

Assemblages à base de polyoxométallates : des interactions fondamentales aux matériaux hybrides supramoléculaires

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UNIVERSITE



Assemblages à base de polyoxométallates : des interactions fondamentales aux matériaux hybrides supramoléculaires

Thèse de doctorat de l'Université Paris-Saclay préparée à Université de Versailles-Sanit-Quentin-en-Yvelines

École doctorale n°571 Sciences chimiques : Molécules, Matériaux, Instrumentation et Biosystèmes Spécialité de doctorat: Chimie

Thèse présentée et soutenue à Versailles, le 25 octobre 2017, par

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Composition du Jury :

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Do not love half lovers Do not entertain half friends Do not indulge in works of the half talented Do not live half a life and do not die a half death If you choose silence, then be silent When you speak, do so until you are finished Do not silence yourself to say something And do not speak to be silent If you accept, then express it bluntly Do not mask it If you refuse then be clear about it for an ambiguous refusal is but a weak acceptance Do not accept half a solution Do not believe half truths Do not dream half a dream Do not fantasize about half hopes Half a drink will not quench your thirst Half a meal will not satiate your hunger Half the way will get you no where Half an idea will bear you no results Your other half is not the one you love It is you in another time yet in the same space It is you when you are not Half a life is a life you didn't live, A word you have not said A smile you postponed A love you have not had A friendship you did not know To reach and not arrive Work and not work Attend only to be absent What makes you a stranger to them closest to you and they strangers to you The half is a mere moment of inability but you are able for you are not half a being You are a whole that exists to live a life not half a life

Gibran Khalil Gibran

In the memory of my grandfather whom we lost last November; it still breaks my heart to have not been around for your last days. I hope I'm making you proud.

Abstract

In this work, we report in the first part the substitution of molybdenum by tungsten within Keplerate-type anions, $[{Mo_6}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42-}$ (E = O or S). Introducing tungsten to the synthesis medium resulted in the isolation of a series of compounds, $[{W_xMo_{6-x}}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42-}$, with variable metal content within their pentagonal units {M₆}. The isolated products were characterized in solid state and in solution using different techniques. An outstanding observation revealed the selective occupation of the central position in the pentagonal unit by the W atoms. This revelation was stretched to reach other historical structures as Mo-blue wheel [Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-} and Krebs [Mo_{36}O_{112}(H_2O)_{16}]^{8-} anions that also showed the same preferential occupation of W atoms for the heptacoordinated site, at the center of the pentagon. Numerous techniques were employed to assess this regioselective substitution process as high field NMR, X-ray diffraction and EXAFS.

In the second part, we focus on the fabrication of a three-component hybrid material based on polyoxometalates (POMs), metallic clusters and y-cyclodextrin (y-CD). Investigation of such material has been conducted using bottom-up approach by investigating the specific interactions between CD and both types of inorganic units. Their ability to interact has been investigated in the solid state by single-crystal X-ray diffraction and in solution using multinuclear NMR methods (including DOSY, EXSY and COSY), ESI-mass and UV-Vis spectroscopies, electrochemistry and ITC experiments. Single-crystal XRD analysis reveals that POM:y-CD constitutes a highly versatile system which gives aggregates with 1:1, 1:2, and 1:3 stoichiometry. Surprisingly, these arrangements exhibit a common feature wherein the γ -CD moiety interacts with the Dawson-type POMs through its primary face. We present also the first structural model involving an octahedral-type metallic cluster with γ -CD. XRD study reveals that the cationic $[Ta_6Br_{12}(H_2O)_6]^{2+}$ ion is closely embedded within two γ -CD units to give a supramolecular ditopic cation, suitable to be used as a linker within extended structure. Solution study demonstrates clearly that pre-associations exist in solution, for which binding constants and thermodynamic parameters have been determined, giving preliminary arguments about the chaotropic nature of the inorganic ions. Finally, the three components associate together to give a well ordered polymer-like hybrid chain that is derived as hydrogel and single crystals.

In the last part, we extend the CD-POM investigation to reach giant POM structures as the Moblue ring. A non-conventional complexation results from this interaction explained by the encapsulation of the organic macrocycle (CD) within the inorganic torus (POM). Increasing the complexity of the system by introducing a third species, e.g. Keggin- or Dawson-type POM, or octahedral cluster, provoked the formation of hybrid supramolecular assembly based on the hierarchical arrangement of organic and inorganic molecules. Such nanoscopic onion-like structure has been characterized by single-crystal X-ray diffraction thus demonstrating the capability of the giant inorganic torus to develop relevant supramolecular chemistry and the strong affinity of the inner and outer faces of the γ -CD for the polyoxometalate surfaces. Furthermore, interactions and behavior in solution have been studied by multinuclear NMR spectroscopy which supports specific interactions between different units. The formation of this three-component hybrid assembly from one-pot procedure, in water and from nearly stoichiometric conditions is discussed in terms of the driving forces orchestrating this highly efficient multi-level recognition process. Finally, combining the concept of mixed Mo/W pentagon-based POM with the hierarchical system generated a mesmerizing architecture.

Résumé

Dans ce travail, nous présentons dans la première partie la substitution du molybdène par du tungstène dans les anions de type Keplerates, $[{Mo_6}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42-}$ (E = O or S). L'introduction du tungstène dans le milieu de synthèse a entraîné l'isolement d'une série de composés, $[{W_xMo_{6-x}}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42-}$, avec une teneur en métal variable dans leurs unités pentagonales ${M_6}$. Les produits isolés ont été caractérisés à l'état solide et en solution en utilisant différentes techniques. Une observation remarquable a révélé l'occupation sélective de la position centrale dans l'unité pentagonale par les atomes W. Cette observation a été étendue à d'autres structures telles que les roues du bleu du molybdène $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ et l'anion Krebs $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ qui ont également montré la même occupation préférentielle des atomes W pour le site héptavalent, au centre du pentagone. De nombreuses techniques ont été employées pour évaluer ce processus de substitution regiosélective telle que la RMN à hauts champs, la diffraction des rayons X et EXAFS.

Dans la deuxième partie, nous nous concentrons sur l'élaboration d'un matériau hybride à trois composantes à base de polyoxométallates (POM), de clusters métalliques et de y-cyclodextrine $(\gamma$ -CD). La conception de ce matériau suivant une approche synthétique basée sur la propagation à l'infini des interactions spécifiques entre la CD et les deux types d'unités inorganiques, donnant lieu à des chaines polymériques hybrides. Leur capacité à interagir mutuellement a été étudiée à l'état solide par diffraction des rayons X (DRX) sur monocristal et en solution en utilisant des méthodes de spectroscopie RMN multinucléaire et UV-Vis, spectrométrie de masse (ESI), ainsi que des expériences d'électrochimie et d'ITC. L'analyse par DRX sur monocristal révèle une diversité structurale du système POM: y-CD conduisant à des agrégats de stoechiométrie variable de type 1:1, 1:2 et 1:3. De façon remarquable, ces arrangements présentent une caractéristique commune dans laquelle la fraction γ -CD interagit avec les POMs de type Dawson à travers sa face frontale. Nous présentons également le premier modèle structural impliquant un cluster métallique de type octaédrique avec γ -CD. L'étude par DRX révèle que l'ion cationique [Ta₆Br₁₂ (H₂O) $_{6}$]²⁺ est intimement intégré dans les cavités de deux unités γ -CD pour donner un cation ditopique supramoléculaire, que l'on peut utiliser comme agent liant pour la conception des structures étendues. L'étude en solution démontre clairement que ces associations sont stables en solution, et les constantes d'association ainsi que les paramètres thermodynamiques des complexes d'inclusion ont été déterminés. Les forces motrices des telles associations fortes sont discutées notamment l'effet chaotropique des ions inorganiques. Enfin, les trois composants, CD, POM et cluster, s'associent pour donner une chaîne hybride de type polymère bien ordonnée, sous forme d'un hydrogel ou des monocristaux.

Dans la dernière partie, nous étendons l'étude des interactions CD-POM aux structures POMs géantes telle que l'anneau du bleu du molybdène. Une complexation non conventionnelle résulte de l'encapsulation du macrocycle organique (CD) dans la cavité centrale du l'anneau inorganique anionique (POM). Accroître la complexité du système en introduisant une troisième espèce, par exemple un POM de type Keggin ou Dawson ou un cluster octaédrique, conduit à la formation d'un assemblage supramoleculaire hybride par agencement hiérarchique des molécules organiques et inorganiques. Cette structure nanoscopique multicouche a été caractérisée par DRX sur monocristal démontrant ainsi la capacité du tore inorganique géant à développer une chimie supramoléculaire hiérarchique grâce à la forte affinité des faces interne et externe du y-CD pour les surfaces des polyoxométalates. De plus, les interactions et le comportement en solution ont été étudiés par spectroscopie RMN multinucléaire qui montre des interactions spécifiques entre différentes unités. La formation de cet assemblage hybride à trois composants suivant une procédure en une seule étape, dans l'eau et à partir de conditions stoechiométriques, est discutée en termes de forces motrices d'auto-organisation et reconnaissance moléculaire. Enfin, la combinaison du concept de POM contenant des unités pentagonales mixtes à base de Mo/W avec le système hybride hiérarchique a généré une architecture fascinante multifonctionnelle.

Publications

The following publications were published or submitted as a result of work undertaken over the course of this thesis.

"Polyoxometalate, cationic cluster and γ -cyclodextrin. From primary interactions to supramolecular hybrid materials". **M. A. Moussawi**, N. Leclerc, S. Floquet, P. A. Abramov, M. N. Sokolov, S. Cordier, A. Ponchel, E. Monflier, H. Bricout, D. Landy, M. Haouas, J. Marrot, E. Cadot. *J. Am. Chem. Soc.* 139 (36) (**2017**) 12793-12803.

"Nonconventional three-component hierarchical host-guest assembly based on Mo-blue ringshaped giant anion, γ -cyclodextrin and Dawson-type polyoxometalate". **M. A. Moussawi**, M. Haouas, S. Floquet, W. E. Shepard, P. A. Abramov, M. N. Sokolov, V. P. Fedin, S. Cordier, A. Ponchel, E. Monflier, J. Marrot, E. Cadot. *J. Am. Chem. Soc.* 139 (41) (**2017**) 14376-14379.

"Supramolecular adduct of γ -cyclodextrin and $[\{\text{Re}_6\text{Q}_8\}(\text{H}_2\text{O})_6]^{2+}$ (Q = S, Se)". P. A. Abramov, A. A. Ivanov, M. A. Shestopalov, **M. A. Moussawi**, E. Cadot, S. Floquet, M. Haouas, M. N. Sokolov. *J. Clust. Sci.* (**2017**), (DOI: 10.1007/s10876-017-1312-z).

"Inclusion compounds based on chalcogenide rhenium clusters and γ -cyclodextrin: toward the control of the association strength". P. A. Abramov, A. A. Ivanov, M. A. Shestopalov, **M. A. Moussawi**, N. B. Kompankov, M. N. Sokolov, S. Floquet, D. Landy, M. Haouas, K. A. Brylev, S. Cordier, E. Cadot. Under preparation.

Other work

"Investigation of the protonation state of the macrocyclic $\{H_nP_8W_{48}O_{184}\}$ anion by modeling ¹⁸³W NMR chemical shifts". M. Haouas, M. Diab, **M. A. Moussawi**, E. Cadot, S. Floquet, M. Henry, F. Taulelle. *New Journal of Chemistry* 42 (**2017**) 6112-6119.

"pH – controlled one pot syntheses of giant $Mo_2O_2S_2$ – containing selenotungstate architectures". **M. A. Moussawi**, S. Floquet, P. A. Abramov, C. Vicent, M. Haouas, E. Cadot. Under revision in *Inorganic Chemistry*.

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General introduction

Polyoxometalates (POMs) are soluble molecular oxides mediating metalate ions and the infinite oxides. They are discrete anions whose unrivalled structural and chemical diversity sparked in numerous domains of scientific research providing interesting properties in fields of catalysis, optics, magnetism, medicine and biology. This family of compounds is increasingly studied, in particular due to the ease of functionalizing these POMs leading to extremely diverse inorganic and hybrid architectures. In the past two decades, studies have focused on POM-hybrid materials supplying additional functionalities due to the synergetic interactions between the POM and the organic moieties. Formation of such hybrids can be based on simple ionic interactions between the organic and inorganic components. Other types of interaction as the hydrophobic effect can serve as the driving force for the preassociation of organic/inorganic complementary species provoking the self-assembly of POMs into highly-ordered complex structures. Understanding the nature of these interactions is essential for the development of such hybrid materials. In this manuscript, we report on the synthesis of a series of compounds derived from historical/classical POMs, as well as the investigation of the formation of new organic/inorganic-hybrid materials. The work is divided into three main parts and explained thoroughly in chapters II, III and IV.

Chapter I. A brief overview of supramolecular chemistry and some historical examples is first presented. Description of polyoxometalates from simple structures to giant architectures, focusing on the pentagonal motif-containing structures as they are the main topic of the coming chapter, however this chapter also presents recent results about POM/cyclodextrin hybrid materials that we will shed the light on in chapters III and IV. Finally, we end this chapter by host-guest chemistry in POMs and some applications.

Chapter II. We demonstrate that Keplerate ion can be built on mixed Mo/W pentagonal motifs $\{M(M_5)\}$, where the tungsten atoms occupy preferentially the central heptacoordinated position decorated by the five $\{MoO_6\}$ octahedra. Such a result means that in such conditions, the polycondensation of the molybdate and tungstate ions correspond to a regioselective process. Study in solution reveals that the kinetic of the Keplerate formation is directly dictated by the W/Mo ratio. Such a result open new insights for nanoscopic pentagonal-based POM species in general like the giant Mo-blue ring and the Krebs anions. A series of new

mixed Mo/W compounds have been synthesized and characterized both in solid and solution.

Chapter III. This chapter focuses on recent results obtained by combining various inorganic species (POMs or clusters) with γ -cyclodextrin (γ -CD) leading to the formation of a variety of POM/CD or cluster/CD hybrid materials. ITC and NMR appeared to be efficient techniques to assess the strength of interactions and pre-association of these species in solution. Finally, we demonstrate the possibility of engineering a three-component system based on POM/cluster/CD that can be derived as hydrogel or single crystals combining the chemistry of the electron rich cluster with that of the electron poor POM using CD.

Chapter IV. Following the same concept stretched in Chapter III, we demonstrate the formation of a nonconventional complexation between CD and Mo-blue ring where CD behaves as a guest, as never seen before, and the ring-shaped POM as a host. Increasing the complexity of the system led to the design of multi-component systems by encapsulating a Dawson-type anion $[P_2W_{18}O_{62}]^{6-}$ within the cavity of the anionic ring showing a hierarchical alternation of organic and inorganic layers. We highlight also the crossover between the mixed pentagons of Chapter II and the hierarchical arrangement to synthesize mesmerizing architecture.

Chapter I- Introduction:

I. From Molecular to Supramolecular Chemistry

Chemistry of covalent bonds or basic molecular chemistry is the field revolving around the molecular species, their properties, transformation and unraveling the mystery behind their structures. Super-molecules are to molecules what molecules are to atoms where intermolecular bonds or interactions play the role of covalent ones, i.e. supramolecular chemistry is the chemistry beyond the molecule. It is based on the organization of larger entities of high complexity resulting from the association of two or more chemical compounds grasped by intermolecular interactions. This multidisciplinary field of chemistry is attractive in its own way, as it includes organic or inorganic chemistry and extends its arms to reach biochemical structures of Nature as well.¹ Complexity in arrangement within natural compounds arises from the association of simple building units that are held together by weak interactions such as hydrogen bonds, π - π stacking or van der Waals and electrostatic interactions resulting in extremely large and sophisticated biomolecules that take the credit for the functional and structural complexity of the cells and beings. A classic example of this process is the formation of proteins that is constituted of a sequence of amino acids covalently bonded then this sequence fold over itself and is held by one or multiple weak interactions mentioned earlier. Then finally, the molecular architecture arises from the interconnections between these folded units.

Chemists have set their minds to construct sophisticated molecular structures on the nanometric scale that can be of use in diverse domains of science or technology such as computer industry, drug delivery and others.²⁻⁴ These nanometric structures can be constructed stepwise and piece by piece and their synthesis differs from the straightforward self-assembly process leading to well-defined and targeted molecules, thus following a puzzle-like ordering with several complementary created molecules.

Over the past few decades, supramolecular architecture attracted a big deal of attention because of their potential to aide reaching quite large and versatile astonishing structures of uses in domains as catalysis, biomedicine and many more.⁵⁻⁷ The introduction of host-guest interactions which can be considered as underlying of the broadest supramolecular interactions that facilitates formation of hierarchical structures with variable sizes and shapes bearing synergistic physical or chemical properties. Host-guest interactions lead to the

formation of inclusion complexes between two or more units, resulting in highly specific arrangement through a controlled manner. This innovative approach has been and still being used in engineering hierarchical and supramolecular materials.

Mastering the art of host-guest interactions has been driving scientists in not only organic and inorganic chemistry but also in fields as coordination chemistry or biochemistry. People working in this domain have been recognized for their efforts and achievements where in 1987 the Nobel Prize for Chemistry was awarded to Lehn, Cram and Pedersen for the development of molecules with structure-specific interactions of high selectivity.⁸ The pioneers work dealt mainly with organic macromolecules (crown ethers and cryptands), their discovery and applications.

Crown ethers are macrocyclic polyethers in which the ethereal groups are separated by two methylene (CH₂-) groups. This family of compounds dates back to 1988 when Pedersen reported their discovery.⁹ They vary in size depending on the number of atoms forming the cycle. Crown ethers are known for their complexation abilities for elements belonging to the first two columns of the periodic table and for ammoniums and alkyl-ammoniums as well. They are flexible and their skeleton usually distorts if needed to optimize the binding in the host-guest arrangement. They usually comprise 12 to 60 atoms including the coordinating oxygen atoms, but the best complexing rings are those made out of 15 to 24 atoms possessing 5 to 8 oxygen atoms as convergent coordinating centers. And the most known example is the [18]-crown-6 that exhibits remarkable adaptation of its geometry when complexed with metallic cations such as sodium ion, for example. The [18]-crown-6 derivative is flexible enough to wrap itself and to distort its framework for maximizing the electrostatic interactions and bonding. Figure 1a shows an example of a K-centered [18]-crown-6.



Figure 1: Structural representation of: a) potassium-centered [18]-crown-6 ether and b) potassium-centered cryptand. Color code: K, green; C, black; H, white; N, blue and O, red.

On the other hand, cryptands discovered by Lehn in 1985,¹⁰ can be considered as a three dimensional analogue of the simpler planar crown ethers. Such a type of ligands acts as bi- or poly-cyclic multidentate ligands and exhibits stronger affinity and selectivity compared to crown ethers. The cage-like interior cavity within the cryptand provides the binding site for the ionic guests to form cryptates. And similar to their simpler counterparts, cryptands also possess the ability to bind organic cations as alkylammonium ions. The shape and size of the bicyclic cage-like molecule enables the discrimination in the encapsulation of different ions due to size and symmetry compatibility. One more difference between cryptands and crown ethers is that in the former nitrogen atoms contribute as well in the binding to the ions as shown in Figure 1b.

Further developments in organic supramolecular hosts lead to a large variety of macrocyclic arrangements, which includes the cucurbit[n]urils (noted CB_n).¹¹ This family of molecular containers results from the cyclic condensation of glycoluril units in the presence of formaldehyde. These compounds contain two symmetric openings lined with ureido-carbonyl groups and provide numerous derivatives with different sizes since the number of constitutive glycoluril units varies from 5 (CB₅) to 14 (CB₁₄). Their chemistry relies on their rigidity and on the properties of the CB_n portals able to generate hydrogen-bonding and ion-dipole interactions.¹ The hydrophobic inner lining of the ring favors the encapsulation of neutral organic species, while the ion-dipole interactions favor the binding of cations to the carbonyl-lined window allowing the solubilization of the resulting adduct in water. These distinct binding environments have overwhelming interferences in the mechanism of exchanging guests,¹² as illustrated by example shown in Figure 2.



Figure 2: Cucurbituril-guest exchange pathway for neutral guests in presence of small mono-cations. (Figure reproduced from reference 1).

Examples of prominent compounds known for their hosting capabilities include cyclodextrins (CDs). These organic macrocycles are synthetic compounds resulting from the enzymatic degradation of polysaccharides (starch). The inner pocket of the macrocycle forms a hydrophobic cavity suitable for hosting other molecules. The encapsulation process leading to a host-guest complex modifies the physical, chemical or biological properties of the guest such as solubility or redox properties. These remarkable changes of the guests properties increased the attention in the use of CDs in most sectors of industry mainly chemistry,¹³ chromatography,¹⁴ catalysis,¹⁵ food,¹⁶ biotechnology,¹⁷ cosmetics,¹⁸ hygiene, textiles,¹⁹ medicine and pharmacy.²⁰⁻²² The discovery of CDs has been attributed to the French scientist Antoine Villiers in the late 1800s.²³ These cyclic oligosaccharides are based on the connection of α -1,4-linked D-glucopyranosyl and they possess the general formula $(C_6H_{10}O_5)_n$ with n = 6, 7 or 8 in the usual α , β and γ CDs respectively as shown in Figure 3. Depending on the number of the repetitive units comprised in the molecule, the size of the internal cavity varies from 0.57 nm in α -CD to 0.78 nm in β -CD and 0.95 nm in γ -CD.²³ Since their discovery, numerous studies have been conducted on these macrocyclic assemblies, shedding light on their remarkable supramolecular capabilities.^{24,25}



Figure 3: a) Lewis representation of the 1,4 D-glucopyranosyl repetitive unit in cyclodextrin, and b) schematic representation of the three cyclodextrins α , β and γ containing 6, 7 and 8 units, respectively. (Figure b reproduced from reference 23).

In the abundant literature about supramolecular properties of CDs, Stoddart *et al.* recently reported the use of CDs as an effective tool to recover gold-containing molecules, where CD acts as a second coordination sphere around the anion of interest.²⁶ In the same study, they proved the efficiency of CD as a possible candidate for the selective capture of radioactive Cs⁺ ions from aqueous solutions as an attempt to remediate environment from the nuclear wastes damages. The isolated complexes were crystallized and their structures showed a one dimensional polymer-like chain with the recovered tetrabromoaurate entrapped between the two primary faces of adjacent CDs while alkali counter cations are strongly coordinated on the exterior border of two secondary faces as shown in Figure 4.



Figure 4: Structural representation of the chain-like polymer of $CsAuBr_4$ and α -cyclodextrin. Color code: Au, yellow wires; Br, green wires; C, grey wires; O, red wires and Cs, white spheres. (Figure reproduced from reference 26).

Aiming to identify organic and inorganic compounds that have the ability to selfassemble and form hybrid systems, Stoddart once again reported on the interactions between β - and γ -CD and a large anionic species, such as the polyoxometalate (abbreviated POM) $[PMo_{12}O_{40}]^{3-}$ anion.²⁷ So attempting to create functional supramolecular hybrid architectures, Stoddart *et al.* evidenced the existence of supramolecular adduct involving the CDs and the anionic POM which penetrates partially the inner cavities of two adjacent CDs. Such an arrangement is described by Stoddart as a decorated or a crowned POM by CDs. The complexation takes place between the 7-membered (β -CD) and 8-membered macrocycles (γ -CD) due to the size compatibility. The association with the γ -CD leads to the formation of a linear chain while that with the β -derivative provide a zig-zag chain. In both chains, the cluster is located between the primary faces of the CDs while the secondary faces of two adjacent CDs are hydrogen bound to each other as shown in Figure 5 and 6.



Figure 5: Capped representation of the linear chain formed from $[PMo_{12}O_{40}]^{3-}$ and γ -cyclodextrin. Color code: Mo, cyan; La, blue; O, red; C, grey and P, orange. (Figure reproduced from reference 27).

Inorganic chemistry offers considerable opportunities to engineer structures of high complexity and impressive architecture. Taking into consideration pure inorganic assemblies or coordination compounds, the coordination modes of the transition metals are flexible and versatile enough to access a vast sea of complex architectures arising from self-assembling through a one-pot synthesis. This self-assembling process arises from the ability of the system to voluntarily design large functional highly ordered complexes of multi-physicochemical properties born from synergies between individual constitutive building units.



Figure 6: Capped representation of the zig-zag chain formed form $[PMo_{12}O_{40}]^{3}$ and β -cyclodextrin. Color code: Mo, cyan; La, blue; O, red; C, grey and P, orange. (Figure reproduced from reference 27)

Among the numerous examples of organic or inorganic species ranging in the supramolecular chemistry category, the well renowned polyoxometalates (POMs) family can be considered as a subset of this department. POMs are known for their structural diversity and astonishing structures which constitutes remarkable functional building block to develop sophisticated supramolecular engineering. Structures and properties of POMs are discussed in the following section.

II. A survey of Polyoxometalates chemistry

II.1. Definition and History

Polyoxometalates (POMs) are discrete polynuclear anionic metal oxide species composed of metal centers in their highest oxidation state(s). These clusters are the result of the unique and remarkable property of the early transition metals such as tungsten W^{VI} , molybdenum Mo^{VI} and vanadium V^{V} for the most common elements. Polyoxometalates are generally formed from condensation of the tetraoxometalate precursors $[MO_4]^{n-}$ in acidic medium giving connected $\{MO_n\}$ polyhedra through corner or edge shared junctions, i.e. the polyhedra are linked via one or two bridging oxygen atoms. As result, an anionic polynuclear molecule with a general formula $[M_xO_y]^{m-}$ is formed. Besides, the structural chemistry of the

POMs is dominated by the specificity of the coordination bond between the metal center (in its highest oxidation state) and the oxo ligand. The presence of empty *d* orbitals on the metal centre favorizes metal-oxo π -bonding,²⁸ which increases the strength of the metal-oxide bond and therefore confers great stability to this class of compounds. This fact is the reason behind the formation of short terminal {M=O} groups that limits the growing process to discrete POM species and then prevents the formation of infinite metal oxides.²⁹ These {M=O} bonds exhibit low basicity due to the strong polarization of the oxygen by the metal center. As a consequence, some POM species exhibit weak binding ability for protons and behave as very strong Brønsted acids behaving as super acidic systems.³⁰ The formation of the polynuclear POMs through the acidic polycondensation of the basic tetraoxometalate ion can be written as follow:

$$x MO_4^{n-} + z H^+ \rightarrow [M_xO_y]^{m-} + z/2 H_2O$$

Although pH plays a vital role in the polycondensation process, other factors such as temperature, concentration, solvent, ionic strength, etc., affect majorly the self-assembling mechanism that allows to produce numerous different POMs even when starting from the same precursor.³¹

The most renowned POMs are those containing tungsten or molybdenum in their highest oxidation state (IV). Besides, development of POM chemistry with other early transition metals of group 5, such as vanadium (V), niobium (V) and tantalum (V) is more recent and further striking progresses are still expected with these elements.²⁸

Historically, the first POM reported dates back to 1826 when J. J. Berzelius noticed the formation of yellow precipitate while acidifying ammonium molybdate solution with phosphoric acid.³² This was the first description of POMs known today as the ammonium salt of phosphomolybdate (NH₄)₃PMo₁₂O₄₀•nH₂O. However, one century later, the structure of 12-phosphotungstic acid was elucidated by Keggin in 1933 from interpreting powder X-ray diffraction images.³³ In the development of this field, X-ray diffraction techniques especially single crystal X-ray diffraction methods have played a crucial role discovering numerous complicated POM arrangements. Development of the structural chemistry of POMs through X-ray diffraction methods has been undoubtedly at the origin of the big expansion of this field with an ever increasing number of publications from 48 in 1990 to more than 8500 by April 2017.³⁴ The tremendous enthusiasm provoked by POMs chemistry can be explained by their unrivalled structural, chemical and physical properties that allowed the development of new

molecule-based materials and devices useful in many societal domains such as medicine, energy, and environment or information storage.^{2,35,36}

II.2. Structural architectures of POMs

Due to the large diversity of POMs species which differ in their i) composition (POMs can include in their framework, almost all the elements of the periodic table), ii) symmetry, iii) size and iv) electronic properties, it becomes puzzling and scarce to establish a well-precise POMs classification. However, POM compounds have been historically distributed into two subclasses namely isopolyoxometalates and heteropolyoxometalates with general formulae $[M_xO_y]^{n-}$ and $[X_zM_xO_y]^{n-}$, respectively.

II.2.1. Isopolyoxometalate compounds [M_xO_y]ⁿ-:

Isopolyoxoanions are built from metal-oxo frameworks lacking the presence of a heteroatom and retain the general formula $[M_xO_y]^{n}$. As a general trend, isopolyoxometalates exhibit weak hydrolytic stability in aqueous solution when compared to their counterparts bearing the heteroatom.²⁸ Some compounds belonging to this subclass display a highly charged surface granting some oxygen atoms a basic character and thus making them building blocks with interesting chemical reactivity.³⁷ In aqueous solution, the self-assembling process is influenced by many parameters, but despite the complexity of the condensation mechanisms, specific compounds can be isolated as pure material from the complicated dynamic library. However, a thorough and comprehensive reaction system should be the way to design finely targeted POMs species. The main members belonging to this family are usually composed of six to twelve metallic centers. The most known isopolyoxometalate are the Lindqvist-type ions $[M_6O_{19}]^{n}$. Some archetypical isopolyoxometalates such as the decavanadate ion $[V_{10}O_{28}]^{6-}$, the paratungstate $[H_2W_{12}O_{42}]^{10-}$ or the Krebs anion $[Mo_{36}O_{112}]^{8-}$ are shown in Figure 7.



Figure 7: Polyhedral representation of some isopolyoxometalates: a) Lindqvist $[M_6O_{19}]^{n-}$, b) decavanadate $[V_{10}O_{28}]^{6-}$, c) paratungstate $[H_2W_{12}O_{42}]^{10-}$ and d) Krebs anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$.

II.2.1.1. Structural descriptions

• The Lindqvist ion $[M_6O_{19}]^{n}$. The Linqvist ion is formed from all metals of group 5 and 6 (except vanadium and chromium) in their highest oxidation state. Examples of $[M_6O_{19}]^{n}$ with metals of group 5 include: $M = Nb^{5+}$ and Ta^{5+} with n = 8, and group 6: $M = Mo^{6+}$ and W^{6+} with n = 2. The hexametalate cluster contains 6 [MO_6] polyhedra connected via edge-shared junctions with each metal center bearing one terminal oxygen (M=O) and sharing 4 μ_2 – bridging oxygen atoms (M-O-M) with its neighboring centers shown in Figure 8. Structural characterization revealed high idealized symmetry (O_h) .³⁸ The reactivity of this POM is directly controlled by the nature of the metal center. For instance, the ionic charge of the vanadate or niobate clusters is high enough to promote coordination of metal centers such as Ir(I), Rh(II) or Ru(III), grafted on the surface of the {M_6O_{19}} ions. On the contrary, the tungstate or molybdate counterparts are known for their inertness toward metallic cations.³⁹⁻⁴¹



Figure 8: Structural representation of the Lindqvist anion $[M_6O_{19}]^{n}$. a) Ball and stick representation and b) polyhedral representation showing the six edge-sharing octahedra that originates the overall octahedral symmetry. Color code: M, white spheres and grey polyhedra; O, red spheres.

• The decavanadate ion $[H_nV_{10}O_{28}]^{(6-n)}$. This species corresponds to one of the most stable vanadates in solution. In the pH ranging from 2 to 6, several protonation states for the decavanadate species have been evidenced with the formula $[H_nV_{10}O_{28}]^{(6-n)}$ where n varies from 0 to 4. The $[V_{10}O_{28}]^{6-}$ ion is formed by the acidification of metavanadate $[VO_3]^-$ at pH 6.⁴² Its structure can be viewed as an extension of the Lindqvist derivative as two fused $\{V_6O_{19}\}$ moieties sharing two $[VO_6]$ polyhedra as shown in Figure 9.



Figure 9: Structural representation of the decavanadate anion $[V_{10}O_{28}]^{6}$. a) Ball and stick representation and b) polyhedral representation. Color code: V, white spheres and grey polyhedra; O, red spheres.

• The Krebs anion $[Mo_{36}O_{112}]^{8}$. A notably large isopolyoxometalate compared to the previous examples can be isolated at pH below 2. The correct formula was reported by Glemser in 1973 with a wrong proposed structure. In 1979, the right formula for $[Mo_{36}O_{112}]^{8}$ was given by Paulatboschen as preliminary results. Then, the complete structural description was definitively established by Krebs in 1982 through the report of the X-ray crystallographic analysis.⁴³⁻⁴⁵ The structure presented in Figure 10 is built from two identical $\{Mo_{17}\}$ moieties related through a center of inversion and scotched together by two $\{Mo_1\}$ bridging units. The open-shell structure can be viewed as 2 flower-like pentagonal motifs $\{Mo(Mo_5)\}$ with a heptacoordinated pentagonal-bipyramidal center and five octahedral petals – This same fragment is found in other POM structures named Keplerate ion or Molybdenum Blue that are discussed below – and two dimeric $\{Mo_2\}$ units. Within each moiety, the two pentagonal motifs are linked via $\{Mo_1\}$ group. The two identical moieties are linked with the $\{Mo_1\}$ units in a corner-sharing mode forming (Mo-O-Mo) bonds.



Figure 10: Structural representation of the Krebs anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$. a) top view and b) side view showing the different building unit. Units color code: {Mo₁}, red; {Mo₂}, blue and {Mo(Mo₅)}, grey.

II.2.2. Heteropolyoxometalates [X_zM_xO_y]ⁿ⁻:

This class of POMs compounds retain the formula $[X_zM_xO_y]^{n-}$ bearing heteroatom in their framework. Usually, the heteroatom combines with oxygen atoms to give either octahedron {XO₆}, tetrahedral {XO₄} or trigonal {XO₃} groups, which act as assembling groups. Heteroatoms belong usually to the p-block and the most common are Si^{IV}, As^{V, III}, P^V or Ge^{IV}, Te^{IV,VI}, Sb^{III,V}, etc..³⁸ These heteroatoms are introduced into the reaction mixture as oxo-ions {XO_p}ⁿ⁻ that directs and orientates the condensation process of the metalate ions until determining the topology, the symmetry and the nuclearity of the resulting POMs. In the final hetero-POM, the assembling groups are generally embedded within the metal-oxo framework.

Furthermore, the nature of the assembling group in POMs governs the charge and reactivity of the hetero-POM. The most distinguished species belonging to this family are the Keggin and Wells-Dawson anions and their derivatives. These two examples are discussed in the following section.

• Description of Keggin ion $[XM_{12}O_{40}]^{n}$. This arrangement is based on a templated $[XO_4]^{n}$ tetrahedral assembling group, located at the center surrounded by four $[M_3O_{13}]$ triads. Each triad is composed of three edge-shared {MO₆} octahedra. The three {MO₆} within the $[M_3O_{13}]$ fragment share a μ_3 -oxygen atom (O_a -type) which is directly connected to the central heteroatom thus forming the X-O_a-M junction. The structure is highly symmetric and retains a tetrahedral environment T_d . Nevertheless, the molybdenum Keggin possesses a lower symmetry in solid state due to the minor displacements of the Mo atoms out of the mirror planes passing through the 4 $[M_3O_{13}]$ triads, thus exhibiting symmetry close to the chiral T group.³⁸ Interestingly, several isomers can be formed based on the single parent arrangement - the α -Keggin structure - to obtain the β , γ , δ and ε isomers, shown in Figure 11. The positional isomers are generated simply by the successive rotation of the four triads by 60° respectively. The α isomer is the most common and stable isomer. Such stability for the α isomer can be attributed to the minimizing of the Coulombic repulsions between the intertriad metallic centers. These unfavorable repulsions increase through the 60° rotation of the {M₃O₁₃} cores.^{46,47} Examples of the β , γ , δ and ε isomers were reported by Sasaki,⁴⁸ Hervé,⁴⁹ Nazar⁵⁰ and Sécheresse,⁵¹ respectively. Based on structural and compositional diversity, the Keggin anion is probably the most popular POM species widely studied in many fields of

science for its multifunctional properties varying from acidic and chemical reactivity⁵² to redox activity or electrochemistry.⁵³



Figure 11: Polyhedral representation of the five different isomers of the Keggin-type anion. Color code: M, blue and grey polyhedra; X, pink polyhedra.

• Description of the Wells-Dawson arrangement $[X_2M_{18}O_{62}]^{n}$. Wells-Dawson or simply Dawson anions are heteropolyoxometalates of the general formula $[X_2M_{18}O_{62}]^{n}$ (M = W or Mo; X = P or As). Dawson reported in 1953 the X-ray diffraction analysis of the $[P_2W_{18}O_{62}]^{6}$ ion.⁵⁴ The anion $[X_2M_{18}O_{62}]^{n}$ arises from the connection of two $\{XM_9O_{34}\}$ fragments sharing six $\{MO_6\}$ corners through quasi-linear M-O-M junctions as shown in Figure 12. The Dawson-type POM exhibits a D_{3h} idealized symmetry and can be seen as two six-membered belts and two three-membered caps. The belts are composed of three $\{M_2O_{10}\}$ dioctahedra connected to each other through edge-shared junctions and centered by one heteroatom linked to the three $\{M_2O_{10}\}$ units by three X-O_a-M coordination bonds. In each belt, three $\{Mo_2O_{10}\}$ units assemble through corner-shared junctions. Caps are composed of $[M_3O_{13}]$ triads similar to those found in the Keggin structure and coordinated to the heteroatom in the same mode. Rotating successively the apical $[M_3O_{13}]$ triads by 60°, lead to the formation of isomeric structures. However, all these isomers have not been neither isolated nor observed. Nevertheless, similarly to the Keggin derivatives, the most stable corresponds to the most symmetric α -isomer. Up to date, most of the studies revolve around the phosphorous-based Dawson derivative, and it showed plenty of application in heterogeneous catalysis,⁵⁵ antibiotic activity,^{56,57} and DNA binding inhibition.⁵⁸ Almost a decade ago, a heteroatom-deficient Dawson derivative was reported with the general formula $[H_4P_1W_{18}O_{62}]^{7-.59}$



Figure 12: Polyhedral representation of α -[X₂M₁₈O₆₂]ⁿ⁻ formed from two trivacant Keggin-type anions [XMo₉O₃₂] (discussed in the following section). Color code: M, grey polyhedra; X, pink polyhedra.

II.2.3. Lacunary Keggin derivatives:

Structural variations on Keggin-based archetypes are not limited to the previously mentioned positional isomers. This variation can be upped by creating vacant POMs, known as lacunary (or polyvacant) anions resulting from the controlled basic hydrolysis of the (saturated) parent compounds. For example, the silica-tungstate Keggin derivative $[SiW_{12}O_{40}]^{4-}$ is able to form three lacunary species (see Figure 13). The monovacant, divacant and trivacant species $[SiW_{11}O_{39}]^{8-}$, $[SiW_{10}O_{36}]^{8-}$ and $[SiW_9O_{34}]^{10-}$ are obtained by controlled hydrolysis in basic medium. These derivatives result from the formal removal of one or several octaedra from the saturated parent Keggin anion.⁶⁰ Such lacunary compounds are of great interest since they have the ability to accept or coordinate a transition metal that can change drastically the initial properties of parent species (e.g. chemical, electrochemical, magnetic, etc.⁶¹).



Figure 13: Polyhedral representation of different lacunary Keggin species: a) monovacant, b) divacant and c) trivacant. color code: M, grey polyhedra and X, pink polyhedra.

II.2.4. Lacunary Dawson clusters.

Through similar routes, the saturated Dawson anions $[X_2M_{18}O_{62}]^{n}$ can undergone selective hydrolysis to produce (poly)vacant derivatives (see Figure 14). The monovacant derivative $[X_2M_{17}O_{61}]^{(n+4)}$ is formally obtained through the removal of one {M=O} group. This derivative has two known isomers based on the position of the vacant site: the α_2 -isomer results from the departure of the {M=O} vertex from the {M_3O_{13}} cap while the α_1 -isomer is generated by the {M=O} departure from the octahedra of the belt.⁶² The latter species is energetically unfavored and it usually undergoes spontaneous re-isomerization $\alpha_1 \rightarrow \alpha_2$. Similar to the Keggin anion, the Dawson is able to give trivacant species.⁶³ Furthermore, a Dawson-type superlacunary species exists in this family, corresponding to the loss of six adjacent metallic centers. This hexalacunary species can be recondensed in acidic condition to give larger POM species such as [NaP₅W₃₀O₁₁₀]¹⁴⁻ and [P₈W₄₈O₁₈₄]⁴⁰⁻.^{64,65}



Figure 14: Polyhedral representation of different lacunary Dawson species: a) cap-monovacant, b) belt-monovacant, c) trivacant and d) hexavacant. Color code: M, grey polyhedra and X, pink polyhedra.

II.2.5. Functionalization of lacunary POMs:

The ability to be functionalized is one of the most attractive features of POMs. Depending on the strategy of functionalization, such an achievement could be a hard task due to the inertness of the outward $\{M=O\}$ groups and the fragility of the formed M-Q bond. Nevertheless, basic coordination of mono⁶⁶ or ditopic⁶⁷ specific organic ligand on hetero-transition metal,⁶⁸ could be the simple way to create a huge library of multifunctional POM-based species with extended utility.

II.2.5.1. Lacunary functionalized Keggin derivatives:

The simplest example in this series is the mono-substituted derivative resulting from the coordination of a solvated transition metal to give compounds of the general formula $[XM_{11}O_{39}(TM)(solvent)]^{n-}$ (M = Mo or W; X = heteroatom; TM = transition metal) where the vacant site is occupied by a solvated TM in an octahedral environment. In the same idea, the coordination of ruthenium cation Ru^{II} by the monovacant Keggin derivative α -[GeW₁₁O₃₉]⁸⁻ leads to "pendant" Ru center attached to the POM species by two oxygen atoms belonging to the vacant POM and the four remaining coordination sites of the Ru(II) were filled by three DMSO molecules and an aqua ligand to give $[Ru^{II}(DMSO)_3(H_2O)\alpha$ -GeW₁₁O₃₉]⁶⁻⁶⁹. Combinations of the POMs with Lanthanide ions correspond also to an important class of functionalized species relevant for their luminescent⁷⁰ and magnetic properties.^{3,71} For instance, Kortz *et al.* reported in 2007 the crystallographic structures of the β_2 -monovacant Kegging with a series of Lanthanides, (Ln = La, Ce, Sm, Eu, Gd, Tb, Yb, and Lu) giving corresponding compounds of the general formula $[Ln(\beta_2-SiW_{11}O_{39})_2]^{13-}$ as shown in Figure 15.72 The use of trivacant Keggin derivative in the presence of different TMs gave rise to more complicated arrangements. Sécheresse *et al.* reported in 2007 a { α -SiW₉} trivacant moiety, which supports a total of four TMs linked to acetate and hydroxo groups as complementary ligands.⁶⁸



Figure 15: Combined polyhedral - ball and stick representation of $[Yb(SiW_{11}O_{39})_2]^{13}$. Color code: W, grey polyhedra; Si, pink polyhedra and Yb, blue sphere.

In the same context, the coordination of a preformed inorganic cluster as linker to the vacant Keggin derivatives is accessible. As exemplified by Cadot' work, highly predictable POM chemistry can be developed with the use of the emblematic dimeric building block $\{Mo_2O_2S_2\}^{2+}$ in the presence of vacant Keggin derivatives.⁷³ The $\{Mo_2O_2S_2\}^{2+}$ is a preformed stable cation formed from the acidic hydrolysis of the $[Mo_{10}O_{10}S_{10}(OH)_{10}]$ molecular rings in aqueous medium. The first isolated compound resulted from the coordination of this dimeric building block to the divacant γ -isomer $[SiW_{10}O_{36}]^{8-}$ giving a nice example of complementary geometry and coordination requirements with a 1:1 stoichiometry,⁷⁴ as shown in Figure 16a. The γ -[SiW₁₀Mo₂S₂O₃₈]⁶⁻ anion shows the perfect fit of the linker in the vacancy with four oxo ligands from the POM replacing the equatorial aqua ligands coordinated to the two centers of the linker and resulting in four direct (Mo-O-W) bridges. The addition of the same linker $\{Mo_2O_2S_2\}^{2+}$ to a trivacant $[PW_9O_{34}]^{9-}$ shows a different binding mode. The isolated compound revealed a pillar-like structure with two $\{PW_9\}$ moieties sandwiching three $\{Mo_2O_2S_2\}^{2+}$ linker to give the $[(PW_9O_{34})_2(Mo_2O_2S_2(H_2O)_2)_3]^{12-}$ sandwich-type structure (see Figure 16b).⁷⁵



Figure 16: Mixed representation of: a) [SiW₁₀Mo₂S₂O₃₈]⁶⁻ and b) [(PW₉O₃₄)₂(Mo₂O₂S₂)₃]³⁻. Color code: W, grey (wires and polyhedra); Mo, blue spheres; P, pink spheres; S, yellow spheres and O, red spheres.

II.2.5.2. Lacunary functionalized Dawson derivatives:

As a general trend in the POM chemistry, the Dawson lacunary species can be also coordinated to organic molecules, transition metals or linkers. In fact, the monovacant $[P_2W_{17}O_{61}]^{10}$ can be functionalized in non-aqueous solvent by different organosilyl groups such as $[(SiC_6H_5)_2O]$,⁷⁶ {[Si(CH₃)₃SH]₂O}.⁷⁷ Lacunary Dawson species are also reacted with

transition metals. A large variety of mixed metal complexes can be isolated as the sandwich structure $[(P_2W_{15}O_{56})_2Cu_4(H_2O)_2]^{16-}$ (presented Figure 17a)⁷⁸ or the tetrameric tetrahedral arrangement $[Fe_{14}O_6(OH)_{13}(P_2W_{15}O_{56})_4]^{31-}$ (see Figure 17b)⁷⁹ formed from the trivacant $[P_2W_{15}O_{56}]^{12-}$. On the other hand, the iron-rich derivative $[H_4P_2W_{12}Fe^{III}_{9}O_{56}(CH_3CO_2)_7]^{6-}$ is formed from the hexavacant $[H_2P_2W_{12}O_{48}]^{12-}$ species where six Fe(III) centers decorates the missing side of the POM as $\{Fe_6O_8\}^{2+}$, then three extra Fe(III) ions are grafted on the $\{Fe_6O_8\}^{2+}$ core to obtain the final arrangement (see Figure 17c).⁸⁰ Lanthanides-containing Dawson derivatives have been also reported. For instance, Francesconi published the europium-containing monovacant dimer, where two moieties of the monovacant $\{P_2W_{17}\}$ are bridged by two Eu²⁺ ions to give $[Eu(H_2O)_3(\alpha_2-P_2W_{17}O_{61})]_2$ (Figure 17d).⁸¹



Figure 17: Mixed representation of: a) $[P_2W_{15}O_{56})_2Cu_4(H_2O)_2]^{16}$, b) $[Fe_{14}O_6(OH)_{13}(P_2W_{15}O_{56})_4]^{31}$, c) $[H_4P_2W_{12}Fe_9O_{56}(OAc)_7]^{6}$ and d) $[Eu(H_2O)_3(P_2W_{17}O_{61})]_2$. Color code: W, grey; Eu, teal; Fe, green; Cu, aqua; P, pink; C, white and O, red.

Complexes of the lacunary Dawson derivatives with the $\{Mo_2O_2S_2\}^{2+}$ mentioned earlier have been investigated as well. Depending on the used precursor, i.e. monocavant or trivacant, the resulting structures are very different. The dimeric species $[(P_2W_{17}O_{61})_2(Mo_4O_4S_4(H_2O_{22})]^{16-}$ are obtained from the monovacant $\{P_2W_{17}O_{61}\}^{10-}$
precursor⁸² while a spectacular tetrameric planar butterfly-like structure $[(H_2P_2W_{15}O_{56})_4\{Mo_2O_2S_2(H_2O)_2\}_4\{Mo_4O_4S_4(OH)_2(H_2O)_2\}]^{28-}$ has been characterized from reaction of $\{Mo_2O_2S_2\}^{2+}$ with the trivacant $[P_2W_{15}O_{56}]^{12-}$ anion (see Figure 18).⁸³



Figure 18: Mixed representation of: a) $[(P_2W_{17}O_{61})_2(Mo_2O_2S_2(H_2O))_2]^{16}$ and b) $[(H_2P_2W_{15}O_{56})_4\{Mo_2O_2S_2(H_2O)_2\}_4\{Mo_4O_4S_4(OH)_2(H_2O)_2\}]^{28}$. Color code: W, grey wires; Mo, orange polyhedra and blue spheres; S, yellow spheres; P, pink spheres and O, red spheres.

II.2.6. Very large POMs species: Molybdenum Blue and Keplerate:

As discussed earlier, the condensation of metalate ions in acidic condition leads to the formation of POMs. However, condensation of molybdates in the presence of reducing agent originates new species known as Molybdenum Blue or Keplerate ion. These two classes of compounds contain both Mo^{VI} and Mo^V metal centers and correspond both to mixed-valence systems. Furthermore, both class of compounds exhibit an important common structural invariant which correspond to the pentagonal motif {Mo(Mo₅)O₂₁}. These giant POMs can be described by their multifunctional and highly complex molecular structures. The compounds are known for their fair stability in solution and remarkable in their large size reaching the nanometric scale. The mechanism of formation of these species is not quite clear yet, but it is possible to direct the reaction (or apply empirical synthetic parameters) to get specifically one species over the others possible by controlling the conditions in the reaction medium. For example: the condensation of molybdates in aqueous solution in acidic medium at pH < 2 leads to the formation of the Krebs anion [Mo₃₆O₁₁₂(H₂O)₁₆]⁸. noted {Mo₃₆}. The same solution in presence of a reducing agent leads to formation of large blue rings [Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀]¹⁴⁻ and [(MoO₃)₁₇₆(H₂O)₆₃(MeOH)₁₇H_n]⁽³²⁻ⁿ⁾⁺ noted {Mo₁₅₄} and

{Mo₁₇₆} respectively. Addition of weak coordinating ligands (such as acetate) to the previous – reducing – solution in a buffered condition (pH ≈ 3.5) changes drastically the condensation mechanism to produce capsule-like structure [Mo₁₃₂O₃₇₂(AcO)₃₀(H₂O)₇₂]⁴²⁻ noted {Mo₁₃₂}, namely the Keplerate anion. All these species are formed directly in solution from self-assembling process of the building units available in the dynamic library. Three representative structures and the invariant building unit [M₆O₂₁]⁶⁻ noted {M(M₅)} are shown in Figure 19.



Figure 19: Ball and stick (a) and polyhedral (b) representations of $\{M(M_5)\} = [M_6O_{21}]^6$. Color code: M, grey and O, red.

II.2.6.1. Bielefeld wheel: Elucidation of the Mo Blue mystery

The blue solution of molybdate has been known for a long time. This chemical system actually exists in nature for example: near Idaho Springs – Colorado and Ouray – Utah, but the exact formula was a mystery for a long time.⁸⁴ In nature, they originate from the dissolution of ilsemannite of the approximate formula ($Mo_3O_8.nH_2O$) that comes from the partial oxidation of molybdenite (MoS_2). Many chemists have been interested in unraveling the mystery behind molybdenum blues as early as Scheele in late 1770s. This enthusiasm towards the topic has been shared by Berzelius in 1826 who reported that the blue powder isolated from the solution is a form of reduced molybdenum of the formula ($Mo_5O_{14}.nH_2O$).⁸⁵ However, the exact composition of this solution remained unknown until mid-1990s when Müller *et al.* reported a series of reduced molybdenum-based giant clusters. The first in this series was the Bielefeld "big wheel" { Mo_{154} } reported in 1995.³⁷ And following discoveries unveiled that beyond this blue solution lies a bunch of clusters varying in size and shape from the ring-shaped { Mo_{154} } and { Mo_{176} } to the lemon-shaped { Mo_{368} }, shown in Figure 20.⁸⁴



The way to unravel the mystery started with the isolation of the first single-crystals from a molybdenum blue solution reduced with hydroxylamine NH₂OH used as a reducing agent.³⁷ This important discovery revealed two features about the structure: i) The 154 Mo atoms are engaged in a large metal-oxo framework lining a large toric arrangement of approximately 4 nanometers in diameter, ii) the structure exhibits a large surface surrounded by a large number of water molecules, conferring high solubility in aqueous medium. The original arrangement containing nitrogen monoxide NO as {Mo=N=O} at the center of the pentagonal motifs has a historical importance, but this derivative has never been obtained in a pure form. On the other hand, substituting the {MoNO}³⁺ by {MoO}⁴⁺ leads to the formation of the more stable counterpart the [Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀]¹⁴⁻ noted {Mo₁₅₄}.⁸⁶ This replacement of the NO-containing groups by the O-containing ones simplified the synthesis, product isolation, crystallization and structural characterizations. The enhanced synthesis can be found in *Inorganic Synthesis*.⁸⁷

• **Structural description of {Mo**₁₅₄**}.** The structure (Figure 20a) is composed of fourteen peripheral {Mo₂} dimeric units equally distributed over the both side of the toric aperture and fourteen central {Mo₁} connecting the fourteen {Mo₈} fragments based on fused {Mo(Mo₅)} pentagonal units. In the pentagons, the central hepta-coordinated Mo center adopts apentagonal bipyramid geometry and is surrounded by five hexa-coordinated Mo centers in an octahedral arrangement by edge-sharing mode. The latter connect to other pentagons through {Mo₁} units. The {Mo₂} dimers at the periphery of the wheel determine the diameter of the cavity. A slight change in the synthetic conditions *i.e.* decreasing the pH to less than 1 and increasing the concentration of molybdate in solution leads to the formation of the {Mo₁₇₆} wheel, hence passing from a tetradecamer to hexadecamer cluster with the addition of two extra units of each fragment found in the {Mo₁₅₄}.⁸⁸ The larger {Mo₁₇₆} can undergo an extraordinary nucleation process to form two cluster-like {Mo₃₆O₉₆(H₂O)₂₄} fragments that occupy the cavity exhibiting a hub-cap arrangement covering the two portals of the $\{Mo_{176}\}$ torus resulting in the formation of a new compound of the blue family of the general formula $[Mo_{248}O_{720}H_{16}(H_2O)_{128}]^{16-}$ noted $\{Mo_{248}\}$, and presented in Figure 21.⁸⁹ Another astonishing species of this family has been published by Cronin et al. in 2010. The authors reported the synthesis of a Krebs-containing blue wheel {Mo₁₈₆} that was obtained in a non-conventional way, which consists in the use of a flow reactor system.⁹⁰ The obtained cluster shown in Figure 22a mimics four octahedra deficient {Mo₁₅₄} noted {Mo₁₅₀} with its cavity filled by a Krebs anion $\{Mo_{36}\}$, interacting with the $\{Mo_{150}\}$ host via sodium-cation bridges. Together, {Mo₂₄₈} and {Mo₁₈₆} can be seen as fully inorganic host-guest systems. After proving their potential in pure inorganic host-guest chemistry, the ability of the molybdenum blue to host organic guests was explored by Aida et al. in 2004 where Zn-centered porphyrins were used as guest components and $[(MoO_3)_{176}(H_2O)_{63}(MeOH)_{17}H_n]^{(32-n)+}$ as host.⁹¹ Detailed characterization including mass spectrometry, spectroscopic studies and electron microscopy investigations showed that the ring is able to engulf up to three Zn-centered porphyrins in its large macrocyclic cavity. In such a host-guest nanoscopic systems, the organic moieties were stacked through π - π interactions with their molecular planes parallel to the wheels equator and arranged perpendicularly to the C8 axis of the {Mo₁₇₆} big wheel (see Figure 22b). Although NMR study in solution provides direct evidence of host-guest interactions, unfortunately no crystallographic data were reported and structural assumptions were built from molecular mechanics modeling.



Figure 21: (Left) side view and (right) top view of structural representation of $\{Mo_{248}\}\$ showing the hub-cap arrangement of the $\{Mo_{36}O_{96}(H_2O)_{24}\}\$ covering the portals of the wheel. (Figure reproduced from reference 89).

However, even though POMs chemistry can produce large nuclearity species and then considered quite large in size, they are still far from usual dimension of natural arrangements observed with proteins. The dream to get larger clusters came true when Müller *et al.* reported the largest POM so far that make molecular POMs objects comparable to protein in size. The Bielefeld group isolated the blue lemon arrangement which consists of 368 metallic centers embedded in a network of oxygen atoms and lined by $SO_4^{2^-}$ bidentate ligands (see Figure 20c).^{92,93} The six nanometers in length is comparable to the size of the protein Human Carbonic Anhydrase II (HCAII).^{85,93} It can be seen that the assembly of 64 {Mo₁}, 32 {Mo₂} and 40 {Mo(Mo₅)} fragments is generated by a symmetry-breaking process inducing a curvature change in the large POM surface. The cluster has the general formula $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]$ and noted {Mo₃₆₈}.



Figure 22: Structural representation of a) fully inorganic host-guest {Mo₁₈₆} and b) hybrid organic-inorganic host-guest arrangement {Zn-centered Mo₁₇₆}. (Figures reproduced from references 90 and 92 respectively).

Emerging properties arising from these well-defined nanoscopic molecular species make them good candidates to further investigate the nano world behavior in different domains. The presence of Mo^V/Mo^{VI} mixed valence centers that correspond to thermally or optically delocalized 4d electrons promises rich electronic, optic and redox behavior.⁸⁶ For instance, the narrow band gap due to the high density of state in the HOMO/LUMO region results in nano-sized semiconductors.⁸⁶ In addition, the specific large cavity and its inherent related properties showed promising results in supramolecular chemistry on both organic or inorganic sides and there is no doubt that relevant development will produce breakthrough

results.^{90,91} Furthermore, molybdenum blue species showed the ability to form hollow spherical species so called Keplerate ions, another important class of giant POMs that are discussed in the following section.

II.2.6.2. The Keplerate-type species

Another renowned self-assembled POMs in the giant molybdenum-containing species is characterized by their spheroidal shape with the general formula $\{M_{72}L_{30}Q_{30}\}$ (M = Mo, W; $L = Mo_2O_4^{2+}, Mo_2O_2S_2^{2+}, Cr^{3+}, Fe^{3+}, VO^{2+}; Q = CH_3CO_2^{-}, SO_4^{2-}, C_4H_4O_6^{2-}, SeO_4^{2-}, etc.).^{84,94-}$ ⁹⁷ As shown in Figure 23, the icosahedral cluster resembles the structure of fullerene.⁸⁸ Once again, the pentagonal motif $\{M_6O_{21}\}^{6-}$ found in the Mo blue derivative is also present and constitutes within the Keplerate derivatives the main POM subunit. The structure can be described as a set of 12 pentagonal fully oxidized {Mo(Mo₅)} fragments distributed on the vertices of the icosahedron and connected via the 30 cationic linkers (L) in a corner-sharing fashion. In the {Mo₁₃₂} Keplerate derivatives, 30 dimeric cationic units such as {Mo₂O₄}²⁺ or ${Mo_2O_2S_2}^{2+}$ connect the twelve pentagonal motifs to give fairly stable arrangement probably due to the Mo^V-Mo^V metal-metal bond. The formation pathway of Keplerate in solution has been of much interest since their discovery by Müller in 1998.⁹⁸ Recently Roy et al. investigated the formation pathway of $\{Mo_{132}\}$ from a molybdenum dynamic library.⁹⁹ They discovered by ESI-mass investigation that the simple dissolution of heptamolybdate [Mo₇O₂₄]⁶⁻ in aqueous solution opens a vast dynamic library in which the fragment of interest $[Mo_6O_{21}]^{6-}$ is an active member. In the presence of concomitant cationic linker and weakly coordinating ligands (usually acetate), these pentagonal fragments then self-assemble spontaneously to form the nanoscopic Keplerate-type capsule. Such a type of hollow speroidal capsule offers unique possibilities in the field of supramolecular properties, catalysis and materials. For instance, it has been found that the presence of the 20 pores distributed on the surface allows the transfer of various substrates from the solvent to the interior of the large cavity of the capsule.¹⁰⁰ Such a process facilitates inner functionalization of the capsule¹⁰¹ for prompting catalysis¹⁰² or chemical reactions¹⁰³ under confined environment. Depending on the type of the linker (monomeric or dimeric) not only the size of these pores differs, but also the nature of the lining atoms differs from fully oxo $\{M_9O_9\}$ to oxo-thio $\{M_9O_6S_3\}$. In the largest cluster, the average diameter of these pores reaches out to 6.5 Å, hence providing large crown-like cavities interesting for host-guest chemistry. These pores can be selectively opened or shut using different types of cations (organic of inorganic). Actually, they mimic individual crown ethers in their receptor abilities but the presence of 20 pores at the surface of the capsule gives rise to unique multi-receptor behavior with a particular insight in surface supramolecular chemistry. These surface properties have been recently investigated thoroughly by Cadot *et al.*, who discovered that a series of alkylammonium cations act as molecular effectors blocking specifically the { Mo_9O_9 } pores. Some of these cations, such as tetramethylammonium [NMe_4]⁺ behave as a tailored plug for the pore and it was shown that the hydrophobic character of the cation contributed to the receptor-effector binding.¹⁰⁴ Playing with Keplerate with the basic concepts of supramolecular chemistry is not restricted to the host-guest surface chemistry, as it has been reported that the { $Mo_{72}Fe_{30}$ } derivative is to engulf in its spherical cavity a Keggin or linqvist POMs species and thus to create new host-guest chemical systems.¹⁰⁵ Beside, Keplerate-based materials are useful to combine at the molecular level as relevant elements for catalysis. For instance, Keplerate ion has been used as precursor for the synthesis of Mo/V/Te multi-element oxide phase, one of the best achievements for the selective catalytic oxidation of light alkanes.¹⁰⁶



Figure 23: Polyhedral representation of the Keplerate anions: a) $\{M_{72}M'_{30}\}\$ and b) $\{M_{72}(M-M)_{30}\}\$. Color code: M^{VI} , grey; M' = Cr, Fe or V, blue and M^V , red.

II.3. Host-guest chemistry with POMs:

Amongst the long list of compounds that can be linked or associated to the host-guest chemistry, POMs correspond to relevant or potential candidates to develop brightly creative host-guest systems. The high negative charge of POM clusters affiliates charge-balancing counter ions that in some cases interact specifically with cryptate-like POMs. Keeping in mind that the self-assembling process of POMs, their catalytic properties and even their redox activity are greatly influenced by the POM-cation alliance, the topic corresponding to the anion-cation interaction/recognition is still of broad interest and numerous researchers have produced immense effort exploring this domain. As starting point, understanding this type of alliance or interaction is of basic interest in the development of a POM-based supramolecular concept aiming to unravel the key-point behind ionic recognition or guest inclusion for the fine tuning or design of these POM-supramolecular assemblies in catalysis¹⁰⁷ or in materials science.^{3,108}

Nice example demonstrating the relevance of the control of the host-guest interaction between cations and POM units are found with the Dawson-derivative structures such as $[P_5W_{30}O_{110}]^{15}$, $[P_6W_{39}O_{147}]^{30}$ or $[P_8W_{48}O_{184}]^{40}$ formed from the connections of several hexavacant $\{P_2W_{12}\}$ moieties. The three structures mimic hollow closed or opened rings suitable for engulfing one or more cations. Examples of inner guest clusters ranging from two to more than a dozen transition metals¹⁰⁹ or p-block¹¹⁰ elements have been reported in literature. The Preyssler anion $[P_5W_{30}O_{110}]^{15}$ noted $\{P_5W_{30}\}$,¹¹¹ exhibit a smaller and closed cavity. It was reported later by Pope *et al.* in 1985 that the Preyssler POM can encapsulates a sodium atom (Figure 24).⁶⁵ Further investigations evidence that the encapsulation process can be extended to other metallic cations such as Ln or An elements.¹¹²



Figure 24: Structural representation of a sodium-centered Preyssler anion $[NaP_5W_{30}O_{110}]^{14}$. Color code: W, grey and Na, green.

A captivating supramolecular inorganic chemistry has been revealed by Cadot *et al.* investigating the supramolecular properties of the $\left[\left\{ Mo_{17}(OH)_6O_{52}(H_2O)_6 \right\}_3 \left\{ Mo_2O_2S_2(H_2O)_6 \right]^{6-} \text{ chalco-cluster toward the apolar } \left[NMe_4 \right]^+ \right]^{-1} \right]^{1/2}$ cation.¹¹³ The cluster shares the same fragment found in the structurally related $[H_3Mo_{57}V_6(NO)_6(H_2O)_{18}]^{21-}$ published by Müller in 1996.¹¹⁴ They are made up of three {Mo₁₇} POM fragments linked by six {Mo₂O₂S₂(H₂O)₆}²⁺ in the former or six {V^{IV}O}²⁺ and three $\{Mo_2^V\}$ units in the latter. Shedding light on the first structure, it seems intuitive that its geometry should induce capability to encapsulate different species. The presence of the larger linkers leads to the expansion of the anionic pockets on the exterior as well as the internal cavity, thus facilitating the supramolecular interaction with organic cations larger than ammonium. The X-ray single crystal structure showed two different sites occupied by the $[NMe_4]^+$ cations, the three peripheral pockets and the internal cavity, each filled by one [NMe₄]⁺. Analysis of the host-guest interactions in the pocket does not allow identifying any short contacts. The distances between the methyl groups and the POM (C-O = 3.56-3.88 Å) remain long enough to exclude any strong attractive contribution within the host-guest process (see Figure 25). In this case, the role of the solvent, i.e. H₂O, should be considered within the host-guest recognition, involving desolvation and solvent re-organization processes.



Figure 25: (a) Top view and (b) side view of mixed polyhedral – space-filling representation of the host-guest complex between $\{Mo_{63}S_{12}\}$ and $[NMe_4]^+$. Color code: Mo^{VI} , grey polyhedra; Mo^V , red polyhedra; C, black sphere and O, red sphere.

Large POMs as Keplerate supply a perfect frame to extend the basic concepts of supramolecular chemistry toward inorganic chemistry, since the presence of twenty pores and accessible channels offers unique opportunity to mimic at the molecular level interdependent phenomena such as mass transfer and transport, chemical confinement, ionic recognition or phase transfer extraction. Exchange through channels is the way to modify the inner sphere of the capsule such as its hydrophobicity/hydrophilicity character or the overall charge of the

capsule by substituting the inner ligands (carbonate,¹¹⁵ carboxylates¹¹⁶ or sulfates¹¹⁷) through post-functionalization process.^{95,96} These studies revealed the flexibility of the pores architecture and their ability to transfer bulky substrates.¹⁰⁴ The overall mentioned properties made Keplerate suitable candidate for investigation of their supramolecular multireceptor behavior. This interesting property has been investigated by Müller *et al.* from analysis the single-crystal X-ray diffraction structure of the smaller sphere { $W_{72}Fe_{30}$ } crystallized in the presence of ammonium cations.¹¹⁸ Solid state analysis demonstrated the presence of twenty ammonium plugging the twenty pores { $Fe_3W_3O_3$ } of the capsule through hydrogen bonding involving the inner oxygen atoms lining the crown ether-like pore shown in Figure 26.



Figure 26: a) Space-filling representation of $\{W_{72}Fe_{30}\}$ with its pores plugged by $[NMe_4]^+$ cations. b) Ball and stick representation of the $[NMe_4]^+$ -plugged pore. Color code: W, green; Fe, orange; N, blue; O, red and H, white. (Figure reproduced from reference 118).

On the other hand, pores of larger Keplerate-type capsule were shown to be plugged in the solid state by organic guanidinium cations $[C(NH_2)_3]^{+,119}$ Even though many structural evidences demonstrate the presence of cationic guest within the pores, there is a lack of knowledges about the host-guest recognition process in solution and many questions arise from the thermodynamics contributions. Recently, Cadot *et al.* investigated thoroughly the host-guest interaction in solution between {Mo₁₃₂} and a series of inorganic and organic cations.¹⁰⁴ The authors demonstrated that the interaction between various alkylammoniums and the capsule increase with increasing the hydrophobic character in the used guest (Figure 27a). The interaction was tracked by ¹H DOSY NMR monitoring the self-diffusion coefficient of the capsule, as well as of the cation, and then allowing to extract interaction parameters between both. All the studied guests exhibit the same charge to equalize electrostatic attraction. By comparing the binding constant of different cations with the Keplerate, it was shown that as the apolar character of the guest increases, the binding constant increases, thus highlighting significant hydrophobic contribution within the host-guest interaction. This observation sheds the light on the importance of the hydrophobic effect in the host-guest interactions compared to the steric effect reported by Lehn *et al.* for the same series of alkylammoniums with [27]-crown-O₉ macrocycle. The comparison between the two effects is shown in Figure 27b.



Figure 27: a) Plot showing the variation of the self-diffusion coefficient (*D*) of different alkyammoniums as function of concentration of the Keplerate anion { Mo_{132} }. b) Correlation between LnKs and the number of the methyl substituents within $H_{(4-x)}NMe_x$ alkylammonium obtained with Keplerate or [27]-crown-O₉. (Figures reproduced from reference 104).

Furthermore, POMs have the ability to host larger entities as mentioned above with $\{Mo_{248}\}$, $\{Mo_{186}\}$ and others. Now shedding the light on a different approach in host-guest chemistry, Cronin *et al.* reported the self-templating and *in situ* assembly of a (cluster-of-clusters) based on inorganic macrocycles.¹²⁰ In their study, they demonstrated the ability of $[Mo_{24}Fe_{12}(EDTA)_{12}O_{72}]^{12}$ macrocycle noted $\{Mo_{24}Fe_{12}\}$ to entrap different POM units such as $[FeMo_6O_{18}(OH)_6]^{3-}$, $[PMo_{12}O_{40}]^{3-}$, $[P_2W_{18}O_{62}]^{6-}$ or $[Mo_{12}O_{36}(HPO_3)(H_2O)_6]^{4-}$ noted $\{FeMo_6\}$, $\{PMo_{12}\}$, $\{P_2W_{18}\}$ and $\{Mo_{12}\}$ respectively. The guest in each case occupies the center of the macrocycle stabilized by the hydrogen bonds formed between the guest and the EDTA ligand, which lines the inner side of the macrocycle. Though in the case of $\{P_2W_{18}\}$, and due to the high charge of the guest, it was found that six sodium ions participate in reducing the electrostatic repulsions between the two anionic host-guest species. In the four cases, the host-guest assemblies are arranged into a supramolecular tetrahedral cage as shown in Figure 28.



Figure 28: Mixed representation of a) $\{P_2W_{18}\}$ -centered $\{Mo_{24}Fe_{12}\}$ and b) tetrahedral arrangement of four $\{P_2W_{18}\}$ -centered $\{Mo_{24}Fe_{12}\}$ units. Color code: Mo, blue polyhedra; W, grey polyhedra; Fe, green polyhedra; N, Blue sphere; P, pink polyhedra; C, white sphere and O, red sphere.

II.4. POM properties and applications

Due to their structural diversity, POMs can be employed in many applicative fields. However, their main application remains undoubtedly for catalysis. They have been exploited for years in laboratories or in industry for either homogeneous¹²¹⁻¹²³ or heterogeneous chemical catalysis^{124,125} or photo-^{126,127} and electro-catalysis.^{128,129} In fact, POMs possess many potential active sites suitable for catalysis. The oxygen atoms on the surface serve as electron donors which impart a weak basic character to the POMs surface. However, protons can be also distributed on the surface conferring superacid behavior for the heteropolyacid H₃PW₁₂O₄₀. Some metal centers display Lewis acid character due to their empty d-orbitals, hence, forming a very versatile class of compounds capable of intervening in a large number of catalytic reactions. In addition, functionalizing these POMs makes possible to provide additional complementary catalytic properties.

Though their main use remains in catalysis, POMs are of great interest in molecular magnetism or in studying remarkable electronic properties such as magnetic exchange or electronic delocalization.^{3,130,131} One of the examples representing this category is once again the well-known Keplerate cluster $\{M_{72}M'_{30}\}$ (M' = Fe^{III}, Cr^{III} or V^{IV}) shown in Figure 23a.^{132,133} Also, the term of single molecule magnet (SMM) came to light when the groups of Cronin¹³⁴ and Coronado¹³⁵ synthesized in 2008 a family of POMs with exceptional magnetic properties. The POM [(XW₉O₃₄)₂Mn₄Mn₂O₄(H₂O)₄]¹²⁻ (X = Ge or Si) synthesized by Cronin *et al.* exhibits a sandwich arrangement with a core based on six manganese atoms encapsulated between two trivacant {XW₉} units. The manganese atoms form a mixed

valence cluster (four Mn^{III} and two Mn^{II}) similar to that found in the $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ that is widely recognized for its molecular magnetic properties.^{136,137} Coronado *et al.* reported $[Ln^{III}W_{10}O_{36}]^{9-}$ (Ln = Er, Ho, etc.) that are formed by the encapsulation of atom of the lanthanides family between tow monovacant lindqvist $\{W_5\}$ units. In this case, the lanthanide is found in an anti-prismatic eight coordinated position. The peculiarity of this POM is that the magnetism no longer comes from a cluster but from a single central Ln^{III} ion, the lacunary POMs serving only as diamagnetic ligands. It therefore no longer forms a molecular magnet, but a mononuclear magnet molecule (or Single Ion Magnet).

POMs have also been studied for their applications in medicine as early as 1970s, in particular for their antiviral, antibacterial and anti-cancerous properties. Numerous studies have shown their efficiency through *in vitro* tests. However, rarely *in vivo* tests revealed the toxicity of some POMs.^{138,139} The antiviral properties of POMs have been used almost since half a century where silicotungstates were used as inhibitors for viruses as rabies, rubella, polio, leukemia, etc.).^{140,141} POMs even showed their efficiency against HIV (Human Immunodeficiency Virus) with $[NaSb_9W_{21}O_{86}]^{18}$ known as HPA-23 (see Figure 29a). Unfortunately, the *in vivo* tests were inconclusive and do not allowed to develop further this class of biologically active drugs.¹⁴² On the other hand, POMs developing weak activity against viruses were found to be active against cancerous tumors. In particular, heptamolybdate $[Mo_7O_{24}]^{6}$ shown in Figure 29b exhibited strong anti-cancer activity in mice against several tumors (sarcoma, breast cancer, colon cancer, lung cancer, etc.). Studies on $[Mo_7O_{24}]^{6}$ biological activity showed inhibition of the tumor's growth while the origin of the biological mechanisms is still not clear yet.¹⁴³



Figure 29: Mixed representation of: a) [NaSb₉W₂₁O₈₆]¹⁸⁻ and b) [Mo₇O₂₄]⁶⁻. Color code: W, grey; Mo, blue; Sb, aqua; Na, green and O, red.

Few other interesting properties of POM have been reported recently such as Awaga's work using POM clusters as active electrode materials in Lithium Ion Batteries (LIBs) in which the Keggin type POM $[PMo_{12}O_{40}]^{3-}$ is able to act as electron sponge storing 24 electrons (see Figure 30 for a schematic interconversion between both charged and discharged states).³⁶ In the discharged state, the clusters negative charge increases formally to 27- as a result in the reduction of the 12 metallic centers from Mo^{VI} to Mo^{IV} with the concomitant formation of Mo-Mo bonds within the four {Mo₃O₁₃} triads and the subsequent contraction of the cluster's size due to shortening of the Mo-Mo distance.



Figure 30: Ball and stick representation of charged $[PMo_{12}O_{40}]^{3-}$ and discharged $[PMo_{12}O_{40}]^{27-}$ showing the change in the structure while charging and discharging the Keggin-type anion. (Figure reproduced from reference 36).

Recently, Wu *et al.* reported on the synthesis of a soft single layer ionic organicinorganic framework to be exploited as a membrane for sieving molecules and nanoobjects.¹⁴⁴ Their work was based on well-known organic host-guest using cyclodextrins as cavitand combined with POM chemistry. Wu's group used the Keggin type anion $[PW_{11}VO_{40}]^{4-}$ as nodes with bolaform Azo-Tr/TeEG.2Br molecules exhibiting two cationic heads azobenzene (Azo) connected via tri-/tetra-ethylene glycol (Tr/TeEG) that can bind to nodes on opposite sides to form the framework. Considering the anionic charge delocalized on the anionic POM, the organic cations can adjust their positions around the nodes only via minimizing steric hindrance. So a well-known host, i.e. α -cyclodextrin was used to form a pseudorotaxane cationic structure with the di-headed cation to provide the suitable steric guidance around the POM nodes. In the presence of the cationic pseudo-rotaxane, the POM nodes are expected to reticulate leading to an unusual hybrid supramolecular framework as presented in Figure 31. After further analyses (TEM and powder X-ray diffraction), it was determined that the components self-arrange to form a two dimensional single layer POMlocked polyrotaxane with square pores. The latter has been used to fabricate and design nanoporous membranes that have shown their high efficacy and size-selectivity in the separation of semiconductor CdTe quantum dots.



Figure 31: Schematic representation of the 2D supramolecular framework constructed from an assembly of the Keggin $[PW_{11}VO_{40}]^4$ and the cationic molecules (Azo-Tr/TeEG). Color code: blue, spheres $[PW_{11}VO_{40}]^4$; yellow sticks, (Azo-TrEG)²⁺; skyblue rings, α -CD. (Reproduced from reference 144).

III. Conclusion and outlook

Exploring the supramolecular properties of POMs or exploring influence of changing their composition has been and still attracts a great deal of attention with regard to emerging new properties. The versatile POMs system has revealed great potential to act as either host or guest depending on the supramoleular system. In addition to the expected electrostatic effect, interaction of POMs with apolar cationic guest is favored by significant hydrophobic contribution arising probably from desolvation and polar solvent (water) reorganization. Chapter 2 aims to present results of changing the composition of some prominent POMs seeking the isolation of new compounds with enhanced properties compared to their parent. Chapter 3 is dedicated to study primary organic-inorganic host-guest noncovalent interactions between POMs and cyclodextrines through a set of methods specific for solution investigations (NMR spectroscopy, ITC, XAS) or solid state characterization (X-ray diffraction analysis). These studies reveal to be of primary importance to understand the formation of hybrid materials containing POMs, y-cyclodextrins and octahedral clusters, promising as functional materials in many modern applications. Chapter 4 is devoted to present extraordinary non-conventional architectures based on the combination of the work previously presented in chapters 2 and 3.

IV. References

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Chapter II- Mo/W regioselectivity within mixed pentagonal building blocks in giant polyoxometalates:

I. Pentagonal transferable motifs from {Mo(Mo)₅} to {W(W)₅} and in between

Over centuries and since their first encounter with large molecules, scientists have always been overwhelmed by their astonishing structures and capabilities. After crossing the molecule boundary, chemists now can fabricate, construct and design functional devices on molecular nano-objects scale.¹ Polyoxometalate (POM) provides unrivalled range of architectures in the field of inorganic chemistry that facilitates supplying more sophisticated multifunctional materials for the ever-increasing demand in rapidly progressing domains as water oxidation,² alkene oxidation³ and photochemical decomposition.⁴ A class of molecular objects lying in this category shares an important structural feature, such as the transferable pentagonal building block $[MM_5O_{21}]^{6-}$ noted $\{M(M)_5\}$, shown in Figure 1.



Figure 1: (a) Ball and (b) stick and polyhedral representations of the $[MM_5O_{21}]^{6-}$ unit (noted $\{M(M_5)\}$).

In the POM chemistry, this unit was first witnessed in a discrete structure namely the Krebs anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, abbreviated $\{Mo_{36}\}$ (Figure 2a),⁵ and it came back to light around mid-1990s when Müller *et al.* reported the isolation and the first structural description of one of the molybdenum blues family $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ $\{Mo_{154}\}$ (Figure 2b) containing fourteen $\{Mo(Mo)_5\}$ units in its metal-oxo framework. More $\{Mo(Mo)_5\}$ containing structures were revealed with the discovery of the spheroidal hollow anion $[Mo_{132}O_{372}(CH_3CO_2)_{30}(H_2O)_{72}]^{42-}$ $\{Mo_{132}\}$ (Figure 2c).⁶ This transferable pentagonal unit was also found in other structures such as $\{H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ $\{Mo_{57}\}$,⁷ $[Mo_{176}O_{528}H_{16}(CH_3OH)_{17}]^{16-}$ $\{Mo_{176}\}$,⁸ $[Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$ $\{Mo_{368}\}$ (Figure 2d),⁹ and many more as previously mentioned in chapter 1. For almost thirty years, the composition

of this pentagonal motif was dominated by molybdenum (VI) as metallic component and no example of any pentagon-containing structure was ever reported with other elements. This fact stood still until Müller *et al.* reported a Telerate-type structure comprised of twelve tungsten-based pentagonal building units linked together by 30 usual linkers {Mo₂O₄} to give the formula [(WW₅O₂₁)₁₂(Mo₂O₄)₃₀(CH₃CO₂)₃₀(H₂O)₇₂]⁴²⁻¹⁰



Figure 2: Polyhedral representation of some structures containing the pentagonal motif $[MM_5O_{21}]^{6-}$ noted $\{M(M)_5\}$: a) $\{Mo_{36}\}$, b) $\{Mo_{154}\}$, c) $\{Mo_{132}\}$ and d) $\{Mo_{368}\}$.

It was the first example of a tungsten-based motif. Other tungsten-comprising Keplerates formed with the sulfurated cationic dimer $\{Mo_2O_2S_2\}^{2+}$ and the monomeric Fe³⁺ or VO³⁺ linkers were reported later on.¹¹⁻¹³ $\{W(W)_5\}$ made one more appearance when Cronin *et al.* reported several structures containing complete and defect pentagonal motifs with formulae $\{W(W)_4\}$ and $\{W(W)_3\}$.^{14,15} Cronin's group also reported the possibility of forming the pentagonal motif from niobium,¹⁶ and recently Zhang's group showed a fullerene-like structure $[Ti_{42}O_{60}\{OCH(CH_3)_2\}_4(OH)_{12}]^{6-}$ noted $\{Ti_{42}O_{60}\}$ made of titanium-based pentagonal motifs. The structure illustrated in Figure 3 shows that each pentagon shares an octahedral $\{TiO_6\}$ with every neighboring pentagon while all the equatorial oxygen atoms behaving as μ -3 junctions in the framework.¹⁷



Figure 3: Structural representation of a) $[H_{12}W_{48}O_{164}]^{28}$ showing the incomplete pentagonal motif $\{WW_4\}$, orange and green polyhedra (reproduced from reference 14), and b) fullerene-like $\{Ti_{42}O_{60}\}$ showing the $\{TiO_6\}$ polyhedra connecting neighboring pentagons. Color code: W, blue, orange and green; Ti, grey.

Mixed addenda POMs have shown quite fascinating properties compared to their regular counterparts. For example, the dimers of Keggin-type ions $[Si_2W_{18}Ta_6O_{78}Cr(H_2O)_4]^{7-1}$ built from two {SiW₉Ta₃O₄₀} units have shown photocatalytic hydrogen evolution activity.¹⁸ Many diverse examples of mixed addenda POMs and their applications can be found in literature.¹⁹⁻²³ So the aim of this work was to investigate the formation of the pentagonal motifs including both Mo (VI) and W (VI) atoms. The first to report on mixed W/Mo pentagonal {M(M)₅} building blocks were Cadot et al., showing two structures containing mixed {M'_x(M)_{5-x}} (M' = W^{VI}; M = Mo^{VI} and x = 1 or 2).²⁴ In their structure, they evidenced that the center of each pentagon is selectively occupied by a hepta-coordinated pentagonalbipyramidal W^{VI} atom surrounded by five hexa-coordinated {MoO₆} octahedra as shown in Figure 4. Actually, it was one of the rare examples showing Mo/W regioselectivity within polyoxometalate structures in contrast to all mixed metal POMs reported so far that show nearly statistical Mo/W distribution over the metallic sites. Usually synthesis of mixed POMs containing non-statistical metallic distribution over their framework, require multistep synthesis procedure using preformed lacunary-POMs as starting material. In such a situation, each step corresponds to the specific condensation of suitable addenda to be embedded in the POMs framework.¹⁸ Thus, varying composition of POMs allows tuning its physical-chemical properties such as redox, catalytic or magnetic behavior.²⁵ Now, mixed-addenda pentagonal motifs are not out of reach anymore, though it has never been reported so far that W/Mo regioselectivity at the central site of the pentagon can lead to isomerically pure $\{W(Mo_5)\}$ mixed pentagons.



Figure 4: Structural representation of $[(BW_{11}O_{39})_2(H_5Mo_{13}W_2O_{48})]^{19}$ showing the connection of two pentagonal motifs $\{WMo_5\}$ to two monovacant Keggin-type anions. Color code: W, grey; Mo, green and B, purple. (reproduced from reference 24)

In this chapter, we demonstrate that Keplerate ion can be built on mixed Mo/W pentagonal motifs $\{Mo_{6-x}W_x\}$. For x = 1, the tungsten atom occupies preferentially the central heptacoordinated position decorated by the five $\{MoO_6\}$ octahedra. Such a result means that in these conditions, the polycondensation of molybdate and tungstate ions correspond to a regioselective process.

Study in solution reveals that kinetics of the Keplerates formation is directly dictated by the W/Mo ratio while theoretical calculations showed that energy of the isolated pentagons $\{Mo_{6-x}W_xO_{21}\}\$ are quite independent upon the Mo/W distribution.²⁶ Experimental and theoretical results are quite consistent with kinetically driven based regioselective process. Such results open new insights for the design of nanoscopic pentagonal-based species derived from the Krebs anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, the giant blue wheel $[Mo_{154}O_{462}(OH)_{14}(H_2O)_{70}]^{14-}$ and derivatives or others.

II. Experimental Part

II.1. Physical methods

Fourier transform infrared (FT-IR) spectra were recorded on a 6700 FT-IR Nicolet spectrometer using diamond ATR technique. ATR correction was applied to the spectra of the non-diluted samples.

Nuclear magnetic resonance (NMR) solution spectra were recorded using 5 mm o.d. tubes. ¹H NMR was measured with a Bruker Avance 400 MHz spectrometer equipped with a BBI probehead and operated at a magnetic field strength of 9.4 T. D₂O was used as the solvent. Translational diffusion measurements were performed using Bruker's "ledbpgs2s" stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy.^{27 95}Mo NMR spectra were recorded on a 900 MHz Bruker Avance III console.

Elemental analyses for C, H, N, and S content were determined by the analytical service of the CNRS at Gif sur Yvette, France, while those of W, Mo, Na, and K were obtained from analytical service of University of Reims, France.

Energy-dispersive X-ray (EDX) spectroscopy measurements were performed on a JEOL JSM 5800LV apparatus. SEM images were recorded on a JEOL model JSM-7001F microscope equipped with an EDX spectrometer using gold-coated samples and a X-Max silicon drift detector (SDD) by Oxford. The EDX spectra were acquired with a voltage acceleration of 15 kV, an acquisition time of 120 s and more than 1000 counts.

Thermal gravimetric analysis (TGA) was used to determine the water content on a Seiko TG/DTA 320 thermogravimetric balance (5 °C.min⁻¹, under O₂).

Single crystal X-ray diffraction data collections at low temperature (200 K) were carried out using a Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS bidimensional detector using a high brilliance I μ S microfocus X-ray Mo K α (λ = 0.71073 Å) monochromatized radiation. Absorption corrections were based on multiple and symmetry-equivalent reflections in the data set using the SADABS program²⁸ based on the method of Blessing.²⁹ The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.^{30,31}

Spectrophotometric studies were carried out on a Perkin Elmer Lambda 19 spectrophotometer at room temperature by using quartz cells of 1 mm path length.

X-ray Absorption Spectroscopy (XAS) including both Extended X-Ray Absorption Fine Structure (*EXAFS*) and X-ray Absorption Near Edge Structure (XANES) spectra were recorded at ROCK beamline Synchrotron SOLEIL, Saint-Aubin, France. Few milligrams of each compound were diluted in boron nitride (BN) to prepare pellets for the solid state or dissolved in distilled water then introduced into adjustable size cell. The samples (solid or solution) were later subjected to the Synchrotron beam with a <Si 111> monochromator for W L_{III}-edge at 10204 eV.

II.2. Syntheses

II.2.1. Precursor

Starting precursor $K_{2-x}(NMe_4)_x[I_2Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5] \cdot 15H_2O$ was prepared according to literature.³² Preparation of 0.3 M sodium salt of $[Mo_2O_4(H_2O)_6]^{2+}$ in HCl 4 M was adapted from preparation reported by Dolbecq *et al.*³³ All other reagents were of commercial quality and used without additional purification.

II.2.2. General synthetic method for sodium salts of sulfurated-type Keplerates

A total of (6 mmol) Na₂MO₄•2H₂O (M = Mo or W) with variable ratios (Mo_{6-x}/W_x with x = 0-6) and sodium acetate (18 g; 220 mmol) were dissolved in 60 mL of distilled water and then acidified by 43.5 mL of glacial acetic acid (725 mmol). In a separate flask, K_{2-x}(NMe₄)_xI₂Mo₁₀S₁₀O₁₀(OH)₁₀(H₂O)₅•15H₂O (2.0 g; 0.87 mmol) was hydrolyzed in HCl (15 mL, 4 mol.L⁻¹) for 15 min at 40 °C. Then, a cloudy light precipitate was filtered off to get a clear orange-red filtrate, which was quickly added to the sodium metalate solution under vigorous stirring. The pH of the resulting solution was ~ 3.5, and the solution was stirred for 15 minutes. Various ratios of sodium molybdate and sodium tungstate were introduced as follow (Mo_{6-x}W_x). In case where x = 0 or 6, slow kinetics of formation was observed and the product was observed where the solution turned turbid after exactly one minute of the addition of the {Mo₂O₂S₂} linker. Abundant quantity of product was then isolated after fifteen minutes. Products obtained were washed with ethanol and dried with ether.

 $(NMe_4)_4Na_{33}K_5[(MoMo_5O_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •150H₂O: 1.1 g, yield 50 %. IR/cm⁻¹: 1621 (ms), 1539 (m), 1481 (w), 1423 (mw), 960 (s), 929 (m), 852 (m), 790 (vs), 667 (w), 647(w), 581 (s), 450 (w). Molecular weight for C₇₆H₅₈₂K₅Mo₁₃₂N₄Na₃₃O₅₉₄S₆₀ is 26601.3 g.mol⁻¹. Elemental analysis Calc. (found): H 2.21 (2.02); C 3.43 (3.49); N 0.21 (0.20); S 7.23 (7.02). EDX atomic ratios Calc. (found): Mo/S = 2.20 (2.22); Mo/Na = 4.00 (3.95); Na/K = 6.60 (6.80). TGA: A weight loss of 15.2 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 15.0 %).

(NMe₄)₂Na₃₆K₅[(WMo₅O₂₁)₁₂(Mo₂O₂S₂)₃₀(CH₃COO)₃₀(H₂O)₇₂]•(CH₃COO)•150H₂O: 1.74 g, yield 76 %. IR/cm⁻¹: 1620 (ms), 1538 (m), 1481 (w), 1425 (mw), 959 (s), 929 (m), 852 (m), 792 (vs), 667 (w), 647 (vw), 576 (s), 451 (w). Molecular weight for $C_{70}H_{561}K_5Mo_{120}N_2Na_{36}O_{596}S_{60}W_{12}$ is 27636 g.mol⁻¹. Elemental analysis Calc. (found): H 2.05 (2.08); C 3.04 (3.25); N 0.10 (< limit of detection); S 6.96 (6.87). EDX atomic ratios Calc. (found): Mo/S = 2.00 (2.01); Mo/Na = 3.33 (3.28); Mo/W = 10.00 (8.38); Na/K = 7.2 (7.70). TGA: A weight loss of 14.4 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 14.4 %).

 $(NMe_4)_2Na_{36}K_4[(W_2Mo_4O_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •148H₂O: 2.16 g, yield 91 %. IR/cm⁻¹: 1623 (ms), 1538 (m), 1481 (w), 1423 (mw), 950 (s), 928 (m), 854 (m), 795 (vs), 667 (w), 646 (vw), 576 (s), 453 (w). Molecular weight for C₆₈H₅₅₄K₄Mo₁₀₈N₂Na₃₆O₅₉₂S₆₀W₂₄ is 28556.7 g.mol⁻¹. Elemental analysis Calc. (found): H 1.96 (1.69); C 2.86 (3.17); N 0.10 (<

limit of detection); S 6.74 (6.7). EDX atomic ratios Calc. (found): Mo/S = 1.80 (1.82); Mo/Na = 3.00 (3.02); Mo/W = 4.50 (4.71); Na/K = 9.00 (8.98). TGA: A weight loss of 14.0% between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 13.9 %).

(NMe₄)Na₄₅K₃[(W₃Mo₃O₂₁)₁₂(Mo₂O₂S₂)₃₀(CH₃COO)₃₀(H₂O)₇₂]•5(CH₃COO)•2Cl•165H₂O : 2.16 g, yield 87 %. IR/cm⁻¹: 1621 (ms), 1536 (m), 1481 (w), 1423 (mw), 944 (s), 929 (m), 854 (m), 794 (vs), 667 (w), 647 (vw), 575 (s), 450 (w). Molecular weight for $C_{74}Cl_2H_{591}K_3Mo_{96}NNa_{45}O_{619}S_{60}W_{36}$ is 30377.7 g.mol⁻¹. Elemental analysis Calc. (found): H 1.96 (1.96); C 2.93 (3.07); N 0.05 (< limit of detection); S 6.33 (6.61). EDX atomic ratios Calc. (found): Mo/S = 1.60 (1.62); Mo/Na = 2.13 (2.15); Mo/W = 2.66 (2.82); Na/K = 15.00 (13.13); K/Cl = 1.5 (1.63). TGA: A weight loss of 14.1 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 14.0 %).

 $(NMe_4)_2Na_{39}K_4[(W_4Mo_2O_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]-2(CH_3COO)-Cl-165H_2O$: 1.97 g, Yield 77 %. IR/cm⁻¹: 1621 (ms), 1537 (m), 1481 (w), 1430 (mw), 965 (m), 945(s), 857 (m), 797 (vs), 667 (w), 646 (vw), 578 (s), 453 (w). Molecular weight for C₇₂ClH₅₉₄K₄Mo₈₄N₂Na₃₉O₆₁₃S₆₀W₄₈ is 31195.3 g.mol⁻¹. Elemental analysis Calc. (found): H 1.92 (1.86); C 2.77 (3.04); N 0.09 (< limit of detection); S 6.17 (6.52). EDX atomic ratios Calc. (found): Mo/S = 1.40 (1.42); Mo/Na = 2.15 (2.18); Mo/W = 1.75 (2.09); Na/K = 9.75 (9.47); K/Cl = 4.00 (2.43). TGA: A weight loss of 13.8 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 13.7 %).

 $(NMe_4)_2Na_{37}K_3[(W_5MoO_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •160H₂O: 1.42 g, yield 54 %. IR/cm⁻¹: 1622 (ms), 1538 (m), 1481 (w), 1423 (mw), 965 (m), 945 (s), 861 (m), 799 (vs), 668 (w), 649 (vw), 578 (s), 453 (w). Molecular weight for C₆₈H₅₇₈K₃Mo₇₂N₂Na₃₇O₆₀₄S₆₀W₆₀ is 31921.5 g.mol⁻¹. Elemental analysis Calc. (found): H 1.83 (1.66); C 2.56 (2.67); N 0.09 (< limit of detection); S 6.03 (6.30). EDX atomic ratios Calc. (found): Mo/S = 1.20 (1.32); Mo/Na = 1.94 (2.00); Mo/W = 1.20 (1.50); Na/K = 12.33 (12.84). TGA: A weight loss of 13.2 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 13.1 %).

 $(NMe_4)_3Na_{35}K_3[(W_5WO_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •158H₂O: 1.57 g, yield 57 %. IR/cm⁻¹: 1622 (ms), 1536 (m), 1481 (w), 1433 (mw), 967 (m), 946 (s), 862 (m), 801 (vs), 667 (w), 650 (vw), 580 (s), 455 (w). Molecular weight for C₇₂H₅₈₆K₃Mo₆₀N₃Na₃₅O₆₀₂S₆₀W₇₂ is 32968.6 g.mol⁻¹. Elemental analysis Calc. (found): H 1.79 (1.57); C 2.62 (1.76); N 0.13 (0.18); S 5.84 (5.36). EDX atomic ratios Calc. (found): Mo/S = 1.00 (1.23); Mo/Na = 1.71

(1.64); Mo/W = 0.83 (0.72); Na/K = 11.66 (11.25). TGA: A weight loss of 12.7 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 12.6 %).

II.2.3. Synthesis of single crystals of sulfurated mixed Keplerate

$(H_2NMe_2)_{29}(NMe_4)_4Na_{11}K_2[(WMo_5O_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H2O)_{72}]\bullet 4(CH_3COO)\bullet 128H_2O:$

(NMe₄)₂Na₃₆K₅[(WMo₅O₂₁)₁₂(Mo₂O₂S₂)₃₀(CH₃COO)₃₀(H₂O)₇₂]•(CH₃COO)•150H₂O (1 g; 0.036 mmol) were dissolved in 47 mL distilled water. NMe₂H₂Cl (0.5 g; 6.11 mmol) were added under vigorous agitation, the solution was then mixed gently for 30 min provoking the precipitation of an orange red powder that was filtered without vacuum and dried in air yielding 0.34 g of final solid. The product isolated was dissolved in 15 mL of distilled water and 4 mL of acetic buffer (3.8 M AcOH; 1.1 M AcONa). Well-shaped hexagonal crystals suitable for XRD appear after two weeks yielding 0.17 g of crystalline product. IR/cm⁻¹: 1620 (ms), 1533 (m), 1479 (mw), 1442 (mw), 1418 (mw), 959 (s), 945 (m), 850 (s), 786 (vs), 667 (mw), 567 (s). Elemental analysis for C₁₄₂H₇₈₂K₂Mo₁₂₀N₃₃Na₁₁O₅₈₀S₆₀W₁₂ Calc. (found): H 2.79 (2.47); C 6.05 (6.15); N 1.64 (1.55); S 6.82 (6.52); Mo 40.81 (38.61); W 7.83 (9.62); Na 0.90 (0.69); K 0.28 (0.33). TGA: A weight loss of 12.9 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 12.8 %).

II.2.4. General synthetic method for crystalline powders of sulfurated mixed Keplerates as dimethylammonium salts

0.3 g of each mixed sulfurated compound of $\{Mo_{6-x}W_x\}$ for x = 0.5 (0.01 mmol on average) were dissolved in 20 mL of acetate buffer solution (1 M AcOH; 0.1 M AcONa) at pH 3.5, and then dimethylammonium chloride (0.1 g; 1.22 mmol) were added. The limpid orange-red solutions are allowed to stand for crystallization in open crystallizing dishes. Well-shaped crystals appear after two days, but they are not suitable for XRD as they diffract at very small angles (20 below 25 °). Crystals are isolated by filtration and dried in air.

$(NH_{2}Me_{2})_{30}(NMe_{4})_{3}Na_{11}K[(W_{2}Mo_{4}O_{21})_{12}(Mo_{2}O_{2}S_{2})_{30}(CH_{3}COO)_{30}(H_{2}O)_{72}]\bullet 3(CH_{3}COO)$

•128H₂O: IR/cm⁻¹: 1623 (ms), 1538 (m), 1478 (mw), 1442 (mw), 1418 (mw), 948 (s), 852 (s), 793 (vs), 667 (mw), 572 (s). Molecular weight for $C_{138}H_{775}KMo_{108}N_{33}Na_{11}O_{578}S_{60}W_{24}$ is 29138.4 g.mol⁻¹. Elemental analysis Calc. (found): H 2.68 (2.55); C 5.96 (5.85); N 1.59 (1.54); S 6.6 (6.33). EDX atomic ratios Calc. (found): Mo/S = 1.80 (1.83); Mo/Na = 9.81

(9.94); Na/K = 11.00 (10.82); Mo/W = 4.5 (4.35). TGA: A weight loss of 12.2 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 12.4 %).

 $(NH_2Me_2)_{32}(NMe_4)Na_8K[(W_3Mo_3O_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •128H₂O: IR/cm⁻¹: 1623 (ms), 1538 (m), 1478 (mw), 1442 (mw), 1420 (mw), 948 (s), 856 (s), 794 (vs), 717 (s), 667 (mw), 574 (s). Molecular weight for C₁₂₈H₇₅₈KMo₉₆N₃₃Na₈O₅₇₂S₆₀W₃₆ is 29891 g.mol⁻¹. Elemental analysis Calc. (found): H 2.56 (2.32); C 5.14 (5.37); N 1.55 (1.62); S 6.44 (6.6); Mo 30.81 (30.48); W 22.14 (21.75); Na 0.62 (0.6); K 0.13 (0.13). TGA: A weight loss of 11.9 % from 25 to 200 °C corresponds to hydration and coordination water (calc. 12.0 %).

$(NH_{2}Me_{2})_{29}(NMe_{4})_{3}Na_{11}K[(W_{4}Mo_{2}O_{21})_{12}(Mo_{2}O_{2}S_{2})_{30}(CH_{3}COO)_{30}(H_{2}O)_{72}] \bullet 2(CH_{3}COO)$

•108H₂O: IR/cm⁻¹: 1627 (ms), 1538 (m), 1479 (mw), 1442 (mw), 1421 (mw), 948 (s), 860 (s), 794 (vs), 713 (s), 667 (mw), 574 (s). Molecular weight for $C_{134}H_{724}KMo_{84}N_{32}Na_{11}O_{556}S_{60}W_{48}$ is 30782.8 g.mol⁻¹. Elemental analysis Calc. (found): H 2.37 (2.34); C 5.23 (5.48); N 1.46 (1.55); S 6.25 (6.65). EDX atomic ratios Calc. (found): Mo/S = 1.40 (1.46); Mo/Na = 7.63 (8.42); Mo/W = 1.75 (2.15); Na/K = 11.00 (11.68). TGA: A weight loss of 10.8 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 10.5 %).

 $(NH_2Me_2)_{30}(NMe_4)Na_{10}K[(W_5MoO_{21})_{12}(Mo_2O_2S_2)_{30}(CH_3COO)_{30}(H_2O)_{72}]$ •108H₂O: IR/cm⁻¹: 1627 (ms), 1538 (m), 1478 (mw), 1445 (mw), 1419 (mw), 945 (s), 863 (s), 798 (vs), 667 (mw), 578 (s). Molecular weight for C₁₂₄H₇₀₂KMo₇₂N₃₁Na₁₀O₅₅₂S₆₀W₆₀ is 30782.8 g.mol⁻¹. Elemental analysis Calc. (found): H 2.37 (2.34); C 5.23 (5.48); N 1.46 (1.55); S 6.25 (6.65). EDX atomic ratios Calc. (found): Mo/S = 1.2 (1.33); Mo/Na = 7.20 (8.03); Mo/W = 1.20 (1.58); Na/K = 10.00 (9.89). TGA: A weight loss of 10.2 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 10.3 %).

II.2.5. General method for oxo-type Keplerates synthesis

 $Na_2MO_4 \cdot 2H_2O$ (M = Mo or W) (3 mmol) and sodium acetate (9 g; 110 mmol) were dissolved in 30 mL of distilled water and then acidified by 22 mL of glacial acetic acid (366 mmol). The sodium salt of $[Mo_2O_4(H_2O)_6]^{6+}$ (7.5 mL) was quickly added to the metalate solution under vigorous stirring. The pH of the resulting solution was ~3.5, and the solution was stirred for 15 minutes. Various ratios of molybdenum and tungsten were introduced as follow ($Mo_{6-x}W_x$). In case where x = 0, slow kinetics of formation was observed and the product was isolated as powder after five days. While for x = 1-6, faster formation of the $\{Mo_2O_4\}$ linker, and abundant quantity of product was isolated after 15 minutes. Products obtained were washed with ethanol and dried with ether. **Na**₄₂[(**MoMoO**₂₁)(**Mo**₂**O**₄)₃₀(**CH**₃**COO**)₃₀(**H**₂**O**)₇₂]•137**H**₂**O**: 0.86 g, yield 79 %. IR/cm⁻¹: 1621 (ms), 1548 (s), 1450 (m), 1420 (w, sh), 970 (s), 934 (m, sh), 853 (s), 792 (vs), 726 (s), 629 (m), 567 (s), 512 (w), 463 (w). Molecular weight for C₆₀H₅₀₈Mo₁₃₂Na₄₂O₆₄₁ is 25270.6 g.mol⁻¹. Elemental analysis Calc. (found): H 2.04 (2.33); C 2.87 (2.92). EDX atomic ratios Calc. (found): Mo/Na = 3.14 (2.99). TGA: A weight loss of 14.9 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 15.0 %).

Na₄₂[(**WMo**₅**O**₂₁)(**Mo**₂**O**₄)₃₀(**CH**₃**COO**)₃₀(**H**₂**O**)₇₂]•4**NaCl**•137**H**₂**O**: 0.96 g, yield 85 %. IR/cm⁻¹: 1625 (ms), 1544 (s), 1452 (m), 1420 (w, sh), 966 (s), 933 (s, sh), 853 (s), 798 (vs), 726 (s), 629 (m) 566 (s), 512 (w), 470 (w). Molecular weight for $C_{60}Cl_4H_{494}Mo_{120}Na_{46}O_{634}W_{12}$ is 26280.5 g.mol⁻¹. Elemental analysis Calc. (found): H 1.94 (2.05); C 2.73 (2.88). EDX atomic ratios Calc. (found): Mo/W = 10.00 (10.14); Mo/Na = 2.60 (2.21); Na/Cl = 11.5 (11.63). TGA: A weight loss of 8.7 % between 25 and 100 °C corresponds to hydration water molecules (calc. 8.9 %).

Na₄₂[(W₂Mo₄O₂₁)(Mo₂O₄)₃₀(CH₃COO)₃₀(H₂O)₇₂]•9NaCl•12(CH₃COONa)•108H₂O: 1.09 g, yield 93%. IR/cm⁻¹: 1630 (ms), 1547 (s), 1448 (m), 1420 (m), 964 (s), 933 (m, sh), 853 (s), 797 (vs), 726 (s), 629 (w), 567 (s), 512 (w), 464 (w). Molecular weight for C₈₄Cl₉H₄₈₆Mo₁₀₈Na₆₃O₆₃₆W₂₄ is 28215.8 g.mol⁻¹. Elemental analysis Calc. (found): H 1.81 (1.85); C 3.55 (3.33). EDX atomic ratios Calc. (found): Mo/W = 4.50 (4.89); Mo/Na = 1.71 (1.73); Na/Cl = 7.00 (7.04). TGA: A weight loss of 10.7 % between 20 and 200 °C corresponds to hydration and coordination water molecules (calc. 11.5 %).

Na₄₂[(**W**₃**Mo**₃**O**₂₁)(**Mo**₂**O**₄)₃₀(**CH**₃**COO**)₃₀(**H**₂**O**)₇₂]•108**H**₂**O**: 1.01 g, yield 88 %. IR/cm⁻¹: 1635 (ms), 1545 (s), 1445 (m, sh), 1420 (m), 961 (s), 933 (m, sh), 857 (m), 801 (s), 727 (s), 636 (2), 567 (s), 512 (w), 465 (w). Molecular weight for C₆₀H₄₅₀Mo₉₆Na₄₂O₆₁₂W₃₆ is 27760.3 g.mol⁻¹. Elemental analysis Calc. (found): H 1.63 (1.90); C 2.60 (2.48). EDX atomic ratios Calc. (found): Mo/W = 2.66 (2.95); Mo/Na = 2.28 (2.05). TGA: A weight loss of 10.9 % from 20 to 200 °C corresponds to hydration and coordination water molecules (calc. 11.7 %).

Na₄₂[(**W**₄**Mo**₂**O**₂₁)(**Mo**₂**O**₄)₃₀(**CH**₃**COO**)₃₀(**H**₂**O**)₇₂]•5(**CH**₃**COONa**)•128**H**₂**O**: 1.04 g, yield 85 %. IR/cm⁻¹: 1633 (ms), 1547 (vs), 1445 (s), 1420 (m, sh), 966 (s), 939 (m, sh), 860 (s), 802 (vs), 729 (s), 640 (m), 570 (s), 515 (w), 471 (w). Molecular weight for $C_{70}H_{505}Mo_{84}Na_{47}O_{642}W_{48}$ is 29585.7 g.mol⁻¹. Elemental analysis Calc. (found): H 1.57 (1.89); C 2.50 (2.63). EDX atomic ratios Calc. (found): Mo/W = 1.75 (1.91); Mo/Na = 1.78 (1.56). TGA: A weight loss of 11.0 % between 20 and 200 °C corresponds to hydration and coordination water molecules (calc. 11.1 %).

Na₄₂[(**W**₅**MoO**₂₁)(**Mo**₂**O**₄)₃₀(**CH**₃**COO**)₃₀(**H**₂**O**)₇₂]•8(**CH**₃**COONa**)•125**H**₂**O**: 1.03 g, yield 81 %. IR/cm⁻¹: 1629 (ms), 1548 (s), 1444 (m), 1421 (m, sh), 965 (s), 937 (m, sh), 860 (m, sh), 804 (s), 730 (s), 643 (w), 572 (s), 513 (w), 469 (w). Molecular weight for $C_{76}H_{508}Mo_{72}Na_{50}O_{645}W_{60}$ is 30832.7 g.mol⁻¹. Elemental analysis Calc. (found): H 1.66 (1.98); C 2.96 (2.93). EDX atomic ratios Calc. (found): Mo/W = 1.20 (1.41); Mo/Na = 1.44 (1.44). TGA: A weight loss of 11.0 % between 20 and 200 °C corresponds to hydration and coordination water molecules (calc. 11.5 %).

Na₃₇[(W₅WO₂₁)(Mo₂O₄)₃₀(CH₃COO)₂₅(H₂O)₈₂]•108H₂O: 0.97 g, yield 76 %. IR/cm⁻¹: 1634 (ms), 1548 (s), 1445 (m), 1421 (m, sh), 1336 (mw), 966 (s), 937 (m, sh), 850 (m, sh), 806 (s), 732 (s), 574 (s), 513 (w), 469 (w). Molecular weight for $C_{50}H_{455}Mo_{60}Na_{37}O_{612}W_{72}$ is 30695 g.mol⁻¹. Elemental analysis Calc. (found): H 1.49 (1.60); C 1.96 (1.89). EDX atomic ratios Calc. (found): Mo/W = 0.83 (0.91); Mo/Na = 1.62 (1.49). TGA: A weight loss of 10.6 % from 20 to 200 °C corresponds to hydration and coordination water molecules (calc. 11.1 %).

II.2.6. Synthesis of mixed blue wheel

Na₁₆[Mo₁₄₀W₁₄O₄₆₂H₁₄(H₂O)₇₀]•2Cl•120H₂O (method 1): The synthesis procedure is inspired by the protocol followed by Müller *et al.* **for Na₁₄[Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀]•xH₂O.³⁴ Na₂MoO₄•2H₂O (2.42 g; 10 mmol) and Na₂WO₄•2H₂O (0.33 g; 1 mmol) were dissolved in 10 mL of distilled water. Then, Na₂S₂O₄ (0.2 g; 1.15 mmol) was added (color changes slowly from colorless to light yellow). 30 mL of 1 M hydrochloric acid were immediately added into the solution (color changes directly to dark blue), leading to pH 0.9. The solution is stirred for 10 minutes then allowed to stand for crystallization in a closed flask. Three weeks later a mixture of deep blue crystals (suitable for X-ray diffraction) is formed together with nonsoluble blue powder. The isolated mixture was dissolved and filtrated. The filtrate was allowed to evaporate and the pure product was collected as crystals by filtration. The isolated mass, 248 mg, corresponds to a 13% yield based on molybdenum. IR/cm⁻¹: 1620 (ms), 995 (mw), 975 (m), 910 (mw), 872 (w), 818 (vw), 627 (w), 547 (w). Molecular weight for Cl₂H₃₉₄Mo₁₄₀Na₁₆O₆₅₂W₁₄ is 27273 g.mol⁻¹. EDX atomic ratios Calc. (found): Na/Cl = 8.00 (7.23); Mo/Na = 8.75 (8.30); Mo/W = 10.00 (10.92). TGA: A weight loss of 12.5 % between 25 and 200 °C corresponds to hydration and coordination water molecules (calc. 12.5 %).**

 $(NH_4)_{15}Na_2[Mo_{140}W_{14}O_{462}H_{14}(H_2O)_{70}] \cdot 3Cl \cdot 120H_2O$ (method 2): $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1.76 g; 1.428 mmol) and $Na_2WO_4 \cdot 2H_2O$ (0.33 g; 1 mmol) were dissolved in 10 mL of distilled water, and $Na_2S_2O_4$ (0.2 g; 1.15 mmol) was added (color changes slowly from colorless to light yellow-green). 30 mL of 1 M hydrochloric acid were immediately added into the solution (color changes directly to dark blue), leading to pH 0.9. The solution is stirred for 10 minutes. A large amount of precipitate is formed that was filtrated and then the filtrate was allowed to stand for crystallization in a closed flask. Three days later crystals appear. The product isolated by filtration and dried in air had comparable composition (EDX) and IR fingerprint observed for method (1) product. The isolated mass, 274 mg, corresponds to a 14% yield based on molybdenum. IR/cm⁻¹: 1620 (ms), 1415 (mw), 991 (m), 974 (m), 909 (w), (w). 871 817 (vw), 628 (w), 545 Molecular (mw), weight for Cl₃H₄₅₄Mo₁₄₀N₁₅Na₂O₆₅₂W₁₄ is 27257.2 g.mol⁻¹. Elemental analysis Calc. (found): H 1.68 (1.55); N 0.77 (0.85); Mo 49.28 (48.92); W 9.44 (9.01); Na 0.17 (0.21). EDX atomic ratios Calc. (found): Na/Cl = 0.66 (0.74). TGA: A weight loss of 12.6 % between 25 and 200 $^{\circ}$ C corresponds to hydration and coordination water molecules (calc. 12.5 %).

II.2.7. Synthesis of mixed Krebs anion

K₈[**Mo**₃₂**W**₄**O**₁₁₂(**H**₂**O**)₁₆]•36**H**₂**O**: K₂MoO₄ (0.425 g; 1.77 mmol) and Na₂WO₄•2H₂O (0.09 g; 0.276 mmol) were dissolved in 10 mL of distilled water at 80°C. Acidifying gradually with 10 mL of 0.4 M nitric acid, lead to pH 1.2. The solution turned cloudy after few minutes, and then mixed for 30 minutes at 80 °C. Filtration was done when the solution reached room temperature to remove the dispersed particles, followed by another filtration after one hour. The resulting filtrate was allowed to stand for crystallization. One day later, rhombus-like crystals suitable for X-ray diffraction were formed. The isolated mass, 100 mg, corresponds to a 28% yield based on molybdenum. IR/cm⁻¹: 1624 (ms), 1405 (mw), 1341 (mw), 980 (s), 952 (ms), 915 (mw), 875 (s), 850 (mw), 787 (mw), 695 (mw), 624 (mw), 565 (mw). Molecular weight for H₁₀₄K₈Mo₃₂O₁₆₄W₄ is 6846.99 g.mol⁻¹. Elemental analysis Calc. (found): Mo 44.84 (45.21); W 10.74 (9.84). EDX atomic ratios Calc. (found): Mo/K = 4.00 (3.76); Mo/W = 8.00 (9.10). TGA: A weight loss of 13.9 % between 25 and 600 °C corresponds to hydration and coordination water molecules (calc. 13.7 %).

III. Sulfurated Keplerate ions based on mixed Mo/W pentagonal building units

III.1. Variation of Mo/W composition in the Keplerate ion

Spherical molecular oxo-clusters, namely Keplerate ions came to light in 1998 after the discovery of fullerenes in 1985,³⁵ and they attracted a great deal of attention since then.³⁶ In POM chemistry, Keplerate⁶ is the most renowned super-fullerene structure and various studies have been conducted, especially on intriguing supramolecular capacity which offers many potentiality in different domains like catalysis, biology or materials. Overall studies and related results about Keplerate-type ions³⁷ reveal that such assemblies are highly tunable and offer many possibilities for functionalization. For instance, the exchange of the inner ligands such as acetate or sulfate generally present in the as-synthesized Keplerate precursors has been widely investigated and allows properties tuning of the inner cavity such as charge density, hydrophobicity/hydrophilicity or acidity/basicity. Furthermore, changing the nature of the linker {Mo₂E₂O₂} which assembles the twelve pentagons from the fully oxo (with E =O) to the oxothio (with E = S) species softens the surface pores of the Keplerate and concomitantly reduces the apertures of the twenty {Mo₉O₃E₃} pores distributed over the spheroid surface. Watfa *et al.* clearly demonstrated that softening the pores of the capsule leads to a dramatic changes of its recognition surface properties.³⁸ In this study, we report on an additional way for modification of the Keplerate ions which consists of the changing in the metal composition of the pentagonal motifs from molybdenum (VI) to tungsten (VI) in the {Mo_{6-x}W_x} series with x = 0-6.

III.1.1. Experimental observations about the Keplerate ion formation

As mentioned in the synthetic procedures, different ratios of molybdenum and tungsten were introduced in a concentrated acetate buffer to vary the content of the pentagonal motifs in Keplerate ions as follows $\{Mo_{6-x}W_x\}$ (x = 0-6). In such conditions, the Keplerate ion is formed spontaneously in the presence of the preformed $\{Mo_2O_2S_2\}$ linker. It should be worth noting that these conditions differ slightly from those reported by Müller *et al.* who used reducing agent (generally hydrazinium sulfate) requires to produce *in situ* the Mo^V-based dimer $\{Mo_2O_4\}^{2+}$ linker. As condensation of molybdate ions occurring *via* acidobasic processes is known to proceed very fast to generate the dynamic library of building blocks, determining rate of the Keplerate ion formation should then correspond mostly to that of the dimer $\{Mo_2O_4\}$ formation. In our case, using preformed linkers, the formation of our sulfurated Keplerate ions becomes then limited to acido-basic condensation and coordination reactions able to produce the pentagonal motif and the overall $\{Mo_{132}\}$ nanocapsule according to symmetry-driven self-assembly.

For x = 0, after adding the linker {Mo₂O₂S₂} to pure molybdate solution, the reaction mixture turned gradually from light to deep red, remained limpid and was allowed to stand for several days to observe the slow formation of bright red crystalline powder. Introducing tungstate ions in the ratio W/Mo = 1:5, a large amount of precipitate appeared suddenly after

about one minute of reaction. Such an observation means that presence of a few amount of tungstate (~16 %) provokes a dramatic increase of the rate of formation of Keplerate ions, according to assumption that solubility of the Keplerate salts should remain quite unaffected through the variation of the W-Mo content of the pentagons. From a practical point of view, the resulting solutions were stirred for 15 minutes then filtrated and the precipitate collected. For x = 6, after acidifying the tungstate solution with acetic acid, the solution turned cloudy. The linker {Mo₂O₂S₂} was then added and the turbid yellowish solution was filtered before it was left for several days where a yellow powder was collected by filtration. The color of the isolated products depends upon the introduced tungsten to molybdenum molar ratio. As the tungsten content introduced increases, color of the isolated solid changes gradually from bright red for x = 0 to yellow for x = 6 as shown in Figure 5.



Figure 5: x-dependent color change in the sodium salt of {Mo_{6-x}W_x}-containing sulfurated Keplerates.

III.1.2. Characterization of the Mo-W mixed Keplerate species by EDX and infrared spectroscopy

The isolated products were examined using energy-dispersive X-ray spectroscopy EDX to compare the W/Mo ratio content with those introduced. From the EDX results, the W^{VI}/Mo^{VI} ratio has been measured for each compound, assuming that each Keplerate ions contains 60 Mo^V (coming from the linkers) and 132 metal centers. As a general trend, the Mo-W composition found in the Keplerate ions matches almost perfectly the introduced W/Mo in the reaction mixture. The results are graphically shown in Figure 6. Such a result is consistent with the close reactivity of tungstates and molybdates and means that in such conditions corresponding to the Keplerate formation, both should react intimately together with no kinetic or thermodynamic discrimination of one metallic species with respect to the other. It indicates also that we can tune the composition of the pentagonal motif of Keplerates as wanted, which can be very interesting for tuning the reactivity of these species.



Figure 6: $W^{VI}/(M^{VI})$ ratio (extracted from EDX) in the pentagons of the isolated products as function of the introduced W/Mo ratio in the sample batches. The straight line of 1:1 slope provides a guideline for the eye.

After verifying their content, the compounds were characterized by IR and they all showed the fingerprint of the Keplerate anion in comparison to that found in literature.³⁹ The spectra are shown in Figure 7 and the spectroscopic data summarized in Table 1.



Figure 7: Infrared spectra of Na-{ $Mo_{6-x}W_x$ }-containing sulfurated Keplerates for x = 0–6. Dashed lines represent a guide for the eye to highlight the changes taking place.

The infrared spectra of the $[\{M'_x M_{6-x}\}_{12}O_{312}S_{60}(AcO)_{30}]^{42-}$ (M' = W^{VI} and M = Mo^{VI}) compounds exhibit the typical feature of Keplerate compounds,⁴⁰ that contain the vibration bands corresponding to the v(COO) for asymmetric and symmetric modes of the coordinated acetate ligands observed in the ranges 1540-1535 and 1430-1420 cm⁻¹ respectively, as well as the vibrations corresponding to the metal-oxo framework of the Keplerate ions observed in the spectral region below 1100 cm⁻¹. These later are roughly attributed to the stretching vibrational modes involving the metal-terminal oxygen double bond v(Mo=O) and the bridging Mo-O-Mo group. It should be mentioned that all the spectra contain a weak absorption at 1481 cm⁻¹ attributed to the v(C-N) stretching mode of some traces of NMe₄⁺ counter-cations, coming from the $\{Mo^VO_2S_2\}$ -based precursor. As observed in the IR spectra shown in Figure 7, the shape of the spectra remains quite unchanged whatever the W/Mo ratio in the pentagons indicating that all the compounds $\{Mo_{6-x}W_x\}$ should retain the archetypical structure of the $\{M_{132}\}$ Keplerate ions. Furthermore, the wavenumber of $\nu(CO)$ vibrational modes appear almost unaffected with the increase of the W content. Such a result could be expected since the thirty acetate ligands are generally coordinated to the $\{Mo_2O_2S_2\}$ linkers and should not interact with the metal atoms belonging to the pentagons. On the contrary, the vibrations arising from the metal-oxo framework display some significant differences in relationship with the Mo-W content. For instance, the shape of the v(M=O) changes significantly as the W content increases and can be interpreted as an decrease of the wavenumber of the v(M=O) from about 962 cm⁻¹ for x = 0 to 946 cm⁻¹ for x = 6. Interestingly, opposite trends are observed on the bridging vibrations, which undergo an increasing wavenumber as W content increases (see Table 1).

This observation could be due to a better $d\pi$ - $p\pi$ overlap between the W and O atoms that involve more diffuse 5*d* orbitals centered on W than those of the Mo centers. As a consequence of the reinforcement of the M=O axial bonds, the equatorial W-O bridging bonds could be weakened in agreement with the experimental infrared data. In conclusion, these infrared result show that all compounds of the {Mo_{6-x}W_x} series retain the structure of the {M₁₃₂} Keplerate-type anion. Furthermore, analysis of the W-Mo content reveals that molybdate and tungstate ions react intimately to be included together within the {M₁₃₂} framework and to produce a {Mo_{6-x}W_x} series wherein x varies monotonously from x = 1 to x = 6.

compound	wavenumber (cm ⁻¹)					
	δ(О–Н)	δ(С–Н)	v(C-O)	$\nu(M=O)$	ν (M-O-M)	non attributed
{Mo ₆ }	1621(<i>m</i>)	1481(w)	1539(<i>m</i>)	960(s)	852(<i>m</i>)	667(w); $647(w)$
			1423(<i>m</i> , <i>br</i>)	929(m, sh)	790(<i>vs</i>)	581(s); $450(w)$
{WM05}	1620(<i>m</i>)	1481(w)	1538(<i>m</i>)	959(s)	852(<i>m</i>)	667(w); 647(vw)
			1425(<i>m</i> , <i>br</i>)	929(m, sh)	792(<i>vs</i>)	576(s); $451(w)$
$\{W_2Mo_4\}$	1623(<i>m</i>)	1481(w)	1538(<i>m</i>)	950(<i>s</i>)	854(<i>m</i>)	667(w); $646(vw)$
			1423(<i>m</i> , <i>br</i>)	928(<i>m</i> , <i>sh</i>)	795(vs)	576(s); $453(w)$
{W ₃ Mo ₃ }	1621(<i>m</i>)	1481(w)	1536(<i>m</i>)	944(<i>s</i>)	854(<i>m</i>)	667(w); $647(vw)$
			1423(<i>m</i> , <i>br</i>)	929(m, sh)	794(<i>vs</i>)	575(s); $450(w)$
$\{W_4Mo_2\}$	1621(<i>m</i>)	1481(vw)	1537(m)	965(m, sh)	857(<i>m</i>)	667(w); $646(vw)$
			1430(m, br)	945(s)	797(vs)	578(s); $453(w)$
(1 ())	1 101 ()	1500()			
{W5M0}	1622(m)	1481(w)	1538(<i>m</i>)	965(<i>m</i> , <i>br</i>)	861(<i>m</i>)	668(w); $649(vw)$
			1423(m, br)	945(s)	799(<i>vs</i>)	578(s); 453(w)
(1117)	1600()	1401()	1526()	$0(7(\dots, 1))$	9(2(m))	(67(m) + 650(m))
{ vv ₆ }	1622(m)	1481(W)	1330(m)	96/(m, sh)	802(m)	007(w); 000(vw)
			1433(m, br)	946(<i>s</i>)	801(<i>vs</i>)	580(s); $455(w)$

Table 1. Infrared data of the sodium salts of the mixed W/Mo Keplerate ions $Na-\{Mo_{6-x}W_x\}$, with x = 0-6.

s = strong; m = medium; w = weak; sh = shoulder; br = broad; vs = very strong; vw = very weak.

III.1.4. Solution study by NMR spectroscopy

• 400 MHz ¹H NMR. All 1D ¹H NMR spectra of the sulfurated { $Mo_{6-x}W_x$ } compounds have been recorded from 3 x 10⁻³ mol.L⁻¹ D₂O solutions in the sodium salt form. They exhibit two sets of resonances corresponding to acetates either coordinated inside the sphere within the range ~0.5-0.9 ppm, or freely solvated in solution at ~1.9 ppm consistent with that reported for typical { Mo_{132} } Keplerates.^{10,39} This observation reflects the equilibrium occurring in solution between the coordinated and free acetates as evidenced for similar compounds.^{39,41} Besides, the presence of three ¹H NMR resonances observed for the inner acetates in { Mo_{132} } capsule have been already reported and interpreted as internal equilibria between different mode of coordination for acetate ligands, either at the { $Mo_2O_2S_2$ } linkers, spanning the { $Mo_2O_2S_2$ } linkers and the pentagons or at the pentagons (see Figure 8). Herein, an intriguing trend is observed in the ¹H NMR spectra where the absolute intensity of lines assigned to coordinated acetates and their linewidths are directly correlated to the W/Mo ratio within the pentagons. As the tungsten content in the pentagon increases, the intensity of these peaks decreases while their linewidths increase leading to broader peaks for the { W_6 } compound as illustrated in Figure 9. The loss in signal integration of these resonances up to ca. 80% is
associated to their extreme line broadening because the signal area of the free solvated acetates (δ 1.9 ppm) did not show any substantial increase with increasing the W content. Then, the ¹H NMR resonances of the coordinated acetates appear highly sensitive to W/Mo composition of the pentagonal motif. This observation could be explained through different ways. In one hand, the W-Mo distribution within the $\{M_{132}\}$ capsule should break the symmetry of the capsule and concomitantly a large distribution of chemical shift should arise in relationship with the chemical environment of the acetate ligands in the vicinity of the pentagonal motif. On the other hand, the presence of W atoms could also influence the binding constants of the acetate ligand in the different situations as described in Figure 8, where it can be bound to the $\{Mo_2O_2S_2\}$ linkers, spanning the linker and the pentagons or directly bound to the pentagon. Furthermore, the presence of tungsten atoms could also affect the dynamic of the exchange process, leading to a significant increase of the linewidths related to the inner acetate resonances. This phenomenon should be dependent on the binding constants but also on the strength or the lability of the bonds between the $\{Mo_2O_2S_2\}$ linkers and the $\{Mo_{6-x}W_x\}$ pentagons. In previous papers, Müller *et al.* demonstrated that the exchange process of bulky ligands between inward and outward situations could be explained by a successive breaking and reformation of constitutive bonds of the capsule.⁴¹ In our case, the presence of W atoms should change significantly the strength of these bonds and then affect dramatically the exchange process.



Figure 8: Schematic representation of the different sites of the inner acetates coordinated to the inward face of the metal-oxo framework of the capsule.



Figure 9: ¹H NMR for Na-{ $Mo_{6-x}W_x$ }-containing sulfurated Keplerates showing coordinated and solvated acetate ligands.

• 900 MHz ¹H NMR. Comparing ¹H high field NMR of the two mixed Keplerate series, i.e. the oxo and the sulfurated, shows the effect of the linker on the signals of the coordinated acetates (Figure 10). As demonstrated by Müller et al., the classical oxo Keplerate $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, exhibits two different signals for coordinated acetates: a major peak assigned to acetates coordinated to the likers $\{Mo_2O_4\}$, type I in Figure 8, and a minor one for acetates coordinated on the pentagonal motif, type III in Figure 8.⁴¹ Interestingly, as represented in Figure 9, the presence of sulfur in the linker gives a small extra peak. It is well-known that the $\{Mo_2O_2S_2\}$ linker displays higher lability of coordinated acetates and then a decreased stability constant compared to its oxo analogous.⁴¹ As a consequence, further coordination modes can be expected, like those of acetate ligands bridging the $\{Mo_2O_2S_2\}$ linker and the pentagon (type II in Figure 8) as observed in the compound $[H_8M_{084}]S_{48}O_{188}(H_2O)_{12}(CH_3COO)_{24}]^{32}$ published by our group in 2012.³⁹ Interestingly, the introduction of W^{VI} atoms within the pentagons increases the percentage of acetates coordinated to the pentagon when compared to that coordinated to the di-nuclear linker, especially for the sulfurated species. Indeed, the 900 MHz spectra evidence at least 5 coordination modes for acetates among the all possible combinations of coordinated neighboring atoms within the pentagons, and between the pentagons and the linkers.



2.5 2.0 1.5 1.0 0.5 0.0 3.5 3.0 2.5 1.0 0.5 0.0 ppm 2.0 1.5 Figure 10: 900 MHz High field ¹H NMR for Na-{Mo_{6-x}W_x}-containing Keplerates for x = 0, 1 or 3 in oxothio- (left) and oxo-compounds (right).

• Variable temperature ¹H NMR. To investigate further the dynamic behavior and then understand the origin of the broadening of the resonances of linked acetates, variable temperature experiments and diffusion ordered spectroscopy (DOSY) were performed. As individual resonances of linked and free acetates are distinguished, the exchange processes between coordinated and solvated species are slow in the NMR time scale. The broadening of the signals should then indicate in this case an increase of the exchange rates. Increase of temperature gives rise to two phenomena with opposite effect on the NMR linewidths (shown in Figure 11): i) the increase of the exchange rates responsible for line broadening, and ii) the decrease of relaxation rates and thus line narrowing. From these experiments, it was not easy to discriminate between both opposite processes.



Figure 11: Variable temperature ¹H NMR for Na-{WMo₅}-containing sulfurated Keplerate showing two opposite effects on the linewidth of linked acetates.

• DOSY ¹H NMR. DOSY experiments of the same series presented in Figure 9 (fixed concentration at 3 mM) provided however more useful insights. Diffusion coefficients of free and linked acetates appear dependent on Mo/W substitution in the mixed Keplerate-type capsules (see Figure 12). Variation of the self-diffusion coefficients appears quite negligible from x = 0 to 4. Above x = 4, one can see the progressive increase of diffusion coefficients for linked acetates from ca. $120 \pm 10 \ \mu m^2/s$ for x = 0-4 to $280 \pm 10 \ \mu m^2/s$ in {W₆} (x = 6). The tendency is also observed for the free acetates from ca. 265 ± 30 to $440 \pm 10 \ \mu m^2/s$ for {Mo₆} and $\{W_6\}$ respectively. This is consistent with increased mobility of both inner and outer acetates that we know are involved in exchange processes.⁴⁰ This means the broadening in the acetates linker signals (0.6–1.0 ppm) with increasing W content in the pentagonal unit is due to increased exchange rates between the different inner linked acetates. Note that resonance of free acetates did not undergo dramatic line broadening like those of inner acetates, although they are involved in a common exchange process. This could be due to an increase of the dynamic that involves strictly the inner acetates over the three linked situations shown in Figure 8. In conclusion, these results indicate that the observed broadening of the resonances of linked acetates should originate mainly from dynamic phenomena. Hence, the presence of W atoms seems to induce a remarkable enhanced lability of the acetate linkers.



Figure 12: Evolution of ¹H DOSY diffusion coefficients of free and linked acetates in Na-{ $Mo_{6-x}W_x$ }-containing sulfurated Keplerates as a function of number of W in the pentagonal unit.

• ⁹⁵Mo high field NMR. To monitor the W/Mo substitution effect on the local Mo environments within the pentagonal unit, ¹⁸³W and ⁹⁵Mo NMR were carried out. Unfortunately, we were not able to analyze the ¹⁸³W NMR spectra for such system in aqueous medium. The spectra were of very poor quality showing no clear signals. Usually giant POMs with high nuclearity, such as Keplerates, are difficult to measure by ¹⁸³W NMR probably due

to the combination of low symmetry of their structures and their slow tumbling motion causing dispersion and broadening of their signals. Figure 13 shows the results of ⁹⁵Mo highfield NMR measurements for the Na-{ $Mo_{6-x}W_x$ }. The ⁹⁵Mo NMR spectrum of the fully molybdenum Keplerate [Mo₁₃₂O₃₁₂S₆₀(CH₃COO)₃₀(H₂O)₇₂]⁴²⁻ showed a spectrum similar to that of [Mo₇O₂₄]⁶⁻ at pH 3.25 exhibiting a signal at ca. 97 ppm assigned to the isomolybdate β -Mo₈O₂₆⁴⁻, present as synthesis impurity since it is stable in the pH range of Keplerate synthesis (3-4.5).⁴² Introduction of W induces slight changes in the range 0-30 ppm as well as the appearance of a novel resonance at ca. -40 ppm that increases with increasing the W amount. This latter is assigned to $[Mo_9S_8O_{10}(OH)_{10}(H_2O)]^{2-1}$ anion (abbreviated $\{Mo_9\})^{43}$ because comparable ⁹⁵Mo NMR spectrum with similar features is obtained for this compound as shown in Figure 13. This may indicate the weak stability of mixed W-Mo oxothio-Keplerates in solution that undergo decomposition into other sub-products upon dissolution in D₂O and the difficulty to observe the Mo centers in these compounds, although long measurements (12 h accumulation) high-field ⁹⁵Mo NMR were carried out on concentrated samples. Globally, introduction of W provokes first low-field shift up to 26 ppm of the ⁹⁵Mo resonances in $\{WMo_5\}$ sample and then high-field shift to 14 ppm for $\{W_3Mo_3\}$ sample.



Figure 13: 58.67 MHz ⁹⁵Mo NMR for $\{Mo_{6-x}W_x\}$ -containing sulfurated-Keplerates, indicating the presence of impurities from side products or decomposition (see text).

Because the previous ⁹⁵Mo NMR spectra of the sulfurated compounds are not resolved enough, similar experiments were conducted on fully oxo-Keplerates to get more insights. ⁹⁵Mo The NMR spectra of the fully oxo-Keplerates, [(Mo₆₋ $_{x}W_{x}O_{21})_{12}\{MO_{2}O_{4}(CH_{3}COO)\}_{30}(H_{2}O)_{72}\}^{42}$ for x = 0-3, shown in Figure 14, exhibit comparable features in the 0 - 30 ppm range than the sulfurated analogs but signals appear narrower. Because the pentagonal units in the Keplerates should be considered as isolated motifs separated by the $\{Mo_2O_2S_2\}$ or $\{MoO_4\}$ linkers, these resonances could represent the signature of Keplerates, since the spectrum does not display any resonance that corresponds to any of the identified dissociated polyoxomolybdate species mentioned earlier. As previously witnessed for the sulfurated series, introduction of W leads to appearance of new low-field resonances. Unfortunately, the resonances can't be accurately assigned to a specific species yet.



Figure 14: 58.67 MHz ⁹⁵Mo NMR for {Mo_{6-x}W_x}-containing fully oxo-Keplerates.

III.1.5. UV-Vis characterization and Kinetic studies of Na-{Mo_(6-x)W_x} sulfurated Keplerates

Experimental observations during the synthesis showed that the kinetic of the Keplerates formation seems to be correlated directly to the tungsten content. Furthermore, the kinetic seems to govern directly the precipitation rate of the Keplerate. As the formation of the Keplerate ion in solution provokes a color change, we attempted to determine

quantitatively kinetic of the Keplerate using UV-Vis spectroscopy after characterization of electronic spectra of pure compounds in aqueous medium.

III.1.5.1. UV-Vis characterization of the Na-{Mo_(6-x)W_x} species

The molar absorption coefficients (ε) have been determined from mother solutions of 7.25 x 10⁻⁵ mol.L⁻¹ in {Mo_{6-x}W_x} (x = 0–6). From each solution, five dilutions were carried out to dispose solutions in the 1 x 10⁻⁵–7 x 10⁻⁵ mol.L⁻¹ range. The spectra were recorded in the visible region between 650 and 320 nm.

As shown in Figure 15, the spectrum of the $\{Mo_6\}$ compound exhibits two maxima at 425 and 360 nm that correspond to ligand to metal charge transfer (LMCT), $E \rightarrow Mo^V$ (E = O, S).³⁹ Moreover, the compounds appear to be stable over the concentration range as assessed by the straight line of the Beer-Lambert plots (not shown). It must be worth noting that the low-energy absorption at $\lambda = 425$ nm corresponds to the fingerprint of the sulfurated Keplerate ion, since molybdate (or tungstate) ions are colorless and that the isolated $\{Mo_2S_2O_2\}$ species give absorptions below 300 nm.⁴⁴ As the tungsten content within the pentagonal motifs increases, the intensity of the maxima at 425 and 360 nm decreases as shown in Figure 15, indicating that the electronic structure of the $\{Mo_2O_2S_2\}$ chromophore is significantly sensitive to the Mo/W composition of the pentagonal motifs. Nevertheless, the intensity of the maximum at 425 nm appears to be more affected as it almost vanishes when reaching the fully tungstate pentagons $\{W_6\}$ within the Keplerate capsule. The molar absorption coefficient ε_{425} of Keplerate ions decreases from about 200 000 to 40 000 mol.L⁻ ¹.cm⁻¹ when the molybdenum atoms of the pentagons are fully substituted for tungsten atoms. This could be due to the decrease of the basicity of oxygen atoms of the pentagonal motif linked to the Mo^V centers when Mo^{VI} atoms are substituted by W^{VI 26}.



Figure 15: UV-Vis spectra in the Na-{ $Mo_{6-x}W_x$ } sulfurated series (rigth) and variations of the molar absorption coefficient at 425 and 360 nm as function of the W content within { W_xMo_{6-x} } pentagons.

Then, the determination of the UV-Vis parameters reveals that the presence of W atoms affect significantly the electronic structure of the chomophore, mainly featured by the dramatic decrease of the visible absorptions. Besides, this study allows further UV-Vis investigations, such as kinetic study.

III.1.5.2. Kinetic study of the mixed sulfurated Keplerate formation.

UV-Vis studies of the solutions have been conducted at 425 nm, at room temperature in experimental conditions mimicking those used in the synthetic procedures. Acetate buffer solution (CH₃CO₂Na = 1.1 M and CH₃CO₂H = 3.8 M), linker {Mo₂O₂S₂} solution (0.11 M) in 4 M HCl and metalate solutions Na₂MO₄.2H₂O M = Mo or W (0.3 M) were prepared. Samples were prepared by adding 0.3 mL of the metalate mixture (following Mo_{6-x}W_x) to 4 mL of the buffer solution, followed by the addition of 0.3 mL of the linker (t = 0) and directly introducing the homogenized sample into a 0.1 mm quartz cell. The kinetics of formation was followed for 100 minutes.

The variation of the absorbance at 425 nm for 100 minutes is graphically shown in Figure 16a. The initial rate of formation was extracted and then calculated from the molar absorption coefficient found for each Keplerate ion of the $\{Mo_{6-x}W_x\}$. The initial rate, noted R° is plotted versus the W content within the pentagon (see Figure 16b). The results show an increase of the initial rate of formation of Keplerate reaching a maximum value for x ranging between 3 and 4, then the initial rate decreases abruptly for x = 6. This result clearly indicates that the presence of W atoms plays a key role in the Keplerate formation. As the color changing corresponds to the formation of the Keplerate ion, it becomes intuitive to conclude that presence of tungstate ions could favor the formation of the pentagons to some extent and then the resulting formation of the Keplerate ions through connections of the formed pentagons by the $\{Mo_2O_2S_2\}$ linkers. Such a result appears quite intriguing because it is generally admitted that condensation of tungstates is much slower than condensation of molybdate species.⁴⁵ In our case, the contrary is observed until a ratio W/Mo ~ 1. Nevertheless, as the ratio increases above 1, the initial rate decreases and reaches a value close to zero for the pure W system. This latter result becomes conventionally compared to that usually reported on the condensation of tungstates. In our case, the tungsten atom could play a determining role within the specific formation of the pentagonal unit, which differs from the usual octahedron by the presence of a heptacoordinated metal atom at the center of the pentagon. One speculative hypothesis could consider that extension of coordination from six to seven would be facilitated from a kinetic point of view with the W at the center with respect to the Mo one. Such an assumption could be justified in part by more diffuse 5d and 7s-7p orbitals of the W atom, then more available to extent coordination number linking a seventh oxygen atom.



Figure 16: a) Variation of the absorbance A at $\lambda = 425$ nm in the {Mo_{6-x}W_x} Keplerate series for 100 min and b) variation of the initial rate of formation R° as a function of the x parameter with x = number of W atom / pentagon.

III.2. Single-Crystal X-Ray diffraction analysis of {W(Mo₅)} pentagonal-based Keplerate-type anion.

Based on results previously reported showing that W/Mo selectivity was achievable at the center of the pentagon,²⁴ and on our kinetic result showing that presence of W atoms as tungstate ions could play a crucial role in the pentagon's formation, we decided to investigate structurally the Keplerate ions based on the {WMo₅} pentagons using X-ray diffraction According analysis. to the above procedures, the crude compound $(NMe_4)_2Na_{36}K_5[Mo_{120}W_{12}O_{312}S_{60}(CH_3COO)_{30}(H_2O)_{72}] \cdot (CH_3CO_2) \cdot 150H_2O$ has been reprecipitated as a dimethylammonium salt and then re-crystallized in acetate buffer. Single then characterized. They crystals were obtained and retain the formula $(H_2NMe_2)_{29}(NMe_4)_4Na_{11}K_2[Mo_{120}W_{12}O_{312}S_{60}(CH_3CO_2)_{30}(H_2O)_{72}] \bullet 4(CH_3CO_2) \bullet 128H_2O$

(noted DMA-{WMo₅}). It must worth noting that getting single-crystals suitable for X-Ray diffraction analysis remain a difficult task for the Keplerate systems. Although numerous attempts have been tried, the quality of crystallographic data of the crystal DMA-{WMo₅} remained modest somehow. Nevertheless, the structure was solved, and selected crystallographic parameters are given in Table 2. The molecular representation of DMA-{WMo₅} is presented in Figure 17.



Figure 17: Structural representation of DMA-{WMo₅} Keplerate type ion showing twelve mixed {WMo₅} pentagons connected by 30 { $Mo_2O_2S_2(ACO)_{30}$ } linkers to give the { M_{132} }-type capsule (left). Ball & stick representation of the mixed pentagons containing a W atom at the center and five Mo octahedra at the periphery (right). The vibrational thermal ellipsoid of Mo (green) and that of the W atom (grey) (80% of probability) are comparable in size and in shape giving consistency to a single W-Mo distribution over the six metallic positions of the pentagon.

Table 2. selected crystallographic parameters of the X-ray diffraction analysis of DMA-{WMo₅}.

Compound	DMA-{WMo ₅ }	Ζ	8
Formula	$C_{142}H_{782}K_2Mo_{120}N_{33}Na_{11}O_{580}S_{60}W_{12}$	$ ho_{ m calc}$, g.cm ⁻³	2.681
FW, g.mol ⁻¹	28209.7	μ (Mo K α), cm ⁻¹	0.465
<i>Т</i> , К	200	λ(Μο Κα), Å	0.71073
crystal size (mm)	0.28×0.20×0.06	θ range, deg	θ max = 19.5°, θ min = 2.2°
crystal system	orthorhombic	data collected	1203839
space group	Cmma	unique data	85325
<i>a</i> , Å	65.1435(24)	unique data I>2o(I)	49295
b, Å	65.3020(24)	no. parameters	2339
<i>c</i> , Å	44.5493(16)	$R(F)^{\mathrm{a}}$	0.482
α, deg	90	$R_w(F^2)^{\mathrm{b}}$	0.158
β , deg	90	GOF	2.22
γ, deg	90		
$V, \text{\AA}^3$	189512(12)		

III.2.1. Molecular structural description of the {W₁₂Mo₁₂₀}-Keplerate type anion (DMA-{WMo₅})

The structure of the $\{M_{132}\}$ Keplerate metal-oxo framework has been reported in numerous articles.³⁷ The present structure exhibits similar molecular arrangement, which consists of a truncated icosahedron with twelve pentagons $\{M(M_5)\}$ and twenty hexagonal pores formed by the connection of the pentagonal building units by thirty $\{Mo_2O_2S_2\}$ linkers (see Figure 17). Nevertheless, the main result of this work corresponds to the location of the twelve tungsten atoms which have been found at the center of the twelve pentagonal motifs. It should be worth noting that locations of the 12 W atoms have been directly found by the direct method. Despite the weak crystalline quality, the structure of DMA-{WMo₅} exhibits no disorder within the metal-oxo framework. Such a result is generally obtained when the space group of the Keplerate-type structure does not range in a cubic crystal system. In our case, the compound DMA-{WMo₅} crystallizes in the orthorhombic system and the structure refinement has been carried out within the *Cmma* space group. The asymmetric unit, which retains the formula { $W_8Mo_{80}S_{40}C_{22}O_{296}$ } is distributed over two Keplerate capsule while the cell contains eight { M_{132} } Keplerate-type capsules (see Figure 18).



Figure 18: Representation of the cell-packing within the DMA-{WMo₅} structure. The crystal system is orthorhombic and the cell contains eight { M_{132} } capsules a) view along the *a* axis (in the {ac} plane). b) view along the *c* axis (in the {*ab*} plane.

All the elements of the capsule have been located such as the 132 metal atoms, the sixty sulfur atoms that belong to the thirty {Mo₂O₂S₂} linkers, the 312 oxygen atoms that ensure the coordination spheres of the 132 metal atoms. Furthermore, the overall acetate ligands have been also found. It should be worth mentioning that the primary result given by the direct method allowed the location of the heaviest atoms Mo and W with the W atoms at the centers of the twelve pentagons and the 120 Mo atoms found at the periphery of the pentagon and at the metal centers of the 30 linkers. The refinements using this Mo-W distribution leads to very similar thermal ellipsoids for Mo and W (see Figure 17), meaning that electronic density of the heptacoordinated sites is quite consistent with that corresponding to tungsten W (Z = 74) rather that Mo (Z = 42). The mean principal values U₁₁, U₂₂ and U₃₃ of the anisotropic displacement parameters of W and Mo in the pentagon are given in Table 3, while the corresponding thermal ellipsoids of the metallic atoms of the pentagon are visualized in Figure 19. Furthermore, these parameters are also compared with those found for

the heptacoordinated Mo atoms (at the center of the pentagons) in the very similar structure $[Mo_{132}S_{60}(AcO)_{30}]^{42-.39}$



Figure 19: Representation of the thermal ellipsoid (80 % of the electronic density) of the metallic centres within the DMA-{ WMo_5 } structure showing the close similarity in size and shape between W and Mo. (green = Mo; grey = W).

Table 3. Main averaged anisotropic displacement parameters of the W at the center and Mo (periphery) atoms within the DMA-{WMo₅} compared to those observed for heptacoordinated Mo atoms in similar structure.³⁹

Anisotropic displacement parameters (Å ²)					
atoms	U ₁₁	\mathbf{U}_{22}	U ₃₃	reference	
W _(center)	0.09022875	0.079065	0.0688525	This work	
Mo _(periphery)	0.08811594	0.0749206	0.0700384	This work	
Mo _(center)	0.10883333	0.1269333	0.0947333	39	

Besides, we did not observe any significant change in the geometrical parameters of the heptacoordinated tungsten atoms {WO₇} compared with those observed for Mo atoms in similar situation. For instance, the interatomic distances (M-O) found for M = W or Mo are given in Table 4. Even if the W-O bonds appear quite shorter than that found in the molybdenum counterparts, these results are difficult to analyze considering the high R_1 value of the DMA-{WMo₅} structure ($R_1 = 0.158$) and the large values of the standard uncertainties for the W-O bond distances. Actually, the closest of the geometrical parameters between the W and Mo polyhedra is nicely illustrated by the high similarities between the Mo or W containing Keggin anions such as [PMo₁₂O₄₀]³⁻ and [PW₁₂O₄₀]³⁻ arrangements.^{46,47}

Table 4. Comparison of the M-O bond lengths within the $\{MO_7\}$ polyhedron (with M = Mo or W).

Bond type	Mo ^a	$\mathbf{W}^{\mathbf{b}}$
M=O	1.734(7)	1.721(10)
Equatorial	1.990(6)	2.021(12)
M-OH ₂	2.317(8)	2.229(9)

^a ref 39; ^b : this work

In conclusion, the single-crystal diffraction study of the DMA-{WMo₅} structure indicates the twelve W atoms (confirmed by elemental analysis) are located rather at the center of the twelve pentagons. Such a result demonstrate that in the case of the pentagon's formation, the co-condensation of tungstate and molybdate does not lead to a statistical Mo-W distribution as generally found for other structural type (like Keggin-type ions, for instance). Herein, for a ratio W:Mo = 1:5, co-condensation leads to a Mo/W selectivity at the heptacoordinated site. To support such an observation, we engaged many systematic studies to evidence definitely the W geometrical environment using other analytical methods. As mentioned above, ¹⁸³W or ⁹⁵Mo liquid NMR (in 400 and 900 MHz spectrometers) failed to identify clearly the central and peripheral metal atoms engaged within the Keplerate framework. ESI-mass spectroscopy could be useful to distinguish the W/Mo distribution within the { M_{132} } capsule, but the resulting ESI-mass spectra were poorly resolved with signals exhibiting very low intensity. Then, we decided to use EXAFS spectroscopy for further characterization of the tungsten atoms in its heptacoordinated environment.

III.2.2. EXAFS analysis of the W atoms at the center of the pentagon

Extended X-ray absorption fine structure (EXAFS) is a powerful tool that allows the determination of the chemical environment of a specific element in terms of the type and number of neighbors, structural disorders or interatomic distances. EXAFS has been proved to be useful technique to study structures in POMs,⁴⁸ including Keplerate-type { Mo_{132} }.⁴⁹ In fact, a total of 12 samples corresponding to the DMA and Na salts of the mixed sulfurated Keplerate { $Mo_{6-x}W_x$ } (x = 1-6) have been investigated by EXAFS (tungsten L_{III}-edge) in both solid and solution to explore the nature and the number of atoms surrounding W atoms in each case. Unfortunately, we were not able to extract and fit the data for all the samples tested (by the time this chapter was written) due to the fact that data treatment is a lengthy process. It is worth mentioning that for each compound, the spectra of the solid and liquid state are superimposed, similarly, for a specific composition when comparing the DMA and Na salts, the spectra are superimposed as well. Figure 20 displays typical tungsten EXAFS spectrum showing the L_{III}-edge used to extract the data corresponding to W coordination spheres.



Figure 20: Plot of the absorption coefficient, μx vs. incident X-ray energy for the W L-edge of a Keplerate sample. The edge energy, E_0 , as well as the XANES and EXAFS regions are denoted on the plot.

The tungsten L_{III}-edge (at 10204 eV) was used to investigate the first and second coordination spheres of the tungsten atoms in the DMA-{WMo₅}-containing Keplerate in solid state. The question we attempted to address by EXAFS is whether or not the tungsten atom occupies uniquely the central position. The raw k^3 weighted L_{III}-edge EXAFS spectrum and its corresponding fit are shown in Figure 21a. The Fourier transform shows two unique peaks around R + Δ = 1.6 Å and R + Δ = 3 Å corresponding to the overlapping W•••O shells (range of real distance 1.7-2.4 Å) and W•••Mo shell (real distance 3.3 Å), respectively. The back transformation from FT to $\chi(k)$ in the two ranges of W•••O and W•••Mo shells gave the corresponding EXAFS oscillation shown in Figure 21b. The data was then fitted with three W•••O shells and one W•••Mo shell, according to the X-ray diffraction data. Careful calculation with a fit at 1.01% ndicated that each W atom in the ring-shaped anion is coordinated by N atoms with a radius R (Å), as follow: (N; R) = (1.48; 1.71 Å), (5.35; 2.01 Å) and (1.49; 2.25 Å) oxygen atoms corresponding to W=O. Mo and W-OH₂ groups, respectively. For the second coordination sphere, each W atom is surrounded by 4.73 Mo atoms at R = 3.29 Å with a 20% uncertainty on N and 0.02 Å on R.



Figure 21: a) k^3 weighted EXAFS and b) Fourier-transform EXAFS signal of DMA-{WMo₅}-containing Keplerate in solid state. Solid line gives experimental curves and dotted lines give fitted curves. The fitted structural EXAFS parameters for the W atoms corresponding to the best agreement with the experimental data reveal to be consistent with an heptacoordinated W atom {WO₇} represented above.

The EXAFS results and those obtained from the X-Ray diffraction structural analysis are compared in Table 5.

Table 5. Comparaison of the EXAFS and XRD structural parameters of the W atoms within DMA-{ WMo_5 } Keplerate-type anion.

		N	Interatomic	distances (Å)
Neighbor type	EXAFS	XRD analysis	EXAFS	XRD
O _(terminal)	1.48	1	1.71	1.72(1)
$\mathbf{O}_{(equatorial)}$	5.35	5	2.01	2.02(2)
OH ₂	1.48	1	2.25	2.22(1)
Мо	4.73	5	3.29	3.30(1)

In conclusion, the EXAFS parameters argue in favor of a heptacoordinated site for the central W atoms ($N_{exp} = 8$ has been found while N = 7 was expected), consistent with the XRD structural determination (see Table 5) and the elemental analysis. Then, these results are of prime importance and point out some difference about condensation of tungstate versus molybdate where the former seems to extend easier the number of its first coordination shell than the second. As there exist other archetypical arrangements built upon pentagonal motifs, we decided to investigate the possibility to build a selection of pentagon-based species with the mixed pentagonal motifs {WMo₅}. Until now, these selected compounds are known as fully molybdenum species and they correspond to the Krebs anion [Mo₃₆O₁₁₂(H₂O)₁₆]⁸⁻ which contains four {Mo(Mo₅)} pentagons and to one of the member of the Mo-blue derivatives [Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀]¹⁴⁻ (abbreviated {Mo₁₅₄} hereafter) for containing fourteen {Mo(Mo₅} pentagons (see Figure 2). Formation of both compounds result from significantly different synthetic reaction schemes. The Krebs anion results from a pure acido-basic condensation of molybdenum under reducing conditions.

IV. Extension to other structural types

IV.1. Variation of Mo/W composition in the blue wheel anion forming {W₁₄Mo₁₄₀}

Müller *et al.* solved the 200 years old molybdenum blue mystery in 1996. While these Mo-blue systems were considered as oligomeric species, Müller *et al.* discovered the molecular nature of the first member of these compounds with the X-ray diffraction analysis of the wheel shaped $[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]^{n-50}$ As Mo-blue ring shaped anion contains fourteen $\{MoNO\}^{3+}$ distributed at the center of the oentagons. Later they reported a more straightforward synthesis by formal exchange of the fourteen $\{Mo(NO)\}^{3+}$ groups by $\{MoO\}^{4+}$ to give a highly crystalline compound with the formula $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ known as $\{Mo_{154}\}^{.34}$ This structure is the most renowned within the Mo-blue family, and numerous studies have been conducted to investigate its supramolecular potential or its functionalization by including different metallic atoms within its framework and thus form various derivatives.⁵¹⁻⁵³ Herein, we report a new modification for the Mo-blue wheel summarized by changing the metal composition of the pentagonal motifs from fully molybdate to tungsten-molybdenum mixed pentagon as seen for Keplerate in the $\{W(Mo)_5\}$ -containing Keplerate.

IV.1.1. Formation and composition

While the synthesis of the fully molybdate wheel { Mo_{154} } can be found in literature,³⁴ a similar approach with some adaptations was followed to synthesize the mixed counterpart [$W_{14}Mo_{140}O_{462}H_{14}(H_2O)_{70}$]¹⁴⁻ noted { $W_{14}Mo_{140}$ }. A stoichiometric ratio of a reducing agent (sodium dithionite, $Na_2S_2O_4$) is added to a mixed W-Mo metalates solution triggering the reducing process of Mo^{VI} into Mo^V , evidenced by a spectacular color change from colorless to dark-blue. The solution is then acidified with HCl 1 M to pH close to 1 forming a dark blue solution known as molybdenum blue. The main difference between the two syntheses lies in the formation of abundant insoluble material at the beginning of the synthesis and in the crystallization rate of suitable X-ray diffraction studies. Therefore, adapted procedure using ammonium molybdate as Mo source allows limiting the formation of the amorphous precipitate and getting single crystals of { $W_{14}Mo_{140}$ } in three days. EDX and elemental analysis showed the expected metal composition for the two salts of { $W_{14}Mo_{140}$ }, namely Na-{ $W_{14}Mo_{140}$ } and NH₄-{ $W_{14}Mo_{140}$ }, displaying a ratio of ten to one for Mo and W

respectively, matching the introduced W/Mo ratio in the reaction mixture. These results are consistent with those seen earlier for Keplerate.

The IR spectra of both compounds (sodium and sodium-ammonium salts of $\{W_{14}Mo_{140}\}$) showed the vibration bands corresponding to the blue wheel as shown in Figure 22 and the spectroscopic data summarized in Table 6.



Figure 22: IR spectra of: a) Na-{Mo_{154}}, b) Na-{ $W_{14}Mo_{140}$ } and c) NH₄-{ $W_{14}Mo_{140}$ }.

The infrared spectra of the three compounds contain the absorptions corresponding to the metal-oxo framework of the ring-shaped anion in the spectral region between 1100 and 400 cm⁻¹ (see Figure 22). Absorptions at 975 and 910 cm⁻¹ are attributed to the vibration of the metal-terminal oxygen bond v(M=O).⁵⁴ Other bands are roughly attributed to the bridging metal-oxygen-metal bonds. The spectrum of the ammonium salt exhibits an extra absorption at 1415 cm⁻¹ corresponding to the vibration of the N-H bond in the ammonium counter cations. Actually, the shape of the spectra remains nearly unchanged revealing that all the compounds retain the archetypical structure of the wheel {Mo₁₅₄}. The shape of the absorption peak corresponding to v(M=O) undergoes minor changes when changing from the fully molybdate {Mo₁₅₄} to the mixed {W₁₄Mo₁₄₀} wheels. This absorption band seems slightly broader due to the appearance of a shoulder around 960 cm⁻¹ that can be tentatively attributed to v(W=O).

compound	wavenumber (cm ⁻¹)				
	δ(О–Н)	ν(N–H)	$\nu(M=O)$	ν (M-O-M)	non attributed
Na-{Mo ₁₅₄ }	1621 <i>(m)</i>	-	975(<i>m</i>)	910(<i>m</i> , <i>sh</i>) 875(<i>w</i>) 820(v <i>w</i>)	992(<i>m</i> , <i>sh</i>) ; 625(<i>w</i>) 546(<i>w</i>)
Na-{W ₁₄ Mo ₁₄₀ }	1620(<i>m</i>)	-	975(<i>m</i>)	910(<i>m</i> , <i>sh</i>) 872(<i>w</i>) 818(v <i>w</i>)	995(<i>m</i> , <i>sh</i>) ; 627(vw) 547(w)
NH4-{W14M0140}	1620(<i>m</i>)	1415 <i>(m)</i>	974(<i>m</i>)	909(m,sh) 871(w) 817(vw)	991(<i>m</i> , <i>sh</i>) ; 628(<i>w</i>) 545(<i>w</i>)

Table 6. Infrared Data of the wheel ions $[(Mo_{(6-x)}W_x)_{14}Mo_{70}O_{462}H_{14}(H_2O)_{70}]^{14}$ for x = 0 or 1.

s = strong; m = medium; w = weak; sh = shoulder; br = broad; vs = very strong; vw = very weak.

IV.1.2. UV-Vis characterization of {Mo₁₅₄} and {W₁₄Mo₁₄₀}

The same protocol for determining the molar attenuation coefficients (ϵ) of Keplerates has been applied again to determine that of {Mo₁₅₄} and {W₁₄Mo₁₄₀}. From each solution, five dilutions were carried out to obtain solutions in the 1 x 10⁻⁵–7 x 10⁻⁵ mol.L⁻¹ range. The spectra were recorded in the visible – near infrared region between 1100 and 320 nm.

The spectra of both compounds shown in Figure 23 exhibit two maxima in the regions 710 - 720 and 1030 - 1040 nm that correspond to intervalence charge transfer (IVCT) from $Mo^V \rightarrow Mo^{VI}$ as reported for this family of compounds which originates the blue color for such species. The compounds appear to be stable over the concentration range as assessed by the straight line of the Beer-Lambert plots (not shown). The intensity of the maxima appear to be sensitive to the metal-oxo composition of the wheel where the presence of W in the frame work increases the molar attenuation coefficient in the region 710-720 nm from about 129,000 to 150,000 mol.L⁻¹.cm⁻¹. This can be attributed to the fact that introducing a tungsten atom at the center of the pentagon changes probably the 4d-electron hopping pathway over the Mo-O framework, which could affect the IVC transition probabilities. Yet this observation seems to be in contradiction with that has been observed for Keplerate where ε decreased with increasing the W ratio within the pentagons. Actually, it must be worth noting that affected visible transition. The opposite trend is related to the nature of the involved transition which corresponds to $L \rightarrow M$ ligand-to-metal charge transfer (LMCT) at the {Mo₂O₂E₂} chromophore in the Kelerate ion and to $Mo^{V} \rightarrow Mo^{VI}$ IVCT within the Mo-ring shaped anion. Molar attenuation coefficients are listed in Table 7 below.



Table 7. Molar attenuation coefficients of $\{Mo_{154}\}$ and $Na-\{W_{14}Mo_{140}\}$ determined from Beer-Lambert plots at different wavelengths.

Figure 23: UV-Vis spectra of fully molybdate wheel {Mo₁₅₄} and mixed wheel NH₄-{W₁₄Mo₁₄₀}.

IV.1.3. Redox titration to determine the number of d electrons

The ring-shaped anion as its molybdenum counterpart contains fourteen electronically uncoupled compartments distributed like pearls on a string forming an electronic necklace where the Mo (4d) electrons are grouped by pairs and each pair of delocalized electrons is held in a separate incomplete double-cubane-type compartment { Mo_5O_6 } shown in Figure 24.⁵⁵ The number of reduction can be easily deduced by a simple redox titration using a strong oxidizing agent as permanganate ion (MnO_4) in acidic conditions.



Figure 24: Structural representation showing the incomplete double-cubane $\{Mo_5O_6\}$ compartment: a) polyhedral and b) ball and stick. Color code: Mo, green; W, grey; O, red.

A stock solution of potassium permanganate (0.01 M) was prepared. Ammonium salt of mixed blue wheel was dissolved (559.3 mg in 20 mL H₂O) to give a titrated solution 1 x 10^{-3} mol.L⁻¹ in {W₁₄Mo₁₄₀}. 10 mL of the blue solution were introduced into a beaker with 5 mL of sulfuric acid (4 M) and then titrated by the 0.01 M KMnO₄ solution. The redox potential of the solution was measured by a platinum electrode and the potential referenced to Ag/AgCl standard potential. The potentiometric titration gradually turned from dark blue to pink passing through colorless solution at the equivalence after adding 5.5 mL of the titrant that indicated the presence of 27.5 4d electrons which corresponds to the 28 Mo^V centers expected for this blue-wheel structure. The potentiometric curve is presented in Figure 25.



Figure 25: Potentiometric titration curve of NH_4 -{ $W_{14}Mo_{140}$ } using [MnO_4]⁻ showing the potential jump at equivalence corresponding to 28 electrons.

IV.2. Single crystal X-ray diffraction analysis of Na-{W₁₄Mo₁₄₀}

Based on the results obtained from the mixed Keplerate DMA-{WMo₅} showing the regioselectivity between W and Mo within the pentagon, and after confirming that the isolated product corresponds to the archetypical structure of the wheel with the expected metal composition, we decided to investigate the { $W_{14}Mo_{140}$ } structure by X-ray diffraction analysis. According to the procedure (see experimental part), single crystals of Na₁₆[Mo₁₄₀W₁₄O₄₆₂H₁₄(H₂O)₇₀]•2Cl•120H₂O (noted Na-{ $W_{14}Mo_{140}$ }) were obtained directly from the reaction mixture. The crystals were of good quality and the X-ray analysis allowed producing reliable structural model shown in Figure 26. The selected crystallographic parameters are included in Table 8.



Figure 26: Top view along the z-axis of Na-{ $W_{14}Mo_{140}$ } wheel showing fourteen mixed { WMo_5 } pentagons (left). Ball & stick representation of the mixed pentagons containing a W atom at the center and five Mo octahedra at the periphery (right). The vibrational thermal ellipsoid of Mo (green) and that of the W atom (grey) are comparable in size and in shape in agreement with a single W-Mo distribution over the six metallic positions of the pentagon.

Fable 8. selected crystallographic paramete	rs of the X-ray diff	fraction analysis of	Na-{W14M0140}
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Compound	Na-{W ₁₄ Mo ₁₄₀ }	Ζ	4
Formula	Cl ₂ H ₃₉₄ Mo ₁₄₀ Na ₁₆ O ₆₅₂ W ₁₄	$\rho_{\rm calc}$, g.cm ⁻³	2.124
FW, g.mol ⁻¹	27273	μ (Mo K α), cm ⁻¹	0.397
<i>Т</i> , К	200	λ (Mo K α), Å	0.71073
crystal size (mm)	$0.30 \times 0.28 \times 0.03$	θ range, deg	θ max = 30.0, θ min = 2.3
crystal system	orthorhombic	data collected	1587063
space group	Cmca	unique data	63460
<i>a</i> , Å	50.1056(24)	unique data I>2σ(I)	47404
b, Å	56.0688(26)	no. parameters	2064
<i>c</i> , Å	30.2558(14)	$R(F)^{\mathrm{a}}$	0.247
α, deg	90	$R_w(F^2)^{\mathrm{b}}$	0.079
β , deg	90	GOF	1.15
γ, deg	90		
$V, Å^3$	84999(7)		

IV.2.1 Structural description of the Na-{W₁₄Mo₁₄₀}

• Description of the molecular ring-shaped arrangement. From X-ray diffraction analysis, it was evident that $\{W_{14}Mo_{140}\}$ retains the same archetypical structure of $\{Mo_{154}\}$. As shown in Figure 27, both structures can be noted as $[\{M(Mo_7)\}\{Mo'_2\}\{Mo_1\}]_{14}$ where M = Mo or W in $\{Mo_{154}\}$ and $\{W_{14}Mo_{140}\}$ respectively. The repetitive unit $\{MO_7(MoO_6)_{10}\}$ connects in an alternate disposition to form the wheel shaped structures. The $\{M(Mo_7)\}$ block is based on the ever-present pentagonal unit $\{M(Mo_5)\}$ (where M occupies the central pentagonal bipyramidal position sharing edges with the surrounding five octahedral $\{MoO_6\}$) and two extra $\{MoO_6\}$ octahedra. The $\{Mo_2O_5(H_2O)_2\}^{2+}$ unit noted $\{Mo'_2\}$ is formed by two $\{MoO_6\}$ octahedra sharing one corner restricting the opening of the ring on both sides whereas one $\{Mo_1\}$ unit lies beneath each pentagonal motif. They exhibit a nano-sized cavity that can be

easily used as a cavitand in host-guest chemistry as illustrated in chapter 1. The 70 H_2O ligands borne by this structure are distributed on the exterior surface close to the portals of the cavity as illustrated by Müller *et al.* for the fully molybdenum anion {Mo₁₅₄}.⁵⁰



Figure 27: Polyhedral representation showing: a) $[{M(Mo_7)}{Mo'_2}]{Mo_1}]$ repetitive unit and b) the alternate disposition of these units to form the ring-shaped anion. Color code: W, grey and Mo, green, yellow and purple.

• **3D** packing of the Na-{ $W_{14}Mo_{140}$ }. Na-{ $W_{14}Mo_{140}$ } crystallizes in an orthorhombic system with *Cmca* space group. The cell contains four { $W_{14}Mo_{140}$ } wheels while all the ring-shaped anions appear connected to give a 3D porous-like network (see Figure 28). These connections are ensured through a formal dehydration process leading to Mo=O•••Mo bridges. These inter-ring bridges are featured by a short Mo=O bonds (Mo-O = 1.39 Å) that alternates with a longer one (Mo•••O = 1.73 Å). In the structure, two neighboring rings are linked together through a single Mo=O•••Mo bridges.



Figure 28: Representation of the cell-packing of the Na-{ $W_{14}Mo_{140}$ } structure. The crystal system is orthorhombic and the cell contains four { M_{154} } wheels. a) view along the *a* axis (in the {ac} plane), b) view along the *c* axis (in the {ab} plane) and c) selected view showing the 3D network formed by the connection of neighboring { $W_{14}Mo_{140}$ } wheels through Mo=O•••Mo bridges.

The direct method was used to locate the heavy atoms (W and Mo) revealing the occupancy of the pentagonal bi-pyramidal position by W atoms only, while Mo occupied all the hexa-coordinated positions. The oxygen atoms and most of the counter ions were located after successive refinements, which allowed finding all the atoms constituting the wheel. However, no counter ions were located due to severe disorders within the large intermolecular void. Refinements using the single W-Mo distribution led to similar ellipsoids for W and Mo, revealing once again that the electronic density at the central position of the pentagon corresponds to W rather than Mo. The mean principal values U_{11} , U_{22} and U_{33} of the anisotropic displacement parameters of W and Mo in the pentagon are given in Table 9, while the corresponding thermal ellipsoids of the metallic atoms of the pentagon are visualized in Figure 29. Furthermore, these parameters are also compared with those found for the heptacoordinated Mo atoms (at the center of the pentagons) in the similar structure $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-.56}$



Figure 29: Representation of the thermal ellipsoid (80 % of the electronic density) of the metallic centers within the Na-{ $W_{14}Mo_{140}$ } structure showing the close similarity in size and shape between W and Mo. (green = Mo; grey = W) within the pentagonal motif.

Table 9. Main anisotropic displacement parameters of the W at the center and Mo (periphery) atoms within Na- $\{W_{14}Mo_{140}\}$ compared to those observed for heptacoordinated Mo atoms in similar structure.⁵⁶

Anisotropic displacement parameters (Å ²)					
atoms	U ₁₁	U_{22}	U ₃₃	reference	
W _(center)	0.04031500	0.0289150	0.0270050	This work	
Mo _(periphery)	0.02254940	0.0186800	0.0180260	This work	
$Mo_{(\text{center})}$	0.02529250	0.0266900	0.0274175	56	

Furthermore, analysis of the structure showed very close geometrical parameters between the hepacoordinated site occupied by W or that occupied Mo. The interatomic distances of M-O bonds for M = W or Mo are given in Table 10 and shown to be comparable.

Table 10. Comparison of the M-O bond lengths within the $\{MO_7\}$ polyhedron (with M = Mo or W).

Bond type	Mo ^a	\mathbf{W}^{b}
M=O	1.687(6)	1.703(3)
Equatorial	2.017(6)	2.008(22)
M-OH ₂	2.222(6)	2.199(3)

^a ref 56; ^b : this work

In the end, the single crystal structure of $\{W_{14}Mo_{140}\}\$ showed the presence of fourteen W atoms at the center of the pentagonal motif which was confirmed by elemental analysis. These results indicate that even in highly acidic solutions (pH ~ 1) and under reducing condition, the co-condensation of W and Mo occurs simultaneously with a preferential occupation of the central position by W. Furthermore, as complementary structural method, EXAFS spectroscopy was used to support this observation as shown in the following section.

IV.2.2. EXAFS analysis of the W environment within NH₄-{W₁₄Mo₁₄₀}

Similar to Keplerate, $\{W_{14}M_{0140}\}$ was examined by EXAFS. Once again, the tungsten L_{III}-edge was used to investigate the first and second coordination spheres of the tungsten atoms in the {WM0₅}-containing blue wheel. The spectra of both the solution and solid state appear to be identical. The Fourier transform (FT) shows two unique peaks around $R + \Delta =$ 1.6 Å and R + Δ = 3 Å corresponding to the overlapping W•••O shells and W•••Mo shell, respectively. The back transformation from FT to $\chi(k)$ in the two ranges of W•••O and W•••Mo shells gave the corresponding EXAFS oscillation shown in Figure 30b. The data was then fitted with three W•••O shells and one W•••Mo shell. Careful calculation with a fit at 0.36% indicated that each W atom in the ring-shaped anion is coordinated by N atoms with a radius R (Å), as follows: (N; R) = (1.44; 1.70), (5.41; 2.01) and (1.40; 2.13) corresponding to W=O, W-O-Mo (equatorial) and W-O-Mo (axial), respectively. Furthermore, or the second coordination sphere, each W atom is surrounded by 5.71 Mo atoms at R = 3.31 Å with a 20% uncertainty on N and 0.02 Å on R. The extra one Mo atom in the second coordination sphere of the blue wheel when compared to that of the Keplerate corresponds to $\{Mo_1\}$ that is located beneath the pentagonal motif and is a part of the incomplete double-cubane compartment.



Figure 30: a) k^3 weighted EXAFS and b) Fourier-transform EXAFS signal of {W₁₄Mo₁₄₀} wheel. Solid lines give experimental curves and dotted lines give fitted curves. The fitted structural EXAFS parameters for the W atoms corresponding to the best agreement with the experimental data are shown to be consistent with a hepta-coordinated W atom {WO₇}.

The EXAFS results are compared to those obtained from the X-ray diffraction analysis in Table 11 below.

Table 11: Comparison of the EXAFS and XRD structural parameters of the W atoms within $\{W_{14}Mo_{140}\}$ wheel.

	Ν		Interatomic distances (Å)	
Neighbor type	EXAFS	XRD analysis	EXAFS	XRD
O _(terminal)	1.44	1	1.70	1.70(1)
O _(equatorial)	5.41	5	2.01	2.00(2)
OH ₂	1.44	1	2.13	2.19(1)
Мо	5.71	6	3.31	3.30(1)

Finally, EXAFS parameters demonstrated and supported what have been seen by Xray diffraction. The heptacoordinated site is selectively occupied by W and there is no statistical distribution of W atoms over the pentagon or other hexacoordinated sites.

IV.3. W at the center of the pentagon within Krebs anion

Krebs anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ noted $\{Mo_{36}\}$ was the first discrete polyoxometalate ever isolated containing the pentagonal motif $\{M(M)_5\}$ and it dates back to 1982 when Krebs *et al.* reported the correct structure.⁵ It was the first large isopolyoxomolybdate and it dominates the polycondensation of molybdate at low pH and has been proposed as the primary building block for the formation of Mo-blue ring-shaped anion. In this section we report on a new Krebs-type open shell structure, $[W_4Mo_{32}O_{112}(H_2O)_{16}]^{8-}$ noted $\{W_4Mo_{32}\}$ by changing the metal composition of the pentagonal motifs within the original structure $\{Mo_{36}\}$.

IV.3.1. Formation and characterization of K-{W₄Mo₃₂}

Similar to {Mo₃₆}, the mixed Krebs anion is formed at highly acidic pH (below 2). The synthesis of Krebs has been adapted to obtain the mixed counterpart (see experimental part). The metalate solution containing W and Mo is heated to 80° and then acidified slowly with nitric acid (0.4 M). During the synthesis, white precipitate appears in the reaction mixture that is filtrated before passing to the crystallization step. The limpid solution generates rhombohedral transparent crystals with elemental analysis consistent with formula $K_8[W_4Mo_{32}O_{112}(H_2O)_{16}]$ •36H₂O, abbreviated K-{W₄Mo₃₂} hereafter. Elemental analysis showed the expected ratio between W and Mo, i.e. W:Mo = 1:8, which would correspond to one tungsten for each pentagon present in the structure. Infrared spectrum of {W₄Mo₃₂} given in Figure 31 showed the same fingerprint of the full Mo-containing {Mo₃₆} anion. The spectroscopic data are presented in Table 12.



Figure 31: IR spectra of: a) the Krebs anion {Mo₃₆} and b) its mixed counterpart {W₄Mo₃₂} both as potassium salt.

The infrared spectra of both compounds display the absorptions corresponding to the metal-oxo framework of the open shell structure in the spectral region between 1100 and 400 cm⁻¹. Absorptions at about 975 cm⁻¹ are attributed to the vibration of the metal-terminal oxygen bond v(M=O).⁵⁴ Other bands are roughly attributed to the bridging metal-oxygen-metal bonds. The spectra exhibit absorptions at 1405 and 1340 cm⁻¹ corresponding to the vibration of the N-O (traces of nitric acid). The shape of the spectra remains unchanged indicating that {W₄Mo₃₂} retains the archetypical structure of {Mo₃₆}.

compound	wavenumber (cm ⁻¹)				
	δ(О–Н)	v(N–O)	$\nu(M=O)$	ν (M-O-M)	Non attributed
{M0 ₃₆ }	1621 <i>(m)</i>	1406(m) 1344(m)	976(<i>m</i>)	913(m,sh) 875 (s)	951(<i>s</i>) ; 788(w); 692(<i>w</i>); 620(<i>w</i>)
{W4M036}	1624(<i>m</i>)	1405(m) 1341(m)	980(<i>m</i>)	851 (m,sh) 915(m,sh) 875 (s)	564(w) 952(s);787(w); 695(w);624(w)
				850 (m,sh)	565(w)

Table 12. Infrared Data of the open shell ions $[(Mo_{(6-x)}W_x)_4Mo_{12}O_{112}(H_2O)_{16}]^{8-}$ for x = 0 or 1.

s = strong; m = medium; w = weak; sh = shoulder; br = broad; vs = very strong; vw = very weak.
IV.4. Single crystal X-ray diffraction analysis of K-{W₄Mo₃₂}

The structure of the isolated single crystal K-{W₄Mo₃₂} was assessed by X-ray diffraction analysis. According to the procedure (see experimental part) crystals of $K_8[W_4Mo_{32}O_{112}(H_2O)_{16}]$ •36H₂O were obtained directly from the reaction mixture within one day after the synthesis. The crystals were of good quality and the structure was solved and presented in Figure 32 while the selected crystallographic parameters are included in Table 13.



Figure 32: Side view of $\{W_4Mo_{32}\}$ open shell structure showing four mixed $\{WMo_5\}$ pentagons (left). Ball & stick representation of the mixed pentagons containing a W atom at the center and five Mo octahedra at the periphery (right). The vibrational thermal ellipsoid of Mo (green) and that of the W atom (grey) are comparable in size and in shape giving consistency to the single W-Mo distribution over the six metallic positions of the pentagons.

Table 13. Selected crystallographic parameters of the X-ray diffraction analysis of $\{W_4Mo_{32}\}$

Compound	${W_4Mo_{32}}$	Ζ	2
Formula	$H_{104}K_8Mo_{32}O_{164}W_4$	$ ho_{ m calc}$, g.cm ⁻³	3.033
FW, g.mol ⁻¹	6846.99	μ (Mo K α), cm ⁻¹	0,596
<i>Т</i> , К	200	λ (Mo K α), Å	0.71073
crystal size (mm)	$0.30 \times 0.15 \times 0.2$	θ range, deg	$\theta \min = 2.8, \ \theta \max = 40.0$
crystal system	Monoclinic	data collected	174421
space group	P1 21/n 1	unique data	21923
<i>a</i> , Å	16.3705(3)	unique data I> $2\sigma(I)$	19612
b, Å	18.6933(4)	no. parameters	930
<i>c</i> , Å	24.9057(5)	$R(F)^{\mathrm{a}}$	0.181
α, deg	90	$R_w(F^2)^{\mathrm{b}}$	0.053
β , deg	99.2205(9)	GOF	1.18
γ, deg	90		
$V, \text{\AA}^3$	7523.1(3)		

IV.4.1. Structural description of {W₄Mo₃₂}

The cluster, related to the Krebs anion archetype is assembled from two identical $\{W_2Mo_{15}\}\$ fragments, both related through a center of inversion. Its two symmetrical fragments are connected via $\{Mo_1\}\$ units that are involved in four corner-shared (Mo-O-Mo) junctions forming an oblate structure. Once again, tungsten atoms occupy the pentagonal bipyramidal position at the center of the pentagon sharing edges with five octahedral $\{MoO_6\}$. The complex structure can be rationalized by breaking it into its smallest building units, i.e. $\{W_4Mo_{32}\} = \{Mo_1\}_4\{Mo_2\}_4\{W(Mo)_5\}_4$ as illustrated in Figure 33.



Figure 33: Polyhedral representation of K-{ W_4Mo_{32} } showing: a) { W_2Mo_{15} } unit, b) side view and c) top view. Color code: W, grey; Mo, green; { Mo_1 } unit, aqua; { Mo_2 } unit, red.

It crystallizes in a monoclinic system in a P21/n space group, and its cell contains two $\{W_4Mo_{32}\}$ open shell structures (See Figure 34).



Figure 34: Representation of the cell-packing of the $\{W_4Mo_{32}\}$ structure. The crystal system is monoclinic and the cell contains two $\{M_{36}\}$ structures a) view along the *a* axis (in the {bc} plane). b) view along the *c* axis (in the {ab} plane). Oxygen atoms and potassium cations have been omitted for clarity.

The heavy atoms were located using the direct method while the counter ions and the oxygen ligands were located after refinement. Once again, W atom occupied preferentially the central position surrounded by Mo atoms in all the hexacoordinated sites. It should be metioned that a splitting of the W atoms have been found on two close positions (separated by ~ 0.5 Å) which represents a statistical occupancy factor of 90% and 10%, respectively. The mean principal values U₁₁, U₂₂ and U₃₃ for W on these two sites are given in Table 14, and the corresponding thermal ellipsoids are visualized in Figure 35. Besides, these parameters are compared with those found for the heptacoordinated Mo atoms (at the center of the pentagons) in the molybdenum derivative $[Mo_{36}O_{112}(H_2O)_{16}]^{14-}$ in Table 14.⁵



Figure 35: Representation of the thermal ellipsoid (80 % of the electronic density) of the metallic centers within the $\{W_4Mo_{32}\}$ structure showing the close similarity in size and shape between W and Mo. Color code: Mo, green; W (90% occupation), white; W (10% occupation), red.

Table 14. Main anisotropic displacement parameters of the W at the center and Mo (periphery) atoms within the $\{W_4Mo_{32}\}$ compared to those observed for heptacoordinated Mo atoms in similar structure.

Anisotropic displacement parameters (\AA^2)								
atoms	\mathbf{U}_{11}	U ₂₂	U ₃₃	reference				
W _(center 90%)	0.0198900	0.0179850	0.0183100	This work				
W _(center 10%)	0.0198900	0.0179850	0.0183100	This work				
Mo _(periphery)	0.0086750	0.0079175	0.0077575	This work				
$Mo_{(center)}$	0.0109500	0.0075000	0.0111000	5				

The interatomic distances presented in Table 15 show that there is almost no change in the bond length when changing W for Mo at the central position in both structures.

Table 15. Comparison of the M-0) bond lengths within the {MO ₇]	<pre>} polyhedron (with M = Mo or W)</pre>
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Bond type	Mo ^a	$\mathbf{W}^{\mathbf{b}}$	
M=O	1.6521(6)	1.6937(9)	
Equatorial	2.0188(5)	2.0095(8)	
M-OH ₂	2.3875(5)	2.3240(8)	

^a ref 5; ^b : this work

Following the same trend observed with Keplerate and the wheel, the $\{W_4Mo_{32}\}$ anion displayed a W-centered pentagonal motif. The presence of W at the heptacoordinated site was observed in the X-ray diffraction analysis. Further evidence of its presence at the center eliminating the possibility of statistical distribution was evidenced using EXAFS technique as discussed in the following section.

IV.4.2. Featuring the tungsten environment in K-{W₄Mo₃₂} arrangement by EXAFS analysis

EXAFS was used to examine the first and second coordination spheres of the W atom within the mixed Krebs structure { W_4Mo_{32} }. The raw k^3 weighted EXAFS spectrum and its corresponding fit are shown in Figure 36. For expected seven oxygens in the first sphere and six molybdenum atoms in the second, the Fourier transform shows two unique peaks around $R + \Delta = 1.6$ Å and $R + \Delta = 3$ Å corresponding to the overlapping W•••O shells and W•••Mo shell respectively as already seen for Keplerate and the wheel. The data was then fitted with three W•••O shells and one W•••Mo shell. Carful calculation with a fit at 0.36% indicated that each W atom in the wheel is coordinated by N atoms with radius R (Å) as follows: (N; R) = (1.43; 1.74), (5.40; 1.99) and (1.28; 2.31) corresponding to W=O, W-O-Mo (equatorial) and W-O-Mo (axial), respectively. For the second coordination sphere, each W atom is surrounded by 5.65 Mo atoms at R = 3.31 Å with a 20% uncertainty on N and 0.02 Å on R. Similar to the mixed blue wheel, Krebs anion contains an extra Mo atom in the second coordination sphere when compared to that of the Keplerate corresponding to $\{Mo_1\}$ that connects the two pentagonal motifs in each half of the open shell. Comparison of the geometrical parameters of the W atoms extracted from EXAFS and X-ray diffraction analysis are shown in Table 16.



Figure 36: a) k^3 weighted EXAFS and b) Fourier-transform EXAFS signal of {WMo₅}-containing Krebs. Solid lines give experimental curves and dotted lines give fitted curves. The fitted structural EXAFS parameters for the W atoms corresponding to the best agreement with the experimental data are shown to be consistent with a hepta-coordinated W atom {WO₇}.

	Ν		Interatomic	Interatomic distances (Å)	
Neighbor type	EXAFS	XRD analysis	EXAFS	XRD	
O _(terminal)	1.43	1	1.74	1.69(1)	
$\mathbf{O}_{(equatorial)}$	5.40	5	1.99	2.00(1)	
OH_2	1.28	1	2.31	2.32(1)	
Мо	5.65	6	3.31	3.30(1)	

Table 16. Comparison of the EXAFS and XRD structural parameters of the W atoms within {W4M032}.

EXAFS analysis gave another argument supporting X-ray diffraction results, indicating that only the pentagonal bipyramidal site is preferentially occupied by W when synthesis is conducted using the adequate W:Mo ratio.

V. Conclusion and perspective

Changing the metal-oxo composition of POMs is expected to modify their physicalchemical properties and corresponds to one possibility for POMs functionalization intensively developed in our group. The aim of this chapter was to transfer this concept to some prominent POM structures in the hope of discovering new structures based on mixed pentagonal motifs while the Mo/W regioselectivity at the pentagon changes drastically the kinetic of formation of pentagons.

For this purpose, a solution studies about the formation of Keplerate anion have been carried out. These studies resulted in the isolation of new mixed pentagonal motifs-containing Keplerates. The isolated products were characterized in both liquid solutions and solid state. One observation stood out concerning the regioselectivity within the pentagonal units, i.e. when synthesizing mixed addenda Keplerate with tungsten and molybdenum; the former occupied preferentially the central pentagonal bi-pyramidal site.

UV-Vis showed that increasing the tungsten content within the pentagon affects the LMCT absorption band directly as the latter decreases drastically with the increasing tungsten character. ¹H NMR signals for the linked acetate are sensitive to the composition of the pentagons. The peaks correlated to the linked acetates are subjected to excessive line broadening when increasing the number of tungsten atoms in the pentagonal motif.

After succeeding in solving the structure of the first mixed pentagon containing Keplerate $\{W_{12}Mo_{120}\}$ showing the regioselectivity within the pentagon, the work has been extended to other structures sharing the same unit. Two additional compounds were isolated and characterized such as the mixed blue wheel $\{W_{14}Mo_{140}\}$ and the mixed Krebs anion $\{W_4Mo_{32}\}$.

It appears that W atoms occupy selectively the central position of the pentagonal motif with no apparent statistical distribution if they are introduced in a stoichiometric ratio in the reaction mixture. This observation was supported fairly by the analysis of the vibrational ellipsoids of W and Mo at the same site that argued in favor of a central W. As single crystal X-ray diffraction analysis allows characterizing long-range order and produces model which correspond formally to one solution among other possibilities, we attempted to investigate local ordering of the W atom using EXAFS method. EXAFS analysis provided another argument supporting that observation indicating that the W atoms within the {WMo₅} pentagons exhibit a coordination close to $N_c = 7$ in the first coordination sphere. Such an extension of coordination from six to seven would be facilitated from a kinetic point of view for the W center with respect to the Mo one probably due to diffuse 5d and 7s-7p orbitals, thus more available to include a seventh oxygen atom. Hence, these results demonstrate that tungstates and molybdtates co-polycondenstation proceeds simultaneously with no kinetic or thermodynamic discrimination for one metallic species with respect to the other but occurs further with a positional selectivity of the W atom at the central position and the Mo located within the peripheral positions.

These new findings may open novel opportunities for synthesizing mixed Keleratetype ions based on multi-metal elements. For instance, one may expect to design enhanced multi-element catalytic phases (so called M1 phases) that are known for their high selectivity in propane oxidation,⁵⁷ as previous studies showed the possibility of synthesizing these phases starting from multi-metal containing Keplerates.⁵⁸

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Chapter III - Polyoxometalate, cationic cluster and γ-cyclodextrin. From primary interactions to supramolecular hybrid materials

I. Insights into supramolecular hybrid assemblies based on organic and inorganic material

Motivation to design sophisticated hybrid materials has directed great attention for the development of challenging scientific projects such as those based on mimicking natural processes involved within energy conversion, biomass valorization or pollutants elimination.¹⁻⁶ Understanding the primary interactions that govern the assembling between molecular components is probably the key for controlling the hierarchical arrangement of complementary active moieties from solution to the functioning material.⁷ In nature, active components are spatially well-ordered to provide the highest efficiency for energy transfer, electrons exchange or catalytic transformation.^{8,9} For example, metallic clusters involved in redox bioprocesses such as nitrogen fixation, CO₂ reduction or respiration are ubiquitous in biology, but generally they are included within highly evolved biochemical environment to perform electron-transferring functions through complex pathways.¹⁰⁻¹² Intense research efforts are deployed in the design of artificial devices integrating active core within simplified biological-like environment. In context, supramolecular chemistry is developing basic concepts and principles that are useful tools to assemble specifically molecular units through weak interactions arising from directed hydrogen bonding, electrostatic or dispersion forces.¹³⁻¹⁵ In addition to these weak attractive effects, polar solvents such as water contribute substantially to the aggregation processes. Desolvation or solvent reorganization around the guest or within the host can be the most determining contribution in shifting the binding equilibrium.¹⁶⁻¹⁸ In many cases, the so-called hydrophobic effect was found to be one of the main driving forces in aqueous medium able to dictate hostguest association, self-assembly processes or ionic recognition.^{19,20} Polyoxometalates (POMs) are anionic all-inorganic molecular metal oxides with highly diverse structures that reach in size nanoscopic dimensions.^{21,22} This class of compounds exhibits a wide structural diversity in relationship with their remarkable chemical and physical properties that make them useful for applications in areas ranging from materials science, and energy conversion to catalysis and
medicine.²³⁻²⁸ Therefore, wider exploitation of POM compounds requires the development of robust and efficient synthetic protocols for their integration into hybrid architectures and devices. In context, supramolecular approach has the intrinsic advantage to self-assemble these POM units through weak and specific interactions into well-ordered hierarchical materials. Recently, cyclodextrin has proved to behave as specific glue to assemble POM units to give 1D nanogrid assembly²⁹ or crystalline materials.³⁰ In this chapter, we report on the formation of extended hybrid materials based on the anionic Dawson-type polyoxometalate α -[P₂W₁₈O₆₂]⁶⁻ or Keggin-type [BW₁₂O₄₀]⁵⁻ (denoted {P₂W₁₈} and {BW₁₂} respectively) and the cationic cluster [Ta₆Br₁₂(H₂O)₆]²⁺ (abbreviated {Ta₆}) mediated through specific interactions with γ -cyclodextrin (noted γ -CD hereafter). Figure 1 shows the structures of such molecular building units.



Figure 1: Structural representation of the molecular components used as building blocks: a) Dawson anion $[P_2W_{18}O_{62}]^{6-1}$ { P_2W_{18} } b) Keggin anion $[BW_{12}O_{40}]^{5-1}$ { BW_{12} } c) γ -cyclodextrin $C_{48}H_{80}O_{40}$ (γ -CD) and d) octahedral cluster $[Ta_6Br_{12}(H_2O_{62})^{2^+}({Ta_6})]$.

The inorganic moieties i.e. POM and octahedral cluster³¹⁻³³ are two complementary units in term of ionic charge and electronic density. Polyoxotungstates such as the archetypical Dawson $[P_2W_{18}O_{62}]^{6-}$ and Keggin $[BW_{12}O_{40}]^{5-}$ contain tungsten atoms in their +VI highest oxidation state and are considered usually as electron-poor polynuclear complexes as exemplified by their ability to undergo multielectron reduction without significant structural changes. On the contrary, the aqua hexatantalum cationic species $[Ta_6Br_{12}(H_2O)_6]^{2+}$ exhibits low oxidation states $Ta^{II,III}$ mixed valence centers giving rise to electron-rich metal-metal bonds and related oxidation processes without damaging the cluster structure. In general, octahedral clusters represent an important class of compounds in the field of solid state chemistry.³⁴ Nevertheless, sophisticated solution chemistry, ranging from coordination chemistry^{35,36} to supramolecular materials^{37,38} can be also developed from octahedral-type clusters allowing investigating a large panel of applications in photocatalysis,³⁹ soft materials,⁴⁰ bio-imaging⁴¹ or phototherapy.⁴² The γ -CD as organic unit is a cyclic oligosaccharide built on eight 1,4-linked D-glucopyranosyl residues, which delimit a toroidal hydrophobic cavity. Their remarkable inclusion properties have given rise to wide applications in many fields of science such as nanotechnology,⁴³ pharmaceutics⁴⁴ or medicine.⁴⁵ Thus CDs represent an interesting class of building blocks for the construction of hybrid assemblies.⁴⁶ In this chapter, we show first of all the existence of relevant supramolecular associations between γ -CD and POMs and between γ -CD and {Ta₆} separately in aqueous solutions as well in the solid state. Strikingly, these interactions give rise to aggregates or host-guest adducts which appear fully complementary for the rational design of ordered supramolecular hybrid inorganic-organic network containing POM / {Ta₆}²⁺ / γ -CD as base units (POM being either {P₂W₁₈} or {BW₁₂}).

II. Experimental Part

II.1. General Methods:

Fourier Transform Infrared (FT-IR) spectra were recorded on a 6700 FT-IR Nicolet spectrophotometer, using diamond ATR technique. The spectra were recorded on non-diluted compounds and ATR correction was applied.

UV-vis spectra were recorded on a Perkin-Elmer Lambda-750 using calibrated 0.1 cm Quartz-cell.

Elemental analyses (C, H, N and S) were carried out by the analytical service of the CNRS at Gif sur Yvette, France. Quantitative analyses of metals were carried out by ICP analysis and Fluo-X analysis and were performed in UCCS laboratory in Lille, France. These elemental analyses were performed by inductively coupled plasma-optic emission spectroscopy 720-ES ICP-OES (Agilent) with axially viewing and simultaneous CCD detection.

Energy-dispersive X-ray spectroscopy_(EDX) measurements were performed using a SEM-FEG (Scanning Electron Microscope enhanced by a Field Emission Gun) equipment (JSM 7001-F, Jeol). The measures were acquired with a SDD XMax 50 mm² detector and the Aztec (Oxford) system working at 15 kV and 10 mm working distance. The quantification is realized with the standard library provided by the constructor using L α lines.

Water and cyclodextrin contents were determined by **thermal gravimetric analysis** (**TGA**) with a Mettler Toledo TGA/DSC 1, STAR^e System apparatus under oxygen flow (50 mL min^{-1}) at a heating rate of 5°C min⁻¹ up to 700°C.

Nuclear Magnetic Resonance (NMR) spectra were measured in D₂O at 25 °C when it is not specified. ¹H and ³¹P NMR spectra were obtained on a Bruker Avance 400 spectrometer at Larmor frequencies 400.1 and 162.0 MHz respectively, using 5 mm standard NMR tubes. The 1D ¹H spectra were recorded with one pulse sequence at 30° flip angle (pulse duration 2.4 μ s), using 1 s recycle delay, 1.6 s acquisition time, and 16 number of scans. Variable temperature ¹H NMR experiments were performed in the temperature range 20-80 °C after at least 30 min of sample temperature stabilization delay. The ³¹P NMR spectra were run with 7.7 µs pulse duration (45° flip angle), 15 s recycle delay, 1 s acquisition time, and an accumulation of 32 transients. 2D ¹H-¹H COSY and EXSY spectra were carried out on some selected samples using standard phase sensitive pulse sequences in States mode and 1 s mixing time in EXSY experiment. Translational diffusion measurements were performed using Bruker's "ledbpgs2s" stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy.⁴⁷ The ¹⁸³W NMR spectra were measured on a Bruker Avance 500 spectrometer at a resonance frequency of 20.8 MHz equipped with a specific low-gamma nuclei 10 mm probehead. Chemical shifts are reported relative to TMS (1 H), 85% H₃PO₄ (31 P), and 1 M aq. Na₂WO₄ (¹⁸³W), using secondary references in case of ¹⁸³W (D₂O/H₂O solution of $H_4SiW_{12}O_{40}$ observed at -103.8 ppm).

Electrospray Ionization Mass Spectrometry (ESI-MS) spectra were collected using a Q-TOF instrument supplied by WATERS. Samples were solubilized in water at a concentration of 10⁻⁴ M and were introduced into the spectrometer via an ACQUITY UPLC WATERS system whilst a Leucine Enkephalin solution was co-injected via a micro pump as internal standard.

Isothermal Titration Calorimetry (ITC) is used to determine formation constants and inclusion enthalpies simultaneously for each γ -CD/[P₂W₁₈O₆₂]⁶⁻, γ -CD/[Ta₆Br₁₂(H₂O)₆]²⁺ and γ -CD/[P₂W₁₈O₆₂]⁶⁻/[Ta₆Br₁₂(H₂O)₆]²⁺ systems by the use of an isothermal calorimeter (ITC₂₀₀, MicroCal Inc., USA). Degassed deionised water solutions were used in both cell (V₀ = 202.8 µL) and syringe (40 µL). After addition of an initial aliquot of 0.2 µL, 10 aliquots of 3.7 µL of the

syringe solution were delivered over 7 s for each injection. This number of ten injections was chosen according to Tellinghuisen's recommendation.⁴⁸ The time interval between two consecutive injections was 90 s, which proved to be sufficient for a systematic and complete return to baseline (when no gelation phenomenon was observed in the cell). The agitation speed was set to 1000 rpm. The resulting heat flow was recorded as a function of time.

Experiments involving γ -CD/[P_2W_{18}O_{62}]^{6-} and γ -CD/[Ta_6Br_{12}(H_2O)_6]^{2+} binary systems :

Since mixtures of 1:1 and 1:2 guest:CD complexes were expected, two distinct ITC titrations were realized at three temperatures (283, 298 and 313 K), in order to merge experimental information on both complexes. Titration 1 was implemented by using a cell filled with a guest solution and a syringe filled with a γ -CD solution. Titration 2 involved a cell filled with an equimolar solution of host and guest, and a syringe filled with a γ -CD solution. The following concentrations were used for the different systems:

Table 1: Concentrations of $[P_2W_{18}O_{62}]^6$, $[Ta_6Br_{12}(H_2O)_6]^{2+}$ and γ -CD used for the first and second calorimetric titrations.

Guest		Cell	Syringe
$[P_2W_{18}O_{62}]^{6}$	Titration 1 Titration 2	$[P_2W_{18}O_{62}]^{6-}0.125 \text{ mM}$ $[P_2W_{18}O_{62}]^{6-}0.25 \text{ mM} + \gamma\text{-CD } 0.25 \text{ mM}$	γ-CD 2.5 mM γ-CD 2.5 mM
$\left[Ta_{6}Br_{12}(H_{2}O)_{6}\right]^{2+}$	Titration 1 Titration 2	$[Ta_6Br_{12}(H_2O)_6]^{2+} 0.33 \text{ mM}$ $[Ta_6Br_{12}(H_2O)_6]^{2+} 0.67 \text{ mM} + \gamma \text{CD} 0.67 \text{ mM}$	γ-CD 3.33 mM γ-CD 3.33 mM

Experiments involving γ -CD/[P₂W₁₈O₆₂]⁶⁻/[Ta₆Br₁₂(H₂O)₆]²⁺ ternary system :

Titrations were realized at 298 K by injecting a 200 μ M [P₂W₁₈O₆₂]⁶⁻ solution on a solution containing [Ta₆Br₁₂(H₂O)₆]²⁺ (90 μ M) and γ -CD (respectively 22.5, 90 and 360 μ M for titration 1, 2 and 3).

The heat of dilution of each partner was eliminated from each titration by subtracting the raw signal obtained for the corresponding blank titrations (i.e. only one partner in cell or syringe, the other compartment being filled with water). The peak area following each addition was obtained by integration of the resulting signal and was expressed as the heat effect per injection.

Electrochemistry was conducted using purified water obtained by passing water through a RiOs 8 unit followed by a Millipore-Q Academic purification set. All reagents were of highpurity grade and were used as purchased without further purification. Cyclic voltammetry (CV) experiments were carried out with a Methrohm Autolab PGSTAT12 potentiostat/galvanostat associated with a GPES electrochemical analysis system (EcoChemie). Measurements were performed at room temperature in a conventional single compartment cell. A glassy carbon (GC) electrode with a diameter of 3 mm was used as the working electrode. The auxiliary electrode was a Pt plate placed within a fritted-glass isolation chamber and potentials are quoted against a saturated calomel electrode (SCE). The solutions were deaerated thoroughly for at least 30 minutes with pure argon and kept under a positive pressure of this gas during the experiments.

Single-Crystal X-ray diffraction data collections were carried out at T = 150(2) or 200(2) K with a Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS bidimensional detector using a high brilliance IµS microfocus X-ray Mo Ka monochromatized radiation ($\lambda = 0.71073$ Å) or at 100(2) K using X-Ray synchrotron beam line ($\lambda = 0.72925$ Å) at PROXIMA2 source in SOLEIL Laboratory (see Table 5). Crystals were glued in paratone oil to prevent any loss of crystallization water. An empirical absorption correction was applied using the SADABS program⁴⁹ based on the method of Blessing.⁵⁰ The structures were solved by direct methods and refined by full-matrix least squares using the SHELX-TL package.⁵¹ Heavier atoms (W or Ta) for each structure were initially located by direct methods. The remaining non-hydrogen atoms were located from Fourier differences and were refined with anisotropic thermal parameters. Positions of the hydrogen atoms belonging to the γ -cyclodextrins were calculated and refined isotropically using the gliding mode. Crystallographic data for single-crystal X-ray diffraction studies are summarized at the end of the chapter in Table 5.

Powder X-ray diffraction data was obtained on a Bruker D5000 diffractometer using Cu radiation ($\lambda = 1.54059$ Å).

II.2. Syntheses

All reagents were purchased from commercial sources and used without further purification. $K_6[P_2W_{18}O_{62}]$ •19H₂O and $K_5[BW_{12}O_{40}]$ were prepared according to literature.^{52,53} Cesium and rubidium salts of $[P_2W_{18}O_{62}]^{6-}$ were prepared by addition of an excess of CsCl or of

RbCl to an aqueous solution of $K_6[P_2W_{18}O_{62}]$ •19H₂O. Their compositions were checked by FT-IR, TGA and EDX.

KNa₅{[**P**₂**W**₁₈**O**₆₂](**C**₄₈**H**₈₀**O**₄₀)}•3.5NaCl•23H₂**O** ({**P**₂**W**₁₈}⊂CD). A mixture of K₆[**P**₂**W**₁₈**O**₆₂]•19H₂O (1.2 g; 0.24 mmol) and γ-CD (0.34 g; 0.24 mmol) in aqueous solution of NaCl (0.5 mol.L⁻¹; 25 mL) was stirred at 35 °C for 15 min. The resulting clear solution was then stirred at room temperature for 15 min and was allowed to stand for crystallization in air. Needle-like colorless crystals of {**P**₂**W**₁₈}⊂CD suitable for single crystal X-ray diffraction appeared within 5 days. They were isolated by filtration and washed with cold water. Yield 1.22 g, 78 %. FT-IR spectrum is given in Figure 2. Elemental analysis for C₄₈H₁₂₆Cl_{3.50}KNa_{8.5}O₁₂₀P₂W₁₈ (FW = 6352.1 g.mol⁻¹) Calc. (found): H 1.98 (2.08); C 9.03 (9.25); Na 3.06 (2.95); K 0.61 (0.66); P 0.97 (1.00); W 52.1 (51.92). TGA showed a weight loss of 6.5 % in the 20-220 °C temperature range corresponding to the hydration water (calculated 6.7 %) and a weight loss of 22.5 % in the 220-700 °C range assigned to the loss of 1 CD and the 3.5 Cl (calculated 21.5 %).

CsNa₅{[P₂W₁₈O₆₂](C₄₈H₈₀O₄₀)₂}•1.2NaCl•23H₂O ({P₂W₁₈}⊂2CD). A solution of Cs₆[P₂W₁₈O₆₂]•19H₂O (0.55 g; 0.1 mmol) in aqueous solution of NaCl (0.5 mol.L⁻¹; 18 mL) was stirred at 30 °C until the total dissolution of the solid. γ-CD (0.26 g; 0.2 mmol) was added to the resulting limpid solution that was stirred at room temperature for 20 min. The obtained mixture was allowed to stand for crystallization in air where needle-like colorless crystals of {P₂W₁₈}⊂2CD suitable for single crystal X-ray diffraction appeared within 8 days. They were isolated by filtration and washed with cold water. Yield 0.42 g, 55 %. FT-IR spectrum is given in Figure 2. Elemental analysis for C₉₆H₂₀₆Cl_{1.2}CsNa_{6.2}O₁₆₅P₂W₁₈ (FW = 7689.8 g/mol) Calc. (found): C 14.99 (14.43); Cs 1.73 (1.82); H 2.70 (2.78); Na 1.85 (2.08); P 0.81 (0.94); W 43.03 (44.45). TGA showed a weight loss of 5.6 % in the 20-220 °C temperature range corresponding to the hydration water (calculated 5.4 %) and a weight loss of 32.7 % in the 220-700 °C range assigned to the loss of 2 CDs (calculated 33.7 %).

 $Rb_4K_{1.5}Na_{0.5}\{[P_2W_{18}O_{62}](C_{48}H_{80}O_{40})_3\}$ •35H₂O ({P₂W₁₈}⊂3CD). A solution of $Rb_6[P_2W_{18}O_{62}]$ •19H₂O (1.5 g; 0.29 mmol) in 25 mL distilled water was stirred at 30 °C until the total dissolution of the solid. γ-CD (1.125 g; 0.86 mmol) were added to the resulting limpid solution that was stirred at room temperature for 20 min. The obtained mixture was allowed to

stand for crystallization in air where hexagonal colorless crystals of $\{P_2W_{18}\}\subset 3CD$ suitable for single crystal X-ray diffraction appeared within 7 days. They were isolated by filtration and washed with ethanol and ether. Yield 1.32 g, 48 %. FT-IR spectrum is given in Figure 2. Elemental analysis for C₁₄₄H₃₁₀K_{1.5}Na_{0.5}O₂₁₇P₂Rb₄W₁₈ (FW = 9293.3 g.mol⁻¹) Calc. (found): C 18.6 (17.97); H 3.33 (3.19); K 0.63 (0.57); Na 0.12 (0.01); P 0.66 (0.85); Rb 3.67 (3.60); W 35.60 (34.83). TGA showed a weight loss of 7.1 % in the 20-220 °C temperature range corresponding to the hydration water (calculated 7.7 %) and a weight loss of 40.3 % in the 220-700 °C range assigned to the loss of 3 CDs (calculated 41.5 %).

{[Ta₆Br₁₂(H₂O)₆](C₄₈H₈₀O₄₀)₂}Br₂•14H₂O ({Ta₆}⊂2CD). (250 mg; 0.108 mmol) [Ta₆Br₁₂(H₂O)₆]Br₂ were dissolved in 10 mL distilled water resulting in a dark green solution. In a separate beaker, (312 mg; 0.22 mmol) γ -CD were dissolved in 5 mL of distilled water resulting in a clear limpid solution. The latter was added in one shot to the former, the obtained solution was stirred gently for 10 min and then allowed to stand for crystallization. Two days later, abundant quantity of square-like dark green crystals of {Ta₆}⊂2CD suitable for single crystal Xray diffraction was obtained. Yield 405 mg, 73 %. FT-IR spectrum is given in Figure 22. Elemental analysis for Br₁₄C₉₆H₂₀₀Ta₆ (FW = 5156.2 g/mol) Calc. (found): C 22.34 (22.20); Br 21.69 (21.51); H 3.87 (3.90); Ta 21.05 (20.95). TGA showed a loss of 6.99 % assigned to coordinated and hydration water molecules in the 20-120 °C temperature range (calculated 7.0 %) and a loss of 66.9 % in the 120-500 °C range corresponding to the loss of 2 CDs and the 14 Br with the formation of Ta₂O₅ (calculated 67.3 %).

Preparation of [Ta₆ \subset 2CD•{P₂W₁₈}]-based hydrogel Gel. [Ta₆Br₁₂(H₂O)₆]Br₂ (100 mg; 0.0432 mmol) were dissolved in 2 mL distilled water. Another solution of K₆[P₂W₁₈O₆₂]•19H₂O (212 mg; 0.0432 mmol) and C₄₈H₈₀O₄₀•6.6H₂O (121 mg; 0.0865 mmol) were dissolved in 5 mL distilled water. The former (green solution) was added dropwise to the latter (clear solution) while gently stirring. Each drop introduced into the solution coagulates and form a micelle-like green droplet. With the continuous addition of the tantalum solution, the viscosity of the solution increases gradually and the magnetic bar struggles to rotate. After the addition of the whole quantity of the green solution, the viscous mixture was stirred gently for five minutes. The resulting green mixture was allowed to stand for one hour in open air where a green gel is obtained. The gel maintains its viscosity and texture if left covered afterwards while it dries up if

left in open air. Composition of the hydrogel was determined by elemental EDX after thoroughly washing the gel through successive centrifugation in excess water to removed mother liquor and then drying in air at room temperature. FT-IR spectrum of the gel after drying is given in Figure 22. Elemental analysis for K₄[Ta₆Br₁₂(H₂O)₆][γ -CD]₂[P₂W₁₈O₆₂]•~60 H₂O : Calc. (found) Br 9.26 (10.04); C 11.13 (11.93); H 2.82 (3.04); K 1.51 (1.43); P 0.59 (0.65); Ta 10.49 (11.82); W 31.99 (30.52).

Synthesis of Single crystals of $K_2H_2[Ta_6Br_{12}(H_2O)_6][\gamma-CD]_2[P_2W_{18}O_{62}].32.5H_2O$. Solutions similar to those used in the preparation of the gel were utilized in the crystallization process. Around 0.5 mL of each solution was introduced on opposite sides of a 0.5 cm diameter H-tube. Two drops of CF₃SO₃H 2 M were added to each side. Then distilled water was layered above both solutions until the H-tube was filled allowing slow diffusion on both sides. After one week needle-like green crystals are formed at the center of the tube. Crystals were isolated and characterized by XRD, FT-IR, TGA and EDX. Yield 50 mg, 47 %. FT-IR spectrum is given in Figure 22. TGA showed a weight loss of 6.5 % assigned to coordinated and hydration water molecules in the 20-120 °C temperature range (calculated 6.0 %) and a loss of 34.8 % in the 120-600 °C range corresponding to the loss of the 2 CDs and the 12 Br with the formation of K₂O, Ta₂O₅, P₂O₅ and WO₃ (calculated 34.2 %). Elemental analysis for Br₁C₉₆H₂₃₉K₂O_{180.5}P₂Ta₆W₁₈ : calc. (found) Br 9.81 (10.21); C 11.78 (11.82); H 2.44 (2.53); K 0.80 (0.78); P 0.63 (0.61); Ta 11.10 (11.43); W 33.86 (32.54). FW = 9772.8 g/mol.

Synthesis of Single crystals of $[Ta_6Br_{12}(H_2O)_6]_2[\gamma-CD]_4[HBW_{12}O_{40}].20H_2O.$ $[Ta_6Br_{12}(H_2O)_6]Br_2$ (100 mg; 0.0432 mmol) were dissolved in 4 mL distilled water. Another solution of K₅[BW₁₂O₄₀]•16H₂O (144 mg; 0.0432 mmol) and C₄₈H₈₀O₄₀•6.6H₂O (123 mg; 0.0865 mmol) were dissolved in 4 mL distilled water. Around 0.5 mL of each solution was introduced on opposite sides of a 0.5 cm diameter H-tube. Two drops of CF₃SO₃H 2 M were added to each side. Then distilled water was layered above both solutions until the H-tube was filled allowing slow diffusion on both sides. After one week needle-like green crystals are formed at the center of the tube. Crystals were isolated and characterized by XRD, FT-IR, TGA and EDX. Yield 30 mg, 43 %. FT-IR spectrum is given in Figure 22. TGA showed a weight loss of 5.0 % assigned to coordination and hydration water molecules in the 20-120 °C temperature range (calculated 4.5 %). Elemental analysis for: BBr₂₄C₁₉₂H₃₈₄O₂₃₂Ta₁₂W₁₂ calc. (found) C 18.14 (17.98); H 3.04 (2.81). EDX calc. (found): Ta/W = 1.00 (1.03); Ta/Br = 0.50 (0.61). FW = 12711.1 g/mol.

III. Binary systems based on POM/CD or Cluster/CD interactions III.1. Formation of the γ-CD based adducts

{P2W18}⊂nCD. Systematic studies have been carried out using different ratios of $\{P_2W_{18}\}$ and γ -CD and different alkali salts of the Dawson anion allowing either to tune solubility of the $\{P_2W_{18}\}/\gamma$ -CD aggregates or to improve the quality of the single crystals. This study showed that this chemical system is highly flexible producing crystalline solids, which contain aggregates with variable $\{P_2W_{18}\}$: γ -CD stoichiometries. The syntheses were straightforward and consist of mixing one, two or three equivalents of γ -CD, respectively dissolved in water or in 0.5 mol.L⁻¹ NaCl aqueous solution containing one equivalent of Dawson anion $[P_2W_{18}O_{62}]^{6-}$ at concentration of about 10^{-2} mol.L⁻¹ as potassium, rubidium or cesium salts. Solutions were allowed to stand at room temperature for crystallization. After several days, single-crystals suitable for XRD, elemental analysis and further characterizations were collected. Then, the three isolated crystalline phases with the respective composition $KNa_5[P_2W_{18}O_{62}] \cdot [\gamma$ - $C_{s}Na_{5}[P_{2}W_{18}O_{62}] \cdot [\gamma - CD]_{2} \cdot 1.2NaCl \cdot 23H_{2}O$ CD]•3.5NaCl•23H₂O, and $Rb_4K_{1.5}Na_{0.5}[P_2W_{18}O_{62}] \bullet [\gamma-CD]_3 \bullet 35H_2O$ have been abbreviated hereafter $\{P_2W_{18}\} \subset CD$, $\{P_2W_{18}\} \subset 2CD$ and $\{P_2W_{18}\} \subset 3CD$, respectively. Infrared spectra of $\{P_2W_{18}\} \subset nCD$ shown in Figure 2 appear to be the summation of the spectrum corresponding to CD and that corresponding to $[P_2W_{18}O_{62}]^{6-}$ with the ratios of the bands corresponding to CD clearly increasing from $\{P_2W_{18}\}\subset CD$ to $\{P_2W_{18}\}\subset 3CD$. The absorption bands in the region 1480 to 1180 cm⁻¹ are assigned to C-H bending vibrations while those located in the 1200 to 1000 cm⁻¹ are attributed to the symmetric stretching of C-O-C and C-O of the polysaccharide. The band at 1084 cm⁻¹ corresponds to P-O asymmetric vibration and those at 800 and 905 cm⁻¹ are attributed to W-O-W asymmetric vibrations. From $\{P_2W_{18}\}\subset CD$ to $\{P_2W_{18}\}\subset 3CD$, the ratio of the bands of CD compared to that of the POM clearly increases (see in the 950-1150 cm⁻¹ range), showing the increases of the ratio $CD/\{P_2W_{18}\}$, accordingly to the TGA curves recorded for the three compounds (see Figure 3).



Figure 2: FT-IR spectra of compounds $\{P_2W_{18}\}\subset CD$, $\{P_2W_{18}\}\subset 2CD$, and $\{P_2W_{18}\}\subset 3CD$, in comparison with the FT-IR spectra of the precursor $K_6[P_2W_{18}O_{62}]$. 19H₂O ($\{P_2W_{18}\}$) and of the γ -cyclodextrin (CD).

 ${Ta_6} \subset 2CD$. The cationic cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ showed high tendency to form a 1:2 inclusion complex with the γ -CD whatever the used ${Ta_6}/\gamma$ -CD ratio. The formation of the 1:2 adduct is nearly quantitative from aqueous mixtures containing stoichiometric proportion of γ -CD and ${Ta_6}$ cluster. The resulting solutions were able to generate greenish plate crystals corresponding to $[Ta_6Br_{12}(H_2O)_6] \cdot [\gamma$ -CD]₂Br₂ \cdot 14H₂O, namely ${Ta_6} \subset 2CD$.



Figure 3: Thermal gravimetric analysis (TGA) of $\{P_2W_{18}\}\subset nCD$ with n = 1, 2 or 3 colored blue, red and green respectively, showing the loss of water and CD between 20 and 700°C.

III.2. Single crystal X-ray analysis

 $\{P_2W_{18}\}\subset nCD \text{ arrangements with } n = 1, 2 \text{ or } 3$. Remarkably, X-ray diffraction analysis of single crystals obtained from $\{P_2W_{18}\}/\gamma$ -CD mixtures revealed three different stoichiometries depending on the used POM/ γ -CD ratio (see Figure 4 below).



Figure 4: Structural representation of the supramolecular $\{P_2W_{18}\}\subset nCD$ assemblies along their X-ray diffraction analysis showing a) the 1:1, b) 1:2 and c) 1:3 arrangements for n = 1, 2, and 3 respectively.

Interestingly, structural analyses in the solid state of the 1:1, 1:2 and 1:3 arrangements exhibit a striking common mode of interaction in which the two components are held together through close contacts involving the primary face of the γ -CD and the longitudinal side of the POM. As generally depicted for such a type of arrangements, the two components are held together through a set of weak attractive interactions including electrostatic, ion-dipole and hydrogen bonding (see Figure 5-7). In the structure of the 1:1 complex (see Figure 4a), the Dawson ion appears literally put down on the primary face of the γ -CD. Structural analyses revealed only one short ion-dipole contact W=O•••C-OH (O•••C = 2.68 Å), while the remaining similar interactions appear weaker as reflected by O•••C distances longer than 3.2 Å. Furthermore, four weak hydrogen bonding contacts are observed leading to O•••O distances in the 3.0-3.3 Å range. Finally, electrostatic interactions must also be considered since attractive interactions are reinforced by O•••K•••O junctions involving terminal W=O groups of the POM unit (O•••K distances, ~ 3.0 Å) and by the hydroxymethyl groups of the glucopyranose moieties belonging to the γ -CD (See Figure 5a). No CD•••CD interactions have been witnessed in the crystal packing of this arrangement (see Figure 5b).



Figure 5: Structural representation of: a) $\{P_2W_{18}\}\subset 1$ CD arrangement showing the involvement of the potassium cations (yellow spheres) within the POM••••γ-CD interactions in addition to the hydrogen bonds (dotted blue sticks) and C-H•••O (red dotted stick), b) crystal packing of this arrangement.

The structure of $\{P_2W_{18}\}\subset 2CD$ assembly consists of one Dawson unit $[P_2W_{18}O_{62}]^{6-1}$ sandwiched by two γ -CD disposed on the two opposite longitudinal faces of the POM at 180° from each other (see Figure 4b). The cohesion forces of the supramolecular 1:2 arrangement are ensured by three hydrogen bonding contact with O•••O distances of about 3.0 Å, supported by electrostatic interactions involving bridging Na⁺ and Cs⁺ cation (see Figure 6a). In this case, the CDs appear quite close to each other in the crystal packing with an (O•••O = 2.65 Å), (see Figure 6b).



Figure 6: Structural representation of: a) $\{P_2W_{18}\}\subset 2CD$ arrangement showing the involvement of the cesium (dark-green spheres) and sodium cations (light-green spheres) within the POM••• γ -CD interactions in addition to the hydrogen bonds (dotted blue sticks), b) crystal packing showing the CD•••CD interaction.

A third POM: γ -CD stoichiometry has been obtained giving an assembly where the $[P_2W_{18}O_{62}]^{6-}$ ion is closely embedded by three γ -CDs as a paddle wheel arrangement (see Figure 4c). As already observed for the 1:1 and 1:2 stoichiometries, the primary faces of the three γ -CD units are directed toward the central POM moiety. Interestingly, the three γ -CDs are related through a C₃ axis and held together through three short hydrogen-bonding contacts (O•••O = 2.69 Å). Furthermore, three equivalent rubidium cations are also involved within the {P₂W₁₈} \subset 3CD arrangement as nodes that associate the POM with three γ -CDs through seven Rb–O contacts (Rb–O = 2.83 – 3.22 Å), as illustrated in Figure 7. Each CD appear closely packed with two other CDs overlapping in a triangular arrangement and sharing three O•••O contacts in the range 2.69-3.01 Å (see Figure 7b).



Figure 7: Structural representation of: a) $\{P_2W_{18}\}\subset 3CD$ arrangement along the C₃ axis showing the involvement of the rubidium cations (light-green spheres) within the POM•••• γ -CD interactions in addition to the hydrogen bonds (dotted blue sticks), b) crystal packing showing CD•••CD interactions.

At last, three additional hydrogen bonds (O•••O = 2.93 Å) ensure direct interactions between {P₂W₁₈} and γ -CD. These results have to be correlated with those previously reported by Stoddart *et al.* on superstructures involving cyclodextrins and the Keggin-type [PMo₁₂O₄₀]³⁻ anion.³⁰ In all cases, the three structures exhibit similar types of molecular recognition wherein POM unit is facing γ -CD through its primary face as two complementary moieties usually described as hydrogen bond acceptor and donor, respectively. In these structural examples, the Keggin or Dawson ions do not penetrate deeply into the cavity of the macrocyclic host but rather interact through multiple weakly bonding interactions array with the hydrophilic OH groups lining the primary faces of the CDs. Actually, such a situation is significantly pronounced with the Dawson anion, a species larger than the $[PMo_{12}O_{40}]^{3-}$ Keggin-type anion.³⁰ Besides, it should be also worth noting the role of the alkali ions (Na⁺, K⁺, Rb⁺ or Cs⁺), which participate also in the reinforcement of the supramolecular POM•••CD associations in the solid state packing. Nevertheless, Stoddart *et al.* mentioned that the La³⁺ counter cation presents as fully hydrated aqua ion $[La(H_2O)_9]^{3+}$ displays only very weak ionic interactions with the $[PMo_{12}O_{40}] \subset 2CD$ supramolecular complexes. In our case, probably due to their low enthalpy hydration,⁵⁴ alkali ions are then able to interact directly with the OH groups of the rims (see Figures 5-7). In this case, such a situation precludes the usual CD•••CD face-to-face organization observed within the $[PMo_{12}O_{40}] \subset 2CD$ arrangement.³⁰

{Ta₆}⊂•2CD arrangement. The supramolecular host-guest arrangement within $[Ta_6Br_{12}(H_2O)_6]$ •[γ-CD]₂Br₂•14H₂O crystal is depicted in Figure 8. The structural analysis reveals a $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster closely embedded into two γ-CDs interacting mutually through multiple hydrogen-bonds (O•••O = 2.9-3.0 Å). The inclusion complex interaction in this case involves the wider rim of the CDs (secondary face). Structural parameters of the encapsulated {Ta₆} cluster remain in the usual range of that generally observed in octahedral tantalum clusters (Ta–Ta = 2.88 – 2.93 Å; Ta–Br = 2.60 – 2.61 Å; Ta–O = 2.15 – 2.39 Å).⁵⁵⁻⁵⁷ However, the cohesion of the supramolecular assembly arises from four short C–H ••• Br contacts (H•••Br = 2.83 Å) involving the inner H-3 hydrogen atoms of each γ-CD and the Br atoms of the cluster (see Figure 8b). In addition, the host-guest stability is supported by a framework of 16 hydrogen bonds connecting the four *in-plane* aquo ligands of the {Ta₆} cluster with the four closest OH groups (O•••O = 3.0 - 3.1 Å) that line the secondary face of the two γ-CD (see Figure 8c).



Figure 8: Mixed representations of the solid state structure of the supramolecular host-guest { $[Ta_6Br_{12}(H_2O)_6] \subset 2\gamma$ -CD}²⁺ complex : a) side view and b) top view highlighting close interactions between inner H-3 hydrogen (white sphere) and four bromide ligands (yellow sphere) with H•••Br = 2.83 Å; c) focus on the intermolecular hydrogen bonding network involving the four *in plane* aquo ligands of the cluster and the hydroxo groups of γ -CD secondary faces (O•••O = 3.0 – 3.1 Å).

As resulting from the multiple intermolecular weak interactions and host-guest disposition, the two stacked γ -CDs appear slightly staggered of about 21° leading to an overall D_4 idealized symmetry. Besides, the tetragonal unit cell displays the common tubular arrangement formed by supramolecular building blocks {Ta₆⊂2CD} running along the *c* axis through short (O•••O = 2.83 Å) and long (O•••O = 6.78 Å) inter-blocks distances (see Figure 9).^{30,58,59} At least, it should be mentioned that the charge balance is ensured by two bromide ions per [Ta₆Br₁₂(H₂O)₆]²⁺ cluster. One half is located on eight equivalent disordered positions and closely intercalated within the {Ta₆⊂2 γ -CD} tubes (see Figure 9), while the other half of the Br⁻ ions is distributed between the tubular assembly.



Figure 9: Representation of the {Ta₆} \subset 2CD structure showing the tubular bamboo-like chains running along the *c* axis. The supramolecular host-guest assembly is alternately stacked through short (O•••O = 2.83 Å) and long (O•••O = 6.78 Å) intermolecular interaction involving the primary face of the γ -CD. These "bamboo-like" chains are mutually connected through the bromide counter ions to give the tetragonal cells. Colour code: yellow sphere = Br; blue sphere = aqua ligand of the {Ta₆}²⁺ cluster; the cyclodextrin are represented by grey-red sticks for C and O respectively.

Among the abundant literature on the cyclodextrin-based host-guest arrangements, it should be mentioned the report of Nau *et al.* about the inclusion complexes of the $[B_{12}X_{12}]^{2^{-1}}$ series (with X = H, Cl, Br or I) who described the crystallographic structure of the $[B_{12}Br_{12}]^{2^{-1}}$

dodecaborates included within two γ -CDs.⁶⁰ Strikingly, both ionic species, *i.e.* cationic with $[Ta_6Br_{12}(H_2O)_6]^{2+}$ or anionic with $[B_{12}Br_{12}]^{2-}$, appear deeply immersed within two facing γ -CDs to give similar host-guest arrangements. Furthermore, structural analogies can be also prolonged to the crystal lattices which display the formal tubular network, both consistent with a tetragonal cell in the I_{422} space group. Such an analogy tends to demonstrate that the lattice is mainly imposed by the tubular packing of the large supramolecular ionic units able to accommodate different types of counter-ions in the large resulting voids, such as Na⁺ with $[B_{12}Br_{12}]^{2-}$ or Br⁻ with $[Ta_6Br_{12}(H_2O)_6]^{2+}$. At least, these striking structural similarities are also supported by close solution behavior revealed by NMR, ITC and electrochemical studies (see following sections).

III.3. Solution studies

Interactions of γ -CD with {P₂W₁₈} POM or [Ta₆Br₁₂(H₂O)₆]²⁺ cluster in aqueous solutions have been confirmed and studied in details by NMR, ESI-MS, ITC measurements, electrochemistry and UV-Vis. These studies and related analyses were able to give clear insights about supramolecular pre-organization processes that occur in solution and to draw a comprehensive description of the interplay of the solvation shell within the recognition processes.

NMR studies. Aqueous solutions of K₆[P₂W₁₈O₆₂]•19H₂O or [Ta₆Br₁₂(H₂O)₆]Br₂ mixed with various amounts of γ-CD have been studied by multinuclear NMR (1D, EXSY or DOSY). NMR results showed contrasted behaviors related to the different shape, size and electronic charge density of the inorganic guest species. The ¹H NMR spectra of γ-CD upon increasing concentration of the [P₂W₁₈O₆₂]⁶⁻ species revealed tiny but significant chemical shift changes of mainly the primary face protons H-6 ($\Delta \delta \sim 0.3$ ppm), as illustrated in Figure 10.⁶¹ This observation suggests that the Dawson units interact weakly with the primary face of the γ-CD to give labile associations in fast chemical exchange regime with respect to the NMR time scale. To determine the stoichiometry of binding between the host and the guest, Job's plot, also known as the method of continuous variation was used. It is based on determining the fraction of the hostguest system for which a maximum is observed corresponding to the product of this fraction from the difference in observed NMR chemical shift provoked by this fraction. Job's plot analysis (see insert in Figure 10) allowed concluding that γ-CD/POM aggregates form in solution with an average stoichiometry close to 1:2 (x_{CD} = CD/(CD + guest) = 0.66).



Figure 10: ¹H NMR spectra of γ -CD solution (3 mM) containing variable amounts of K₆[P₂W₁₈O₆₂], showing effect on signal H6 as a result of inclusion complex formation (H6'). Insert: Job's plot for γ -CD and POM obtained by plotting the chemical shift changes H-6/6' protons of the γ -CD.

Furthermore, such aggregates formation has been nicely evidenced concomitantly by ¹H and ³¹P DOSY NMR allowing access to the self-diffusion coefficient of the γ -CD and that of the POM species, respectively. The DOSY investigation, graphically shown in Figure 11 reveals that the self-diffusion coefficients of the interacting substrates decrease significantly in the POM/ γ -CD mixture that underline the formation of stable aggregates in solution. Interestingly, the *D* value of both interacting components reach together the same minimum value at *D* = 210 µm².s⁻¹ observed for the composition range close to the 1:2 ratio ($x_{CD} = 0.66$). While the chemical shift changes of the γ -CD are small and those of the ³¹P or ¹⁸³W resonances nearly undetectable, they feature tiny conformational or electronic changes induced through aggregates formation. On the contrary, the DOSY analysis of the POM/ γ -CD mixture revealed clearly that stable aggregates are formed provoking large changes of self-diffusion coefficients (see Figure 11). These DOSY NMR data corroborate nicely the analysis given by Stoddart *et al.* from SAXS/WAXS measurements carried out on aqueous solution containing the Keggin-type anion and γ -CD.³⁰ Noticeably,

apparent contradictions arise from these finding because structural analysis reveals that POMs and CDs assemble together through weak interactions evidenced by only tiny variations of NMR chemical shifts (¹H, ¹⁸³W and ³¹P), while DOSY or SAXS/WAXS investigations demonstrate that these hydrophilic species form stable aggregates in aqueous solution. Such an apparent discrepancy shed light on the prominent role of the water molecules as solvent when interacting species like POMs and γ -CD exhibit significant solvent-accessible surface.⁶²



Figure 11: Variation of the self-diffusion coefficient of POM (black curve) and γ -CD (red curve) measured by ³¹P and ¹H DOSY NMR spectroscopy, respectively, as a function of the fraction of the CD in the POM-CD system. The significant variation of the D values reveals that both γ -CD and POM move together for compositions close to the 1:2 ratio ($x_{CD} = 0.66$).

In the presence of the octahedral $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cationic cluster, the ¹H NMR spectra of the γ -CD undergoes strong changes characterized mainly by the disappearance of the H-1 and H-3 initial resonances of the γ -CD for the benefit of new signals, (see Figure 12). ¹H NMR titration showed that such changes are nearly completed for the 1:2 ratio that is fully consistent with the X-ray diffraction analysis. Actually, the presence of additional ¹H NMR resonances is characteristic of dynamically slow equilibrium process (on the NMR time scale) in D₂O solution involving deeply embedded tantalum cluster through the two secondary faces of γ -CD tori. EXSY ¹H NMR spectrum (see Figure 13), recorded for a ratio cluster:CD = 0.25 revealed correlations between resonances of the free and complexed γ -CD, both involved in slow exchange processes.



Figure 12: Selected ¹H NMR spectra (298 K, D₂O, 1 mM) of γ -CD in the presence of the different equivalent of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ dication. The appearance of new resonances, clearly observed for the H-1 and H-3 protons suggests that the cluster is deeply inserted into the cavity of the γ -CD at their secondary faces, giving a non-labile 1:2 host-guest arrangement.



Figure 13: ¹H EXSY NMR spectrum of γ -CD solution (3 mM) containing $[Ta_6Br_{12}(H_2O)_6]Br_2$ in the molar ratio $[Ta_6Br_{12}(H_2O)_6]^{2+}/CD = 0.25$, showing exchange correlations between protons of free (Hn) and complexed (Hn') CDs, and protons of the two types of glucopyranose units (H_n' & H_n") present in the complexed CD.

Thus, under complexation process, H-1 undergoes a significant low frequency shift giving broader new signal at 4.93 ppm. At the same time, H-3 resonance splits into two signals at 4.34 and 4.05 ppm that reflect the symmetry lowering of the macrocycles in the host-guest arrangement from C₈ to C₄. Interestingly, EXSY experiment revealed also slow intramolecular dynamic consisting of a wheeling movements of the CD tori around the C₄ axis that result in an exchange of position between H-3' and H-3". Variable temperature ¹H NMR experiments carried out in a mixture at a ratio {Ta₆}: γ -CD = 1:4 confirm plentifully such a dynamic behaviors showing illustrative coalescence phenomena from about 50-60 °C for the most affected H-1 and H-3 signals (see Figure 14).



Figure 14: Variable temperature ¹H NMR spectra of γ -CD solution (3 mM) containing $[Ta_6Br_{12}(H_2O)_6]Br_2$ in the molar ratio $[Ta_6Br_{12}(H_2O)_6]^{2+}/CD = 0.25$, showing magnetization exchange between protons of free (H_n) and complexed (H_n') CDs, and protons of the two types of glucopyranose units (H_n' & H_n") present in the complexed CD.

Furthermore, analysis of the COSY ¹H NMR spectrum of the 1:2 association allowed the confirmation of these ¹H NMR assignments of the γ -CD as host (see Figure 15).



Figure 15: ¹H COSY NMR spectrum of γ -CD solution (3 mM) containing $[Ta_6Br_{12}(H_2O)_6]Br_2$ in the molar ratio $[Ta_6Br_{12}(H_2O)_6]^{2+}/CD = 2.3$, showing correlations between resonances of the two distinguished glucopyranose units $(H_n, \& H_n)$ present in the complexed CD.

Actually, the significant downfield shifts concomitant to the splitting of the inner H-3 protons appear in fair concordance with that observed by X-ray diffraction analysis. In the solid state structure, four H-3 protons of each γ -CD exhibit very close contacts with four Br atoms of

the tantalum cluster (Br•••H = 2.83 Å), while the four remaining H-3 are engaged within significantly longer interactions (Br•••H = 3.19 Å) as illustrated in Figure 8b. Then, the decrease of the local symmetry of the γ -CD from C₈ to C₄ generates two groups of four equivalent glucopyranosyl units that should provoke the splitting of all the ¹H resonances. This is clearly observed for the most affected H-3 protons while line broadening and probably accidental degeneracy prevent any clear resolutions for the other signals arising from the two sets of nonequivalent glucopyranosyl units. In conclusion, NMR results reveal a frozen complex that should feature a high host-guest affinity. Such a situation is fully consistent with the X-ray structural analysis which reveals a deeply embedded tantalum cluster within the γ -CDs pocket. These observations have been further supported by ITC analysis (see below).

ESI-MS studies. The γ -CD based systems containing either the Dawson anion or the {Ta₆} octahedral dicationic cluster give explicit ESI-MS spectra in fair accordance with our previous results. As shown in Figure 16a, ESI-MS spectrum of 1.10^{-4} mol.L⁻¹ aqueous solution in {P₂W₁₈} \subset 3CD assembly, carried out in the negative mode contains three well-defined massifs which have been attributed unambiguously to [{P₂W₁₈} \subset 2CD]⁶⁻ at m/z = 1159.6, [H{P₂W₁₈} \subset CD]⁵⁻ at m/z = 1132.2 and CD-free POM identified as [H₂P₂W₁₈O₆₂]⁴⁻ at m/z = 1091.4 and [P₂W₁₈O₆₁]⁴⁻ at m/z = 1086.7. It is quite surprising that such aggregates which have been characterized as labile adduct by ¹H NMR can even be observed in the conditions required for ESI-MS experiments.



Figure 16: ESI-MS spectra of the inclusion compounds in aqueous solution. (a) $\{P_2W_{18}\}\subset 3CD$ showing the 1:1 and the 1:2 adducts while the 1:3 complex is not observed. (b) $\{Ta_6\}\subset 2CD$ containing the m/z peak related to the 1:2 (red trace) and 1:1 (green trace) adducts. The side peaks separated from each other by m/z = 9 are unambiguously attributed to either hydrated or dehydrated complexes.

Nevertheless, initial complex $\{P_2W_{18}\}\subset 3CD$ was not observed in the ESI-MS spectrum, probably due to a weaker stability than that of the smaller aggregates $\{P_2W_{18}\}\subset 2CD$ and $\{P_2W_{18}\}\subset CD$. This is consistent with ITC measurements, which indicate also that higher aggregates such as $\{P_2W_{18}\}\subset 3CD$ do not contribute significantly within the thermodynamic of the overall host-guest process. Conversely, the $\{Ta_6Br_{12}(H_2O)_6\subset 2CD\}^{2+}$ host-guest arrangement in aqueous solution gives an ESI-MS spectrum in the positive mode that contains two main massifs, each characteristic of the 1:2 and 1:1 assembly, respectively (see Figures 16b and 17).



Figure 17: Full ESI-MS spectrum of the inclusion complexes in aqueous solution of $\{Ta_6\} \subset 2CD$ (black trace) with a zoom into the m/z peaks related to the 1:2 (red trace) and 1:1 (green trace) adducts with dehydration of cyclodextrin (blue trace).

The highest m/z massif contains peak at 2372.2 corresponding to the expected dicationic 1:2 species ${Ta_6Br_{12}(H_2O)_6 \subset 2CD}^{2+}$. Furthermore, this peak is flanked on each side by two additional signals giving an overall set of five peaks all separated exactly by m/z = 9 that is consistent with gain or loss of one or two water molecules. Therefore, the two right side-peaks located at m/z = 2380 and 2389 are attributed to mono- and di-hydrated dicationic derivatives, while the two other peaks located on the left side result from the loss of one or two water

molecules. Aqua ligands attached to the octahedral tantalum cluster could be involved in such dehydration process and especially the two axial coordination water molecules. These water molecules are directed along the γ -CD axis and probably more exposed than the four remaining equatorial aqua ligands, intimately encaged within the two γ -CD tori (see Figure 8). The other massif is constituted of several peaks corresponding to different hydration state of the 1:1 dication host-guest arrangement. The expected species {Ta₆Br₁₂(H₂O)₆⊂CD}²⁺ and related mono-and di-hydrated derivatives are observed at m/z = 1724, 1733 and 1742, respectively. On the left side, the presence of the first six peaks at lower m/z value is rather consistent with the sequential dehydration of the octahedral cluster until the loss of the six coordination aqua ligands to give the anhydrous species {Ta₆Br₁₂⊂CD}²⁺, while the rest of the peaks are attributed to the dehydration of the cyclodextrin as shown in Figure 17.

These ESI-MS results seem to indicate that a supramolecular control of the desolvation process of the $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster is allowed, selectively restricted to the two axial aquo ligands within the closed 1:2 arrangement and extended to the six aquo ligands and cyclodextrin dehydration within the 1:1 open shell complex. Such ESI-MS observations tend to demonstrate that supramolecular coordination chemistry based on selective ligand exchange process should be achievable from aqua octahedral clusters, using their remarkable host-guest complementarity with γ -CD.

ITC measurements. ITC was used to analyze from a thermodynamic point of view the interactions of the γ -CD with {P₂W₁₈} POM or [Ta₆Br₁₂(H₂O)₆]²⁺ cluster, respectively.^{58,63} ITC results including binding constants, enthalpy $\Delta_r H^*$ and entropy $\Delta_r S^*$ are given at 298 K in Table 2.

Table 2: Binding constants K involving	Dawson anion	1 and tantalum	octahedral	cluster	cation	with γ-CD	and	associated
thermodynamic parameters (in kcal.mol	$^{-1}$) at T = 298 K	Κ.						

Guest	Step	$K(10^3 M^1)$	$\Delta_r H^*$	$T\Delta_r S^*$	$\Delta_r G^*$
$[P_2W_{18}O_{62}]^{6}$	1:1	3.2	-12.6	-7.8	-4.8
	1:2	0.37	-11.9	-8.4	-3.5
$[Ta_6Br_{12}(H_2O)_6]^{2+}$	1:1	150	-8.2	-1.2	-7.0
	1:2	130	-5.2	+1.9	-7.0

The ITC data obtained from $\{P_2W_{18}\}/\gamma$ -CD system were analyzed using a two-site binding model involved within a sequential process. As X-Ray diffraction data revealed that a 1:3 aggregate $\{P_2W_{18}\} \subset 3CD$ can be isolated in the solid state, but introducing a third sequence within the binding model does not improve fits significantly between experimental and calculated data. This means that recognition process is mainly dominated by the formation of the 1:1 and 1:2 aggregates and that presence of higher order aggregates remains negligible in solution. Actually, the ITC results confirm nicely the above results showing a quite significant affinity between {P₂W₁₈} and γ -CD with $K_{11} = 3.2 \ 10^3 \ \text{M}^{-1}$ and $K_{12} = 3.7 \ 10^2 \ \text{M}^{-1}$, associated with enthalpy driven processes, each compensated by entropy penalty. These data appear quite surprising because such large enthalpy gains observed for both 1:1 and 1:2 successive processes do not reflect anymore the weakness of the intermolecular interactions of the Dawson ion with the γ -CD. Actually, a partial inclusion could be expected involving the two polar sites of the Dawson ion, structurally similar to that found by Stoddart et al. with the Keggin ion derivative.³⁰ Nevertheless, as evidenced by our ¹H NMR studies in solution and supported by X-ray diffraction analysis, aggregates formation results mainly from close contacts between the largest lateral sides of the POM and the hydrophilic primary face of the γ -CD species. Furthermore, overall results are rather consistent with weak interactions as shown by ¹H NMR in solution and solid-state structural analysis even though the resulting aggregates exhibit fair stability as exemplified by large variations of DOSY self-diffusion coefficient of both species (see Figure 11) and by large binding constants K_{11} and K_{12} . These apparent inconsistencies fade away whilst the prime role of the solvent is considered. Since a pure hydrophobic effect cannot account within the interacting process, water structure recovery resulting of solvent depletion from binding interfaces should contribute in a significant extent. Thermodynamic fingerprints (see Table 2) could be consistent with a "chaotropic" recognition process involving "water structure breakers" species. This idea that POM anions can range in the chaotropic category is supported by the low charge density distributed at the POM surface and by the intrinsic weak ability of the POM anion to be strongly solvated. Furthermore, evidences of interaction between Keggin-type POMs and organic materials such as lipids or biomolecules are also consistent with the chaotropic nature of POMs.⁶⁴



Figure 18: Microcalorimetric titration data obtained at 298 K from sequential injections of 3.33 mM γ -CD solution into a 0.33 mM [Ta₆Br₁₂(H₂O)₆]Br₂ solution showing ITC thermogram (left) and isotherm (right). Dots and full lines correspond to experimental and calculated heats obtained from thermodynamic parameters describing a two-step sequential binding process (bottom).

Guest affinity of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ octahedral cluster has been determined by ITC titration experiments which have been analyzed using a two-step sequential binding model (see Figure 18). The thermodynamic parameters and binding constants included in Table 2 and Figure 18 reveal that both 1:1 and 1:2 processes are enthalpy driven and associated to opposite entropy changes which is slightly unfavorable for the first 1:1 step and then switches to positive for the following 1:2 step. Binding constants related to the sequential host-guest recognition exhibit very high values, i.e., $K_{11} = 1.5 \ 10^5 \ \text{M}^{-1}$ and $K_{12} = 1.3 \ 10^5 \ \text{M}^{-1}$, which are comparable to that reported by Nau *et al.* on the 1:1 binding process between γ -CD and the perhalogenated dodecaborate ion $[B_{12}X_{12}]^{2}$ (X = F, Cl, Br and I).⁶⁰ Among the series, the highest binding constant was obtained with the bromo-derivative $[B_{12}Br_{12}]^{2-}$ with $K_{11} = 9.6 \ 10^5 \ M^{-1}$ that led the authors to conclude that size-matching effect and polarizability of the X groups should contribute to the host-guest recognition process. In our case, the $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cationic guest exhibits similar globular shape and size to those of the $[B_{12}Br_{12}]^{2-}$ anion.⁶⁰ Furthermore, the positive charge of the cluster does not affect anymore the host-guest affinity which rivals and even exceeds usual values found for γ -CD with anionic substrates.^{58,65} Such a large affinity corroborates nicely the X-Ray diffraction analysis and solution ¹H NMR. In the solid state, the identified network of convergent

weak hydrogen bonding interactions should obviously contribute in part as *pulling factor* to the supramolecular assembly stability. Actually, formation of this host-guest arrangement in aqueous medium remains very intriguing because both components are considered as hydrophilic units, mainly due to the six agua ligands located at the corner of the dicationic octahedral cluster or due to the 24 hydroxyl groups that line the primary and the secondary faces of the γ -CD. Hence, the role of the solvent should be pointed out, acting as a pushing factor which consists of selfreorganization of water molecules relocated from the solvation shell to the bulk. Such a contribution has been considered by Nau et al. as the main factor governing the inclusion process, based on the chaotropic or *super* chaotropic nature of the dodecaborate series.^{60,66-68} This example gives first indications about the solvated character of the hexatantalum cluster and should be the starting point for further development using various octahedral type clusters that differ in their metallic centers, inner or outer ligands or ionic charge as the hexarhenium clusters $[\text{Re}_6 X_8(\text{CN})_6]^{4-}$ (X = S, Se or Te).^{36,69} Although these isostructural rhenium clusters share an octahedral metallic core similar to that present in $[Ta_6Br_{12}(H_2O)]^{2+}$ (see Figure 19), they are different when it comes to charge, nature and number of ligands. These clusters are anionic in charge and they bear eight inner chalcogen ligands (X) compared to the twelve halogens borne by {Ta₆} and they exhibit six cyano groups as outer ligands compared to the aquo ones in the tantalum cluster.



Figure 19: Ball and stick representation of the isostructural arrangement of $[Re_6X_8(CN)_6]^{4-}$ (X = S, Se or Te). Color code: Rem orange; X, purple; C, black and N, blue.

In an ongoing work to compare the host-guest affinity of the tantalum cluster with other octahedral structures, the inclusion complex formation between γ -CD and the [Re₆X₈(CN)₆]⁴⁻ (with X = S, Se or Te) has been investigated by ITC (using the same parameters for the cationic

Ta-containing cluster) to quantify the strength of the host-guest interaction. Table 3 summarizes the corresponding thermodynamic parameters. While both 1:1 and 1:2 cluster:CD complexes are observed for the selenium and tellurium clusters, only 1:1 complexes are formed with the S-containing cluster $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$. The strength of interaction increases weakly but significantly from sulfur to selenium, and then rises by one order of magnitude for the tellurium cluster. These remarkably high values compare well with the published data obtained with the polyoxometalate inclusion complexes and dodecaborate anions.^{30,60} In addition, the inclusion process is enthalpically driven, whatever the cluster. Such a thermodynamic profile arises from the desolvation of the cluster and expelling water from CD cavity when the inclusion complex forms. Note that the magnitude of inclusion enthalpy and entropy strongly decreases from sulfur to selenium, and then more weakly from selenium to tellurium. In addition, this magnitude rises for 1:2 cluster:CD complexes, if compared to 1:1 inclusion compounds.

Table 3: Binding	constants K	involving	$[{\rm Re}_{6}{\rm X}_{8}({\rm CN})_{6}]^{4-}$	cluster	anion	with	□-CD	and	associated	thermodynamic
parameters (in kca	l.mol ⁻¹) at T =	298 K.								

Х	step	$K(10^3 M^{-1})$	ΔH°	TΔS°	ΔG°
S	1:1	0.9	-63.2	-46.4	-16.8
	1 :2	no	no	no	no
Se	1:1	1.5	-30.4	-12.3	-18.1
	1:2	0.3	-56.5	-42.7	-13.8
Te	1:1	37.7	-25.3	+0.8	-26.1
	1:2	12.7	-51.0	-27.6	-23.4

no = not observed

Although the clusters in this series exhibit elevated binding constants they remain inferior to that observed for the cationic tantalum cluster by one to four orders of magnitude. This phenomenon is consistent with that observed by Nau *et al.* for the perhalogenated dodecaborates and it is attributed to the ideal size matching of the cationic cluster to the inner cavity of CD.

Electrochemistry. As both inorganic moieties are redox active and display complementary electrochemical properties, influence of γ -CD upon the electrochemical properties have been examined. Dawson anion $[P_2W_{18}O_{62}]^{6-}$ exhibits the general electrochemical behavior of POM compounds that corresponds to ability to undergo quasi-reversible multi-

electron reductions,⁷⁰ thus conferring electrons reservoir properties interesting for many applications with regard to energy conversion or storage.⁷¹ Whatever the equivalent number of γ -CD, cyclovoltammograms (CVs) of the Dawson remain almost unchanged with respect to that previously reported for the CD-free Dawson anion (not shown).⁷⁰ Such results are probably the fingerprint of labile and weakly bound adducts {P₂W₁₈}⊂nCD, previously identified by ¹H NMR and by structural analysis. Conversely, the electron-rich [Ta₆Br₁₂(H₂O)₆]²⁺ cluster gives two successive monoelectronic waves observed at E₁° = +0.37 V and E₂° = +0.67 V *vs*. SCE in 0.025 mol.L⁻¹ HClO₄ aqueous solution (see Figure 20).⁷²



Figure 20: Cyclovoltammograms of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ (0.5 mM, 298 K, scan rate 10 mV.s⁻¹; 2.5 10⁻² mol.L⁻¹ HClO₄ aqueous solution) in the presence of increasing amounts of γ -CD (from 0 to 5 equivalents). Insert : plot of the first anodic peak potential versus equivalent number of γ -CD showing a break point for the stoichiometric conditions.

These monoelectronic transfers are reversible ($\Delta E_p \sim 60 \text{ mV}$) and correspond to the redox couples {Ta₆}²⁺/{Ta₆}³⁺ and {Ta₆}³⁺/{Ta₆}⁴⁺, respectively. Upon addition of γ -CD, these two redox peaks shift gradually toward higher potential with a large change for the first exchange ($\Delta E_1^\circ = +130 \text{ mV}$) and a smaller one for the second ($\Delta E_2^\circ = +30 \text{ mV}$). These observations evidences clearly that binding situation occurs altering significantly the electrochemical properties of the guest. In addition, loss of electrochemical reversibility is observed and characterized by an increase of potential difference between the cathodic and anodic peaks ΔE_p of 140 mV and 100 mV for the first and the second exchange, respectively. Then, changing the charge state of the guest from 2+ to 4+ in the non-polar environment of the γ -CD pocket might be difficult and should affect the thermodynamic stability of the host-guest assembly giving rise to the observed redox shifts and change of the kinetic barrier. In accordance with this reasonable and well-documented assumption,⁷³ the UV-Vis spectrum of the cluster undergoes only very small variations, indicating that electronic structure of the reduced state of the cluster is almost unaffected by γ -CD complexation (see Figure 21).



Figure 21: UV-Vis spectra of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ aqueous solution in presence of 0, 2, 4 and 10 γ -CD equivalents. For amount of γ -CD upper than 2 equivalents, the UV-Vis features of the $\{Ta_6\}^{2+}$ cluster remain almost unchanged.

These preliminary results tend to demonstrate that electrochemical changes should involve mainly the oxidized forms, namely $\{Ta_6\}^{3+}$ and $\{Ta_6\}^{4+}$. In the visible region, the electronic spectra of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster in aqueous solution is dominated by charge-transfer Ta \rightarrow Ta and Ta \rightarrow Br transitions (see Figure 21). The main UV-Vis data are collected in Table 4. In the presence of various amount of γ -CD, the UV-Vis spectrum of the $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster undergoes tiny changes mainly characterized by a "red" shift of the two band initially located at $\lambda_{max} = 743$ and 648 nm.

Table 4: UV-Vis data of the $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster and the host-guest $\{[Ta_6Br_{12}(H_2O)_6] \subset 2CD\}^{2+}$ assembly in aqueous solution with concentration ranging between 10^{-4} and $8 \ 10^{-4}$ mol.L⁻¹.

Compound	λ_{max} (nm) / ϵ (mol ⁻¹ L cm ⁻¹)
$[Ta_6Br_{12}(H_2O)_6]Br_2$	354 / 15125; 420 / 3875 ; 640 / 6000 ; 745 / 3875
${[Ta_6Br_{12}(H_2O)_6] \subset 2CD}Br_2 \cdot 14H_2O$	354 / 13250 ; 418 / 3625 ; 648 / 5125 ; 751 / 3375

IV. Three-component supramolecular system

The overall presented results offer fundamental bases to build hybrid materials combining the three components γ -CD, the cationic octahedral cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ and the Dawsontype POM. The γ -CD component exhibits a remarkable high affinity with the cationic cluster to consider the 1:2 resulting host-guest complex as a highly stable cationic hybrid building block. Besides, the Dawson $[P_2W_{18}O_{62}]^{6-}$ anion and the γ -CD constitutes a versatile chemical system able to form supramolecular adducts which differ from their stoichiometry but are invariably built on a selective interplay mode involving the primary face of the γ -CD and the largest side of the POM (see Figure 4). Then, high affinities, selective interactions and dynamic flexibility are harnessed to associate the ditopic hybrid cation and the polyoxometalate unit together. This approach will offer undoubtedly new perspectives in the design of unprecedented functional materials that combine the key properties of the electron-rich (cluster donor) and the electronpoor (POM acceptor) moieties, both specifically and spontaneously associated by γ -CD as ditopic linker.

VI.1. Three component system, from hydrogel to single crystals

First attempts have been carried out by mixing directly 2.10^{-2} mol.L⁻¹ aqueous solutions containing the ditopic hybrid cation {Ta₆Br₁₂(H₂O)₆⊂2CD}Br₂•14H₂O and the POM K₆P₂W₁₈O₆₂•19H₂O. In such conditions, the resulting greenish solution becomes viscous until complete gelification in few minutes. Formation of hydrogel-type material indicates that metathesis reaction takes place and results in polymerization process involving the ditopic cation and the POM. The hydrogel has been characterized through a set of analytical methods revealing composition consistent with the formula K₄[Ta₆Br₁₂(H₂O)₆][γ -CD]₂[P₂W₁₈O₆₂]•nH₂O (see experimental section). Infrared spectra confirm the incorporation of the three components assembled within the hydrogel network (see Figure 22). Since {Ta₆} is mute, the spectrum of {Ta₆}⊂2CD almost correspond to that of CD. Thus, the spectrum corresponding to the threecomponent system exhibits the absorption bands corresponding to {P₂W₁₈}⊂2CD where the bands in the region 1480 to 1180 cm⁻¹ are assigned to C-H bending vibrations while those located in the 1200 to 1000 cm⁻¹ are attributed to the symmetric stretching of C-O-C and C-O of the polysaccharide. The band at 1084 cm⁻¹ corresponds to P-O asymmetric vibration and those at 800 and 905 cm⁻¹ are attributed to W-O-W asymmetric vibrations. Besides, the hydrogel assembly reveals birefringence properties under polarized optical micrograph but the most surprising outcome is probably the presence of diffraction peaks in the powder X-Ray diffraction diagram that suggests long-range order exists to a certain extent (see Figure 23).



Figure 22: FT-IR spectra of compounds {Ta₆ \subset 2CD} and {Ta₆ \subset 2CD.POM}, as gel and single crystals, in comparison with the FT-IR spectra of the precursor K₆[P₂W₁₈O₆₂].19H₂O and of the γ -CD.



Figure 23: Powder-X-Ray diffraction pattern of the three-component hydrogel assembly built from hierarchical organization of γ -cyclodextrin, polyoxometalate $[P_2W_{18}O_{62}]^{6-}$ and octahedral cluster $\{Ta_6\}^{2+}$ (see insert); experimental (black) and calculated from single-crystal X-Ray diffraction data (red).

Such a result prompts us to get single-crystals from slow-diffusion techniques using conventional H-tube method. From similar 2.10^{-2} mol.L⁻¹ aqueous solutions used for the hydrogel preparation, small but well-shaped greenish single-crystals suitable for X-ray diffraction analysis were formed in the interfacial region of both solutions for about one week. Elemental analysis of crystals, supported by usual set of analytical methods leads to the similar composition found for hydrogel-based the material with the formula $K_{2}H_{2}\{[Ta_{6}Br_{12}(H_{2}O)_{6}] \subset (C_{48}H_{80}O_{40})_{2}\}[P_{2}W_{18}O_{62}] \cdot 32.5 H_{2}O \text{ (abbreviated } [Ta_{6} \subset 2CD \cdot \{P_{2}W_{18}\}]).$ Besides, the IR spectrum of single crystals is similar to that of the hydrogel as shown in Figure 22. In this regard, $\{P_2W_{18}\}$ POM, γ -CD and $\{Ta_6\}$ octahedral cluster behave as a versatile system, allowing a structuring control from hydrogel to single-crystals using supramolecular bottom-up approach.

VI.2. Single-crystal X-ray diffraction analysis of the three-component system

Single-crystal X-ray diffraction study of $[Ta_6 \subset 2CD \cdot \{P_2W_{18}\}]$ reveals a 1D infinite sandwich-type structure wherein the Dawson POM anions alternate with the ditopic supramolecular cation $\{Ta_6 \subset 2CD\}^{2+}$ (see Figure 24). The linear infinite ionic polymers run along the *c* axis and stack together symmetrically as parallel pillars to give tetragonal packing (see Figure 24b). Besides, the ditopic hybrid cation incorporated within the three-component system exhibits very close geometrical features that those observed previously in the crystallographic structure of $[Ta_6Br_{12}(H_2O)_6] \cdot [\gamma - CD]_2Br_2 \cdot 14 H_2O$ (see Figure 8), especially with regard to the host-guest interactions, mainly expressed through hydrogen bonds distribution. In a same way, arrangement between the γ -CD and the POM remains quite unchanged and involves primary faces of the γ -CD, similar to the structural models of $\{P_2W_{18}\} \subset nCD$, depicted in Figure 4. Interesting observations can be noticed with regard to the expression of the chirality within the solid state arrangement. As usually observed with solid-state structures of cyclodextrins, the $[Ta_6 \subset 2CD \cdot \{P_2W_{18}\}]$ crystallographic structure is consistent with the $P4_12_12$ chiral space group which imposes 4_1 helicoidal axis along centers of the tubular chains. Then, related 4_1 operations generate four different positions for the POM units that wheel helicoidally around the tube axis while orientation of the $\{Ta_6 \subset 2CD\}^{2+}$ units remains unchanged (see Figure 24a and 24c).



Figure 24: Structural representations resulting from the single-crystal X-ray diffraction analysis of the three-component system [Ta₆ \subset 2CD•{P₂W₁₈]: a) tubular chain showing periodic alternation of the ditopic cation {Ta₆ \subset 2CD²⁺ and the [P₂W₁₈O₆₂]⁶ POM running along *c* axis with *c* = 89.17 Å; b) highlight of the tubular chain packing in the *ab* plane; c) POM moieties within the tubular chain are symmetrically related through 4₁ helicoidal axis generating successively four equivalent POM units colored in yellow, green, red and blue, respectively; d) highlight of two POM units sandwiching the {Ta₆²⁺ cluster through short hydrogen bonds such as O-O = 2.64 Å (the two γ -CD have been omitted for clarity).

Finally, additional hydrogen bonds are found, involving the axial aqua ligand of the ${Ta_6Br_{12}(H_2O)_6}^{2+}$ and terminal oxygen atoms of the POM. The shortest distances O•••O that are in the 2.64-2.83 Å range suggest that electrostatic interactions may reinforce hydrogen bonding. Besides, the long-range ordering within the hydrogel can be understood partly from the structural analysis of the single-crystals, by considering that stacked tubular chains, shown in Figure 24 are flexible enough to self-interpenetrate in the supramolecular 3D network. Nevertheless, further investigations are still progressing for the full understanding of the long-range ordering of our hybrid hydrogel.

Keeping in mind that Keggin-type anions also showed tendency to interact with CD as reported by Stoddart *et al.*,³⁰ {Ta₆Br₁₂(H₂O)₆}²⁺ cluster was added to a solution containing γ -CD and a tungsten based Keggin anion [BW₁₂O₄₀]⁵⁻ noted {BW₁₂}. A different behavior was observed compared to that seen with the Dawson-type anion discussed earlier. For the former, a green precipitate was obtained corresponding to a salt formation from charge neutralization between the ditopic cation and the small POM. In the latter case, gelation takes place resulting in a polymer-like chain. Following the same procedure for the crystallization of the first three-component system, {BW₁₂}, {Ta₆} and γ -CD were introduced in an H-tube. Well-shaped green platelets identical to those found for {Ta₆}⊂2CD arrangement were obtained. The crystal didn't only mimic the shape of the {Ta₆}⊂2CD arrangement, but it retained a similar unit cell (see Table 5). Both structures displayed the formal tubular network consistent with a tetragonal cell *I*₄₂₂ space group.

Similar to $\{Ta_6\} \subset 2CD$, the lattice was imposed by the tubular packing of the sandwich host-guest assembly but in this case the accommodated counter anions within the voids are the larger ions $\{BW_{12}\}$ that occupied three distinct positions as demonstrated from the unit cell packing shown in Figure 25. $\{BW_{12}\}$ replaced the Br⁻ ions that filled the void between two neighboring $\{Ta_6\} \subset 2CD$ in the tubular chain and they filled the two gaps generated from the packing of four tubular chains where one centers eight $\{Ta_6\} \subset 2CD$ units and the other is aligned with the $\{BW_{12}\}$ separating two $\{Ta_6\} \subset 2CD$ of the same chain (see Figure 25c). Structural analysis revealed a $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster closely embedded into two γ -CDs interacting through multiple hydrogen bonds (O•••O = 2.9-3.0 Å) through their secondary face (wider rim) identical to that observed for $[Ta_6Br_{12}(H_2O)_6]^{\bullet}[\gamma$ -CD]₂Br₂•14H₂O (see section III for further details). On the other hand, $\{BW_{12}\}$ within the *c* axis along the chain is hydrogen bound to the axial aqua ligands of the cluster through its terminal oxygens (O•••O = 3.0 Å) while the two other $\{BW_{12}\}$ filling the void generated by the packing are hydrogen bound to the primary faces of two successive CDs (O•••O = 2.9 Å).



Figure 25: Mixed representation of the {Ta₆} \subset 2CD•BW₁₂ structure showing the tubular bamboo-like chains running along the *c* axis. The supramolecular host-guest assembly is alternately stacked through short (O•••O = 2.83 Å) and long (O•••O = 6.78 Å) intermolecular interaction involving the primary face of the γ -CD. These "bamboo-like" chains are mutually connected through BW₁₂ in tetragonal cells. Color code: yellow sphere = Br; red sphere = O; grey spheres = C. BW₁₂ is represented in ball and stick mode with white spheres = W and red spheres = O.

ITC measurements. As $[P_2W_{18}O_{62}]^{6-}$ and $[Ta_6Br_{12}(H_2O)_6]^{2+}$ proved their ability to form various supramolecular complexes with γ -CD, the possibility of forming materials involving the three partners was then explored by ITC. Interestingly, when $\{P_2W_{18}\}$ was injected on a mixture of $\{Ta_6\}$ and γ -CD, significant heats were systematically recorded, whereas negligible signals should be expected in the hypothesis of a simple competition between the two distinct 1:1 and 1:2 γ -CD complexes of $\{P_2W_{18}\}$ and $\{Ta_6\}$, as the $\{Ta_6\}$ complexes are significantly stronger than those involving $\{P_2W_{18}\}$. These heats demonstrated the existence of hetero-ternary complexes.

On one hand, when the initial concentrations of {Ta₆} and γ -CD lead essentially to 1:1 complexes, a clean thermogram was obtained (see Figure 26). Strikingly, the corresponding binding isotherm has been calculated with a satisfactory agreement with the experimental data by considering the possibility to associate up to three {Ta₆⊂CD}²⁺ complexes with one POM molecule, as illustrated in Figure 26. The estimated binding constant for the interaction between one {Ta₆}⊂CD complex with one {P₂W₁₈} molecule was close to 4 10⁴ M⁻¹, which is one order of magnitude higher than that for fixing one γ -CD on one {P₂W₁₈} molecule in the absence of
{Ta₆}. Actually, it has to be stressed that the quantitative analysis of this single isotherm by our theoretical model is probably over-parametrized, with respect to the presence of a large distribution of aggregates arising from available combinations of the three building blocks. Nevertheless, the rapid decrease of the ITC isotherm is clearly in favor of strong and multiple bindings between {P₂W₁₈} and {Ta₆}⊂CD entities.



Figure 26: ITC thermograms (upper part) and isotherms (lower part) for the titration of a mixture of γ -CD (22.5 μ M) and $[Ta_6Br_{12}(H_2O)_6]^{2+}$ (90 μ M), by a 200 μ M { P_2W_{18} } solution. Dots correspond to the experimental heats. Red line corresponds to the theoretical heats when considering the presence of { Ta_6 } \subset CD, { Ta_6 } \subset 2CD, { P_2W_{18} }[{ Ta_6 } \subset CD], { P_2W_{18} }[{ Ta_6 } \subset CD]₃

On the other hand, when $\{Ta_6\}\subset 2CD$ complexes were initially favored in the cell by increasing the initial γ -CD concentration, important deformations were observed on the ITC thermograms (not shown). Concomitantly, turbid solutions were extracted from the cell at the end of the titrations. Such observations indicate that interactions between the ditopic cationic complexes $\{Ta_6\subset 2CD\}$ and the $\{P_2W_{18}\}$ favor polymerization process. Both observations of deformed thermograms and turbid solutions during the ITC experiment corroborate our previous observations that such ternary system leads to supramolecular polymer. Unfortunately, the consecutive variation of viscosity and the heterogeneous character of the solutions hindered any quantitative interpretation of the ITC thermograms and further characterizations of interactions between $\{P_2W_{18}\}$ and $\{Ta_6\}\subset 2CD$ complexes are not reliably possible.

Table 5: Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis

Compound	$\{P_2W_{18}\}\subset CD$	$\{P_2W_{18}\}\subset 2CD$	$\{P_2W_{18}\}\subset 3CD$
Formula	C48H116Cl3.50KNa8.50O120P2W18	C96H206Cl1.20CsNa6.20O165P2W18	C144H310K1.50Na0.50O217P2Rb4W18
FW, g.mol ⁻¹	6343.23	7689.82	9297.17
<i>T</i> , K	100	200	200
crystal size (mm)	$0.08 \times 0.06 \times 0.04$	$0.30 \times 0.04 \times 0.02$	$0.30 \times 0.28 \times 0.03$
crystal system	Orthorhombic,	Orthorhombic	Trigonal
space group	P212121	P212121	P321
<i>a</i> , Å	17.671 (4)	17.2589 (16)	21.1963 (4)
b, Å	24.533 (5)	31.374 (3)	21.1963 (4)
<i>c</i> , Å	40.756 (8)	41.297 (3)	35.5050 (17)
$V, Å^3$	17669 (6)	22362 (3)	13814.7 (8)
Ζ	4	4	2
$ ho_{ m calc}$, g.cm ⁻³	2.385	2.284	2.235
μ (Mo K α), cm ⁻¹	1.224	0.953	0.832
λ (Mo K α), Å	0.72925	0.71073	0.71073
θ range, deg	$\theta \min = 1.0, \ \theta \max = 25.5$	$\theta \min = 2.2, \ \theta \max = 25.1$	θ min = 2.2, θ max = 30.0
data collected	184384	249509	168660
unique data	29038	38493	26908
unique data I> $2\sigma(I)$	21536	32586	20542
no. Parameters	855	2330	1142
restraints	452	2915	3
$R_w(F^2)$	0.293	0.318	0.146
R(F)	0.097	0.130	0,049
GOF	1.03	1.11	1.02

Compound	Ta ₆ ⊂2CD	$Ta_6 \subset 2CD \subset P_2W_{18}$	$Ta_6 \subset 2CD \subset BW_{12}$
Formula	C96H200Br14O100Ta6	C96H239Br12K2O180.50P2Ta6W18	$BBr_{24}C_{192}H_{384}O_{232}Ta_{12}W_{12}$
FW, g.mol ⁻¹	5158.99	9775.92	12711.1
<i>Т</i> , К	200	100	150
crystal size (mm)	$0.20 \times 0.12 \times 0.06$	$0.01 \times 0.01 \times 0.01$	$0.20 \times 0.12 \times 0.06$
crystal system	Tetragonal	Tetragonal	Tetragonal
space group	<i>I</i> 422	P41212	1422
<i>a</i> , Å	23.8984 (11)	23.985 (3)	24.0026 (11)
b, Å	23.8984 (11)	23.985 (3)	24.0026 (11)
<i>c</i> , Å	34.8186 (19)	89.175 (18)	35.0473 (19)
$V, Å^3$	19886 (2)	51301 (18)	20192 (2)
Ζ	4	8	4
$ ho_{ m calc}$, g.cm ⁻³	1.723	2.531	1.861
μ (Mo K α), cm ⁻¹	0.619	1.303	0.634
λ (Mo K α), Å	0.71073	0.72931	0.71073
θ range, deg	$\theta \min = 2.1, \ \theta \max = 25.1$	$\theta \min = 0.9, \ \theta \max = 25.6$	$\theta \min = 2.9, \ \theta \max = 35.1$
data collected	129482	532679	485694
unique data	8872	44271	22437
unique data I>2 $\sigma(I)$	7074	22525	13707
no. Parameters	521	1718	551
restraints	10	878	16
$R_w(F^2)$	0.212	0.280	0.358
R(F)	0.072	0.103	0.119
GOF	1.14	1.01	2.32

V. Conclusion

We have shown that recognition process of γ -cyclodextrin in host-guest binding can be used for the building of hierarchical non-covalent materials using POMs and octahedral clusters. We report discovery of a remarkable versatility featuring interactions between the Dawson anion $[P_2W_{18}O_{62}]^{6}$ and the primary portal of γ -CD allowing the selective isolation of the 1:1, 1:2 or 1:3 adducts in the solid state. We report also on the first inclusion complex built from a cationic octahedral cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ and γ -CD wherein the structural model displays the conventional host-guest 1:2 assembly involving close intermolecular contacts. Solution studies, including NMR methods, ITC and electrochemistry reveal that organic and inorganic moieties are pre-assembled together in solution for giving stable aggregates while all these species are considered as hydrophilic. Such a behavior gives insights about the true nature of these solvated ions which seem to range within the category of chaotropic species. Nevertheless, given the large structural diversity of both classes of compounds, offering species that differ in their composition, shape, size, symmetry and ionic charge, there should be extensive solution chemistry to determine the factor dictating their supramolecular interplay with substrates of interest.

Besides, the {POM⊂nCD}ⁿ⁻ aggregates, POM being either P₂W₁₈ or BW₁₂, and the ditopic {Ta₆⊂2CD}²⁺ arrangement reveal striking complementary structural and chemical properties, which have been exploited successfully to design novel three-component phases derived as supramolecular hydrogel or single-crystals with similar composition. X-Ray diffraction study shows that in the supramolecular assembly, {Ta₆⊂2CD}²⁺ acts as a ditopic ionic linker able to produce 1D tubular chain resulting from periodic alternation of POMs and clusters. This first example highlights promising route to design a new class of responsive and adaptable multifunctional materials built from deliberate associations of functionalities by the three well-ordered components. Given the scope of these domains, including POM and cluster chemistries, there is great interest to develop relevant hybrid multifunctional materials using the straightforward supramolecular approach. This strategy will pave the way toward exciting, extensive and challenging physical-chemistry or physics in this new area.

VI. References

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Chapter IV- Nonconventional three-component hierarchical host-guest assemblies:

I. *In situ* assembly and self-templating in host-guest chemistry:

Supramolecular chemistry dates back to the late 1960's and 1970's from the pioneering work of the Nobel Prize winners Pedersen,^{1,2} Cram³ and Lehn.⁴ Their contributions have led to the development of concepts allowing the fabrication of gigantic host-guest supramolecular materials with increased complexity and functionalities, which represent many examples supporting the cliché that the whole is better than the sum of parts.⁵ Actually, supramolecular complexes result from molecular recognition processes that arise from a set of complementary noncovalent interactions such as hydrophobic, coulombic, ion-dipole, dipole-dipole or hydrogen bonding.⁶ Thus, functional moieties specifically self-assembled into mesmerizing supramolecular architectures are able to promote a wide range of chemical and physical events that encompass electrons carrier, energy transfer, binding and release of substrates or ions transportation.^{7,8} Therefore, engineering synergies between these intrinsic functionalities could represent a versatile route to develop promising and inventive applications in the areas of electronic device, bioimaging,⁹ chemical sensing or chemical transformation.¹⁰

As illustrated in chapter III, unprecedented hybrid systems based on the spontaneous selfassembling of complementary organic and inorganic molecular units have been reported,¹¹⁻¹³ with the driving idea that interplays between the organic and inorganic moieties within the designed hybrid architectures inaugurate new phenomena of basic and fundamental interest in different areas such as data storage,¹⁴ gas sorption,¹⁵ molecular recognition,¹⁶ catalysis¹⁷ or medicine.¹⁸

In the context, polyoxometalates (POMs) represent a unique class of all-inorganic metaloxygen anionic clusters, which exhibit remarkable physical-chemical properties in relationship with their vast structural diversity.¹⁹⁻²³ Actually, this class of molecular objects offers huge potentialities for their use as sub-components in supramolecular hybrid materials owing to their specific shapes such as torus,^{24,25} hollow spheroidal capsule,²⁶⁻²⁹ cylinder or cubic box,³⁰ associated to their outer or inner surface functionalities and charge which can be adequately selected for specific and deliberate combinations with organic counterparts.³¹ As POMs display a marked preference toward hosting positively charged guest species in their sizable anionic cavities, they constitute a remarkable class of inorganic cryptands.³² Furthermore, POMs interact also with biological matter such as proteins that confer biological activities, which include in vitro and in vivo anticancer, antiviral and antibiotic activities.³³ Recent results shed light on the origin of primary interactions occurring between POMs and specific patches of proteins that include cooperation of non-specific interactions, driven by fine balancing between electrostatic and hydrophobic effects directly related to the charge and the surface extent of the POM species.³⁴ At the end, specificity of the recognition process is ensured through hydrogen bonding or ion-dipole contacts between the metal-oxide framework of the POMs and adequately designed domains of the protein. Besides, better understanding mechanisms that govern non-covalent inorganic-organic associations will provide new opportunities for the development of efficient and productive methods for POMs incorporation in multifunctional devices and hybrid architectures.

In 1996, elucidation of the molybdenum blue mystery by Müller *et al.* revealed an unrivalled subclass of POM species,³⁵ corresponding to a series of extremely large molecular architectures strikingly characterized by huge Mo nuclearities ranging from 154 to 368.^{36,37} Big wheels deriving from these species which exhibit typical toroidal architectures lining a large shape-persistent cavity represent a class of receptors ideal for the construction of hybrid assemblies. For instance, the archetypical Mo-blue ring-shaped anions exhibit remarkable host-guest properties with ability to encapsulate large organic substrates such as porphyrins,³⁸ or inorganic polynuclear clusters.³⁹ However, taking into account the large diameter of these available cavities, supramolecular properties of these ring-shaped compounds remain unexploited.

In this chapter we report the formation of hybrid hierarchical assemblies based on $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ and $[W_{14}Mo_{140}O_{462}H_{14}(H_2O)_{70}]^{14-}$ molecular wheels (abbreviated $\{Mo_{154}\}^{35}$ and $\{W_{14}Mo_{140}\}$ respectively hereafter), that include in their central cavity the supramolecular adduct built from the archetypical Dawson polyoxometalate $[P_2W_{18}O_{62}]^{6-}$ capped by two γ -cyclodextrins (see Figure 1). The underlying project of these investigations was to demonstrate that hydrophobic contributions play a key role in recognition processes involving polyoxometalates and organic substrates. γ -cyclodextrin with the formula $C_{48}H_{80}O_{40}$ (noted γ -CD

hereafter) has been selected as organic unit for its specific ring-shaped architecture and sizematching with the inward dimension of the large hole delimited by the giant ring-shaped $\{Mo_{154}\}$ anion (see Figure 1). Besides, cyclodextrins are distinguished as prominent synthetic receptors alongside crown ethers and calixarenes.^{40,41} Their hydrophobic cavity lined by glucopyranosyl residues conical-rings exhibits remarkable inclusion properties which gave rise to wide applications in many fields of science such as nanotechnology,⁴² pharmaceutics⁴³ or medicine.⁴⁴ In addition, recent results showed that CDs have also the ability to encapsulate anionic species such as dodecaborate clusters,⁴⁵ Keggin-type or Dawson-type POMs¹² (see chapter III) even though these species exhibit fair solubility in water to be considered as hydrophilic species. Actually, Nau et al. have proposed a precise description about contributors to the recognition process identified as "chaotropic" or "super chaotropic" effect (water structure destruction ability) that involves mainly bulk-water structure recovery.⁴⁵ Polyoxometalates, such as Keggintype and Dawson-type ions could be ranged in this category of chaotropic ionic species,⁴⁶ a basic property that could be extended to any ionic species featured by low charge surface density and large solvent-exposed surface area. Giant polyoxometalates deriving from archetypical Keplerate-type arrangements or molybdenum blue ring-shaped anions should originate such "chaotropic" phenomena within any specific or non-specific aggregation process.



Figure 1: Space-filling representation of the anionic POMs, $[P_2W_{18}O_{62}]^{6-}$ and $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$, cationic cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$, and γ -CD, showing size-matching between host and guest components involved within hierarchical supramolecular assemblies.

II. Experimental Part

II.1. Physical methods

Fourier transform infrared (FT-IR) spectra were recorded on a 6700 FT-IR Nicolet spectrometer using diamond ATR technique. ATR correction was applied to the spectra of the non-diluted samples.

Nuclear magnetic resonance (NMR) spectra were measured in D_2O at 25 °C. ¹Hand ³¹P NMR spectra were obtained on a Bruker Avance 400 spectrometer at Larmor frequencies 400.1 and 162.0 MHz respectively, using 5 mm standard NMR tubes. The 1D ¹H spectra were recorded with one pulse sequence at 30° flip angle (pulse duration 2.4 µs), using 1 s recycle delay, 1.6 s acquisition time, and 16 number of scans. ³¹P NMR spectra were run with 7.7 µs pulse duration (45° flip angle), 15 s recycle delay, 1 s acquisition time, and an accumulation of 32 transients. 2D ¹H-¹H NOESY spectra were carried out on some selected samples using standard phase sensitive pulse sequences in States mode and 1 s mixing time. Translational diffusion measurements were performed using Bruker's "ledbpgs2s" stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy.⁴⁷ The ¹⁸³W NMR spectra were measured on a Bruker Avance 500 spectrometer at a resonance frequency of 20.8 MHz equipped with a specific low-gamma nuclei 10 mm probehead. Chemical shifts are reported relative to TMS for ¹H, 85% H₃PO₄ for ³¹P, and 1 M aq. Na₂WO₄ (¹⁸³W), using secondary references in case of ¹⁸³W (D₂O/H₂O solution of H₄SiW₁₂O₄₀ observed at -103.8 ppm).

Elemental analyses for C and H were carried out by the analytical service of the CNRS at Gif sur Yvette, France. W, Mo, P, Na, and K were carried out by the analytical Laboratory of NIIC SB RAS 630090, Novosibirsk, Russia.

Energy-dispersive X-ray spectroscopy (**EDX**) measurements were performed on a JEOL JSM 5800LV apparatus. SEM images were recorded on a JEOL Model JSM-7001F microscope equipped with an EDX spectrometer using gold-coated samples and a X-Max silicon drift detector (SDD) by Oxford. The EDX spectra were acquired with a voltage acceleration of 15 kV, an acquisition time of 120 s and more than 1000 counts.

Thermal gravimetric analysis (TGA) was used to determine the water content on a Seiko TG/DTA 320 thermogravimetric balance (5 °C min⁻¹, under O_2).

Single crystal X-ray diffraction data collections at low temperature (200 K) were carried out using a Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS bidimensional detector using a high brilliance IµS microfocus X-ray Mo K α (λ = 0.71073 Å) monochromatized radiation. Absorption corrections were based on multiple and symmetryequivalent reflections in the data set using the SADABS program⁴⁸ based on the method of Blessing.⁴⁹ The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.^{50,51}

II.2. Syntheses

Na₁₄[{Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀}(C₄₈H₈₀O₄₀)₂]•2NaCl•200(H₂O): Na₂MoO₄.2H₂O (1.5 g; 6.2 mmol) were dissolved in 5 mL H₂O. Na₂S₂O₄ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with a pH ~ 0.8. γ-cyclodextrin (0.1g; 0.08 mmol) were added and the resulting mixture was stirred further for 10 min after the addition of 5 mL H₂O. The mixture obtained at pH ~ 1 was filtrated then sealed in a flask. Well-shaped crystals suitable for XRD were obtained within 24 hours. The mass isolated was 0.5 g, yield 41 % based on molybdenum. Molecular weight of C₉₆C₁₂H₇₁₄Mo₁₅₄Na₁₆O₈₁₂ is 30077.7 g.mol⁻¹. Elemental analysis Calc. (found): H 2.39 (2.12); C 3.83 (3.54) EDX Calc. (found): Mo/Na 9.62 (9.23); Na/Cl 8.00 (10.85). TGA: A weight loss of 11.8 % between 25 and 130 °C corresponds to hydration water molecules (calc. 12.0 %) and a weight loss of 11.5 % in the 120-450 °C range corresponding to the loss of coordination water and 2 γ-CD (calculated 12.8 %).

Na₁₄[{Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀}(C₄₈H₈₀O₄₀)4]•5NaCl•160(H₂O): Na₂MoO₄.2H₂O (1.5 g; 6.2 mmol) were dissolved in 5 mL H₂O. Na₂S₂O₄ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with a pH ~ 0.8. γ -cyclodextrin (0.1g; 0.08 mmol) were added and the resulting mixture was stirred further for 10 min after the addition of 5 mL H₂O. The mixture obtained at pH ~ 1 was filtrated then sealed in a flask. Well-shaped crystals suitable for XRD were obtained within 24 hours. The mass isolated was 0.67 g, yield 51 % based on molybdenum. Molecular weight of C₁₉₂Cl₅H₇₉₄Mo₁₅₄Na₁₉O₈₅₂ is 32126.7 g.mol⁻¹. Elemental analysis Calc. (found): H 2.49 (2.28); C 7.18 (6.91). EDX Calc. (found): Mo/Na 8.10 (8.09); NaCl 3.80 (3.25). TGA: A weight loss of 8.7 % between 25 and 120 °C corresponds to hydration water molecules (calc. 8.9 %) and a weight loss of 19.3 % in the 120-450 °C range corresponding to the loss of coordination water and 4 γ -CD (calculated 20 %).

Na₁₅K₄H[{Mo₁₅₄O₄₆₂H₁₄(H₂O)₇₀}P₂W₁₈O₆₂(C₄₈H₈₀O₄₀)₂]•200(H₂O): Na₂MoO₄.2H₂O (1.5 g; 6.2 mmol) were dissolved in 5 mL H₂O. Na₂S₂O₄ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with a pH ~ 0.8. K₆P₂W₁₈O₆₂.19H₂O (0.2 g; 0.04 mmol) and γ -cyclodextrin (0.1g; 0.08 mmol) were added and the resulting mixture was stirred further for 10 min after the addition of 8 mL H₂O. The mixture obtained at pH ~ 1 was filtrated then sealed in a flask. Well-shaped crystals suitable for XRD were obtained within 24 hours. The mass isolated was 0.52 g, yield 37 % based on molybdenum. Molecular weight of C₉₆H₇₁₅K₄Mo₁₅₄Na₁₅O₈₇₄P₂W₁₈ is 34504.5 g.mol⁻¹. Elemental analysis Calc. (found): H 2.09 (1.85); C 3.34 (3.41). EDX Calc. (found): Mo/W 8.55 (8.40); Mo/Na 10.26 (10.55); Na/K 3.75 (3.95). TGA: A weight loss of 10.6 % between 25 and 120 °C corresponds to hydration water molecules (calc. 10.4 %) and a weight loss of 7.8 % in the 120-450 °C range corresponding to the loss of 2 γ -CD (calculated 7.5 %).

 $Na_{15}K_{3}H_{2}[\{Mo_{154}O_{462}H_{14}(H_{2}O)_{70}\}P_{2}W_{18}O_{62}(C_{48}H_{80}O_{40})_{2}]\bullet 2(C_{48}H_{80}O_{40})\bullet 225(H_{2}O):$

Na₂MoO₄.2H₂O (1.5 g; 6.2 mmol) were dissolved in 5 mL H₂O. Na₂S₂O₄ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with a pH ~ 0.8. K₆P₂W₁₈O₆₂.19H₂O (0.2 g; 0.04 mmol) and γ -cyclodextrin (0.2 g; 0.16 mmol) were added and the resulting mixture was stirred further for 10 min after the addition of 8 mL H₂O. The mixture obtained at pH ~ 1 was filtrated then sealed in a flask. Well-shaped crystals suitable for XRD were obtained within 24 hours. The mass isolated was 0.57 g, yield 40 % based on molybdenum. Molecular weight of C₁₉₂H₉₂₆K₃Mo₁₅₄Na₁₅O₉₇₉P₂W₁₈ is 37511 g.mol⁻¹. Elemental analysis Calc. (found): H 2.49 (2.50); C 6.15 (5.95); Mo 39.39 (38.50); W 8.82 (8.57); Na 0.92 (0.87); K 0.31 (0.24). TGA: A weight loss of 10.7 % between 25 and 120 °C corresponds to hydration water molecules (calc. 10.8 %) and a weight loss of 15.0 % in the 120-450 °C range corresponding to the loss of 4 γ -CD (calculated 14.5 %).

$Na_{12}K_{3}H_{5}[\{W_{14}Mo_{140}O_{462}H_{14}(H_{2}O)_{70}\}P_{2}W_{18}O_{62}(C_{48}H_{80}O_{40})_{2}]\bullet 200(H_{2}O):$

 $Na_2MoO_4.2H_2O$ (1.21 g; 5 mmol) and $Na_2WO_4.2H_2O$ (0.16 g; 0.5 mmol) were dissolved in 5 mL H_2O . $Na_2S_2O_4$ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with

a pH ~ 0.9. K₆P₂W₁₈O₆₂.19H₂O (0.2g; 0.04 mmol) and γ -cyclodextrin (0.1 g; 0.08 mmol) were added and the resulting mixture was stirred further for 10 min after the addition. The mixture obtained at pH ~ 1 was filtrated then closed in a flask. Well-shaped crystals suitable for XRD were obtained within 24 hours. The mass isolated was 0.4 g, yield 32 % based on molybdenum. Molecular weight of C₉₆H₇₁₉K₃Mo₁₄₀Na₁₂O₈₇₄P₂W₃₂ is 35631.2 g.mol⁻¹. Elemental analysis Calc. (found): H 2.03 (1.81); C 3.24 (3.32). EDX Calc. (found): Mo/W 4.37 (4.95); Mo/Na 11.66 (12.22); Na/K 4.00 (3.88). TGA: A weight loss of 9.8% between 25 and 120 °C corresponds to hydration water molecules (calc. 10.1 %) and a weight loss of 7.5 % in the 120-450 °C range corresponding to the loss of 2 γ -CD (calculated 7.3 %).

$Na_{10}H_{2}[\{Mo_{154}O_{462}H_{14}(H_{2}O)_{70}\}\{Ta_{6}Br_{12}(H_{2}O)_{6}\}(C_{48}H_{80}O_{40})_{2}]\bullet 4NaCl\bullet 200(H_{2}O):$

Na₂MoO₄.2H₂O (1.5 g; 6.2 mmol) were dissolved in 5 mL H₂O. Na₂S₂O₄ (0.1 g; 0.575 mmol) were added where the color changed gradually to yellow. The obtained solution was acidified by 15 mL of 1 M HCl, the mixture turned instantly dark blue with a pH ~ 0.8. [Ta₆Br₁₂(H₂O)₆]•2Br (0.1 g; 0.04 mmol) and γ -cyclodextrin (0.1g; 0.08 mmol) were dissolved in 15 mL H₂O then added to the previous solution. The resulting mixture was stirred further for 10 min, then filtrated and sealed in a flask at 2 °C. An amorphous product was isolated after two weeks 0.25 g, yield 20 % based on molybdenum. Molecular weight of Br₁₂C₉₆Cl₄H₇₂₈Mo₁₅₄Na₁₄O₈₁₈Ta₆ is 32257.3 g.mol⁻¹. Elemental analysis Calc. (found): H 2.27 (2.03); C 3.57 (3.38). EDX Calc. (found): Mo/Ta 25.66 (22.23); Br/Ta 2.00 (1.86); Mo/Na 11.00 (11.03); Na/Cl 3.50 (3.26). TGA: A weight loss of 10.9 % between 25 and 120 °C corresponds to hydration water molecules (calc. 11.2 %).

III. Hierarchical host-guest hybrid materials

After $[PMo_{12}O_{40}]^{3-}$, $[P_2W_{18}O_{62}]^{6-}$ showed its potential in forming hybrid organic/inorganic-based materials when mixed with CDs. The latter system showed great versatility represented by the isolation of three components depending on the introduced ratio as shown in chapter III. As POMs species exhibit strong affinity toward the hydrophobic interior of the cyclodextrins,¹² there is no apparent limitation that hydrophobic exterior of CDs could also interact with adequately designed POM surface such as {M₁₅₄} ring-shaped anions (see Figure 1). To investigate the feasibility of this assumption, the interaction between {Mo₁₅₄} and γ -CD was studied by ¹H NMR in D_2O . Knowing that { Mo_{154} } should encapsulate CDs, nonconventional interactions between the prominent wheel and the organic macrocycle is expected.

III.1. Experimental observations

Although γ -CD has symmetry (C₈) different than that of the wheel (C₇), it was employed due to the size compatibility as it is expected to fit in the wheel's portals (See Figure 1). ¹H NMR showed a pronounced complexation-induced deshielding of the H2 proton ($\Delta\delta \sim + 0.5$ ppm) (see Figure 2), which is located outside the cavity near the secondary hydroxyl rim. Similar effect, but to a lower extent was observed on the outer H1 proton while the H4 proton appears quite unaffected. Besides, the inner protons H3, H5 and H6 undergo a significant shielding effect. Furthermore, the assignment of the most affected signal to the H2 proton has been confirmed by ¹H-¹H NOESY NMR experiment showing the through space interaction between protons H1 and H2 in the interacting CD (see Figure 3). Job's plot of H2's chemical shift change indicated a 1:1 average stoichiometry of binding between the two interacting molecules in solution extracted from the maximum at (0.5) as shown in Figure 2.



Figure 2: ¹H NMR spectra of 3 mM γ -CD in presence of different equivalents of {Mo₁₅₄} ring-shaped anion displaying the deshielding effect on the outer H2 nuclei suggesting the formation of { γ -CD \subset Mo₁₅₄} inclusion complex involving the secondary large face of cyclodextrin and the inner cavity of the Mo-blue wheel. Insert: Job's plot for γ -CD and {Mo₁₅₄} obtained by plotting the chemical shift changes of H2 proton of the γ -CD as a function of the fraction of the host (γ -CD).

These ¹H NMR observations differ significantly from that noticed for the Dawson-type anion $[P_2W_{18}O_{62}]^{6-}$ with γ -CD seen in chapter III or that reported by Stoddart *et al.*, who identified conventional inclusion complex between γ -CD and the Keggin-type anion $[PMo_{12}O_{40}]^{3-}$ through a significant down-field shift of the H6 proton.¹² In this case, the NMR results suggest that γ -CD penetrates deeply into the large cavity of the {Mo₁₅₄} anion, leading to a deshielding effect for the outer protons in contact with the inner oxygen of the {Mo₁₅₄} ring-shaped anion and to a screening effect for the other type of protons belonging to the γ -CD, induced by {Mo₁₅₄} inorganic shell. In addition, the formation of supramolecular adduct involving {Mo₁₅₄} and γ -CD is also nicely supported by ¹H DOSY NMR experiments, showing a clear monotonous decrease of the self-diffusion coefficient of the γ -CD from 280 µm².s⁻¹ for the free-solvated species to 108 µm².s⁻¹ in the presence of two equivalents of {Mo₁₅₄} as shown in Table 1.

Table 1. Diffusion coefficients of different CD:{Mo₁₅₄} compositions measured by ¹H DOSY NMR.

Composition of the system CD:{Mo ₁₅₄ }	Diffusion coefficient $D \ (\mu m^2 s^{-1})$
1:0	280
1:1	138
1:2	108
1:5.55	106



Figure 3: Left: ¹H NOESY NMR of 3mM γ -CD solution containing {Mo₁₅₄} in a molar ratio {Mo₁₅₄}/CD = 5.55, confirming the assignment of resonance H2 next to H1. Right: structure of γ -CD highliting the particular position of H2 at the exterior surface of the CD, as being the most exposed proton to a direct contact with the POM in the CD \subset {Mo₁₅₄} inclusion complex.

After evidencing the incorporation of γ -CD within the ring-shaped POM, several approaches were followed in attempt to isolate the inclusion complex. One pot synthesis proved to be the best way to isolate this complex where γ -CD was introduced into the reaction mixture after the acidification of the reduced sodium molybdate solution to pH = 1. The presence of the organic macrocycle sped up the crystallization process behaving as a template for the construction of the wheel where crystals of the inclusion complex based on {Mo₁₅₄} and CD appeared within about twenty four hours of the synthesis compared to about three days to isolate {Mo₁₅₄} in absence of cyclodextrin. Although the crystals were of good quality, we were not able to locate the cycodextrins. Yet, crystals contained both components as confirmed by infrared (Figure 4) that showed the absorption bands corresponding to C-O-C and C-H vibrations of CD (in the 1200 – 1000 cm⁻¹ and 1450 – 1250 cm⁻¹ region, respectively) and that of Mo=O and Mo-O-Mo of {Mo₁₅₄} (at 975 and 910 cm⁻¹).



Figure 4: FT-IR spectra of the precursors and the inclusion complexes: cyclodextrin (black), Mo-ring shaped anion (red), binary complex of Mo-wheel and CD (purple and blue), Dawson-type anion (brown) and three component complex (green).

¹H NMR on the other hand showed the fingerprint of a complexed CD with the most affected exterior protons H1 and H2 and the shielding of H3, H5 and H6 while ¹H DOSY NMR revealed a slow exchange in solution between free and complexed CD evidenced by the presence of correlation signals corresponding to the two species. Elemental analysis and TGA revealed the direct relation between the introduced cyclodextrin and that obtained in the isolated product as it is possible to synthesize $\{Mo_{154}\}\subset 2CD$ and $\{Mo_{154}\}\subset 4CD$ simply by doubling the quantity of cyclodextrin introduced. The impotence in obtaining a structural model is attributed to mismatched symmetries between the wheel and the macrocycle where the wheel-encapsulated CDs suffered severe disorder that hindered distinguishing the electronic density of CD from that of solvent molecules and thus obstructed the obtainment of the XRD structure.

III.2. Three-component host-guest system, formation and characterization

A more complex scenario has been examined by introducing a third component able to interact with the inner face of the γ -CD. Size-matching polyoxometalates (Dawson-type anion $[P_2W_{18}O_{62}]^{6-}$) or octahedral clusters ($[Ta_6Br_{12}(H_2O_6)]^{2+}$) species have been selected for their fair ability to form inclusion complexes with γ -CD (see chapter III). After exploring and repeating different synthetic approaches as well some analytical test procedures and comparing the final products, it became evident that selected POMs or clusters, γ -CD and {Mo₁₅₄} ring-shaped anion were able to interact together to produce chemically pure assemblies. Finally, one-pot synthesis revealed to be the most convenient procedure to isolate products containing the three components {Mo₁₅₄} / γ -CD / POM or cluster with a relatively good yield for these systems (~ 20 – 40 %). The syntheses were merely inspired from that previously reported by Müller et al.⁵² with some adaptation and consists of acidification until pH = 1 of Na₂MoO₄ aqueous solution under reducing condition (sodium dithionite was used as reducing agent) in the presence of ycyclodextrin and a guest (guests = Dawson-type anion $\{P_2W_{18}\}$ or cationic cluster $\{Ta_6Br_{12}\}$) in ratios Mo: γ-CD: guest = 154:2:1 (see experimental part for further details). The first tested system containing $\{P_2W_{18}\}$ generated crystals corresponding to the formation of a three-component hostguest assembly while that containing $\{Ta_6Br_{12}\}$ as a guest led to the formation of an amorphous product. Elemental analysis and EDX were the key techniques confirming the presence of the three components within both compounds especially in case of the octahedral cluster (see experimental part) since such cluster is mute when it comes to infrared, but in case of the guest POM, infrared provided the first indication of the complex formation by showing the absorption bands corresponding to $\{P_2W_{18}\}$ as shown in Figure 4 which alongside EDX and elemental analysis gave a strong manifestation about the composition of the formed inclusion complexes.

On the upside, single-crystals with abbreviated formula Na₁₅K₃H₂[{Mo₁₅₄}(P₂W₁₈O₆₂)(γ -CD)₂]•200H₂O (noted {P₂W₁₈⊂2CD}⊂{Mo₁₅₄} hereafter) was readily achieved and related characterization will be discussed in the following section. The infrared spectrum of {P₂W₁₈⊂2CD}⊂{Mo₁₅₄} presented in Figure 4 contain the absorption bands corresponding to the metal-oxo framework of the wheel {Mo₁₅₄} and the Dawson-type anions in the spectral region 1100 and 400 cm⁻¹ besides the strong absorption at 1085 cm⁻¹ corresponding to P-O asymmetric vibration of the {P₂W₁₈}. Absorptions at 975 and 910 cm⁻¹ are attributed to the vibration of the metal oxygen bonds v(M=O and Mo-O-Mo), while that at 800 cm⁻¹ corresponds to W-O-W asymmetric vibration. Infrared spectrum confirms the integrity of these two POM components is maintained in the crystals. The presence of cyclodextrin is also easily witnessed from the absorption bands in the 1200 to 1000 cm⁻¹ region attributed to the symmetric stretching of C-O-C and C-O of the organic macrocycle.

III.2.1. Structural description

X-Ray diffraction analysis of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ allowed giving structural models depicted in Figure 5. As shown in Figure 5, crystal analysis of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ reveals a striking three-component supramolecular adduct arranged within a remarkable hierarchical organization, wherein the Dawson anion $[P_2W_{18}O_{62}]^{6-}$ occupies a central position. This Dawson POM species appears capped by two γ -CDs both interacting symmetrically with the two opposite caps $\{W_3O_{13}\}\$ of the anion Figure 5a. Such a type of arrangement resembles to some extent that observed by Stoddart *et al.* with the Keggin-type anion encapsulated by two γ -CDs¹² but differs from what have been witnessed for $[P_2W_{18}O_{62}]^{6-}$ with γ -CD alone as shown in chapter III where cyclodextrins were scotched to the longitudinal face of the Dawson-type anion. Furthermore, in the structure of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$, such a classical supramolecular assembly appears embedded deeply within the large inner cavity of the $\{Mo_{154}\}\$ torus to give the non-conventional striking $([P_2W_{18}O_{62}]\subset 2\gamma-CD\subset \{Mo_{154}\})\$ inclusion complex Figure 5c and d.



Figure 5: Mixed representation of the supramolecular hierarchical compound $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}$: a) highlight of the inner adduct built from a Dawson anion $[P_2W_{19}O_{62}]^{6-}$ capped by two γ -CD tori. b) Representation showing the deep inclusion of the Dawson anion within the large inner cavity of the Mo-blue ring-shaped anion (CDs have been omitted for clarity). c) Profile and d) Top views of the hybrid supramolecular adduct showing the hierarchical organization between three components with the Dawson anion (green and red space-filling spheres) at the center capped by two γ -CDs (wires and transparent space-filling spheres) encaged into the large $\{Mo_{154}\}$ torus (yellow sticks).

Actually, the two inner γ -CDs appear severely disordered within the {Mo₁₅₄} torus that should be due to i) host-guest symmetry mismatching considering the difference in idealized symmetry of the isolated ring-shaped objects, D_{7d} for {Mo₁₅₄} and C_8 symmetry for the γ -CD, ii) intrinsic positional host-guest disorders of the γ -CD within the {Mo₁₅₄} anion and iii) the presence of inversion center imposed by the large number of Mo and W heavy atoms distributed within highly symmetric arrangements. Nonetheless, we propose a disorder scheme by succeeding to rebuild backbones of the two inner γ -CDs from electronic density. Such a structural solution appears quite consistent with the expected geometrical parameters and then gives strong arguments to demonstrate the steric host-guest compatibility between γ -CDs and the {Mo₁₅₄} torus (see Figure 6).



Figure 6: Structural representations of $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\}\$ showing the hydrogen bonding networks between the γ -CD guest and some oxygen atoms of the $\{Mo_{154}\}\$ host wherein a) the secondary face of the γ -CD is outward directed (a) or inward directed (b) according to the proposed disorder scheme. The O•••O distances are within the 2.75-3.20 Å range.

It should be worth mentioning that at this level, it would be highly speculative to give any firm conclusion about the interacting rim of the y-CD, *i.e.* secondary or primary CD face, directed toward the cavity center of the $\{Mo_{154}\}$ anion. However, the proposed structural model allows identifying a network of convergent hydrogen bonds which involve hydroxo groups of the γ -CD and either some oxygen atoms of the $\{Mo_{154}\}$ outer host or those of the $[P_2W_{18}O_{62}]^{6-}$ inner guest (see Figure 6). These intermolecular hydrogen-bonding interactions give rise to quite short O•••O contacts observed in the 2.75-3.20 Å range. In this case, the structure shows spectacular complementarity between the two inorganic species and the CD as the latter fits perfectly in the space between the anchored $\{P_2W_{18}\}$ and its host $\{Mo_{154}\}$ where cyclodextrins behaved as an adhesive fixing the Dawson-type anion within the cavity and blocking the portals of the wheel. The latter appears to retain the same archetypical structure of {Mo₁₅₄} alone, as there is no change in the arrangement of the building blocks or the loss of any metallic centers as seen in Cronin and coworkers' work where {Mo154} lost four metallic centers generating $[Mo_{150}O_{442}(OH)_{10}(H_2O)_6]^{14-}$ to host a Krebs-type anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-39}$ The matryoshka doll-like system based on alternating inorganic and organic layers in a hierarchical manner crystallizes in a monoclinic system in the C2/m space group, while its large unit cell (46650 Å³) contains two $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\}$ units (see Figure 7).



Figure 7: Mixed representation of the packing of compound $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\}$: a) through the *b*-axis in the *ac* plane and b) selected view of one plane showing the large holes created by the packing of the ring-shaped inclusion complexes. Mo: blue polyhedra, W: grey polyhedra and cyclodextrin: ball and stick.

Introducing two more equivalents of cyclodextrin into the reaction mixture led to the isolation of another crystalline species with abbreviated formula $Na_{15}K_{3}H_{2}[\{Mo_{154}\}(P_{2}W_{18}O_{62})(\gamma-CD)_{2}]\bullet 2CD\bullet 225H_{2}O$ (noted {P₂W₁₈⊂2CD}⊂{Mo₁₅₄}•2CD hereafter). Single-crystals of $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \cdot 2CD$ were achieved as well and X-ray structural analysis supported by its elemental analysis revealed an unexpected result which corresponds to the presence of two additional γ -CDs per {Mo₁₅₄} unit literally stuck on the outward surface of the $\{Mo_{154}\}$ ring-shaped anion sandwiching it (see Figure 8).



Figure 8: Mixed representations of the $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \cdot 2CD$ supramolecular assembly a) showing the presence of two outer γ -CDs which interact symmetrically with the surface of the $\{Mo_{154}\}$ anion. b) Selected view of $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \cdot 2CD$ showing large holes delimited by the $\{Mo_{154}\}$ packing which are filled by two outer γ -CD units.

Still here, these additional γ -CD units appear disordered and no definitive conclusion can be given about the type of face interacting directly with the {Mo₁₅₄} surface. However, such a result demonstrates that γ -CD unit is able to interplay with {Mo₁₅₄} anion either through highly specific host-guest recognition process with its large inner cavity or through less specific interactions involving its large exposed surface area. Actually, it should be worth noting that composition of {P₂W₁₈⊂2CD}⊂{Mo₁₅₄}•2CD corresponds precisely to the composition of the synthetic mixture and we noted experimentally that presence of these two additional equivalents of γ -CD in the solution allowed in one hand to increase the crystallization rate and in other hand to get single-crystals of fair-quality while increasing the quantity of the introduced cyclodextrin even more, had no further effect on the composition of the product as the latter appears unable to accept more than four cyclodextrins per {Mo₁₅₄}. The product crystallizes in a triclinic system in the *P-1* space group with its unit cell containing just one {P₂W₁₈⊂2CD}⊂{Mo₁₅₄}•2CD unit.



Figure 9: Mixed representations of the supramolecular assembly of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\bullet 2CD$: a) showing the interaction of the two outer γ -CDs with the surface of the three adjacent $\{Mo_{154}\}$ anions. b) Zoom in displaying the two types of hydrogen-bonds through the hydroxyl groups of the primary face (green) or the secondary face (pink) with terminal oxygens of $\{Mo_{154}\}$ anions.

The close packing is supported by a network of intermolecular hydrogen bonding interactions with O••••O contacts observed in the ~2.5 - 3 Å range between the scotched CD on the surface of its corresponding {Mo₁₅₄} and two adjacent {Mo₁₅₄} wheels as shown in Figure 9. The crystallographic data of both compounds is presented in Table 1. Based on the results

obtained from $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\circ 2CD$ showing the packing of CDs inside and outside the Mo-blue ring, by analogy one can suppose that the structure of $\{Mo_{154}\}\subset 2CD$ and $\{Mo_{154}\}\subset 4CD$ should exhibit the same arrangement where CDs can fill the void within the cavity and the excess will be scotched to the exterior surface of the torus.

Compound	{P ₂ W ₁₈ ⊂2CD}⊂{Mo ₁₅₄ }	{P ₂ W ₁₈ ⊂2CD}⊂{Mo ₁₅₄ }•2CD
Formula	$C_{96}H_{715}K_4Mo_{154}Na_{15}O_{874}P_2W_{18}$	$C_{192}H_{926}K_{3}Mo_{154}Na_{15}O_{979}P_{2}W_{18}$
FW, g.mol ⁻¹	34504.5	37511
Т, К	100	200
crystal size (mm ³)	$0.12 \times 0.14 \times 0.02$	$0.14 \times 0.10 \times 0.02$
crystal system	monoclinic	triclinic
space group	<i>C2/m</i>	P-1
a, Å	36.776 (7)	25.010 (2)
b, Å	43.336 (9)	28.505 (3)
<i>c</i> , Å	30/312 (6)	38.129 (3)
a, °	90	104.196 (4)
β,°	105.06 (3)	101.863 (4)
𝔅 °	90	91.090 (5)
$V, Å^3$	46650 (17)	25721 (4)
Ζ	2	1
$ ho_{ m calc}$, g.cm ⁻³	2.154	2.422
μ (Mo K α), mm ⁻¹	0.431	3.95
λ (Mo K α), Å	0.72931	0.71073
θ range, deg	θ min = 0.7°, θ max = 22.1°	θ min = 2.1°, θ max = 25.4°
data collected	184778	772174
unique data	29276	92697
unique data I > $2\sigma(I)$	22001	53368
no. Parameters	1923	3829
restraints	0	2048
$R_w(F^2)$	0.426	0.478
R(F)	0.142	0.172
GOF	1.01	1.09

Table 2. Selected crsytallographic parameters of the X-ray diffraction analysis of $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\}\$ and $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \circ 2CD$.

III.2.2. Solution study

Preliminary multinuclear NMR studies (including 1D and 2D experiments) in aqueous solution have been carried out on this striking three-component chemical system. Though formation of such a hierarchical assembly including $[P_2W_{18}O_{62}]^{6-}$ and γ -CD within the large $\{Mo_{154}\}$ host leads to broad signals, NMR analysis affords some important features about solution behavior. The ³¹P NMR spectrum of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}$ (5 mmol.L⁻¹ in aqueous solution) shown in Figure 10a contains in addition to the resonance attributed to solvated

 $[P_2W_{18}O_{62}]^{6-}$ observed at $\delta = -12.34$ ppm, three additional signals at -12.43, -12.53 (shoulder) and -12.69 ppm (deconvolution is shown in Figure 10b).



Figure 10: ³¹P NMR spectra of: a) different solution mixtures of $[P_2W_{18}O_{62}]^{6-}$ ion, γ -CD, and the blue wheel {Mo₁₅₄}, showing that only the simultaneous presence of the three components provokes a clear change of ³¹P NMR spectrum. b) The presence of four ³¹P NMR signals with 32 : 52 : 8 : 8 intensity ratio is consistent with three distinct $[P_2W_{18}O_{62}]^{6-}$ species; as solvated ion ($\delta = -12.34$ ppm), and as central guest species into the three-component assemblies either capped by two CDs ($\delta = -12.43$) or one CD leading to an asymmetric complex ($\delta = -12.53$ and -12.69 ppm). The presence of three shielded ³¹P resonances should be interpreted as slow equilibrium occurring between bicapped and monocapped guest species as depicted in scheme inserted on the upper ³¹P NMR spectrum.

The presence of shielded ³¹P nuclei should be related to the screening effect of the {Mo₁₅₄} host onto the deeply embedded [P₂W₁₈O₆₂]⁶⁻ guest. For instance, such a shielding effect corresponds to a general behavior usually observed for any guest species included within the inner cavity of the {Mo₁₃₂} Keplerate nanocapsule (for instance, see chapter II, page 60). However, the presence of these three low-frequency signals suggests that guest [P₂W₁₈O₆₂]⁶⁻ species could be involved within dynamic equilibria, slow on the NMR time scale. As a preliminary hypothesis, these different species could result from the successive release of the inner γ -CD component from {P₂W₁₈⊂2CD}⊂{Mo₁₅₄} (observed at -12.43 ppm) leading to the monocapped guest species (δ = -12.53 and -12.69 ppm) and to the solvated species (δ = -12.34 ppm), respectively.

Furthermore, the attribution of the low-frequency signals to the supramolecular threecomponent system has been confirmed by ³¹P DOSY NMR (see Figure 11a). Two systems with different chemical composition have been investigated for which large excess of the host {Mo₁₅₄} is used to favor inclusion complexes formation. In the stoichiometric ratio CD:{Mo₁₅₄}:{P₂W₁₈} of 2:4:1, the species involved in the ternary hierarchical system (observed at -12.43 ppm) showed a very low diffusion coefficient $D = 73 \ \mu m^2/s$, while the solvated interacting species at $\delta = -12.34$ ppm is characterized by an intermediate value D of 181 $\mu m^2/s$ compared to the same species without any interaction in pure D₂O ($D = 325 \ \mu m^2/s$). When excess of Dawson POM is used in the molar ratio CD:{Mo₁₅₄}:{P₂W₁₈} of 2:4:2, the fraction of free species ($\delta = -12.34$ ppm) increased significantly as well as the observed diffusion coefficient ($D = 285 \ \mu m^2/s$). In the same time, diffusion coefficient of the three-component species also raised up to $D = 181 \ \mu m^2/s$. These observations are typical of dissociation behavior in solution of the three-component complex in slow chemical exchange regime.



Figure 11: ³¹P DOSY NMR spectra in ternary system γ -CD:{Mo₁₅₄}:K₆[P₂W₁₈O₆₂] at two different P₂W₁₈O₆₂⁶⁻ molar ratio showing the effect on diffusion coefficients of bound and free species involved in a dissociative exchange process.

Besides, ¹H NMR spectrum of { $P_2W_{18}\subset 2CD$ } \subset { Mo_{154} } and various NMR titrations revealed that formation of three-component system leads to complex ¹H NMR spectra characterized by significant line width broadening and by the appearance of many new ¹H NMR resonances (see Figure 12). In few lines, the presence of additional ¹H NMR resonances is characteristic of dynamically slow equilibria processes (on the NMR time scale) in D₂O solution involving deeply embedded components through the inner and outer faces of γ -CD tori. For instance, starting from the stoichiometric molar ratio CD:{ Mo_{154} }:{ P_2W_{18} } of 2:1:x or 2:x:1 when varying x from 0 to ca. 4, either for the host { Mo_{154} } (see Figure 12a) or the guest { P_2W_{18} } (see Figure 12b), common broad features (indicated by red arrows in Figure 12) are observed when varied component is introduced in large excess. In such particular chemical composition conditions equilibria should be shifted favorably toward the formation of complex multicomponent inclusion complexes.



Figure 12: ¹H NMR spectra of γ -CD solution (3 mM) in the ternary system γ -CD:{Mo₁₅₄}:{P₂W₁₈O₆₂}, with variable amounts of a) [P₂W₁₈O₆₂]⁶⁻ or b) {Mo₁₅₄} showing appearance of new features due to hierarchical inclusion system {[P₂W₁₈O₆₂]⁶⁻ CD}⊂{Mo₁₅₄}. Note the presence of free CD and binary inclusion complex {[P₂W₁₈O₆₂]⁶⁻ CD} involved in fast chemical exchange (blue arrows) as a result of dissociation equilibrium in these molar ratio conditions. The CD involved in strongly interacting ternary system are shown by red arrows.

¹H DOSY NMR also revealed that these new resonances are characterized by a significant low self-diffusion ($D = 106 \ \mu m^2 . s^{-1}$) in agreement with the nanoscopic dimension of the onionlike supramolecular assembly (see Figure 13). These results joint also and complement the ³¹P DOSY NMR results.



Figure 13: ¹H DOSY NMR spectrum of γ -CD solution in the ternary system γ -CD:{ Mo_{154} }:{ $P_2W_{18}O_{62}$ } with molar ratio 2:1:2, showing signatures of complexed and excess CDs involved in an dynamically slow exchange process. Inset: plots of measured diffusion coefficients as a function of { Mo_{154} }/CD molar ratio in presence (red) and absence (black) of [$P_2W_{18}O_{62}$]⁶. Note that in the system γ -CD:{ Mo_{154} }:{ $P_2W_{18}O_{62}$ } 2:1:2, $Mo_{154}/CD = 0.5$ (the one shown here), two types of CD are distinguished, the one involved in the three-component complex ({ $P_2W_{18}\subset 2CD$ } \subset { Mo_{154} }) with $D = 106 \ \mu m^2/s$ represented by close symbol and the CD in equilibrium between free CD and simple inclusion complex such as the binary [$P_2W_{18}O_{62}$]⁶- \subset 2CD showing and intermediate $D = 180 \ \mu m^2/s$ represented by an open symbol.

 13 C NMR were also conducted to probe the interaction experienced by the CD as host and guest as well in the ternary CD:{Mo₁₅₄}:{P₂W₁₈} system. For comparison the binary systems CD:{Mo₁₅₄} and CD:{P₂W₁₈} were also investigated (see Figure 14). The spectrum of CD is

mostly affected in the presence of the Mo-blue ring either in the binary or the ternary systems, whereas little changes are observed in the binary system involving the Dawson POM. These results suggest that conformational changes in the CD are more important when this latter is embedded in the blue wheel ring as a guest than when it accommodates a Dawson POM in its cavity as a host.



Figure 14: ¹³C NMR spectra of the parent γ -CD, the binary systems γ -CD:{P₂W₁₈} and γ -CD:{Mo₁₅₄}, and the ternary system γ -CD:{Mo₁₅₄}:{P₂W₁₈} showing the effect of {Mo₁₅₄} on the C resonances of the CD.

¹⁸³W NMR is complementary to ³¹P NMR providing further characterization of the Dawson POM component. The spectrum of the ternary CD:{ Mo_{154} }:{ P_2W_{18} } system displays two new broad signals corresponding to the new complexed species attributed to the apical and belt tungsten atoms of the Dawson-type anion as well as the two original peaks of the free species resulting from the equilibrium between free and complexed anions in solution (see Figure 15). It is worth noting that in absence of { Mo_{154} }, the signals of ¹⁸³W NMR present no change whatever the introduced ratio of cyclodextrin as observed previously by ³¹P NMR (Figure 10a).



Figure 15: ¹⁸³W NMR spectra of different solution mixtures showing that the simultaneous presence of the three components provokes a change of ¹⁸³W NMR spectrum. The presence of two new broad ¹⁸³W NMR signals (indicated by the arrows) is consistent with the formation of the three-component inclusion complex.

However, these preliminary NMR characterizations allowed identifying the fingerprint of the three-component system in aqueous solution, and then constitute bases for further investigations of this exciting supramolecular chemical system.

In order to verify the integrity of the Mo-blue ring, potentiometric titrations for $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ and $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ were conducted allowing the determination of the reduction number in these structures. Titrations were carried out using permanganate ion (MnO_4^{-}) in acidic conditions. The potential jump associated with a color change revealed the equivalence corresponding to 28 Mo^V centers expected for the blue wheel structure in both cases, indicating no effect of the organic macrocycle or the $\{P_2W_{18}\}\$ on the electronic feature of the ring. The potentiometric curve of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ is displayed in Figure 16.



Figure 16: Potentiometric titration curve of $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \cdot 2CD$ using (MnO_4) showing the potential jump corresponding to the equivalence point for 28 Mo^V metallic centers.

III.3. Variation of Mo/W composition within the wheel

Based on the results obtained from the mixed blue wheel $[W_{14}Mo_{140}O_{462}H_{14}(H_2O)_{70}]^{14}$ { $W_{14}Mo_{140}$ } showing the regioselectivity between W and Mo within the pentagon (see chapter II), and after confirming that the isolated product corresponds to the archetypical structure of the wheel { Mo_{154} }, we decided to investigate the possibility of following the same concept to synthesize a three-component system based on the mixed blue wheel { $W_{14}Mo_{140}$ }, cyclodextrin and { P_2W_{18} }. This scenario was examined by acidification of an sodium molybdate and sodium tungstate solution under reducing conditions until pH 1 in the presence of [$P_2W_{18}O_{62}$]⁶⁻ and γ -cyclodextrin in ratios Mo:W: γ -CD:{ P_2W_{18} } = 140:14:2:1 (see experimental part). The system generated well shaped crystals of $Na_{12}K_3H_5$ [{ $W_{14}Mo_{140}$ }($P_2W_{18}O_{62}$)(γ -CD)₂]•200H₂O (noted { $P_2W_{18}\subset 2CD$ }] \subset { $W_{14}Mo_{140}$ } hereafter) within 24 hours of the synthesis. Infrared spectrum of { $P_2W_{18}\subset 2CD$ } \subset { $W_{14}Mo_{140}$ } showed the same finger print observed for such species displaying the vibration bands of CD, { P_2W_{18} } and the wheel { $W_{14}Mo_{140}$ }.

III.3.2. Structural description

Single crystal X-ray diffraction analysis of $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}\$ revealed the same order concerning the arrangement of the three components within the structure as seen for $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ where the Dawson-type anion is similarly embedded within the cavity of the wheel $\{W_{14}Mo_{140}\}\$ crowned by two γ -cyclodextrins in a hierarchical fashion. Once again the two CDs appear severely disordered, however, a scheme has been proposed based on the construction of the backbone of the cyclodextrins form the conical electronic density intermediating $\{P_2W_{18}\}\$ and $\{W_{14}Mo_{140}\}\$. The structure and arrangement are in accordance with what have been seen for such system in the structures of $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ and $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ and $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}\$ and the terminal oxygens of both POMs with intermolecular hydrogen-bonding interactions give in the 2.75-3.25 Å range. The ring retains the exact archetypical structure of $\{Mo_{154}\}\$ with the heptacoordinated site occupied solely with tungsten W^{IV} . The system crystallizes in a monoclinic C12/c1 space group with its unit cell containing eight $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}\$ units that are packed in a zig-zag manner (see Figure 17).



Figure 17: Mixed representation of: a) the supramolecular hierarchical compound $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}\)$ and b) selected view of the packing within the unit cell. Mo: blue polyhedra, W: grey polyhedra, O: red spheres, W: white spheres and C: grey spheres.

Refinements using W-Mo distribution led to close ellipsoids for W and Mo, revealing that the electronic density at the central position of the pentagon corresponds to W rather than Mo. The mean principal values U_{11} , U_{22} and U_{33} of the anisotropic displacement parameters of W at the center of the pentagon are given in Table 2 compared to that obtained in chapter II. In addition, no change in the geometrical parameters of the heptacoordinated site was observed if occupied by either W or Mo as observed when comparing $\{P_2W_{18}\subset 2CD\}\subset \{Mo_{154}\}$ and $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}$.

Table 3. Main anisotropic displacement parameters of the W at the center of pentagonal motifs in $2 \subset 2CD$ compared to those observed for Na-{W₁₄Mo₁₄₀} from chapter II.

Anisotropic displacement parameters (Å ²)				
atoms	\mathbf{U}_{11}	\mathbf{U}_{22}	U ₃₃	Compound
W _(center)	0.040315	0.028915	0.027005	Na-{W ₁₄ Mo ₁₄₀ }*
W _(center)	0.047535	0.061930	0.059690	$\{P_2W_{18} {\sub} 2CD\} {\sub} \{W_{14}Mo_{140}\}$

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Finally, the crystal structure of $\{P_2W_{18} \subset 2CD\} \subset \{W_{14}Mo_{140}\}$ revealed the presence of the same striking arrangement { $(P_2W_{18}O_{62}) \subset 2 \gamma$ -CD $\subset (M_{154})$ } decorated by fourteen tungsten atoms at the center of each pentagonal motif as confirmed by EDX indicating that *in situ* self-assembly and self-organization of such hierarchical system can be based on both mixed Mo/W and homogenous Mo wheels. Table 3 below shows the crystallographic data of $\{P_2W_{18} \subset 2CD\} \subset \{W_{14}Mo_{140}\}.$

Table 4. Selected crystallographic parameters of the X-ray diffraction analysis of $\{P_2W_{18} \subset 2CD\} \subset \{W_{14}Mo_{140}\}$.

Commound	$(\mathbf{D}, \mathbf{W}, \mathbf{\sigma}) = (\mathbf{W}, \mathbf{M})$	7	0
Compound	$\{P_2 v_{18} \subseteq 2 \subseteq D\} \subseteq \{v_{14} v_{10140}\}$	Z	0
Formula	$C_{96}H_{719}K_3Mo_{140}Na_{12}O_{874}P_2W_3$	$\rho_{\rm calc}$, g.cm ⁻³	0.574
7 7777 1-1	2		0.725
FW, g.mol ⁻¹	35631.2	μ (Mo K α), cm ⁻¹	0.725
<i>Т</i> , К	150	λ (Mo K α), Å	0.71073
crystal size (mm)	$0.15 \times 0.14 \times 0.03$	θ range, deg	θ min = 2.1, θ max = 25.1
crystal system	monoclinic	data collected	1368043
space group	C2/c	unique data	81954
<i>a</i> , Å	67.093 (4)	unique data I> $2\sigma(I)$	53316
b, Å	34.2942 (19)	no. parameters	2410
<i>c</i> , Å	40.768 (2)	$R(F)^{\mathrm{a}}$	0.483
α, deg	90	$R_w(F^2)^{\mathrm{b}}$	0.171
β , deg	99.821 (3)	GOF	3.35
γ, deg	90		
$V, Å^3$	92429 (9)		

Potentiometric titration of 1 mM $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}\$ revealed 28 electrons corresponding to 28 Mo^V centers as expected for such system. Titration was carried out using a strong oxidizing agent (10 mM MnO₄⁻) in acidic conditions. Both potential jump and color change revealed the equivalence at 5.5 mL corresponding to 28 electrons per blue wheel. The potentiometric curve of $\{P_2W_{18}\subset 2CD\}\subset \{W_{14}Mo_{140}\}\$ is displayed in Figure 18.



Figure 18: Potentiometric titration curve of $\{P_2W_{18} \subset 2CD\} \subset \{W_{14}Mo_{140}\}$ (C = 1 mM) using (10 mM MnO₄⁻) showing the potential jump corresponding to the equivalence point for 28 Mo^V metallic centers, similar to what is expected for such system.

III.4. From anionic to cationic guest

Passing from the Dawson-type anion to the octahedral cationic cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ led to the formation of an amorphous product instead of well-defined crystals. Although getting a structural model for such system was not achieved, the interaction between the three components was investigated by NMR. Samples in the ternary γ -CD:{Mo₁₅₄}:{Ta_6Br_{12}} system at 3 mM CD concentration and fixed CD/{Mo₁₅₄} = 2 ratio and variable ratios of cluster as well as fixed CD/cluster = 2 ratio and variable ratios of {Mo₁₅₄} were prepared and characterized by proton NMR. The results illustrated in Figure 19 allowed understanding to some extent the interactions involved in such a complex system. Broad new peaks appear as soon as the three components are present altogether and for certain chemical compositions coexist with narrower resonances that could account for the binary complexes {Ta₆Br₁₂}⊂CD or CD⊂{Mo₁₅₄}. This could be particularly visible with the H1 proton resonance at ca. 5 ppm. These narrower signals disappear as soon as the chemical composition reaches the 2:1:1 ratios in CD:{Mo₁₅₄}:{Ta₆Br₁₂}. This means that broadening of CD spectrum is directly related to the association of the three components and thus constitutes an evidence of ternary complexes formation similar to those observed with the Dawson POM system. The characteristic signature of H3 at ca. 4.25 ppm whatever the chemical composition of the ternary system demonstrates that a strong interaction takes place between the cluster and the γ -CD, as previously evidenced (see chapter III). It is thus most probably that the large components are due to the complexes involving the cluster together with the blue wheel. These experiments seem to indicate that the stoichiometry of the most probable complex in the ternary system would be, like in the case of the Dawson POM, $CD: \{Mo_{154}\}: \{Ta_6Br_{12}\} = 2:1:1 \text{ that was supported by the disappearance of the narrow peaks of}$ excess CD (in binary complexes) as soon as the characteristic stoichiometry CD: $\{Mo_{154}\}$: $\{Ta_6Br_{12}\} = 2:1:1$ is reached. After this ratio, the spectra no longer evolve showing the six expected resonances for the Hn (n = 1-6) for the CD, but undergoing severe line broadening, Such stoichiometry was confirmed by elemental analysis and EDX when checking the composition of the amorphous compound obtained from such system. Finally, all the results show the specific interactions between the CD and the blue wheel on one hand and the cluster on the other hand, which are still different than that present in the three-component system.



Figure 19: ¹H NMR spectra of γ -CD solution (3 mM) in the ternary system γ -CD:{ Mo_{154} }:{ Ta_6Br_{12} }, with variable amounts of a) [$Ta_6Br_{12}(H_2O)_6$]²⁺ or b) { Mo_{154} } showing appearance of broad features that could be due to hierarchical inclusion system {[$Ta_6Br_{12}(H_2O)_6$]²⁺ \subset CD} \subset { Mo_{154} }.

IV. Conclusion

In summary, we report the discovery of remarkable hierarchical three-component assemblies based on the combination of $\{M_{154}\}$ ring-shaped anions, cyclodextrins and polyoxometalate or cluster. Such unprecedented hybrid assemblies are built from the three functional components which are specifically self-assembled through a one pot procedure, meaning that this striking multi-level recognition process has required neither specific precautions nor sophisticated strategies of multi-step synthesis. Besides, it is also remarkable that $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\},\$ $\{P_2W_{18} \subset 2CD\} \subset \{Mo_{154}\} \bullet 2CD$ compounds and $\{P_2W_{18} \subset 2CD\} \subset \{W_{14}M_{0140}\}$ were formed and isolated as pure crystalline material from solution containing stoichiometric mixture in metalate ions, γ -CD and Dawson-type anion. It transpires that the recognition processes and the related contributors to the effective driving force must be strongly efficient. An ongoing study revealed that it is also possible to extend this concept to other POMs such as the Keggin-type anion $[BW_{12}O_{40}]^{5-}$ and $[SiW_{12}O_{40}]^{4-}$ or anionic octahedral clusters as $[\text{Re}_6X_8(\text{CN})_6]^{4-}$ (X = S, Se or Te) that showed promising preliminary results. The new systems mimic the original one in terms of synthesis and characterization where the new products are obtained as well-defined crystals containing the expected ratios Mo_{154} :CD:guest = 1:2:1 as assessed by elemental analysis and EDX.

Actually, formation of this onion-like supramolecular architecture in aqueous solution should be suspected highly improbable because the three functional subunits are highly soluble in water and thus considered as hydrophilic species. Furthermore, the final arrangement results from the encapsulation of a cationic or anionic guest into an anionic host, wherein the electrostatic repulsion should be screened by the γ -CD units and circumvents by the efficiency of the recognition processes in the latter. Generic driving forces leading to this multi-level assembly could arise from a pronounced "*chaotropic*" effect that operates through an effective water structure recovery. Magnitude of the "*chaoptropic*" nature of polyoxometalates remains unknown especially for those ranging within nanosocopic dimension even though such a behavior has been identified within interactions mechanism between POMs and lipid bilayers interface.⁵³ Given the scope of this area, it becomes obvious that such a preliminary study should open new avenues toward exciting, extensive and challenging physical-chemistry or physics of complex nanoscopic composites.
V. References

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General conclusion

Polyoxometalate (POM) chemistry is a key contributor in the development of sophisticated materials for various fields of science ranging from catalysis and medicine, to data storage. Synthesizing unique POMs having compelling properties can be achieved by either producing new structures or tuning the initial metal composition. Introducing POMs into supramolecular chemistry generated astonishing hybrid materials by combining the properties of organic and inorganic moieties. The wide structural flexibility of the newborn system makes possible the rational design of hybrid architectures ensuring that the interplay between organic and inorganic parts originates phenomena of elemental and essential interest in different areas. The work presented in this thesis shows the synthesis and characterization of new compounds based on historical/classical POMs as well as hierarchical hybrid materials with different properties.

In the first part, the main purpose was to tune the metal composition of the $\{M(M_5)\}$ transferable unit found in prominent structures as Keplerate, Mo-blue ring and Krebs anions aiming to modify their properties. Investigating the Mo/W distribution within the pentagonal unit led to the synthesis of a series of compounds. Surprisingly, introducing tungsten increased the rate of formation of these species. ¹H NMR studies of the Keplerate series showed a direct relation between the metal composition of the pentagons and the lability of the acetate ligands. Interestingly, the introduced tungsten had a preferential occupation for the central heptacoordinated site where it showed the same behavior on three different occasions in Keplerate, blue wheel or in Krebs anions. Such observation was supported by several techniques of characterization mainly in the solid state. EXAFS analysis reinforced this observation by assuring the occupation of W for the central site coordinated by seven oxygen and five or six molybdenum atoms in the first and second coordination spheres, respectively. The selectivity appeared to be kinetically driven that can be due to the presence of more diffuse 5d, 7s and 7p orbitals in the W atom to coordinate a seventh oxygen atom. Such results open the way to investigate the influence of W on the chemical and physical properties of the new compounds and the possibility to synthesize functional materials of enhanced activities based on the mixed species.

In the second part, specific interactions between γ -cyclodextrin and two types of inorganic guests have been tested. The system with POMs as anionic guest showed high versatility giving rise to three arrangements depending on the synthetic conditions, while that with the cationic guest showed a strong affinity of γ -CD for the cluster which appeared closely embedded within two γ -CD units generating a ditopic cation. Solution studies demonstrated the pre-association of host and guest units in solution for which binding constants and thermodynamic parameters have been determined. Designing carefully a complementary system based on the combination of three different chemistries involving POM anions, cationic cluster and γ -cyclodextrin has been investigated. The three moieties appeared to interact together giving rise to a three-component well-ordered hybrid material derived as supramolecular hydrogel or single crystals. The supramolecular chemical complementarity between these components offers new perspective to design unrivaled functional materials that combine the key properties of electron-rich and electron-poor moieties through non-covalent host guest interactions using cyclodextrin.

In an attempt to fabricate nonconventional gigantic host-guest supramolecular materials, and to demonstrate that hydrophobic contributions play a key role in recognition processes involving POMs and organic substrate, the interaction between γ -CD and Mo-blue ring has been investigated. NMR gave an indication about the mode of interaction between the two species suggesting the deep penetration of γ -CD into the large cavity of the Mo-ring and the formation of an inclusion complex. A more complex scenario has been examined by introducing a third size-matching component (POM or cluster) capable of interacting with the inner face of CD. Exploration of the new system gave rise to two new arrangements containing the three components. The arrangements were characterized in liquid and solid state showing unprecedented hierarchy based on alternating organic and inorganic layers encapsulating anionic [P₂W₁₈O₆₂]⁶⁻ species within an anionic Mo-ring. Finally, a cross over between the mixed pentagonal motifs and the gigantic hierarchical system gave rise to a mesmerizing arrangement summarizing the work done in the course of this thesis. Such results will hopefully guide the design of new host-guest arrangements which seems a desirable goal in light of the promising and inventive applications in different areas.

Appendix



Polyoxometalate, Cationic Cluster, and γ -Cyclodextrin: From Primary Interactions to Supramolecular Hybrid Materials

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Supporting Information

ABSTRACT: Herein, we report on a three-component supramolecular hybrid system built from specific recognition processes involving a Dawson-type polyoxometalate (POM), $[P_2W_{18}O_{62}]^{6-}$, a cationic electron-rich cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$, and γ -cyclodextrin (γ -CD). Such materials have been investigated using a bottom-up approach by studying the specific interactions between γ -CD and both types of inorganic units. Their ability to interact has been investigated in the solid state by single-crystal X-ray diffraction (XRD) and in solution using multinuclear NMR methods (including DOSY, EXSY, and COSY), electrospray ionization mass and UV–vis spectroscopies, electrochemistry, and isothermal titration calorimetry experiments. Single-crystal XRD analysis reveals that POM: γ -CD constitutes a highly versatile system which gives aggregates with 1:1, 1:2, and 1:3 stoichiometry. Surprisingly, these arrangements exhibit a



common feature wherein the γ -CD moiety interacts with the Dawson-type POMs through its primary face. We present also the first structural model involving an octahedral-type metallic cluster with γ -CD. XRD study reveals that the cationic $[Ta_6Br_{12}(H_2O)_6]^{2+}$ ion is closely embedded within two γ -CD units to give a supramolecular ditopic cation, suitable to be used as a linker within extended structure. Solution study demonstrates clearly that pre-associations exist in solution, for which binding constants and thermodynamic parameters have been determined, giving preliminary arguments about the chaotropic nature of the inorganic ions. Finally, both building blocks, i.e., the ditopic supramolecular cation $\{[Ta_6Br_{12}(H_2O)_6]@2CD\}^{2+}$ and the Dawson-type anion, react together to give a three-component, well-ordered hybrid material derived either as a supramolecular hydrogel or single crystals. The solid-state structure shows an unprecedented helicoidal tubular chain resulting from the periodic alternation of POM and supramolecular cation, featuring short hydrogen-bonding contacts between the electron-poor POM and electron-rich cluster. The 1D tubular ionic polymer observed in the single crystals should make it possible to understand the long-range ordering observed within the hydrogel hybrid material. The supramolecular chemical complementarities between the γ -CD-based ditopic cation and POM open a wide scope for the design of hybrid materials that accumulate synergistic functionalities.

1. INTRODUCTION

Motivation to design sophisticated hybrid materials has directed great attention to the development of challenging scientific projects such as those based on mimicking natural processes involved within energy conversion, biomass valorization, or pollutants elimination.¹ Understanding the primary interactions that govern the assembling between molecular components is probably the key for controlling the hierarchical arrangement of

complementary active moieties from solution to the functioning material.² In nature, active components are spatially wellordered to provide the highest efficiency for energy transfer, electrons exchange, or catalytic transformation.³ For example, metallic clusters involved in redox bioprocesses such as

Received: July 13, 2017 **Published:** August 18, 2017 nitrogen fixation, CO₂ reduction, or respiration are ubiquitous in biology, but generally, they are included within a highly evolved biochemical environment to perform electron-transfer functions through complex pathways.⁴ Intense research efforts are deployed in the design of artificial devices integrating an active core within a simplified biological-like environment. In context, supramolecular chemistry is developing basic concepts and principles that are useful tools to assemble specifically molecular units through weak interactions arising from directed hydrogen-bonding, electrostatic, or dispersion forces.⁵ In addition to these weak attractive effects, polar solvents such as water contribute substantially to the aggregation processes. Desolvation or solvent reorganization around the guest or within the host can be the most determining contribution in shifting the binding equilibrium.⁶ In many cases, the so-called hydrophobic effect was found to be one of the main driving forces in aqueous medium able to dictate host-guest association, self-assembly processes, or ionic recognition.⁷ Polyoxometalates (POMs) are anionic all-inorganic molecular metal oxides with highly diverse structures that reach in size nanoscopic dimensions.⁸ This class of compounds exhibits a wide structural diversity in relationship with their remarkable chemical and physical properties that make them useful for applications in areas ranging from materials science and energy conversion to catalysis and medicine.9 Therefore, wider exploitation of POM compounds requires the development of robust and efficient synthetic protocols for their integration into hybrid architectures and devices. In context, a supramolecular approach has the intrinsic advantage to self-assemble these POM units through weak and specific interactions into well-ordered hierarchical materials. Recently, cyclodextrin (CD) has proved to behave as a specific glue to assemble POM units to give 1D nanogrid assembly¹⁰ or crystalline materials.¹¹ Herein, we report on the formation of extended hybrid materials based on the anionic Dawson-type POM α - $[P_2W_{18}O_{62}]^{6-}$ and the cationic cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ (abbreviated $\{Ta_6\}$), mediated through specific interactions with γ -cyclodextrin (γ -CD, see Figure 1). The inorganic



Figure 1. Structural representation of the molecular components used as building blocks: (a) Dawson anion $[P_2W_{18}O_{62}]^{6-}$ (POM), (b) γ -cyclodextrin $C_{48}H_{80}O_{40}$ (γ -CD), and (c) octahedral cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ ({Ta₆}).

moieties, i.e., POM and the octahedral cluster,¹² are complementary units in terms of ionic charge and electronic density. Polyoxotungstates such as the archetypical Dawson anion $[P_2W_{18}O_{62}]^{6-}$ contain tungsten atoms in their +VI highest oxidation number and are considered usually as electron-poor polynuclear complexes, as exemplified by their ability to undergo multi-electron reduction without significant structural changes. In contrast, the aqua hexatantalum cationic species $[Ta_6Br_{12}(H_2O)_6]^{2+}$ exhibits low-oxidation-state $Ta^{II,III}$ mixed-valence centers, giving rise to electron-rich metal–metal

bonds and related oxidation processes without damaging the cluster structure. In general, octahedral clusters represent an important class of compounds in the field of solid-state chemistry.¹³ Nevertheless, sophisticated solution chemistry, ranging from coordination chemistry¹⁴ to supramolecular materials,¹⁵ can be also developed from octahedral-type clusters, making it possible to investigate a large panel of applications in photocatalysis,¹⁶ soft materials,¹⁷ bioimaging,¹⁸ or phototherapy.¹⁹

 γ -CD as an organic unit is a cyclic oligosaccharide built on eight 1,4-linked D-glucopyranosyl residues which delimit a toroidal hydrophobic cavity. Their remarkable inclusion properties have given rise to wide applications in many fields of science, such as nanotechnology,²⁰ pharmaceutics,²¹ and medicine.²² Thus, CDs represent an interesting class of building blocks for the construction of hybrid assemblies.²³ In this report, we show the existence of relevant supramolecular associations between γ -CD and POM and between γ -CD and {Ta₆} separately in aqueous solutions as well as in the solid state. Most importantly, we demonstrate that such interactions could be combined in a rational way to give rise to ordered supramolecular hybrid organic—inorganic network based on [P₂W₁₈O₆₂]⁶⁻, {Ta₆}²⁺, γ -CD as primary building units.

2. RESULTS AND DISCUSSION

2.1. Formation of the *γ***-CD-Based Adducts.** *POM@nCD*. Systematic studies have been carried out using different ratios of POM and γ -CD and different alkali salts of the Dawson anion, making it possible either to tune the solubility of the POM/γ -CD aggregates or to improve the quality of the single crystals. This study showed that this chemical system is highly flexible, producing crystalline solids which contain aggregates with variable POM: γ -CD stoichiometries. The syntheses were straightforward and consisted of mixing 1, 2, or 3 equiv of γ -CD, respectively, dissolved in water or in 0.5 mol L^{-1} NaCl aqueous solution containing 1 equiv of Dawson anion $[\bar{P}_2W_{18}O_{62}]^{6-}$ at a concentration of ~10⁻² mol L⁻¹ as potassium, rubidium, or cesium salt. The nature of these alkali cations is expected to tune the solubility of the POM/CD aggregate, thus favoring selective crystallization of the 1:1, 1:2, or 1:3 assembly. Solutions were allowed to stand at room temperature for crystallization. After several days, single crystals suitable for XRD, elemental analysis, and further characterizations were collected. Further details about the synthetic procedures and routine characterization are given in the Supporting Information (SI), section 2. The three isolated crystalline phases with compositions $KNa_{5}[P_{2}W_{18}O_{62}]\cdot[\gamma-CD]\cdot$ 3.5NaCl·23H₂O, CsNa₅[$P_2W_{18}O_{62}$]·[γ -CD]₂·1.2NaCl·23H₂O, and $Rb_4K_{1.5}Na_{0.5}[P_2W_{18}O_{62}]\cdot[\gamma-CD]_3\cdot35H_2O$ are abbreviated hereafter as POM@CD, POM@2CD, and POM@3CD, respectively.

 $[Ta_6]@2CD$. The cationic cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ showed a high tendency to form a 1:2 inclusion complex with cyclodextrins, whatever the $\{Ta_6\}/\gamma$ -CD ratio used. Formation of the 1:2 adduct is nearly quantitative from aqueous mixtures containing stoichiometric proportions of γ -CD and $\{Ta_6\}$ cluster. The resulting solutions were able to generate greenish plate crystals corresponding to $[Ta_6Br_{12}(H_2O)_6]\cdot[\gamma$ -CD]₂Br₂· 14H₂O, namely $\{Ta_6\}@2CD$ (see SI, section 2, for further details).

2.2. Single-Crystal X-ray Analysis. POM@nCD Arrangements with n = 1, 2, or 3. Remarkably, X-ray diffraction (XRD) analysis of single crystals obtained from POM/ γ -CD

mixtures revealed three different stoichiometries depending on the used POM/ γ -CD ratio (see Figure 2). Interestingly,



Figure 2. Structural representation of the supramolecular POM@nCD along their X-ray diffraction analysis showing (a) the 1:1, (b) 1:2, and (c) 1:3 arrangements.

structural analyses in the solid state of the 1:1, 1:2, and 1:3 arrangements exhibit a striking common mode of interaction in which the two components are held together through close contacts involving the primary face of the γ -CD and the longitudinal side of the POM. As generally depicted for such a type of arrangements, the two components are held together through a set of weak attractive interactions including electrostatic, ion-dipole, and hydrogen-bonding (see Figures S3–S5, SI section 4). In the structure of the 1:1 complex (see Figure 2a), the Dawson ion appears literally put down on the primary face of the γ -CD. Structural analyses revealed only one short ion-dipole contact W=O···C-OH (O···C = 2.68 Å), while the remaining similar interactions appear weaker as reflected by O…C distances longer than 3.2 Å. Furthermore, four weak hydrogen-bonding contacts are observed leading to O…O distances in the 3.0-3.3 Å range. Finally, electrostatic interactions must also be considered since attractive interactions are reinforced by O…K…O junctions involving terminal W=O groups of the POM unit (O…K distances, ~3.0 Å) and by ether or methanolic groups of the glucopyranose moieties belonging to the γ -CD. The structure of POM@2CD assembly derives from the former and consists of one Dawson unit $[P_2W_{18}O_{62}]^{6-}$ sandwiched by two γ -CD disposed on the two opposite longitudinal faces of the POM at 180° from each other (see Figure 2b). The cohesion forces of the supramolecular 1:2 arrangement are ensured by three hydrogen-bonding contacts with O…O distances of ~3.0 Å, supported by electrostatic interactions involving bridging Na⁺ and Cs⁺ cations (see Figure S4, SI section 4). A third POM:γ-CD stoichiometry has been

obtained, giving an assembly where the $[P_2W_{18}O_{62}]^{6-}$ ion is closely embedded by three γ -CDs as a paddle wheel arrangement (see Figure 2c). As already observed for the 1:1 and 1:2 stoichiometries, the primary faces of the three γ -CD units are directed toward the central POM moiety. Interestingly, the three γ -CDs are related through a C_3 axis and held together through three short hydrogen-bonding contacts (O··· O = 2.69 Å). Furthermore, three equivalent rubidium cations are also involved within the POM@3CD arrangement, as nodes that associate the POM with two γ -CDs through seven Rb–O contacts (Rb-O = 2.83-3.22 Å) (see Figure S5, SI section 4). At last, three additional hydrogen-bonds ($O \cdots O = 2.93$ Å) ensure direct interactions between POM and γ -CD. These results have to be correlated with those previously reported by Stoddart et al. on superstructures involving CDs and the Keggin-type $[PMo_{12}O_{40}]^{3-}$ anion.¹¹ In all cases, the three structures exhibit similar types of molecular recognition wherein POM unit is facing γ -CD through its primary face as two complementary moieties usually described as hydrogen bond acceptor and donor, respectively. In these structural examples, the Keggin or Dawson ions do not penetrate deeply into the cavity of the macrocyclic host but rather interact through multiple weakly bonding interactions array with the hydrophilic OH groups lining the primary faces of the CDs. Actually, such a situation is significantly pronounced with the Dawson anion, a species larger than the $[PMo_{12}O_{40}]^{3-}$ Keggintype anion.¹¹ Besides, it should be also worth noting the role of the alkali ions (Na⁺, K⁺, Rb⁺, or Cs⁺), which participate also in the reinforcement of the supramolecular POM…CD associations in the solid state packing. Nevertheless, Stoddart et al. mentioned that the La³⁺ countercation presents as fully hydrated aqua ion $[La(H_2O)_9]^{3+}$ displays only very weak ionic interactions with the [PMo₁₂O₄₀]@2CD supramolecular complexes. In our case, probably due to their low enthalpy hydration,²⁴ alkali ions are then able to interact directly with the OH groups of the rims (see Figures S3-S5, SI section 4). In this case, such a situation precludes the usual face-to-face organization observed within the [PMo₁₂O₄₀]@2CD arrangement.¹¹ At last, it should be mentioned that in the 3D packing of the POM@2CD and POM@3CD, some close contacts and partial inclusions between γ -CDs can be depicted in addition to the POM…CD interactions.

 ${Ta_6}@2CD$ Arrangement. The supramolecular host-guest arrangement within $[Ta_6Br_{12}(H_2O)_6] \cdot [\gamma - CD]_2Br_2 \cdot 14H_2O$ crystal is depicted in Figure 3. The structural analysis reveals a $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster closely embedded into two γ -CDs interacting mutually through multiple hydrogen bonds (O---O = 2.9-3.0 Å) involving their wider rim (secondary face). Structural parameters of the encapsulated ${Ta_6}$ cluster remain in the usual range of that generally observed (Ta-Ta = 2.88-2.93 Å ; Ta–Br = 2.60–2.61 Å ; Ta–O = 2.15–2.39 Å).^{25a–c} However, the cohesion of the supramolecular assembly arises from four short C-H \cdots Br contacts (H \cdots Br = 2.83 Å) involving the inner H-3 hydrogen atoms of each γ -CD and the Br atoms of the cluster (see Figure 3b). In addition, the hostguest stability is supported by a framework of 16 hydrogen bonds connecting the four *in-plane* aquo ligands of the $\{Ta_6\}$ cluster with the four closest OH groups (O - O = 3.0 - 3.1 Å) that line the secondary face of the two γ -CDs (see Figure 3c). As resulting from the multiple intermolecular weak interactions and host-guest disposition, the two stacked γ -CDs appear slightly staggered of $\sim 21^{\circ}$, leading to an overall D_4 idealized symmetry. Besides, the tetragonal unit cell displays the



Figure 3. Mixed representations of the solid-state structure of the supramolecular host-guest { $[Ta_6Br_{12}(H_2O)_6]@2\gamma$ -CD}²⁺ complex: (a) side view and (b) top view highlighting close interactions between inner H-3 hydrogen (white sphere) and four bromide ligands (yellow sphere) with H…Br = 2.83 Å; (c) focus on the intermolecular hydrogen-bonding network involving the four *in plane* aquo ligands of the cluster and the hydroxo groups of γ -CD secondary faces (O…O = 3.0–3.1 Å).

common tubular arrangement formed by supramolecular building blocks {Ta₆@2CD} running along the c axis through short (O···O = 2.83 Å) and long (O···O = 6.78 Å) interblocks distances (see Figure S6, SI section 4).^{11,26} At least, it should be mentioned that the electric balance is ensured by two bromide ions per $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster. One half is located on eight equivalent disordered positions and closely intercalated within the {Ta₆@2 γ -CD} tubes (see Figure S6, SI section 4), while the other half of the Br⁻ ions is distributed between the tubular assembly. Among the abundant literature on the CD-based host-guest arrangements, we should mention the report by Nau et al. about the inclusion complexes of the $[B_{12}X_{12}]^{2-}$ series (with X = H, Cl, Br, or I), describing the crystallographic structure of the $[B_{12}Br_{12}]^{2-}$ dodecaborates included within two γ -CDs.²⁷ Strikingly, both ionic species, i.e., cationic with $[Ta_6Br_{12}(H_2O)_6]^{2+}$ or anionic with $[B_{12}Br_{12}]^{2-}$, appear deeply immersed within two facing γ -CDs to give similar host-guest arrangements. Furthermore, structural analogies can be also prolonged to the crystal lattices which display the formal tubular network, both consistent with a tetragonal cell in the I_{422} space group. Such an analogy tends to demonstrate that the lattice is mainly imposed by the tubular packing of the large supramolecular ionic units able to accommodate different types of counterions in the large resulting voids, such as Na⁺ with $[B_{12}Br_{12}]^{2-}$ or Br^- with $[Ta_6Br_{12}(H_2O)_6]^{2+}$. At least, these striking structural similarities are also supported by close solution behavior revealed by NMR, isothermal titration calorimetry (ITC), and electrochemical studies (see following sections).

2.3. Solution Studies. Interactions of γ -CD with POM or $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster in aqueous solutions have been confirmed and studied in detail by NMR, ESI-MS, ITC

measurements, electrochemistry, and UV-vis. These studies and related analyses were able to give clear insights about supramolecular pre-organization processes that occur in solution and to draw a comprehensive description of the interplay of the solvation shell within the recognition processes.

NMR Studies. Aqueous solutions of $K_6[P_2W_{18}O_{62}]\cdot 19H_2O$ or $[Ta_6Br_{12}(H_2O)_6]Br_2$ mixed with various amounts of γ -CD have been studied by multinuclear NMR (1D, EXSY, or DOSY). NMR results showed contrasted behaviors related to the different shape, size, and electronic charge density of the inorganic guest species. The ¹H NMR spectra of γ -CD upon increasing concentration of the $[P_2W_{18}O_{62}]^{6-}$ species revealed tiny but significant chemical shift changes which involve mainly the primary face protons H-6/6' ($\Delta \delta \approx 0.3$ ppm) (see Figure S9, SI section 5).²⁸ This observation suggests that the Dawson units interact weakly with the primary face of the γ -CD to give labile associations in fast chemical exchange regime with respect to the NMR time scale. Furthermore, Job's plot analysis (see inset in Figure 4) allowed concluding that γ -CD/POM



Figure 4. Variation of the self-diffusion coefficient of POM (black curve) and γ -CD (red curve) measured by ³¹P and ¹H DOSY NMR spectroscopy, respectively. The significant variation of the *D* values reveals that both γ -CD and POM move together for compositions close to the 1:2 ratio ($x_{CD} = 0.6$). Inset: Job's plot for γ -CD and POM obtained by plotting the chemical shift changes H-6/6' protons of the γ -CD.

aggregates form in solution with an average stoichiometry close to 1:2. In fact, such aggregates formation has been nicely evidenced concomitantly by ¹H and ³¹P DOSY NMR allowing access to the self-diffusion coefficient of the γ -CD and that of the POM species, respectively. The DOSY investigation, graphically shown in Figure 4 reveals that the self-diffusion coefficients of the interacting substrates decrease significantly in the POM/ γ -CD mixture that underline the formation of stable aggregates in solution. Interestingly, the D value of both interacting components reach together the same minimum value at $D = 210 \ \mu m^2 s^{-1}$ observed for the composition range close to the 1:2 ratio ($x_{CD} = 0.66$). While the chemical shift changes of the γ -CD are small and those of the ³¹P or ¹⁸³W resonances nearly undetectable (see Figures S7 and S8, SI section 5), they feature tiny conformational or electronic changes induced through aggregates formation. In contrast, the DOSY analysis of the POM/ γ -CD mixture revealed clearly that stable aggregates are formed provoking large changes of selfdiffusion coefficients (see Figure 4). These DOSY NMR data

corroborate nicely the analysis given by Stoddart et al. from SAXS/WAXS measurements carried out on aqueous solution containing the Keggin-type anion and γ -CD.¹¹ Noticeably, apparent contradictions arise from these finding because structural analysis reveals that POMs and CDs assemble together through weak interactions evidenced by only tiny variations of NMR chemical shifts (¹H, ¹⁸³W, and ³¹P), while DOSY or SAXS/WAXS investigations demonstrate that these hydrophilic species form stable aggregates in aqueous solution. Such an apparent discrepancy shed light on the prominent role of the water molecules as solvent when interacting species like POMs and γ -CD exhibit significant solvent-accessible surface.²⁹

In the presence of the octahedral $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cationic cluster, the ¹H NMR spectra of the γ -CD undergo strong changes characterized mainly by the disappearance of the H-1 and H-3 initial resonances of the γ -CD for the benefit of new signals (see Figure 5). ¹H NMR titration showed that such



Figure 5. Selected ¹H NMR spectra (300 MHz, 298 K, D₂O, 1 mM) of γ -CD in the presence of different equivalents of {[Ta₆Br₁₂(H₂O)₆]²⁺ dications. Arising of new resonances, clearly observed for the H-1 and H-3 protons, suggests that the cluster is deeply inserted into the cavity of the γ -CD at their secondary faces, giving a non-labile 1:2 host–guest arrangement.

changes are nearly completed for the 1:2 ratio that is fully consistent with the XRD analysis and ITC analysis (see below). The species distribution calculated using the binding constants of ITC measurements in experimental conditions of NMR measurements supports that the prominent species above cluster/CD ratio 0.25 is the 1:2 complex and the 1:1 species remains negligible in the cluster/CD ratio range studied (see Figure S11, SI section 5).

Actually, the presence of additional ¹H NMR resonances is characteristic of dynamically slow equilibrium process (on the NMR time scale) in D₂O solution involving deeply embedded tantalum cluster through the two secondary faces of γ -CD tori. EXSY ¹H NMR spectrum (see Figure S12, SI section 5), recorded for a 1:1 ratio revealed correlations between resonances of the free and complexed γ -CD, both involved in slow exchange processes. Thus, under complexation process, H-1 undergoes a significant low-frequency shift giving broader new signal at 4.93 ppm. At the same time, H-3 resonance splits into two signals at 4.34 and 4.05 ppm that reflect the symmetry lowering of the macrocycles in the host-guest arrangement from C₈ to C₄. Variable temperature ¹H NMR experiments carried out at a ratio $\{Ta_6\}/\gamma$ -CD = 1:4 ratio confirm plentifully such a dynamic behaviors showing illustrative coalescence phenomena from ~50 to 60 °C for the most affected H-1 and H-3 signals (see Figure S13, SI section 5). Furthermore, analysis of the COSY ¹H NMR spectrum of the 1:2 association allowed confirmation of these ¹H NMR assignments of the γ -CD as host (see Figure S14, SI section 5). Actually, the significant downfield shifts concomitant to the splitting of the inner H-3 protons appear in fair concordance with that observed by XRD analysis. In the solid state structure, four H-3 protons of each γ -CD exhibit very close contacts with four Br atoms of the tantalum cluster (Br····H = 2.83 Å), while the four remaining H-3 are engaged within significantly longer interactions (Br - H = 3.19 Å) (see Figure 3b). Then, the decrease of the local symmetry of the γ -CD from C₈ to C₄ generates two groups of four equivalent glucopyranosyl units that should provoke the splitting of all the ¹H resonances. This is clearly observed for the most affected H-3 protons, while line broadening and probably accidental degeneracy prevent any clear resolutions of signals arising from the two sets of nonequivalent glucopyranosyl units. In conclusion, NMR results reveal a frozen complex that should feature a high host-guest affinity. Such a situation is fully consistent with the X-ray structural analysis which reveals a deeply embedded tantalum cluster within the γ -CDs pocket. These observations have been further supported by ITC analysis (see below).

ESI-MS Studies. The γ -CD-based systems containing either the Dawson anion or the ${Ta_6}$ octahedral dicationic cluster give explicit ESI-MS spectra in fair accordance with our previous results. As shown in Figure 6a, ESI-MS spectrum of 1 \times 10⁻⁴ mol L⁻¹ aqueous solution in POM@3CD assembly, carried out in the negative mode contains three well-defined massifs which have been attributed unambiguously to [POM@ 2CD⁶⁻ at m/z = 1159.6, [HPOM@CD]⁵⁻ at m/z = 1132.2, CD-free POM identified as $[H_2P_2W_{18}O_{62}]^{4-}$ at m/z = 1091.4, and $[P_2W_{18}O_{61}]^{4-}$ at m/z = 1086.7. It is quite surprising that such aggregates which have been characterized as labile adduct by ¹H NMR can even be observed in the conditions required for ESI-MS experiments. Nevertheless, initial complex POM@ 3CD was not observed in the ESI-MS spectrum, probably due to a weaker stability than that of the smaller aggregates POM@ 2CD and POM@CD. This is consistent with ITC measurements which indicate also that higher aggregates such as POM@3CD do not contribute significantly within the thermodynamic of the overall host-guest process.

Conversely, the $\{Ta_6Br_{12}(H_2O)_6@2CD\}^{2+}$ host-guest arrangement in aqueous solution gives a ESI-MS spectrum in the positive mode that contains two main massifs, each characteristic of the 1:2 and 1:1 assembly, respectively (see Figures 6b and S15, SI section 6). The highest m/z massif contains peak at 2372.2 corresponding to the expected dicationic 1:2 species $\{Ta_6Br_{12}(H_2O)_6@2CD\}^{2+}$. Furthermore, this peak is flanked on each side by two additional signals giving an overall set of five peaks all separated exactly by m/z = 9 that is consistent with gain or loss of one or two water molecules. Therefore, the two right side-peaks located at m/z = 2380 and 2389 are attributed to mono- and dihydrated dicationic derivatives, while the two other peaks located on the left side result from the loss of one or two water molecules. Aqua ligands attached to the octahedral



Figure 6. ESI-MS spectra of the inclusion compounds in aqueous solution. (a) POM@3CD showing the 1:1 and the 1:2 adducts while the 1:3 complex is not observed. (b) $\{Ta_6\}$ @2CD containing the m/z peak related to the 1:2 (red trace) and 1:1 (green trace) adducts. The side peaks separated from each other by m/z = 9 are unambiguously attributed to either hydrated or dehydrated complexes.

tantalum cluster could be involved and especially the two axial coordination water molecules. These water molecules are directed along the γ -CD axis and probably more exposed than the four remaining equatorial aqua ligands, intimately encaged within the two γ -CD tori (see Figure 3). The other massif is constituted of nine peaks corresponding to different hydration state of the 1:1 dication host-guest arrangement. The expected species {Ta₆Br₁₂(H₂O)₆@CD}²⁺ and related mono- and dihydrated derivatives are observed at m/z = 1724, 1733, and 1742, respectively. On the left side, the presence of six peaks at lower m/z value is rather consistent with the sequential dehydration of the octahedral cluster until the loss of the six coordination aqua ligands to give the anhydrous species ${Ta_6Br_{12}(@CD)^{2^+}}$. These ESI-MS results seem to indicate that a supramolecular control of the desolvation process of the $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster is allowed, selectively restricted to the two axial aquo ligands within the closed 1:2 arrangement and extended to the six aquo ligands within the opened 1:1 shell. Such ESI-MS observations tend to demonstrate that supramolecular coordination chemistry based on selective ligand exchange process should be achievable from aqua octahedral clusters, using their remarkable host-guest complementarity with γ -CD.

Isothermal Titration Calorimetry Measurements. ITC was used to analyze from a thermodynamic point of view the interactions of the γ -CD with POM or $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster, respectively.^{30,26a} ITC results including binding constants, enthalpy $\Delta_r H^*$, and entropy $\Delta_r S^*$ are given at 298

K in Table 1 while further details about ITC experiments are supplied in SI section 7. The ITC data obtained from POM/ γ -

Table 1. Binding Constants K Involving Dawson Anion and Tantalum Octahedral Cluster Cation with γ -CD and Associated Thermodynamic Parameters (in kcal·mol⁻¹) at T = 298 K

guest	step	$K(M^{-1})$	$\Delta_{ m r} H^*$	$T\Delta_{\rm r}S^*$	$\Delta_{ m r}G^*$
[P ₂ W ₁₈ O ₆₂] ⁶⁻	1:1	3.2×10^{3}	-12.6	-7.8	-4.8
	1:2	3.7×10^{2}	-11.9	-8.4	-3.5
$[Ta_6Br_{12}(OH_2)_6]^{2+}$	1:1	1.5×10^{5}	-8.2	-1.2	-7.0
	1:2	1.3×10^{5}	-5.2	+1.9	-7.0

CD system were analyzed using a two-site binding model involved within a sequential process. As XRD data revealed that a 1:3 aggregate POM@3CD can be isolated in the solid state, introducing a third sequence within the binding model does not improve fits significantly between experimental and calculated data. This means that the recognition process is mainly dominated by the formation of the 1:1 and 1:2 aggregates and that the presence of higher order aggregates remains negligible in solution. Actually, the ITC results confirm nicely the above results, showing a quite significant affinity between POM and γ -CD, with $K_{11} = 3.2 \times 10^3 \text{ M}^{-1}$ and $K_{12} = 3.7 \times 10^2 \text{ M}^{-1}$ associated with enthalpy-driven processes, each compensated by entropy penalty. It is worth mentioning that these binding constants are of ~ 1 order of magnitude lower than those reported by Stoddart et al. for both 1:1 and 1:2 complexes between the γ -CD and the Keggin POM $[PMo_{12}O_{40}]^{3-.11}$ This lower affinity with the Dawson-type structure is consistent with the elongated Dawson structure compared to the spherical shape of the Keggin ion. These data appear quite surprising because such large enthalpy gains observed for both 1:1 and 1:2 successive processes do not reflect anymore the weakness of the intermolecular interactions of the Dawson ion with the γ -CD. Actually, a partial inclusion could be expected involving the two polar sites of the Dawson ion, structurally similar to that found by Stoddart et al. with the Keggin ion derivative.¹¹ Nevertheless, as evidenced by our ¹H NMR studies in solution and supported by XRD analysis, aggregates formation results mainly from close contacts between the largest lateral sides of the POM and the hydrophilic primary face of the γ -CD species. Furthermore, overall results are rather consistent with weak interactions as shown by ¹H NMR in solution and solid state structural analysis even though the resulting aggregates exhibit fair stability as exemplified by large variations of self-diffusion coefficient of both species (see DOSY NMR in Figure 4) and by large binding constants K_{11} and K_{12} . These apparent inconsistencies fade away when the prime role of the solvent is considered. Since a pure hydrophobic effect cannot account within the interacting process, water structure recovery resulting of solvent depletion from binding interfaces should contribute in a significant extent. Thermodynamic fingerprints (see Table 1) could be consistent with a "chaotropic" recognition process involving "water structure breakers" species. This idea that POM anions can range in the chaotropic category is supported by the low charge density distributed at the POM surface and by the intrinsic weak ability of the POM anion to be strongly solvated. Furthermore, evidence of interaction between Keggin-type POMs and organic materials

such as lipids or biomolecules is also consistent with the chaotropic nature of POMs.³¹

Guest affinity of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ octahedral cluster has been determined by ITC titration experiments which have been analyzed using a two-step sequential binding model (see Figure 7). The thermodynamic parameters and binding constants



Figure 7. Microcalorimetric titration data obtained at 298 *K* from sequential injections of 3.33 mM γ -CD solution into a 0.33 mM [Ta₆Br₁₂(H₂O)₆]Br₂ solution showing ITC thermogram (left) and isotherm (right). Dots and full lines correspond to experimental and calculated heats obtained from thermodynamic parameters describing a two-step sequential binding process (bottom).

included in Table 1 and Figure 7 reveal that both 1:1 and 1:2 processes are enthalpy driven and associated with opposite entropy changes, which is slightly unfavorable for the first 1:1 step and then switches to positive for the following 1:2 step. Binding constants related to the sequential host-guest recognition exhibit very high values such as $K_{11} = 1.5 \times 10^5$ M^{-1} and $K_{12} = 1.3 \times 10^5 M^{-1}$, which are comparable to those reported by Nau et al. on the 1:1 binding process between γ -CD and the perhalogenated dodecaborate ion $[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, and I). Among the series, the highest binding constant was obtained with the bromo-derivative $[B_{12}Br_{12}]^{2-}$ with $K_{11} =$ $9.6 \times 10^5 \text{ M}^{-1}$ that led the authors to conclude that sizematching effect, and polarizability of the X groups should contribute to the host-guest recognition process. In our case, the ${Ta_6Br_{12}(H_2O)_6]^{2+}}$ cationic guest exhibits globular shape and size similar to those of the $[B_{12}Br_{12}]^{2-}$ anion.² Furthermore, the positive charge of the cluster does not affect anymore the host-guest affinity which rivals and even exceeds usual values found for γ -CD with anionic substrates.^{32,26a} Such a large affinity corroborates nicely the XRD analysis and solution ¹H NMR. In the solid state, the identified network of convergent weak hydrogen-bonding interactions should obviously contribute in part as pulling factor to the supramolecular assembly stability. Actually, formation of this hostguest arrangement in aqueous medium remains very intriguing because both components are considered as hydrophilic units, mainly due to the six aqua ligands located at the corner of the dicationic octahedral cluster or due to the 24 hydroxyl groups that line the primary and the secondary faces of the γ -CD. Hence, the role of the solvent should be pointed out, acting as a pushing factor which consists of self-reorganization of water molecules relocated from the solvation shell to the bulk. Such a contribution has been considered by Nau et al. as the main factor governing the inclusion process, due to the chaotropic or superchaotropic nature of the dodecaborate series.^{27,33} This example gives first indications about the solvated character of the hexatantalum cluster and should be the starting point for further development using various octahedral type clusters that

differ in their metallic centers, inner or outer ligands, or ionic charge. $^{34,14\mathrm{b}}$

Electrochemistry. As both inorganic moieties are redox active and display complementary electrochemical properties, influence of γ -CD upon the electrochemical properties have been examined. Dawson anion $[P_2W_{18}O_{62}]^{6-}$ exhibits the general electrochemical behavior of POM compounds that corresponds to ability to undergo quasi-reversible multielectron reductions,³⁵ thus confering electrons reservoir properties interesting for many applications with regard to energy conversion or storage.³⁶ Whatever the equivalent number of γ -CD, cyclovoltammograms (CVs) of the Dawson remain almost unchanged with respect to that previously reported for the CD-free Dawson anion (not shown).³⁵ Such results are probably the fingerprint of labile and weakly bound adducts POM@nCD, previously identified by ¹H NMR and by structural analysis. Conversely, the electron-rich $[Ta_6Br_{12}(H_2O)_6]^{2+}$ cluster gives two successive monoelectronic waves observed at $E_1^{\circ} = +0.37$ V and $E_2^{\circ} = +0.67$ V vs SCE in 0.025 mol L⁻¹ HClO₄ aqueous solution (see Figure 8).³⁷ These



Figure 8. Cyclovoltammograms of $[Ta_6Br_{12}(H_2O)_6]^{2+}$ (0.5 mM, 298 K, scan rate 10 mV s⁻¹; 2.5 × 10⁻² mol L⁻¹ HClO₄ aqueous solution) in the presence of increasing amounts of γ -CD (from 0 to 5 equiv). Inset: plot of the first anodic peak potential versus equivalent number of γ -CD showing a break point for the stoichiometric conditions.

monoelectronic transfers are reversible ($\Delta E_{\rm p} \approx 60$ mV) and correspond to the redox couples ${Ta_6}^{2+}/{Ta_6}^{3+}$ and ${Ta_6}^{3+}/{Ta_6}^{3+}$ ${Ta_6}^{4+}$, respectively. Upon addition of γ -CD, these two redox peaks shift gradually toward higher potential with a large change for the first exchange ($\Delta E_1^{\circ} = +130 \text{ mV}$) and a smaller one for the second ($\Delta E_2^{\circ} = +30$ mV). These observations evidence clearly that binding situation occurs altering significantly the electrochemical properties of the guest. In addition, loss of electrochemical reversibility is observed and characterized by an increase of potential difference between the cathodic and anodic peaks $\Delta E_{\rm p} = 140$ and 100 mV for the first and the second exchange, respectively. Then, changing the charge state of the guest from 2+ to 4+ in the nonpolar environment of the γ -CD pocket might be difficult and should affect the thermodynamic stability of the host-guest assembly giving rise to the observed redox shifts and change of the kinetic barrier. In accordance with this reasonable and welldocumented assumption,³⁸ the UV-vis spectrum of the cluster undergoes only very small variations, indicating that electronic structure of the reduced state of the cluster is almost unaffected by γ -CD complexation (see SI section 7). These preliminary results tend to demonstrate that electrochemical changes should involve mainly the oxidized forms, namely $\{Ta_6\}^{3+}$ and $\{Ta_6\}^{4+}$. Nevertheless, ongoing works are in progress including spectro-electrochemistry and characterization of the specific interactions of the γ -CD with the oxidized states $\{Ta\}^{3+}$ and $\{Ta\}^{4+}$.

2.4. Three-Component Supramolecular System. The overall presented results offer fundamental bases to build hybrid materials based on combination of three components such as γ -CD, the cationic octahedral cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$, and the Dawson-type POM. The γ -CD component exhibits a remarkable high affinity with the cationic cluster to consider the 1:2 resulting host-guest complex as a highly stable cationic hybrid building block. Besides, the Dawson $[P_2W_{18}O_{62}]^{6-}$ anion and the γ -CD constitute a versatile chemical system able to form supramolecular adducts which differ from their stoichiometry but are invariably built on a selective interplay mode involving the primary face of the γ -CD and the largest side of the POM (see Figure 2). Then, high affinities, selective interactions, and dynamic flexibility are harnessed to associate the ditopic hybrid cation and the POM unit together. This approach will offer undoubtedly new perspectives in the design of unprecedented functional materials that combine the key properties of the electron-rich (cluster donor) and the electron-poor (POM acceptor) moieties, both specifically and spontaneously associated by γ -CD as ditopic linker. Besides, it should be mentioned that when the POM and cluster components were mixed in similar conditions, but in the absence of the γ -CD, amorphous and poorly defined materials were systematically obtained. Furthermore, ITC measurements on the POM-cluster binary system do not reveal any significant heat exchange, consistent with no direct POM…cluster interaction in such conditions.

From Hydrogel to Single Crystals. First attempts have been carried out by mixing directly 2.10^{-2} mol L⁻¹ aqueous solutions containing the ditopic hybrid cation {Ta₆Br₁₂(H₂O)₆@2CD}-Br₂·14H₂O and the POM K₆P₂W₁₈O₆₂·19H₂O. In such conditions, the resulting greenish solution becomes viscous until complete gelification in few minutes. Formation of hydrogel-type material indicates that a metathesis reaction takes place and results in a polymerization process involving the ditopic cation and the POM. The hydrogel has been characterized through a set of analytical methods revealing composition consistent with the formula $K_4[Ta_6Br_{12}(H_2O)_6][\gamma$ - $CD]_2[P_2W_{18}O_{62}] \cdot nH_2O$. Infrared spectra confirm the incorporation of the three components assembled within the hydrogel network (see Figure S2, SI section 3). Besides, the hydrogel assembly reveals birefringence properties below polarized optical micrograph, but the most surprising outcome is probably the presence of diffraction peaks in the powder XRD diagram that suggests long-range order exists to a certain extent (see Figure 9). Such a result prompts us to get single crystals from slow diffusion techniques using conventional Htube method. From similar 2.10^{-2} mol L⁻¹ aqueous solutions used for the hydrogel preparation, small but well-shaped greenish single crystals suitable for XRD analysis were formed in the interfacial region of both solutions for ~ 1 week. Elemental analysis of crystals, supported by the usual set of analytical methods, leads to the similar composition found for the hydrogel-based material with the formula $K_{2}H_{2}\{[Ta_{6}Br_{12}(H_{2}O)_{6}] @ (C_{48}H_{80}O_{40})_{2}\}[P_{2}W_{18}O_{62}] \cdot 32.5 H_{2}O_{10}$ (abbreviated {Ta₆@2CD·POM}). In this regard, POM, γ -CD, and {Ta₆} octahedral cluster behave as a versatile system,



Figure 9. Powder-X-ray diffraction diagram of the three-component hydrogel assembly built from hierarchical organization of γ -cyclodextrin, polyoxometalate $[P_2W_{18}O_{62}]^{6-}$, and octahedral cluster $\{Ta_6\}^{2+}$ (see inset); experimental (black) and calculated from single-crystal X-ray diffraction data (red).

allowing a structuring control from hydrogel to single crystals using supramolecular bottom-up approach.

Single-Crystal X-ray Diffraction Analysis of the Three-Component System. Single-crystal XRD study of {Ta₆@2CD· POM} reveals a 1D infinite sandwich-type structure wherein the Dawson POM anions alternate with the ditopic supramolecular cation ${Ta_6(@2CD)^{2+}}$ (see Figure 10). The linear infinite ionic polymers run along the c axis and stack together symmetrically as parallel pillars to give tetragonal packing (see Figure 10b). Besides, the ditopic hybrid cation incorporated within the three-component system exhibits very close geometrical features that those observed previously in the crystallographic structure of $[Ta_6Br_{12}(H_2O)_6] \cdot [\gamma - CD]_2Br_2 \cdot 14$ H_2O (see Figure 3), especially with regard to the host-guest interactions, mainly expressed through hydrogen bonds distribution. In a same way, arrangement between the γ -CD and the POM remains quite unchanged and involves primary faces of the γ -CD, similar to the structural models of POM@ nCD, depicted in Figure 2. Interesting observations can be noticed with regard to the expression of the chirality within the solid state arrangement. As usually observed with solid-state structures of CDs, the {Ta₆@2CD·POM} crystallographic structure is consistent with the P41212 chiral space group which imposes 41 helicoidal axis along centers of the tubular chains. Then, related 41 operations generate four different positions for the POM units that wheel helicoidally around the tube axis while orientation of the ${Ta_6@2CD}^{2+}$ units remain unchanged (see Figure 10a,c).

Finally, additional hydrogen bonds are found, which involve the axial aqua ligand of the ${Ta_6Br_{12}(H_2O)_6}^{2+}$ and terminal oxygen atoms of the POM. The shortest distances O…O that are in the 2.64–2.83 Å range suggest that electrostatic interactions may reinforce hydrogen bonding. Besides, the long-range ordering within the hydrogel can be understood partly from the structural analysis of the single crystals, by considering that stacked tubular chains, shown in Figure 10 are flexible enough to self-interpenetrate in the supramolecular 3D network. Nevertheless, further investigations are still progressing for the full understanding of the long-range ordering of our hybrid hydrogel.

ITC Measurements. As $[P_2W_{18}O_{62}]^{6-}$ and $[Ta_6Br_{12}(H_2O)_6]^{2+}$ proved their ability to form various



Figure 10. Structural representations resulting from the single-crystal X-ray diffraction analysis of the three-component system {Ta₆@2CD·POM}: (a) tubular chain showing periodic alternation of the ditopic cation {Ta₆@2CD}²⁺ and the [P₂W₁₈O₆₂]⁶⁻ POM running along *c* axis with *c* = 89.17 Å; (b) highlight of the tubular chain packing in the *ab* plane; (c) POM moieties within the tubular chain are symmetrically related through 4₁ helicoidal axis generating successively four equivalent POM units colored in yellow, green, red, and blue, respectively; (d) highlight of two POM units sandwiching the {Ta₆}²⁺ cluster through short hydrogen bonds such as O–O = 2.64 Å (the two γ -CDs have been omitted for clarity).

supramolecular complexes with γ -CD, the possibility of forming materials involving the three partners was then explored by ITC. Interestingly, when POM was injected on a mixture of $\{Ta_6\}$ and γ -CD, significant heats were systematically recorded, whereas negligible signals should be expected in the hypothesis of a simple competition between the two distinct 1:1 and 1:2 γ -CD complexes of POM and $\{Ta_6\}$, as the $\{Ta_6\}$ complexes are significantly stronger than those involving POM (see SI section 6 for simulation details). These heats demonstrated the existence of hetero-ternary complexes.

On one hand, when the initial concentrations of $\{Ta_6\}$ and γ -CD led essentially to 1:1 complexes, a clean thermogram was obtained (see Figure 11). Strikingly, the corresponding binding isotherm has been calculated with a satisfactory agreement with the experimental data by considering the possibility to associate up to three ${Ta_6 @CD}^{2+}$ complexes with one POM molecule, as illustrated in Figure 11. The estimated binding constant for the interaction between one ${Ta_6}$ @CD complex with one POM molecule was close to 4×10^4 M⁻¹, which is 1 order of magnitude higher than that for fixing one γ -CD on one POM molecule in the absence of $\{Ta_6\}$. Actually, it has to be stressed that the quantitative analysis of this single isotherm by our theoretical model is probably over-parametrized, with respect to the presence of a large distribution of aggregates arising from available combinations of the three building blocks. Nevertheless, the rapid decrease of the ITC isotherm is clearly in



Figure 11. ITC thermograms (upper part) and isotherms (lower part) for the titration of a mixture of γ -CD (22.5 μ M) and $[Ta_6Br_{12}(H_2O)_6]^{2+}$ (90 μ M) by a 200 μ M POM solution. Dots correspond to the experimental heats. Red line corresponds to the theoretical heats when considering the presence of $\{Ta_6\}$ @CD, $\{Ta_6\}$ @CD], POM[$\{Ta_6\}$ @CD], POM[$\{Ta_6\}$ @CD]₂, and POM[$\{Ta_6\}$ @CD]₃.

favor of strong and multiple bindings between POM and $\{Ta_6\}$ @CD entities.

On the other hand, when ${Ta_6}@2CD$ complexes were initially favored in the cell by increasing the initial γ -CD concentration, important deformations were observed on the ITC thermograms (see Figure S18, SI section 7). Concomitantly, turbid solutions were extracted from the cell at the end of the titrations. Such observations indicate that interactions between the ditopic {Ta_6@2CD} cationic complexes and the POM favor polymerization process. Both observations of deformed thermograms and turbid solutions during the ITC experiment corroborate our previous observations that such ternary system leads to supramolecular polymer. Unfortunately, the consecutive variation of viscosity and the heterogeneous character of the solutions hindered any quantitative interpretation of the ITC thermograms for further characterizations about interactions between POM and {Ta_6}@2CD complexes.

3. CONCLUSIONS

We have shown that recognition process of γ -cyclodextrin in host-guest binding can be used for building hierarchical noncovalent materials using POMs and octahedral clusters. We report the discovery of a remarkable versatility featuring interactions between the Dawson anion $[P_2W_{18}O_{62}]^{6-}$ and the primary portal of γ -CD, allowing the selective isolation of the 1:1, 1:2, or 1:3 adducts in the solid state. We report also on the first inclusion complex built from a cationic octahedral cluster $[Ta_6Br_{12}(H_2O)_6]^{2+}$ and γ -CD wherein the structural model displays the conventional host-guest 1:2 assembly involving close intermolecular contacts. Solution studies,

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including NMR methods, ITC, and electrochemistry, reveal that organic and inorganic moieties are pre-assembled together in solution, giving stable aggregates, while all these species are considered as hydrophilic. Such a behavior gives insights about the true nature of these solvated ions which seem to range within the category of chaotropic species. Nevertheless, given the large structural diversity of both classes of compounds, offering species that differ in their composition, shape, size, symmetry, and ionic charge, there should be extensive solution chemistry to determine the factor dictating their supramolecular interplay with substrates of interest.

Besides, the $\{POM@nCD\}^{6-}$ aggregates and the ditopic ${Ta_6 @2CD}^{2+}$ arrangement reveal strikingly complementary structural and chemical properties, which have been exploited successfully to design novel three-component phases derived as supramolecular hydrogel or single crystals with similar composition. X-ray diffraction study shows that, in the supramolecular assembly, ${Ta_6@2CD}^{2+}$ acts as a ditopic ionic linker able to produce a 1D tubular chain resulting from periodic alternation of POMs and clusters. This first example highlights promising route to design a new class of responsive and adaptable multifunctional materials built from deliberate associations of functionalities by the three well-ordered components. For instance, combination of luminescent clusters¹⁶ as solar light sensitizer with POMs as electron acceptor could be useful to design light-driven devices relevant in photocatalysis or chemical detection. Given the scope of these domains, including POM and cluster chemistries, there is great interest to develop relevant hybrid multifunctional materials using the straightforward supramolecular approach. This strategy will pave the way toward exciting, extensive, and challenging physical chemistry or physics in this new area.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b07317.

General methods, syntheses, FT-IR spectra, single-crystal X-ray diffraction including crystallographic parameters and additional figures, NMR data, ITC measurements, and UV–visible spectra (PDF)

X-ray crystallographic data (CIF files) for POM@CD, POM@2CD, POM@3CD, $\{Ta_6\}$ @2CD and $\{Ta_6\}$ @ 2CD@POM (ZIP)

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Notes

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Nonconventional Three-Component Hierarchical Host–Guest Assembly Based on Mo-Blue Ring-Shaped Giant Anion, γ -Cyclodextrin, and Dawson-type Polyoxometalate

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Supporting Information

ABSTRACT: In this communication, we report on a noteworthy hybrid supramolecular assembly built from three functional components hierarchically organized through noncovalent interactions. The one-pot synthesis procedure leads to the formation of large Mo-blue ringshaped anion $\{Mo_{154}\}$, which contains the supramolecular adduct based on the symmetric encapsulation of the Dawson-type $[P_2W_{18}O_{62}]^{6-}$ anion by two γ -cyclodextrin units. Such a nanoscopic onion-like structure, noted $[P_2W_{18}O_{62}]@2\gamma$ -CD@ $\{Mo_{154}\}$ has been characterized by single-crystal X-ray diffraction, thus demonstrating the capability of the giant inorganic torus to develop relevant supramolecular chemistry, probing the strong affinity of the inner and outer faces of the γ -CD for the polyoxometalate surfaces. Furthermore, interactions and behavior in solution have been studied by multinuclear NMR spectroscopy, which supports specific interactions between y-CD and POM units. Finally, the formation of this three-component hybrid assembly from one-pot procedure, in water and using nearly stoichiometric conditions, is discussed in terms of the driving forces orchestrating this highly efficient multilevel recognition process.

C upramolecular chemistry dates back to the late 1960s and 1970s from the pioneering work of Pedersen,^{1,2} Cram,³ and Lehn.⁴ Their contributions have led to the development of concepts allowing fabrication of gigantic host-guest supramolecular materials with increased complexity and functionalities,⁵ that arise from a set of complementary noncovalent interactions such as hydrophobic, coulombic, ion-dipole, dipole-dipole, or hydrogen bonding.⁶ Thus, self-assembled mesmerizing supramolecular architectures are able to promote a wide range of chemical and physical events that encompass

electron carriers, energy transfer, binding and release of substrates, or ion transportation.

In context, polyoxometalates (POMs) represent a unique class of all-inorganic metal-oxygen anionic clusters, which exhibit remarkable physical-chemical properties in relationship with their vast structural diversity.⁸ Actually, this class of molecular objects offers huge potentialities for their use as subcomponents in supramolecular hybrid materials^{9,10} owing to their specific shapes such as torus,¹¹ hollow spheroidal capsule,^{12,13} cylinder, or cubic box.^{14,15} POMs interact also with biological matter that confer biological activities.¹⁶ Recent results shed light on the origins of primary interactions between POMs and specific patches of proteins that include cooperation of nonspecific interactions, driven by fine balancing between electrostatic and hydrophobic effects directly related to the charge and the surface area of the POM species.¹⁷ Big wheels deriving from molybdenum blue chemical system^{18–20} exhibit typical toroidal architectures lining a large shape-persistent cavity able to encapsulate large organic substrates such as porphyrins,²¹ or inorganic polynuclear clusters.²² However, taking into account the large diameter of these available cavities, supramolecular properties of these ring-shaped compounds remain unexploited.

Herein we report the first hybrid hierarchical assembly based on the $[\mathrm{Mo}_{154}\mathrm{O}_{462}\mathrm{H}_{14}(\mathrm{H}_{2}\mathrm{O})_{70}]^{14-}$ molecular wheel (abbreviated $\{Mo_{154}\}$ hereafter),¹⁸ which includes in its central cavity the supramolecular adduct built from the archetypical Dawson polyoxometalate $[P_2W_{18}O_{62}]^{6-}$ capped by two γ -cyclodextrins (see Figure 1). γ -cyclodextrin $C_{48}H_{80}O_{40}$ (noted γ -CD hereafter) has been selected as organic unit for its specific ring-shaped architecture and size-matching with the inward dimension of the large hole delimited by the ring-shaped ${Mo_{154}}$ anion (see Figure 1). Besides, cyclodextrins are

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Figure 1. Space-filling representation showing size-matching between host and guest components involved within hierarchical supramolecular assembly.

distinguished as prominent synthetic receptor,^{23,10} useful for wide applications in many fields of science such as nano-technology,²⁴ pharmaceutics²⁵ or medicine.²⁶

The interactions of γ -CD with {Mo₁₅₄} were investigated by ¹H NMR in D₂O. Especially, we witnessed a pronounced complexation-induced deshielding of the H2 proton ($\Delta \delta \sim$ +0.5 ppm) (see Figure 2), which is located outside the cavity



Figure 2. Selected ¹H NMR spectra (400 MHz, 298 K, D₂O, 3 mM) of γ -CD in the presence of different equivalents of {Mo₁₅₄} ring-shaped anion. The marked deshielding effect occurring for the outer H2 nuclei suggests the inclusion complex formation { γ -CD@Mo₁₅₄} involving the secondary face of the γ -CD and the large inner cavity of the Mo-blue wheel.

near the secondary hydroxyl rim. Similar effect, but in a lower extent was observed on the outer H1 proton while the H4 proton appears quite unaffected. Furthermore, the assignment of the most affected signal to the H2 proton has been confirmed by ¹H NOESY NMR experiment (see Supporting Information, Figure S3, sec. 5).

These NMR results suggest that γ -CD penetrates deeply into the large cavity of the {Mo₁₅₄} anion, leading to a deshielding effect for the outer protons in contact with the inner oxygen of the {Mo₁₅₄} ring-shaped anion. In addition, the formation of supramolecular adduct involving {Mo₁₅₄} and γ -CD is also nicely supported by ¹H DOSY NMR experiments, showing a clear monotonous decrease of the self-diffusion coefficient of the γ -CD from 280 for the free-solvated species to 106 μ m² s⁻¹ in the presence of {Mo₁₅₄} (Figure S4, SI, sec. 5).

A more complex scenario has been examined by introducing $[P_2W_{18}O_{62}]^{6-}$ species as a third component able to interact with the inner face of the γ -CD. After exploring and repeating different synthetic approaches as well some analytical test procedures, it became evident that selected POMs, γ -CD and $\{Mo_{154}\}$ ring-shaped anion were able to interact together to

produce a chemically pure assembly. Lastly, one-pot synthesis allowed isolating well-shaped three-component single crystals with good yield (\sim 40%). The synthesis was merely inspired from that previously reported by Müller et al.²⁰ and consists of acidification until pH = 1 of Na_2MoO_4 aqueous solution under reducing conditions (sodium dithionite was used as reducing agent) in the presence of γ -CD and Dawson anion $[P_2W_{18}O_{62}]^{6-}$ in ratios Mo: γ -CD: $[P_2W_{18}O_{62}]^{6-} = 154:4:1$ (see SI, sec. 2 for further details about synthesis conditions). Formation of three-component single-crystals with abbreviated formula $Na_{15}K_{3}H_{2}[\{Mo_{154}\}(P_{2}W_{18}O_{62})(\gamma-CD)_{4}]\cdot 225H_{2}O$ (noted 1 hereafter) was readily achieved through slow evaporation of the resulting solution. X-ray diffraction analysis of 1 gave a structural model which reveals a striking threecomponent supramolecular adduct arranged within a remarkable hierarchical organization, wherein the Dawson anion $[P_2W_{18}O_{62}]^{6-}$ appears capped by two γ -CDs both interacting symmetrically with the two opposite caps of the anion (see



Figure 3a). Such a type of arrangement resembles to some

Figure 3. Mixed representations of the supramolecular hierarchical compound 1 {[$P_2W_{18}O_{62}$]@2 γ -CD@Mo₁₅₄}. (a) Highlight of the inner adduct built from a Dawson anion [$P_2W_{18}O_{62}$]^{6–} capped by two γ -CD tori. (b) Representation showing the deep inclusion of the Dawson anion within the large inner cavity of the Mo-blue ring-shaped anion. (c) Side and (d) top views of the hybrid supramolecular adduct showing the hierarchical organization between three components with the Dawson anion at the center (green and red space-filling spheres) capped by two γ -CD (wires and transparent space-filling spheres) encaged into the large {Mo₁₅₄} torus (yellow sticks).

extent that observed by Stoddart et al. with the Keggin-type anion encapsulated by two γ -CD.¹⁰ Furthermore, this supramolecular assembly appears embedded deeply within the large inner cavity of the ${Mo_{154}}$ torus to give the nonconventional $([P_2W_{18}O_{62}]@2\gamma-CD@\{Mo_{154}\})$ inclusion complex. Actually, the two inner γ -CDs appear severely disordered within the $\{Mo_{154}\}$ torus but we succeeded to rebuild backbones of the two inner γ -CDs from electronic density. This disorder scheme appears quite consistent with usual geometrical parameters and then give reliable arguments to demonstrate the steric hostguest compatibility between γ -CDs and the {Mo₁₅₄} torus (see Figure S2, SI sec. 4.3), but it would be highly speculative to give any firm conclusion about the interacting rim of the γ -CD, i.e., secondary or primary CD faces directed toward the cavity center of the $\{Mo_{154}\}$ anion. Nevertheless, the proposed structural model allows identifying a network of convergent hydrogen bonds which involves hydroxo groups of the γ -CD and either some oxygen atoms of the $\{Mo_{154}\}$ outer host or those of the $[P_2W_{18}O_{62}]^{6-}$ inner guest (see Figure S2, SI sec. 4.3). These intermolecular hydrogen-bonding interactions give rise to quite short O…O contacts observed in the 2.75–3.20 Å range.

Finally, X-ray structural analysis of 1 supported by its elemental analysis revealed two additional γ -CD units per {Mo₁₅₄} unit literally stuck on the outward surface of the {Mo₁₅₄} ring-shaped anion and located within holes delimited by the {Mo₁₅₄} packing (see Figure 4). Still here, these γ -CD



Figure 4. Selected view of 1 showing large holes delimited by the $\{Mo_{154}\}$ packing, which are filled by two outer γ -CD units.

units appear disordered and no definitive conclusion can be given about the type of face interacting directly with the $\{Mo_{154}\}\$ surface. However, such a result demonstrates that γ -CD unit is able to interplay with $\{Mo_{154}\}\$ anion either through highly specific host–guest recognition process with its large inner cavity or through less specific interactions involving its large exposed surface area. Actually, it should be worth noting that composition of 1 corresponds precisely to the composition of the synthetic mixture. Further details about the X-ray diffraction analysis are given in Supporting Information (sec. 1 and sec. 4).

Preliminary multinuclear NMR studies (including 1D and DOSY experiments) in aqueous solution have been carried out on this three-component chemical system. The ³¹P NMR spectrum of 1 (5 mmol L^{-1} in aqueous solution) shown in Figure 5 contains in addition to the resonance attributed to solvated $[P_2W_{18}O_{62}]^{6-}$ observed at $\delta = -12.34$ ppm, three additional signals at -12.43, -12.53 (shoulder), and -12.69ppm (deconvolution is shown in Supporting Information, Figure S5, sec. 5). The presence of shielded ³¹P nuclei must be related to the screening effect of the $\{Mo_{154}\}$ host onto the deeply embedded $[P_2W_{18}O_{62}]^{6-}$ guest. Such a shielding effect is usually observed for any guest species included within the inner cavity of metal-oxo shell.²⁷ However, the presence of these three low-frequency signals suggests that $[P_2W_{18}O_{62}]^{6-}$ species are involved within slow dynamic processes which could correspond to the successive release of the inner γ -CD component from 1 (observed at -12.43 ppm) leading to the monocapped guest species ($\delta = -12.53$ and -12.69 ppm) and to the solvated species ($\delta = -12.34$ ppm), respectively. Furthermore, the attribution of the low-frequency signals to the supramolecular three-component system has been confirmed by ³¹P DOSY NMR (see Figure S7, SI sec. 5.4). The species involved in the ternary hierarchical system (observed at -12.43ppm) exhibit a very low diffusion coefficient $D = 73 \ \mu m^2/s$, while the solvated interacting species at $\delta = -12.34$ ppm is



[P₂W₁₀O₀₂]^{s.} -11 -12 -13 -14 δ/ ppm

Figure 5. ³¹P NMR spectrum of **1** (top) showing that only simultaneous presence of the three components provokes a clear change of ³¹P NMR spectrum. The presence of four ³¹P NMR signals with 32:52:8:8 intensity ratio is consistent with $[P_2W_{18}O_{62}]^{6-}$ ion as solvated ion ($\delta = -12.34$ ppm) or as central guest species into the three-component assemblies ($\delta = -12.43$, -12.53, and -12.69 ppm). The presence of three shielded ³¹P resonances should be interpreted as slow equilibria occurring between bicapped and monocapped guest species as depicted in scheme inserted on the upper ³¹P NMR spectrum.

characterized by an intermediate D value of 181 $\mu m^2/s$ compared to the same species without any interaction in pure solvent ($D = 325 \ \mu m^2/s$). Such an intermediate D value is not only due to slow exchange processes between free and embedded species (see SI sec. 5.4, Figure S6) but also to interactions between solvated $\{P_2W_{18}O_{62}\}^{6-}$ species and outer γ -CDs, which form labile aggregates.²⁸ Besides, ¹H NMR of 1 reveals that formation of three-component system leads to complex ¹H NMR spectra characterized by significant line width broadening and by the appearance of many new ¹H NMR resonances (see Figures S8-S9, SI sec. 5.3). In few lines, these NMR results are consistent with dynamically slow equilibria in D₂O solution involving deeply embedded components through the inner and outer faces of γ -CD tori. Besides, ¹H DOSY NMR revealed that these new resonances are characterized by a significant low self-diffusion (D = 106 $\mu m^2 s^{-1}$ in agreement with the nanoscopic dimension of the onion-like supramolecular assembly (see Figure S4, SI sec. 5.5). These preliminary NMR characterizations constitute bases for further investigations of this exciting supramolecular chemical system.

In summary, we report the discovery of a remarkable hierarchical assembly, built from three functional components specifically formed through a one pot procedure. It transpires that the recognition processes and the related contributors to the effective driving force must be strongly efficient. Actually, formation of this onion-like supramolecular architecture in aqueous solution should be suspected highly improbable because the three individual functional subunits are highly soluble in water and thus considered as hydrophilic species. Generic driving forces leading to this multilevel assembly could arise from a pronounced "*chaotropic*" effect that remains not well understood with polyoxometalates,²⁹ especially for those ranging within nanoscopic dimension. Given the scope of this area, it becomes palpable that such a preliminary study should open new avenues toward exciting, extensive and challenging physical-chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08058.

General methods; syntheses; FT-IR spectra; single crystal X-ray diffraction including crystallographic parameters (Table S1) and additional figures; NMR data (PDF) Crystal data CIF file (ZIP)

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Notes

The authors declare no competing financial interest.

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Investigation of the protonation state of the macrocyclic $\{H_n P_8 W_{48} O_{184}\}$ anion by modeling ¹⁸³W NMR chemical shifts[†]

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A semi-empirical approach based on the partial charge formalism has been used to calculate ¹⁸³W NMR chemical shifts in polyoxotungstates (POTs). Good consistency between calculations and experimental measurements allowed determining the main effective parameters for modeling the electronic state of the { $W^{VI}O_{6}$ } centers. As the three ¹⁸³W NMR chemical shifts of the { $P_8W_{48}O_{184}$ } macrocycle exhibit strong pH dependence, partial charge model calculations have been carried out for the investigation of the protonation of the metal–oxo framework. Furthermore, these calculations highlight the effect of the potassium ions embedded within the internal cavity. In this work, NMR parameters were computed using the PACHA software, distinguishing and assigning ¹⁸³W NMR resonances.

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Introduction

Polyoxotungstates (POTs) are built from the self-assembly of basic octahedral WO₆ units by sharing either edges, vertexes or in some rare cases faces offering a large variety of structures with various nuclearities.1 183W NMR spectroscopy has been proved to be a very powerful tool to elucidate their molecular structures in solution.^{2,3} Despite its low receptivity due to the combination of low resonance frequency and low natural abundance, the ¹⁸³W nucleus remains attractive because of the nuclear spin I = 1/2 that leads generally to very narrow resonance lines.^{4–6} This helps to identify the individual W sites and to quantify easily their frequency of occurrence in the structure. The multiplicity, relative proportion of the independent W sites and the spin-spin correlation through ${}^{2}J_{W-O-W}$ scalar coupling constitute the bases for the information about the symmetry, and thus the structural analysis.⁷⁻¹⁰ The ¹⁸³W chemical shifts span over more than 5500 ppm for paramagnetic POTs $(-2000 \text{ ppm} < \delta < +3600 \text{ ppm}, \text{ with respect to WO}_4^{2-})^{2,3}$ and

800 ppm for diamagnetic POTs (-400 ppm < δ < +420 ppm, with respect to WO₄²⁻).^{3,6,11} Often the spectroscopic features are correlated with the structural properties to describe and rationalize the local electronic environment around the W nuclei and to understand the parameters influencing the chemical shifts.¹²⁻¹⁴ In particular, theoretical approaches are found to be useful to calculate and reproduce the experimental ¹⁸³W NMR parameters.¹⁵⁻¹⁸

Numerous experimental studies supported by DFT calculations about ¹⁸³W NMR chemical shifts showed a strong dependency on the geometry of some archetypical structures of POTs.¹⁶ The geometry optimization step has been found to be of primary importance to compute ¹⁸³W chemical shifts accurately. The method was successfully applied to small molecules and highly symmetrical POT structures. Nevertheless, with larger and lesser symmetrical anions, such as lacunary POTs, classical computational methods showed certain limitations. Thus, alternative theoretical tools demanding less computational time are needed. Semiempirical methods based on charge density models have also been used to calculate ¹⁸³W chemical shifts.^{5,19}

The major problems with empirical approaches are the lack of universality of the adjusted parameters with little physical meaning and the mostly unknown influence of chemical substitution. A nonempirical model based on prior knowledge about the relative spatial distribution of the identified chemical elements only is thus needed to be applicable with no size limits to any synthesized chemical architecture. A mathematical scheme based on clearly identified approximations of quantum-mechanical laws should be used to generate pertinent chemical information such as bond energies, equilibrium constants, chemical shifts, polarities, *etc.* Over the past few years, one of us has developed an approach

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for chemical bonding based on a spherical-atom approximation of density functional theory.²⁰ The spherical approximation used in this formalism allows us to treat considerably larger objects than what can be achieved using standard quantum mechanics computations.

In this context, the Partial Atomic Charge and Hardness Analysis (PACHA) algorithm has shown to be useful to calculate ²⁹Si and ¹³C NMR chemical shifts^{21,22} and help spectral assignment. The advantage of such empirical methods is the limited computational expense required for chemical shift calculations for large molecular systems. In this contribution, we report the empirical evaluation of ¹⁸³W chemical shifts in POTs using a partial charge modeling approach. By comparing the experimentally observed ¹³⁸W chemical shifts with those calculated from structurally dependent W partial charge, q(W), a model for the electronic environment in WO₆ octahedra of POTs is obtained and its main relevant parameters are established. By using these parameters, the variation of ¹⁸³W chemical shifts as a function of protonation in [{8K}] \subset {H_nP₈W₄₈O₁₈₄}]⁽³²⁻ⁿ⁾⁻ can be modeled revealing the protonic exchange ability of this POT.

Experimental section

Sample preparation

The mixed potassium/lithium salt of the crown-type heteropolyanion, $K_{28}Li_5H_7[P_8W_{48}O_{184}]\cdot92H_2O$, and the equivalent ammonium/lithium salt, $(NH_4)_{21}Li_{17}H_2[P_8W_{48}O_{184}]\cdot85H_2O$, were prepared according to the procedures reported by Contant and Tézé²³ and Boyd *et al.*,²⁴ respectively. The products were characterized using FT-IR spectroscopy and thermogravimetric analyses. Samples for NMR measurements were prepared by dissolving each compound in 1 M LiCl in D₂O at a fixed concentration of $[P_8W_{48}O_{184}]^{40-}$, *ca.* 2.2 mM. The pH was adjusted using 1 M HCl aqueous solution.

¹⁸³W NMR experiments

All NMR experiments were recorded at room temperature (27 °C). The ¹⁸³W NMR (20.8 MHz) spectra were recorded in 10 mm outer diameter tubes, using a Bruker AVANCE 500 FT-NMR spectrometer equipped with a Bruker BBO low-frequency tunable probe. These spectra were referenced to an external standard (saturated Na₂WO₄/D₂O solution) using the substitution method (H₄SiW₁₂O₄₀/ D₂O δ = -103.8 ppm). Chemical shifts were reported on the δ scale with resonances up-field of 1 M Na₂WO₄ (δ = 0 ppm) as negative. The data were processed and analyzed using the NMRNoteBook software.

Modeling of NMR shifts

All calculations were made using the PACHA software, available online (http://complex-matter.unistra.fr/equipes-de-recherche/ laboratoire-de-chimie-moleculaire-de-letat-solide/logiciels/). The algorithm allows retrieving a partial charge distribution from the molecular structure. These charges are recovered after application of the electronegativity equalization principle. The NMR shielding around a given nucleus is generally composed of diamagnetic and paramagnetic terms. While both contributions depend on the electronic screening around the nucleus and thus the partial charge *q*, the paramagnetic shielding is often the most dominant and effective. Thus the chemical shift δ with respect to a reference can be expressed as follows:

$$\delta = \sigma_{\rm ref} - \sigma_{\rm dia}(q) - \sigma_{\rm para}(q) \tag{1}$$

The paramagnetic term arises from the distortion of the spherical distribution of the electrostatic potential around the nucleus, and involves mixing of the ground and the excited states by the magnetic field. Following the Jameson and Gutowsky formalism,²⁵ a general expression can be written as follows:^{2,26}

$$\sigma_{\text{para}} = -\frac{\mu_0 \mu_B^2}{\pi a_0^3 \Delta E} \left[\left\langle \left(\frac{a_0}{r}\right)^3 \right\rangle_{\text{p}} P_u + \left\langle \left(\frac{a_0}{r}\right)^3 \right\rangle_{\text{d}} D_u \right]$$
(2a)

where μ_0 is the vacuum permeability, μ_B the Bohr magneton, and a_0 the Bohr radius. ΔE is the average transition energy of the excitation states of the correct symmetry, connected to the ground state by magnetic-dipole allowed transitions. P_u and D_u represent the unbalance of the valence electrons in orbitals p and d, and $\langle r \rangle_{p/d}$ is the mean radius of these orbitals. In the specific case of W^{VI}, one can assume that the most diffuse W orbitals in W–O bonds of POTs are 6p and 6s. The population in the molecular orbitals of W in d orbitals is supposed to be unchanged (5d⁴). The unbalance of population in bonding d orbitals of W in this case can be neglected ($D_u \ll P_u$) and the paramagnetic contribution of the shielding can be approximated as follows:

$$\sigma_{\text{para}} \approx -\frac{\mu_0 \mu_{\text{B}}^2}{\pi a_0^3 \Delta E} \left\langle \left(\frac{a_0}{r}\right)^3 \right\rangle_{\text{p}} P_u \tag{2b}$$

$$P_{u} = (P_{xx} + P_{yy} + P_{zz}) - \frac{1}{2}(P_{xx} \cdot P_{yy} + P_{yy} \cdot P_{zz} + P_{zz} \cdot P_{xx}) + \frac{1}{2}(P_{xy} \cdot P_{yx} + P_{xz} \cdot P_{zx} + P_{yz} \cdot P_{zy})$$
(3a)

Assuming that the cross term contributions are negligible $(P_{ij} = 0, i \neq j)$, eqn (3a) becomes:

$$P_{\rm u} = (P_{xx} + P_{yy} + P_{zz}) - \frac{1}{2}(P_{xx} \cdot P_{yy} + P_{yy} \cdot P_{zz} + P_{zz} \cdot P_{xx}) \quad (3b)$$

Thus, at first approximation the ¹⁸³W chemical shielding can result from the fine balance between mainly four terms, σ_{dia} , $\langle (a_0/r)^3 \rangle_{6p}$, ΔE , and P_u . All these parameters can be related to the partial atomic charge of tungsten q(W) = Z - N, where Z is the oxidation state of W (here Z = 6) and N corresponds to the population of electrons occupying the bonding orbitals 5d⁴, 6pⁿ and 6s^m (N = 4 + P_{ss} + P_{xx} + P_{yy} + P_{zz}).

Preliminary tests showed that the most relevant model corresponds to one full p-orbital and an empty s-orbital scheme with $P_{ss} = 0$, $P_{xx} = 2$, $P_{yy} = P_{zz} = [2 - P_{ss} - P_{xx} - q(W)]/2 = -q(W)/2$. Under such conditions, the population asymmetry can be deduced from eqn (3b):

$$P_{\rm u} = [2 - q({\rm W})] + q({\rm W}) \cdot ([8 - q({\rm W})]/8)$$
(4)

The radial term $\langle (a_0/r)^3 \rangle_{6p}$ reflects the strength of the electric field gradient (efg) generated by the electronic cloud around the nucleus and varies with partial charge q(W) as following:

$$\langle (a_0/r)^3 \rangle_{6p} = \langle (a_0/r)^3 \rangle_{6p}^{\circ} \cdot [1 + f \cdot q(\mathbf{W})] = \mathrm{efg}^{\circ} \cdot [1 + f \cdot q(\mathbf{W})] \quad (5)$$

where efg° is the atomic efg corresponding to the ground state and f is an adjustable parameter. Finally, using eqn (1) and (2b)calculations of ¹⁸³W chemical shifts with respect to WO₄²⁻ $(\sigma_{\rm ref} = -175.8 \text{ ppm}^{18})$ are achieved after determining $\sigma_{\rm dia}$ and q(W) parameters fixed by molecular geometry (either from the experimental X-ray structure or optimization using ab initio methods) and the assumptions about the electronegativity and hardness of the atoms by using the PACHA software. With the determined q(W) values P_u and $\langle (a_0/r)^3 \rangle_{6p}$ can be calculated using eqn (4) and (5). The approach outlined in this manuscript entails the initial optimization of the parameters efg°, f, and ΔE for a standard set of reference POT molecules for which structures and ¹⁸³W chemical shifts are known. The average excitation energy (ΔE) can be estimated from the mean value of observed chemical shifts (δ_{mean}). In practice, f, efg°, and δ_{mean} are input parameters in the PACHA software that are optimized manually by iteration until calculated and experimental shifts fit. These parameters obtained for the reference compounds constitute the basis set of parameters as a representative model for POT structures.

The references used in this work, *i.e.*, $[P_2W_{18}O_{62}]^{6-}$, $\beta \text{-} [\text{SiW}_{12}\text{O}_{40}]^{4-}, \gamma \text{-} [\text{SiW}_{12}\text{O}_{40}]^{4-}, [\text{W}_{10}\text{O}_{32}]^{4-}, \text{are those previously}$ studied by Poblet et al.¹⁶ These related POTs contain more than one W site and their DFT-optimized geometries were reported in the original paper.¹⁶ The structures of the crown-type POTs, $[\{8M\} \subset \{H_n P_8 W_{48} O_{184}\}]^{(32-n)-}$ where M = K or NH₄, were adapted from experimental X-ray diffraction data structural analyses.^{14,24,27} The eight inner cations, *i.e.*, potassium or ammonium present in disordered positions are placed in average positions keeping the ideal D_{4h} high symmetry of the POT. The protonation sites are the basic oxygen atoms of the lacunary sites positioned in the internal cavity. Standard values for bonds involving H-atoms were used: O-H length 97 pm, and W-O-H angle 109°. The Cartesian coordinates of the structures of $[{8K}] \subset {H_n P_8 W_{48} O_{184}}]^{(32-n)-}$ as well as of the reference compounds used in calculations are presented in Tables S1-S6 (ESI⁺).

Results and discussion

Validation of partial charge formalism to calculate ¹⁸³W chemical shifts of POTs

To test the ability of the PACHA software to calculate the ¹⁸³W chemical shifts, some representative POT compounds studied in the past using DFT methods have been investigated in this work.¹⁶ The geometries employed are those of the optimized structures achieved in the previous DFT studies.¹⁶ From these structures, the software calculates the partial charges q(W) and thus the diamagnetic contribution of the shielding around W nuclei. The paramagnetic term is dependent on the three main parameters, $P_{\rm u}$, $\langle (a_0/r)^3 \rangle_{\rm 6p}$, and ΔE . The former can be readily determined from the partial charges q(W) only as shown in eqn (4). The second is also dependent on the partial charges q(W), but requires additional adjustable parameters f and efg^o according to eqn (5). The excitation energy, ΔE , is however estimated from a mean value of the chemical shifts, also an

adjustable parameter. Finally, for a given structure, the three manually adjustable parameters are f, efg[°], and δ_{mean} and their validation can be done based on the significance of the magnitude of the calculated $\langle (a_0/r)^3 \rangle_{6p}$ and ΔE with respect to the usually observed values of the efg and HOMO–LUMO gap energies in POTs.

Table 1 summarizes the overall results obtained from the evaluation of PACHA to calculate chemical shifts in some representative POT structures. Typical values of the adjustable parameters are included together with a comparison between experimental chemical shifts and calculated values either with the current semi-empirical formalism or with conventional DFT methods. Fig. 1 shows a plot of the PACHA calculated *versus* the experimental ¹⁸³W chemical shifts for all the studied POT model compounds, showing the unity slope with small deviations from a straight line.

From Table 1 and Fig. 1, it appears clearly that the partial charge formalism provides satisfactory results to reproduce experimental ¹⁸³W chemical shifts of the POTs studied. The models used, although simplified by considering unbalance of valence electrons in p orbitals only, proved to be relevant enough to calculate the chemical shifts in POTs. Nevertheless, the parameter *f* introduced to calculate the local efg ($\langle (a_0/r)^3 \rangle_{6p}$) is found to be structure dependent and varies from *ca*. 0.0 to 0.7 for the examples studied. The value of the mean chemical shifts (δ_{mean}) has to be adjusted to fit the calculated chemical shifts with those of the observed ones.

The excitation energy (ΔE) was found to vary from *ca.* 1.79 to 3.86 eV for efg^o = 10 a.u. and it is directly proportional to efg^o. The typical values of the efg ($\langle (a_0/r)^3 \rangle_{6p}$) vary from 10 to 22 a.u. These values increase in the same way as the energy gaps (ΔE) since both parameters are proportional to efg^o. Consequently, the quantity ($\langle (a_0/r)^3 \rangle_{6p}/\Delta E$) and thus the final calculated chemical shift (δ) are independent of efg^o. It is worth noting that this ratio ($\langle (a_0/r)^3 \rangle_{6p}/\Delta E$) should be the most effective contribution influencing the chemical shifts since the unbalance in the orbital population parameter P_u hardly varied within the range 1.58–1.74.

Chemical shifts in $[P_8W_{48}O_{184}]^{40-}$

Modeling of the large POT structures is still nowadays a challenging task with conventional *ab initio* methods. The PACHA method could be applied in these cases and could provide useful insights. The $[P_8W_{48}O_{184}]^{40-}$ anion is a large macrocyclic POT built from connection of four lacunary species $[P_2W_{12}O_{48}]^{14-}$. The first report of the ¹⁸³W NMR spectrum of $[H_8P_8W_{48}O_{184}]^{32-}$ was published in 1985 by Contant and Tézé.²³ The ¹⁸³W NMR spectrum recorded in lithium perchlorate aqueous solution showed three resonances of equal intensity at -203.7, -204.4, and -216.6 ppm in full agreement with the idealized D_{4h} symmetry of the compound.

More recently, Sousa *et al.* reported the ¹⁸³W NMR spectrum of $[K_8 \subset \{H_7 P_8 W_{48} O_{184}\}]^{25-}$ displaying three resonances at -190.1, -191.0, and -207.6 ppm,³¹ which fall about 10 ppm lower field compared to the original spectrum of Contant and Tézé.²³ The authors attributed this difference to the ionic strength effect

Table 1 Parameters used to compute ¹⁸³W shifts for some representative POTs and observed and calculated shifts relative to WO4²⁻

		Inpu	t parameters	Computed parameters								
РОТ	Solvent	f	δ_{mean} (ppm)	ΔE (eV)	q (W)	$\langle (a_0/r)^3 \rangle^a$ (a.u.)	$P_{\rm u}^{\ b}$	$\sigma_{\mathrm{para}}{}^{c}$ (ppm)	$\sigma_{\rm dia}~({\rm ppm})$	$\delta_{\mathrm{PACHA}}{}^{d}$ (ppm)	δ_{\exp}^{e} (ppm)	$\delta_{\mathrm{DFT}}^{f}(\mathrm{ppm})$
$[P_2W_{18}O_{62}]^{6-}$	H ₂ O	0.39	18.7	3.00	1.7411 1.8429	16.7 17.1	$1.6207 \\ 1.5750$	-8737.8 -8691.6	8690.1 8689.3	-128.1 -173.5	$-128.1 \\ -173.6$	$-126.0 \\ -170.0$
$\beta \text{-} [SiW_{12}O_{40}]^{4-}$	H ₂ O	0.00	58.3	1.79	1.7471 1.7472 1.7515	10.0 10.0 10.0	1.6180 1.6180 1.6161	-8751.1 -8750.8 -8740.6	8690.0 8690.0 8690.0	-114.7 -115.0 -125.2	-110.0 -114.5 -129.8	-103.0 -111.9 -133.3
$\beta \text{-}[SiW_{12}O_{40}]^{4-}$	DMF	0.00	66.2	1.79	1.7470 1.7471 1.7514	10.0 10.0 10.0	1.6181 1.6180 1.6161	-8759.0 -8758.7 -8748.5	8690.0 8690.0 8690.0	-106.8 -107.1 -117.3	-103.5 -104.0 -120.5	-102.6 -109.5 -130.9
$\gamma \text{-} [SiW_{12}O_{40}]^{4-}$	DMF	0.67	52.5	3.86	1.7491 1.7595 1.6569 1.7394	21.6 21.7 21.0 21.6	1.6172 1.6126 1.6564 1.6214	-8748.2 -8751.3 -8706.6 -8744.8	8690.0 8689.9 8690.8 8690.1	-117.7 -114.4 -160.0 -121.1	-127.4 -104.7 -160.1 -116.8	-135.8 -108.1 -154.7 -126.6
$\left[W_{10}O_{32}\right]^{4-}$	DMF	0.66	126.8	3.77	$1.4285 \\ 1.5701$	19.5 20.4	1.7446 1.6915	-8702.8 -8844.9	8692.5 8691.4	$-165.5 \\ -22.4$	$-165.5 \\ -22.5$	$-171.4 \\ -8.6$

^{*a*} Calculated according to eqn (5) with efg° = 10 a.u. ^{*b*} Calculated according to eqn (4). ^{*c*} Calculated according to eqn (2b). ^{*d*} Calculated according to eqn (1) with $\sigma_{ref} = -175.8$ ppm. ^{*e*} Experimental values.^{5,7,28-30 f} Calculated from DFT methods.¹⁶



Fig. 1 Plot between experimental ^{183}W chemical shifts and those calculated with PACHA for $[P_2W_{18}O_{62}]^{6-},\,\beta\text{-}[SiW_{12}O_{40}]^{4-},\,\gamma\text{-}[SiW_{12}O_{40}]^{4-},\,\text{and}\,[W_{10}O_{32}]^{4-}.$

of the medium. Indeed, the solubility of the compound, $K_{28}Li_5H_7[P_8W_{48}O_{184}]$, is strongly dependent on the pH and the lithium content of the solution.

To illustrate this fact, ¹⁸³W NMR of $K_{28}Li_5H_7[P_8W_{48}O_{184}]$ was recorded under different pH and ionic strength conditions and highly contrasted spectra were obtained (Fig. 2). The spectrum in an acidified medium of pH 1.1 (Fig. 2a) exhibited three resonances at -177.6, -205.1, and -205.5 ppm, very different from those reported in the literature. The spectrum recorded at the same pH but in 1 M LiCl solution (Fig. 2b) showed a comparable spectrum with only changes in the chemical shifts (-180.1, -205.2, and -207.9 ppm). The *ca*. 2 ppm up-field shifts could account for the differences in the ionic strength. The spectrum in 1 M LiCl but without adjusting the pH (Fig. 2c), at spontaneous pH 5.5, led to three broader resonances at -191.1, -193.3, and -208.5 ppm. The spectrum is now comparable to the spectrum published by Contant and Tézé.²³



Fig. 2 183 W NMR spectra of 2.2 mM D₂O solution of K₂₈Li₅H₇[P₈W₄₈O₁₈₄] at (a) pH 1.1, (b) 1 M LiCl and pH 1.1, and (c) 1 M LiCl and pH 5.5.

It is noteworthy to conclude that the pH effect is much stronger than the ionic strength, leading to very different spectra. The pH-dependent ¹⁸³W NMR spectra have also been observed for $[H_4As_8W_{48}O_{184}]^{36-}$ and other POTs.^{32,33} Such a situation could be related to the ability of the POT to fix and release the protons on its structure.

The ³¹P nucleus is also an interesting NMR probe for phosphorus containing POTs. The pH dependency of ³¹P NMR of $[P_8W_{48}O_{184}]^{40-}$ has been reported in previous studies.^{24,34} The ³¹P NMR spectra of K₂₈Li₅H₇[P₈W₄₈O₁₈₄] aqueous solutions are depicted in Fig. 3. Again, the ionic strength effect is much smaller compared to the pH effect although this latter appeared weak. While only ~0.4 ppm of difference is observed for the ³¹P NMR chemical shift when the pH jumps from 4 to *ca.* 6, several ppm shifts are observed in the case of ¹⁸³W. It is clear that ¹⁸³W nuclei are more sensitive to pH effect than the ³¹P nucleus.



Fig. 3 ³¹P NMR spectra of 2.2 mM D₂O solution of $K_{28}Li_5H_7[P_8W_{48}O_{184}]$ at (a) pH 1.1, (b) 1 M LiCl and pH 1.1, and (c) 1 M LiCl and pH 5.5. Inset: Plot of the observed ³¹P chemical shift of 2.2 mM $K_{28}Li_5H_7[P_8W_{48}O_{184}]$ D₂O solution at 1 M LiCl as a function of pH.

pH-Dependency of ¹⁸³W NMR

Fig. 4 shows the selected ¹⁸³W spectra of $K_{28}Li_5H_7[P_8W_{48}O_{184}]$ in 1 M LiCl D₂O solution at a fixed concentration (2.2 mM) in pH ranging from ca. 1 to 6. Due to the too low solubility of the POT, measurement for pH > 6 was not possible. All the three resonances underwent important shifts upon the pH change. In Fig. 5a, plots of the variation of the chemical shifts as a function of pH show two resonances evolving together toward a low-field with increasing pH while the third signal evolves in the opposite direction. Note that resonances $\delta 2$ and $\delta 3$ are close and their curves may cross each other as presented in Fig. 5 based on the prediction using the partial charge formalism (see below Fig. 7). The plots of the chemical shifts as a function of proton/POT ratio (Fig. 5b) show the S-shape curves indicating the saturation of protonation sites at low pH and almost complete deprotonation at a high pH limit. Such chemical shift variations are typical acid-base dependency behaviors.35



ppm-160 -170 -180 -190 -200 -210 -220 -230 -240

Fig. 4 ^{183}W NMR spectra in 1 M LiCl D_2O solution of 2.2 mM $K_{28}Li_5H_7[P_8W_{48}O_{184}]$ at (a) pH 1.1, (b) pH 2.2, (c) pH 3.1, (d) pH 4.0, (e) pH 5.0 and (f) pH 5.8.

The wide range chemical shift variations, over nearly 40 ppm, are indicative of polyacidity despite the absence of resolution of individual successive titration S-shape type curves. Baroudi *et al.* titrated the crown-type POT $[P_8W_{48}O_{184}]^{40-}$ and sixteen protonation sites have been established.³⁴

Modeling of ¹⁸³W shifts in $[{8K} \subset {H_nP_8W_{48}O_{184}}]^{(32-n)-}$ as a function of protonation

In order to understand these chemical shift variations due to the pH change, we used the PACHA software to calculate the effect of protonation on the ¹⁸³W chemical shifts of the three types of tungsten in the structure. We consider that the protons are located on the most basic oxygen atoms, which correspond to those lining the lacunary sites. Fig. 6 shows the location of these protons, as well as those of internal potassium and the three nonequivalent W. Besides the terminal oxo group (W=O), additional unsaturated terminal oxygen is present on the internal W sites (W1). The two other W atoms on the external peripheral sites are either on the cap position (W2) or on the belt position (W3) of the {P₂W₁₂O₄₀} subunits.

First, one has to ensure that the same model used to calculate the shifts of the reference POTs also applies to the case of crown-type POT $[P_8W_{48}O_{184}]^{40-}$. Indeed, the observed chemical shifts at the most acidic medium (pH 1) can be calculated at the highest protonation state $[{8K}] \subset [H_{16}P_8W_{48}O_{184}]^{16-}$, and the adjustable parameters are determined. The input parameters fand δ_{mean} were found to be 0.48 and -20.6 ppm and the output parameters, ΔE , $\langle (a_0/r)^3 \rangle_{6p}$, and P_u were calculated as *ca.* 3.3 eV, 18-19 a.u., and 1.6 respectively, falling in typical ranges for previous POTs studied. In a second stage, by fixing all input parameters and varying the protonation state in $[{8K}] \subset$ $[H_n P_8 W_{48} O_{184}]^{(32-n)-}$, from n = 16 to 0, the ¹⁸³W shifts are thus calculated on the basis of the global charge change only. Indeed, the atomic partial charges should be affected while the structural features are kept unchanged. The overall results are summarized in Table S7 (ESI⁺) and Fig. 7 plots the evolution of the calculated chemical shifts as a function of the number of protons in $[\{8K\} \subset \{H_n P_8 W_{48} O_{184}\}]^{(32-n)-}$. It should be mentioned that when adding multiple protons to the structure many configurations may occur with some degeneracy that may lead to different computed shifts for a given W depending on the position of the proton within the structure. However, because we consider an average value of calculated shifts for all sites of the same type of W, globally the final results do not vary so much from a configuration to another.

As one can see in Fig. 7, the resonance of W2 sites decreases from -181 to -213 ppm when the number of protons decreases from 16 to 0 while those of W1 and W3 increase from -203to -189 ppm and from -210 to -192 ppm respectively. Experimentally, a couple of resonances are observed at -191and -193 ppm at pH 6 or at -206 and 208 ppm at pH 1, while the third isolated resonance also changes with a decrease of the pH from -209 to -181 ppm (Fig. 4 and 5). The comparison with the calculated curves allows us to identify and assign the three resonances and to follow their evolutions.



Fig. 5 183 W NMR chemical shifts of $[P_8W_{48}O_{184}]^{40-}$ as a function of (a) pH and (b) the molar ratio H/POT.



Fig. 6 Top and side views of the structure of $[\{8K\} \subset \{H_{16}P_8W_{48}O_{184}\}]^{16-}$ used to compute the ¹⁸³W chemical shifts of the three types of W, *i.e.*, the internal (W1) and external (W3) belt sites and the bridging cap (W2) of the subunit $\{P_2W_{12}O_{48}\}$, in $[\{8K\} \subset \{H_nP_8W_{48}O_{184}\}]^{(32-n)-}$. Dark gray spheres: the eight internal potassium cations; light gray spheres: protons on the terminal oxygen atoms of the exposed lacunary sites; yellow spheres: phosphorus atoms; magenta spheres: tungsten atoms; red spheres: oxygen atoms.

These results highlight the ability of the partial charge formalism to predict the evolution of chemical shifts with the charge density changes. It is worthy of note that such a result



Fig. 7 Calculated chemical shifts of sites W1, W2, and W3 in [{8K} \subset {H_nP₈W₄₈O₁₈₄}]⁽³²⁻ⁿ⁾⁻ as a function of number of proton in the structure. The observed chemical shifts for different pHs are included in the graph.

was obtained only when considering the presence of the eight potassium cations inside the cavity of the POT. When ignoring the occupancy of these sites or replacing the potassium by smaller cations such as Li^+ or Na^+ , we could not reproduce the experimentally observed trends, *i.e.*, two up-field and one low-field evolutions with decreasing pH. Instead, we record one up-field and two low-field changes as a function of number of protons in the POT. However, by occupying these inner sites by large cations (K, Rb, or Cs), resonance of site W3 changes in the direction of its evolution from low-field to up-field when increasing the protonation state of the POT. These results may emphasise the important template role of potassium in stabilizing the structure of this particular POT.

To further investigate this effect, a similar study was conducted with the mixed ammonium–lithium salt using $(NH_4)_{21}Li_{17}H_2[P_8W_{48}O_{184}]\cdot85H_2O$ as a starting material. With this compound, the solubility is enhanced and the pH range extended from 1 to *ca.* 8. The ¹⁸³W NMR spectra for different pHs (Fig. S1, ESI†) showed a similar behavior and comparable chemical shift changes to those observed with the potassium salt samples are observed (Fig. S2, ESI†). Although we are not able to reproduce the shift change trends using PACHA by replacing the potassium by ammonium cations, the similarity between the experimental data should indicate the comparable stabilizing effect of the template cations.

The substitution of potassium for ammonium in these key sites reflects the host-guest chemistry of $\{P_8W_{48}O_{184}\}^{40-}$. These bound cations should confer a unique stabilization effect in solution in this case of large lacunary POT. The templating role of voluminous cations is obvious as evidenced in more complex systems.³⁶ Though similarly sized the binding modes of ammonium and potassium to crown-type polyoxometalates can be distinguished.³⁷ While the ammonium ions bind to the POT through hydrogen bonds, the potassium cations coordinate directly to nucleophilic oxygen atoms of the lacunary faces. The functionalization of the internal surfaces of the crowntype $[P_8W_{48}O_{184}]^{40-}$ had led to novel complex molecules³⁸⁻⁴⁰ and materials.^{41,42} The guest encapsulation ability of this POT is certainly linked to the high nucleophilicity of its internal cavity. The supramolecular chemistry in this case should be governed not only by the size and shape adaptability of the guest with respect to the intrinsic porosity but also by the electronic affinity between the cation and the templating pocket.

Conclusion

Calculations of ¹⁸³W chemical shifts of POTs have successfully been performed using semi-empirical formalism based on partial atomic charge and hardness analysis. By using an approximate model considering only the most diffuse bonding orbitals, the domination of the paramagnetic shielding can sufficiently be described by the orbital unbalance $P_{\rm u}$ term. This finding opens up the way for the evaluation of ¹⁸³W shifts of large POT clusters, more difficult to compute with conventional *ab initio* methods. PACHA software is a useful tool for identification and assignment of the different W sites in non-symmetrical and complex POTs. In this sense, it should be considered as a computer assisted method to help in the interpretation of the NMR spectra,⁴³ and certainly not in any case to predict and calculate NMR parameters at the absolute magnitude level independently, as *ab initio* calculation methodologies do.

The intriguing variation in the ¹⁸³W NMR spectra of the crown-type POT $[P_8W_{48}O_{184}]^{40-}$ with pH change has been modeled to understand the strong pH-dependency of the shifts of the three resonances. The evolutions of the shifts up to more than 30 ppm can be described by the change in the protonation state at different degrees from 0 to 16 protons per POT. The analysis also revealed the importance of the inner cavity potassium sites stabilizing the crown structure of the POT. The mixed ammonium–lithium salt showed comparable behavior over the wide pH range of the stability of the compound (pH 1–8), albeit the effect of ammonium could not yet be modeled.

Finally, this work showed that chemical shifts could be approached considering a simple representation of the molecular orbital population model that is usually difficult to access. Such information about the orbital occupancy would provide useful insights for the chemist to control the chemistry of these objects.

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pH-controlled one pot syntheses of giant Mo₂O₂S₂-containing selenotungstate architectures

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Supporting Information Placeholder

ABSTRACT: Self-assembly reactions between Na₂WO₄, SeO₂/SeO₃²⁻ and [Mo₂O₂(μ -S)₂(H₂O)₆]²⁺ give, depending on the pH value, two new large polyoxometalate complexes, *i.e.* [(W₁₄Se₂O₅₂)₃(Mo₂O₂(μ -S)₂(H₂O)₂)₆]²⁺ (1) isolated at pH 3.5 and [(Se₂W₁₄O₅₂)₄(WO₃(H₂O))₈(W₂O₅)₂(W₄O₁₂)₂(Mo₂O₂(μ -S)₂(H₂O)₂)₄(Mo₂O₂(μ -S)₂(SeO₃))₄]³⁶⁻ (2) isolated at pH 2. The two compounds were characterized in the solid state by single crystal X-Ray diffraction, EDX, elemental analysis, TGA and FT-IR and in solution by ESI-MS.

Introduction

Owing to their structural versatility and potential applications in many fields such as catalysis,¹ electrocatalysis,² medicine,³ magnetism,⁴ materials sciences, and nanotechnology,⁵⁻⁶ the number of publications concerning polyoxometalates (POMs) exploded over the last decade. This increased interest largely arises from the suitability of pre-formed lacunary POM clusters in which vacancies in the cluster shell can be occupied by additional metal ions or may support the formation of larger metal moieties. Nevertheless, the chemists stay fascinated by the rational design and synthesis of gigantic POMs from a fundamental point of view or for applications in various domains. In the field of polyoxomolybdates, Müller et al. discovered in 1998 a new class of nanoscopic hollow spherical molecules, which were called Keplerate-type clusters containing 132 molybdenum atoms.⁷ This family of compounds has been considerably enriched in the last two decades by number of derivatives synthesized by numerous groups in the world for a large panel of applications and especially for catalysis in confined space. This family of compounds was also complemented by other giant POMs namely the "big wheels" {Mo-154}, {Mo-176} and {Mo-248}, and the "blue lemon" {Mo-368}, which expanded the frontiers of inorganic chemistry to the mesoscopic world.⁷⁻⁸ In contrast, the synthesis of polyoxotungstate clusters with high nuclearity remains more challenging and limited despite wonderful examples published in the recent years. To date, the use of extra linking heteroatoms are required to generate large architectures and the chemists have to choose wisely both the linkers and the building units that will serve to construct such

spectacular supramolecular entities. As building blocks, the heteropolyoxotungstates are built from the assembly of $W^{VI}O_6$ octahedra around heteroanions, which can be for examples $PO_4^{3^\circ}$, $AsO_4^{3^\circ}$, $SiO_4^{4^\circ}$, $GeO_4^{4^\circ}$, $AsO_3^{3^\circ}$, $SbO_3^{3^\circ}$ or $IO_6^{5^\circ}$. A controlled hydrolysis of the latter provides to the chemists a large panel of vacant reactive heteropolyoxotungstates, which can be seen as inorganic ligands. The choice of the heteroelement is determinant since it can seriously affect the final architectures and their physical properties by controlling the range and the connectivity of the building blocks. As linkers, 3d or 4f metals can be chosen, as well as preformed coordination complexes or clusters. In Versailles, our group focused his attention on the use of cationic sulfurated clusters such as $[Mo_2^VO_2S_2(H_2O_2)^{2+}]^{2+}$. While the self-condensation of the aqua complexes $[Mo_2O_2S_2(H_2O)_6]^{2+}$ produces versatile inorganic macrocyclic structures featuring adjustable host-guest properties,⁹ the same $[Mo_2O_2S_2(H_2O_3)_6]^{2+}$ unit proved to be an efficient ditopic unit for reaction with highly negatively charged polyoxotungstates. The coordination requirements of the ${Mo_2O_2S_2}^{2+}$ core are mainly restricted to two equatorial and one axial sites of the two equivalent Mo atoms and predispose the coordinating groups to predictable self-assembly processes. The control of the formation of the $[Mo_2O_2S_2(H_2O_6)]^{2+}$ cation by choosing an appropriate precursor allows to adapt the synthetic conditions to the stability and coordination requirements of the vacant heteropolyoxotungstate. A series of polyoxothiometalate compounds has been obtained by controlled addition of the ${Mo_2O_2S_2}^{2+}$ unit on preformed vacant mono-, di-, tri-, tetra- and superlacunary macrocyclic polyoxotungstates. During the last fifteen years it has been combined with almost all common vacant polyoxotungstates such as $\{XW_9\}$ (X = P, Si, Sb, As), $\{XW_{10}\}$ (X = Si, P), {XW₁₁} (X = B, Si, P), {P₂W₁₅}, {P₂W₁₇}, or {P₈W₄₈} for producing a large panel of nano-sized architectures exhibiting some remarkable flexibility in solution.¹⁰ Among the most inter-esting systems were by far those obtained with $\{AsW_9\}$, probably due to the lone pair steric effect of the As^{III} center.¹¹ For these systems, depending on the experimental conditions and especially the nature of counter cations and the concentration, different assemblies with the same stoichiometry between the POM and the linkers were obtained, i.e., sandwich, tetrahedral, or hexameric arrangements. By the same manner, combination of $[Mo_{2}^{V}O_{2}S_{2}(H_{2}O_{2})]^{2+}$ with ammonium heptamolybdate or sodium

molybdate in one-pot syntheses led to a family of compounds varying from a square $\{Mo_{40}\}^{12}$ to a discotic compound $\{Mo_{63}\}^{,13}$ to a cube $\{Mo_{84}\}^{14}$ or to some keplerates $\{Mo_{132}\}^{,13-14}$ Once again, the experimental conditions play a crucial role for the selective synthesis of such systems and the nature of the counter cations, the molar ratio of the reactants, the concentrations and the pH must be carefully controlled.

In this context, we were motivated by formation in one-pot proassociating cedure of new original architectures $[Mo_2O_2S_2(H_2O)_6]^{2+}$, tungstate and selenite anion SeO₃²⁻. The Se¹ atom of this anion contains a lone-pair which can be exploited since it can generate lacunary polyoxotungstates without the need for hydrolysis of pre-existing parent clusters, allowing for the preparation of unique, often high nuclearity POM architectures and for further expansion when associating to transition metals. Structurally, the use of the selenite SeO_3^{2-} anion prevents the closure of the cluster assemblies to the Keggin or the Dawsontype clusters, and instead gives rise to open lacunary units ${SeW_9}$ or ${Se_2W_{12}}$ and their derivatives. The former is usually obtained when pH is above 4 while the latter is easier obtained in more acidic medium. In the last years, very spectacular supramolecular assemblies were published by different groups. By one pot-synthesis, various architectures were recently reported such as $\begin{array}{l} [H_2 SeW_{18}O_{60}]^{6^{-},15^{-}} [(Se_2W_{12}O_{46}(WO(H_2O))_3]^{2^{4}}, 16^{-} [H_{12}Pd_{10}Se_{10}\\ W_{52}O_{206}]^{28^{-}} and [H_{14}Pd_{10}Se_{10}W_{52}O_{206}]^{2^{6},17} [H_2W_{43}Se_{3}O_{148}]^{2^{4}}, \\ [H_4W_{77}Se_5O_{265}]^{4^{4}-} and [H_6W_{63}Se_{6}O_{221}]^{3^{4},18}\\ [H_{19}Co_{2,5}(W_{3,5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})]^{17^{-}}, [H_4COWO(H_2O)_{3^{4}})^{4^{4}} \end{array}$ $\begin{array}{l} (Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]^{40-} & \text{and} & [H_{14}Ni_2W_2O_2Cl(H_2O)_3\\ (Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2]^{43-}, {}^{19} & [\{(SeO_3)W_{10}O_{34}\}_8\{Ce_8(H_2O)_{20}\}\\ (WO_2)_4(W_4O_{12})]^{48-} & \text{and} & [\{(SeO_3)W_{10}O_{34}\}_8\{Ce_8(H_2O)_{20}\}(WO_2)_4\} \end{array}$ $\{(W_4O_6)Ce_4(H_2O)_{14}(SeO_3)_4(NO_3)_2\}]^{34-20}$ or $[(\alpha-SeW_9O_{34})]$ ${Zr(H_2O)}{WO(H_2O)}(WO_2)(SeO_3){\alpha-SeW_8O_{31}Zr(H_2O)}]_2^{12}$ $[(Se_2W_{18}O_{60})_2(\mu_2-O)_4]^{16-}, [Se_2W_{18}O_{62}(H_2O)_2]^{8-}, \\ SeW_9O_{33})_2\{Ce_2(CH_3COO)(H_2O)_3W_3O_6\}(\alpha-Se_2W_{14}O_{52})]^{17-}$ [(αand $[(\alpha-SeW_9O_{33})_2\{Ce_2(H_2O)_4W_3O_6\}\{\alpha-Se_2W_{14}O_{51}(OH)\}]^{15-21}$ For all of them the reactions were performed in aqueous medium at a controlled pH, which appears as a key parameter for the formation of these systems and especially its building blocks. Based upon similar approach we investigated the ternary system $WO_4^{2/2}/SeO_3^{2/2}$ $/{Mo_2O_2S_2}^{2+}$ at different pH values. At pH ca 3.5 a triangle-like hybrid complex 1 was isolated while at lower pH it recombines to a giant complex 2. Their syntheses and characterizations are described in this study.

Experimental part

Physical methods

Fourier Transformed Infrared (FT-IR) spectra were recorded on a 6700 FT-IR Nicolet spectrophotometer, using diamond ATR technique. The spectra were recorded on non-diluted compounds and ATR correction was applied. Elemental analyses (C, H, N, S) were carried out by the analytical service of the CNRS at Gif sur Yvette, France. Energy-dispersive X-ray spectroscopy (EDX) measurements were performed on a JEOL JSM 5800LV apparatus. Water content was determined by thermal gravimetric (TGA) analysis with a Seiko TG/DTA 320 thermogravimetric balance (5°C min⁻¹, under O_2). NMR studies in D_2O solution at room temperature were carried out on a Bruker Avance 400 spectrometer operating at 76.41 MHz for 77Se nucleus and 16.67 MHz for 183W nucleus. Typical spectra were acquired with 8k to 16k and 32k number of scans for ⁷⁷Se and ¹⁸³W requiring ca. 18-20 h and 18 h measurement times, respectively. ⁷⁷Se chemical shift was referenced to external Na₂SeO₃ ($\delta = 1273$ ppm) and then recalculated vs SeMe₂ ($\delta = 0$ ppm).22 The ¹⁸³W NMR scale was calibrated relative to the signal of D2O/H2O solution of $H_4SiW_{12}O_{40}$ at -103.8 ppm with respect to the saturated Na2WO4 solution. The ⁷⁷Se MAS NMR experiments were performed on a Bruker Avance 500 spectrometer equipped with a 11.7 T wide-bore magnet. The resonance frequency was 95.50 MHz and the experiments were performed with a 3.2 mm MAS probe and a spinning rate of 20 kHz. Hahn echo MAS spectra were recorded with 32K data points and a recycle delay of 61 s.

Electrospray Ionization Mass Spectrometry. A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, U.K.) was used. The temperature of the source block was set to 100°C, while the desolvation temperature was set to 200°C. A capillary voltage of 3.3 kV was applied in the negative scan mode, and the cone voltage was set to 10 V to control the extent of fragmentation of the identified species. TOF mass spectra were acquired in the V-mode operating at a resolution of ca. 10000 (FWHM). At this resolution, the isotopic pattern of the large 1 and 2 polyanions could not be resolved; however, an estimation of the molecular weight can be conveniently assessed taking into consideration the spacing between the series of peaks in the ESI mass spectra. Mass calibration from m/z 50 to 3000 was performed with a solution of sodium iodide in a 2-propanol/water (50:50) mixture. Aqueous sample solutions were infused via a syringe pump directly connected to the ESI source at a flow rate of 10 µL·min⁻¹.

X-Ray diffraction on single crystals. Crystallographic data and refinement details are given in Table 1. Because crystals of Na-1 and Na-2 quickly lose water of crystallization and become amorphous in air, mineral oil was used to protect the crystals from decay. The diffraction data were collected on a Bruker Apex Duo diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) by doing φ and ω scans of narrow (0.5°) frames at 150 K. An empirical absorption correction was applied using the SADABS program²³ Both structures were solved by direct methods and refined by fullmatrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7 set²⁴ using ShelXle program.²⁵

The opposition between high X-ray absorption of mediumsized polyoxometalate crystals and poor x-ray diffraction of smaller crystals poses a particular problem for x-ray analysis of large POMs. In the case of complex **Na-1** we could find optimal crystal size and minimize artifact electronic density down to 2.8 e. The resulting refinement gives 14 sodium cations and absence of voids in the crystal packing, leaving 10 additional protons to balance the charge of $[(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6]^{24-}$. The anion $\{(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6\}^{24-}$ has six $\{Mo_2O_2(\mu-S)_2(H_2O)_2\}^{2+}$ bridges connecting three $\{W_{14}Se_2O_{52}\}$ units. Four of these linkers are disordered over two positions. The disorder can be modeled by rotation of each *cis*- $\{Mo_2O_2(\mu-S)_2(\mu-S)_2(\mu-S)_2(\mu-S)_2)^{2+}$ unit by 180 ° while keeping equal the positions of S, O and H₂O. A related case of such disorder was reported by Cadot et al. in $[(PW_{11}O_{39})_2(Mo_4S_4O_4(OH_2)_2)]^{10-.26}$

In Na-2 the highest difference peak of 3.97 e is a truncation error arising from Fourier series, and it is typical for the structures with a large number of heavy atoms, and in particular for tungsten containing polyoxometalates. The appearance of such artifacts is due to high X-ray absorption of heavy metals. Smaller crystals of complex Na-2 diffract poorly. Four outer $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ units have disordered Mo atoms over two close positions with 0.1/0.9 occupancies. This disordering is not influenced to the geometry of ligand arrangement due to positions of oxygen atoms of Mo=O and Mo-H₂O are overlapped. This situation can be viewed as a rotation of $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ unit by 180°. Furthermore, two $\{WO(H_2O)\}^{4+}$ fragments (W=O 1.715(2), W-O_{H2O} 2.341(2) Å) connected to the four $\{Se_2W_{14}O_{52}\}$

Table 1. Crystallographic data for compounds Na-1 and Na-2. Experiments were carried out at 150 K with Mo Kα radiation using a Bruker Apex Duo. Absorption was corrected for by multi-scan methods, *SADABS* (Bruker-AXS, 2004).

	Na-1	Na-2				
Chemical formula	$H_{158}Mo_{12}Na_{14}O_{242}S_{12}Se_6W_{42}\\$	$K_{0.80}Mo_{16}Na_{17.20}O_{416}S_{16}Se_{12}W_{76}$				
Mr	14084.58	24050.83				
Crystal system, space group	Orthorhombic, Pbcm	Triclinic, P ⁻ 1				
a, b, c (Å)	17.9677 (7), 43.3408 (15), 37.8230 (14)	17.6801 (17), 23.857 (2), 31.133 (3)				
α, β, γ (°)	90, 90, 90	101.709 (2), 90.277 (2), 105.394 (2)				
$V(Å^3)$	29454.1 (19)	12373 (2)				
Ζ	4	1				
μ (mm ⁻¹)	17.76	19.04				
Crystal size (mm)	$0.10\times0.05\times0.05$	$0.15 \times 0.12 \times 0.08$				
T_{\min}, T_{\max}	0.494, 0.745	0.310, 0.745				
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	1171656, 31808, 19109	107431, 50323, 29898				
<i>R</i> _{int}	0.099	0.045				
θ values (°)	$\theta_{\text{max}} = 27.6, \ \theta_{\text{min}} = 1.6$	$\theta_{\text{max}} = 26.4, \ \theta_{\text{min}} = 1.2$				
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.651	0.625				
Range of h, k, l	$-23 \le h \le 23, -56 \le k \le 50, -49 \le l \le 40$	$-22 \le h \le 22, -28 \le k \le 29, -38 \le l \le 38$				
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.078, 0.164, 1.12	0.065, 0.201, 1.05				
No. of reflections, parameters, restraints	31808, 1533, 36	50323, 2465, 24				
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0184P)^2 + 2575.1055P] w = 1/[\sigma^2(F_0^2) + (0.0777P)^2 + 778.140P]$					
	where $P = (F_0^2 + 2F_c^2)/3$	where $P = (F_0^2 + 2F_c^2)/3$				
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	2.78, -3.50	3.96, -3.32				

Computer programs: APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS2014 (Sheldrick, 2014), SHELXL2014 (Sheldrick, 2014), SHELXLE (Sheldrick, 2011), CIFTAB-2014 (Sheldrick, 2014).

units show disordering of W atoms over two close positions with 0.65/0.35 or 0.55/0.45 occupancies, the positions of oxygen atoms also overlapping. The possible reason of such disordering is the rotation of the {Mo₂O₂(μ_2 -S)₂(H₂O)₂}²⁺ units causing water molecules of the {WO(H₂O)} groups to be outside the cavity when the water molecules of the Mo/S cluster units are inside the cavity. The positions of Na⁺ and K⁺ cations were found according to typical distances and geometry. The structure contains very large solvent accessible voids. Composition of the complex was found with EDX and TGA. Moreover, in the structure of Na-2, more complicated disordering of all central moieties was found. The reason of this arises from two different orientations of [(Se₂W₁₄O₅₂)₄(WO₃(H₂O))₈(W₂O₅)₂(W₄O₁₃)₂(Mo₂O₂(μ -

 $S_{2}(H_{2}O)_{2}(M_{2}O_{2}(\mu-S)_{2}(SeO_{3}))_{4}]^{40}$ anion in the crystal structure depicted on Figure S7 (supporting Information). The left orientation is dominant and fills 92% of all positions in the crystal. The occupancies of W atoms from right orientation are only 8% that doesn't allow finding positions of its oxygen ligands. The existence of these orientations is possible due to the fact of practically identical positions of four {Se₂W₁₄O₅₂ units, which are the heaviest parts of the anion. Crystallographic data for Na-1 and Na-2 are summarized in Table 1 whereas Figures 1 to 4 give some pictures of the polyoxometalate moieties. Further details may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) under the CSD numbers 433197 and 433198.

Syntheses

Synthesis of $Na_{18}H_6[(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6]$ •65H₂O (Na-1). 5.0 g of Na₂WO₄.2H₂O (15.15 mmol) were dissolved in distilled water (20 mL) and 0.25 g of SeO₂ (2.25 mmol) were then added (pH 8.4). The pH was lowered to 4.7 with 4 M HCl and a milky white precipitate formed locally by addition of HCl re-dissolved rapidly upon stirring. The resulting colorless solution was stirred at room temperature for further 30 min and 1 precursor of the compound $K_{2-x}(NMe_4)_x$ $[I_2Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5] \cdot 20H_2O$ (0.416 mmol of Mo_{10} which give 2.08 mmol of $[Mo_2O_2S_2]^{2+}$ clusters) were then added. The yellow solid dissolved within some minutes, whereupon the pH was lowered to 3.5 with 4 M HCl. The resulting clear red solution was stirred at room temperature for 2 h and left to evaporate in an open beaker. Slow evaporation yielded 1.81 g of dark-red crystals which were isolated by filtration and recrystallized in 0.1 M NaCl aqueous solution (60 mL) to give after 10 days well-shaped prismatic dark-red crystals of Na18H6[(W14Se2O52)3(Mo2O2(µ-S)₂(H₂O)₂)₆]·65H₂O, denoted hereafter compound Na-1. After recording of the X-Ray structure, the crystals were isolated by filtration, washed with cold water, ethanol and ether. Yield 1,1 g, 22%. IR/cm⁻¹ (see Figure S1, Supporting Information): 1622 (s), 951 (ms), 889 (w), 831 (s), 821 (sh), 758 (vs), 663 (sh), 597 (sh), Elemental analysis calcd (%) for Na₁₈H₆[(W₁₄Se₂O₅₂)₃(Mo₂O₂(µ- $S_{2}(H_{2}O_{2})_{6}$]·70H₂O (M = 14326.6 g.mol⁻¹) H 1.7; S 2.69. Found (%): H 1.15; S 2.65. Absence of C and N which could be due to traces of TMA⁺ cations from the precursor. EDX atomic ratios calculated for $Na_{18}H_6[(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2 (H_2O)_2)_6]$ ·65H₂O (found): Mo/S = 1 (1.10); W/Mo = 3.5 (3.3); W/Se = 7.0 (7.8); Mo/Se = 2 (2.4) W/Na = 2.3 (2.3). TGA: A weight loss of 10.7% between *RT* and 300 °C corresponds to crystallization and coordinated water molecules (cald: 10.3%).

Synthesis of $Na_{35}K_{3}H_{2}[(W_{16}Se_{2}O_{58}(H_{2}O_{2}O_{2})_{4}(W_{2}O_{5})_{2}(W_{4}O_{13})_{2}$ $(Mo_2O_2(\mu-S)_2(H_2O)_2)_4(Mo_2O_2(\mu-S)_2(SeO_3))_4] \cdot 120H_2O \ (Na-2): \ 5$ g of Na2WO4.2H2O (15.15 mmol) and 0.25 g (2.25 mmol) of SeO₂ were solubilized in water (20 ml, pH = 8.4). The pH was lowered to 4.7 with 4 M HCl (about 5 mL added) and the resulting colorless solution was stirred at room temperature for further 30 0.76 of $K_{2-x}(NMe_4)_x[I_2Mo_{10}]$ min. g $O_{10}S_{10}(OH)_{10}(H_2O)_5] \cdot 20H_2O$ were then added (0.32 mmol of Mo_{10} which give 1.58 mmol of $[Mo_2O_2S_2]^{2+}$ clusters). The yellow solid dissolved within some minutes, whereupon the pH was lowered to 2.1 with 4 M HCl (the solution turned dark-red at pH below 2.5). The clear dark-red solution was stirred at room temperature for 2 h, and then was kept in air for slow evaporation at room temperature. After one week, dark red single crystals mixed with powder were obtained (1.1 g). The crystals were isolated by filtration on a glass frit n°4 and were recrystallized in water at pH = 2.1 to give dark red single crystals suitable for X-Ray diffraction study after 10 days. Yield 0.53 g, 10 %. They were isolated by filtration and kept in air. IR/cm⁻¹ (see Figure S2, Supporting Information): 1624 (s), 956 (ms), 889 (m), 831 (s), 750 (vs), 600 (sh), 501 (br., w.). Elemental analysis calcd (%) for $Na_{35}K_{3}H_{2}[(W_{16}Se_{2}O_{58}(H_{2}O)_{2})_{4}(W_{2}O_{5})_{2}(W_{4}O_{13})_{2}(Mo_{2}O_{2}(\mu - M_{2}O_{2})_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(Mo_{2}O_{2})_{4}(W_{2}O_{3})_{2}(W_{2}O_{3})_{$

 $S_{2}(H_{2}O)_{2}(Mo_{2}O_{2}(\mu-S)_{2}(SeO_{3}))_{4}] \cdot 120H_{2}O$ (found): W/Mo = 4.75 (4.53); Mo/S = 1.0 (1.02); W/S = 4.75 (4.60); Mo/Se = 1.33 (1.66), W/Na = 2.16 (2.17), Na/K = 11.66 (12.35). TGA: A weight loss of 9.7% between *RT* and 300 °C corresponds to crystallization and coordinated water molecules (cald: 9.76%).

Results and discussion

Syntheses and structures

By mixing sodium tungstate, selenium dioxide and K2-_x(NMe₄)_x[I₂Mo₁₀O₁₀S₁₀(OH)₁₀(H₂O)₅]·20H₂O in water at pH 3.5, the resulting solution turns to red, a color which is typical of the reaction of nucleophilic $[Mo_2O_2S_2]^{2+}$ clusters with vacant polyox-otungstates.¹⁰⁻¹¹, ²⁸⁻²⁹ At this pH, condensation process of $[Mo_2O_2S_2]^{2+}$ complexes can also occur to give cyclic assemblies around various ligands^{9, 30} and especially around monotungstate group, which leads to the formation of a very stable yelloworange compound [Mo₈O₈S₈(OH)₈(HWO₅(H₂O))]^{3.31} This species is evidenced by the formation of a yellow precipitate during the synthesis when reactants are introduced in stoichiometric ratios. In order to avoid the formation of the latter, the quantity of the $K_{2-x}(NMe_4)_x[I_2Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5] \cdot 20H_2O$ precursor was reduced until obtaining only a limpid red solution. The quantity of $[Mo_2O_2S_2]^{2+}$ is thus introduced below the stoichiometry corresponding to the target compound $[(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6]^{24}$, denoted hereafter 1. After several days the synthesis solution yields dark-red crystals, which were recrystallized from 0.1 M NaCl. Elemental analysis, EDX and TGA measurements lead to the formula $Na_{18}H_6[(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu S_{2}(H_{2}O_{2})_{6}$ · 65H₂O, denoted hereafter Na-1. It crystallizes in the orthorhombic P_{bcm} space group and the resulting refinement gives

only 14 sodium cations and absence of voids in the crystal packing, leaving 10 additional protons to balance the charge of $\{(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6\}^{24-}$. This discrepancy about the formula determined by other techniques can be explained by the presence of at least 65 water molecules, which can be also disordered with Na⁺ cations. The molecular structure of 1 is depicted in Figure 1, whereas the crystallographic data are summarized in Table 1.



Figure 1. Top (a) and side (b) views of the molecular structure of anion 1. $\{Se_2W_{14}\}$ units are represented in grey polyhedra while the Se atoms of two central SeO_3^{2-} anions are given in pink; $[Mo_2O_2S_2(H_2O)_2]^{2+}$ linkers are depicted in ball and stick (Mo in blue, S in yellow, O in red); central Na⁺ cation and H₂O molecule are also depicted in green and red respectively.

It consists of triangular $\{(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6\}^{24}$ macrocyclic anions, with ideal D_{3h} geometry, connected together with sodium cations into two types of puckered layers (Figure S3, SI). The anion has six $\{Mo_2O_2(\mu-S)_2(H_2O)_2\}^{2+}$ bridges connecting three $\{Se_2W_{14}O_{52}\}$ units, which are derivatives from Dawson-like parent $[Se_2W_{14}O_{52}]^{8-}$. These $\{Se_2W_{14}\}$ units differ slightly from the $\{\alpha-Se_2W_{14}\}$ units reported by Izarova and Kögerler³² and by Yan and Su²¹ and are related to the $\{Se_2W_{12}\}$ reported by Kalinina and Kortz¹⁶ or by Long and Cronin³³ in cyclic systems $[(Se_2W_{12}O_{46}(WO(H_2O)_3)]^{24-}$ and $[Se_8W_{48}O_{176}]^{32-}$. To our knowledge, the structure of this $\{Se_2W_{14}\}$ unit is reported for the second time in the literature since it was first reported by Cronin et al. in 2014 and described as a W_{18} -'Trojan Horse' structure.¹⁷ Moreover, it is also similar to the $\{P_2W_{14}O_{54}\}^{14-}$ unit reported by Gouzerh et al. in 2005.³⁴

Due to the lone pair of selenium, a tetravacant Dawson-type structure is obtained. As shown in Figure 2a, eight nucleophilic

oxygen atoms are available and organized for coordinating four clusters $[Mo_2O_2(\mu-S)_2(H_2O)_2]^{2+}$ each, in two equatorial positions of the Mo(V) atoms (Figure 2b). Two dispositions of the $[Mo_2O_2(\mu-S)_2(H_2O_2)]^{2+}$ are possible, i.e. Mo=O short bonds or longer Mo-OH₂ bonds orientated towards the cavity. Therefore, one of the six $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ linkers has water molecules oriented towards the inside of the cavity of the anion $\{(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6\}^{24}$, another one has outward-coordinated H₂O (Figure S4, SI), and the four remaining units show disorders between these two positions with a statistical distribution of water and oxo ligands pointing towards the cavity. This kind of disorder can be found for other [Mo₂O₂S₂]containing POMs, such as $[(PW_{11}O_{39})_2(Mo_4S_4O_4(OH_2)_2)]^{10}$, ²⁶ and $[(P_2W_{17}O_{61})_2(Mo_4S_4O_4(OH_2)_2)]^{16}$. ³⁵ Finally, the cavity of $\{(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6\}^{24}$ is occupied with two atoms with the distance of 2.475 Å between them, and with full occupancy. Hence, these atoms can be assigned as Na⁺ and H₂O distributed statistically over the two positions. The presence of a sodium cation and a water molecule inside the cavity confirms the possibility of the orientation of $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ with Mo=O bonds orientated towards the cavity, to form hydrogen bonds between water molecule and oxo ligands (O-O distance 2.9-3.1 Å), or to coordinate to Na by oxo ligands (Na-O distance in the range 2.56-3.20 Å). These Na cation and water molecule may play a role of template or stabilizing agent for such an architecture. In 2014, we reported the formation of the discotic compound $[{Mo_{17}O_{52}(OH)_4(H_2O)_6}_3(Mo_2O_2S_2(H_2O)_2)_6]^{6-}$, which associates three $\{Mo_{17}O_{52}(OH)_4(H_2O)_6\}$ units connected together by six $\{Mo_2O_2S_2(H_2O)_2\}$ clusters.¹³ The molecular arrangement appears similar and we evidenced for this compound the presence of a NMe₄⁺ cation inside the cavity as template agent for the synthesis of the compound. In other compounds associating $\{AsW_9\}$ units and $(Mo_2O_2S_2(H_2O_2))$ linkers, various supramolecular architectures were obtained, strongly depending on the experimental conditions.¹¹ In particular triangular moieties { $(AsW_9)_3(Mo_2O_2S_2(H_2O_2)_3$ } incorporating Na⁺, K⁺ or H₂O in the cavity were studied. Interestingly, we evidenced the stabilizing role of the K⁺ cation for such assemblies. When K⁺ are removed, the structure is irreversibly modified. A similar stabilizing role of Na⁺ cation in { $(Se_2W_{14}O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6$ }²⁴⁻ is expected and could explain the degradation of this compound which could occur in water, while it is possible to recrystallize it in NaCl medium.



Figure 2. (a) Representation of the tetravacant Se_2W_{14} unit found in anions 1 and 2. The eight nucleophilic oxygen atoms are highlighted in red. (b) Picture of the connection of four $[Mo_2O_2S_2(H_2O)_2]^{2+}$ linkers to the eight available oxygen atoms of the Se_2W_{14} units found in 1. (b) Picture of the connection of two $[Mo_2O_2S_2(H_2O)_2]^{2+}$ linkers and two WO_6 octahedra (in fact $\{WO_3(H_2O)\}$) depicted in blue to the Se_2W_{14} units found in compound 2. The eight available oxygen atoms of the Se_2W_{14} units are coordinated in similar modes to those found in 1.



Figure 3. Molecular structure of polyanion 2. $\{Se_2W_{14}O_{52}\}$ units are represented in grey polyhedral; $[Mo_2O_2S_2(H_2O)_2]^{2+}$ linkers are depicted in ball and stick (Mo in blue, S in yellow, O in red); $\{WO_3(H_2O)\}$ units are depicted as blue octahedra; isopolytun-states moieties $\{W_2O_5\}$ and $\{W_4O_{12}\}$ are given in red and green respectively; additional SeO_3^{2-} anions can be identified through the Se atoms depicted as pink spheres.



Figure 4. Highlights of the central part of the anion 2 showing the connections $[Mo_2O_2S_2]^{2+}$ linkers (Mo in blue, S in yellow, O in red), $\{WO_3(H_2O)\}$ units (blue octahedra); isopolytunstates moieties $\{W_2O_5\}$ and $\{W_4O_{12}\}$ (red and green polyhedra respectively), the additional SeO₃²⁻ anions (Se as pink spheres) and the two central sodium cations (green spheres).

By mixing the same synthetic components in aqueous medium, the color becomes much darker when the pH is decreased below 2.5 and a synthetic solution kept in air at pH 2 gave single crystals compound of а of formula $Na_{35}K_{3}H_{2}[(Se_{2}W_{14}O_{52})_{4}(WO_{3}(H_{2}O))_{8}(W_{2}O_{5})_{2}(W_{4}O_{13})_{2}(Mo_{2}O_{2}(\mu - M_{2}O_{2})_{3})_{2}(Mo_{2}O_{2})_{2}(Mo_{2}O$ S)₂(H₂O)₂)₄(Mo₂O₂(µ-S)₂(SeO₃))₄]·120H₂O, abbreviated hereafter Na-2. At this pH, the formation of the [Mo₈O₈S₈(OH)₈(HWO₅(H₂O))]³⁻ compound does not occur and the synthetic one pot procedure have been optimized by using stoichiometric amounts of each components. Na-2 crystallizes in the triclinic P-1 space group. As depicted in Figure 3 and in Figure S5 (Supporting Information), the large anion $[(Se_2W_{14}O_{52})_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2(\mu - MO_2O_2))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2)_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2)_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2)_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2)_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(MO_2O_2)_4(WO_2O_2)_2(W_2O$

 $S_{2}(H_{2}O_{2})_{4}(Mo_{2}O_{2}(\mu-S)_{2}(SeO_{3}))_{4}]^{40-}$, namely 2, possesses nanometric dimensions 3×2.2 nm. In contrast to the synthesis of 1, the synthesis of 2 is performed at lower pH, which does not favor the condensation of side product POMs such as isopolytungstates. The anion 2 can be decomposed within 6 building blocks of different sizes: four tetravacant {Se₂W₁₄O₅₂} units (in grey in Figure 3); eight monotungstate groups $\{WO_3(H_2O)\}$ (in blue), two dinuclear units $\{W_2O_5\}$ (in green), two tetratungstate units $\{W_4O_{12}\}$ (in purple), eight $\{Mo_2O_2S_2\}$ clusters divided in two types (depicted in ball and stick representation), and from four additional selenite anions SeO_3^{2-} (Se in pink sphere). The main part of the hybrid anion consists of four tetravacant {Se₂W₁₄O₅₂} fragments on which are coordinated two outside $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{24}$ clusters and two tungstate $\{WO_3(H_2O)\}$ units (see Figure 2c). The two $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ are connected on their opposite equatorial positions with another {Se₂W₁₄O₅₂} fragment to give a $\{(Se_2W_{14}O_{52})_2(Mo_2O_2S_2(H_2O)_2)_2\}$ moiety which can be seen as a common part with the anion 1. Furthermore, as observed in 1, both outside $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ clusters experience disorder over two closed positions with 0.65/0.35 SOF values. This fact can be viewed as rotation of the $\{Mo_2O_2(\mu_2-S)_2(H_2O)_2\}^{2+}$ units, probably, due to formation of additional hydrogen bonds or contacts to Na⁺ cations. The composition of the cavities could not be determined by XRD because of the disorder. Each $\{WO_3(H_2O)\}$ unit connected to $\{Se_2W_{14}O_{52}\}$ POM bridges either $\{W_2O_5\}$ or $\{W_4O_{12}\}$ unit and the two latter are also connected together by sharing summits (see Figure S5, SI). Finally, the inner ${Mo_2O_2(\mu_2-S)_2}^{2+}$ units have two SeO_3^{2-} ligands coordinated into trans positions to the Mo=O units, which connect two $\{Mo_2O_2(\mu_2 - \mu_2)\}$ S_{2}^{2+} fragments together. Such coordination of SeO_{3}^{2-} is not surprising if we consider the family of cyclic compounds discovered by Miras and Cronin.³⁶⁻³⁷ All Mo=O bonds are directed outside the POM (Figures S6, SI). Moreover, these clusters are coordinated through oxygen atoms of $\{W_2O_5\}$ groups in the cispositions (one of oxygen atom of SeO_3^{2-} participates in the formation of $\{W_2O_6\}$ moiety). Other cis-positions are occupied by oxygen atoms of the rhombohedral $\{W_4O_{12}\}$ fragment (Figures S5-S6, SI). Four inner $\{Mo_2O_2(\mu_2-S)_2\}^{2+}$ units, two $\{W_4O_{12}\}$ and two $\{W_2O_5\}$ groups form the cavity in the central part of this hybrid polyoxometalate which is depicted in Figure 4. Finally, as observed for 1, the cavity of 2 is partially filled by two sodium cations with SOF = 0.6 in interaction with two bridging sulfide of two $\{Mo_2O_2(\mu_2-S)_2\}^{2+}$ clusters (Na-S = 2.972 and 3.031 Å), two water molecules (Na-Ow = 2.267 and 2.432 Å), and two terminal oxo ligands of the {W₄O₁₂} units (Na-O = 2.491 and 2.495 Å) leading to distorted octahedra.

Nuclear magnetic resonance spectroscopy

The two polyanions were tentatively characterized by ⁷⁷Se and ¹⁸³W NMR in H₂O-D₂O solution. Unfortunately, as shown in Figure S8 (SI), we were not able to confidently analyze the ¹⁸³W spectra we got for these two compounds in aqueous medium. The spectrum of 2 was too poor and only some broad signals can be hardly seen. Usually giant POMs with high nuclearity exceeding 60 W are difficult to measure by 183 W NMR probably due to the combination of low symmetry of their structure and their slow tumbling motion causing dispersion and broadening of their signals. In the case of compound 1, a complex spectrum is obtained containing at least twenty-six resonances. All these observations could be due to partial decomposition, to some equilibria in solution and/or to local disorders of the components of 1 and 2, which produces mixture of isomers with lower symmetries. In line with this, ⁷⁷Se NMR (Figure S9) also showed many resonances instead of a single signal expected for the idealized high symmetrical structure of 1, and broad signals for 2 ranging from 1260 to 1360

ppm. Similar difficulties were also reported by Kortz and Kalinina for cyclic compound resulting from the connection of three $\{Se_2W_{12}\}$ fragments to $\{WO(H_2O)\}^{4+}$ groups.¹⁶ They showed evolution of the ⁷⁷Se spectrum with time leading to a myriad of signals within the range 1240-1350 ppm. They concluded the sample is unstable in aqueous solution and the solid-state ⁷⁷Se MAS spectrum exhibited a broad signal covering the 1287-1293 ppm range. In Figure 5, the ⁷⁷Se MAS spectra of samples 1 and 2 show similar resonances at ca. 1305-1308 and 1294-1301 ppm respectively, that should account for typical selenium sites in selenotungstate derivatives.



Figure 5. MAS ⁷⁷Se NMR spectra of (a) Na-1 and (b) Na-2.

Electrospray Ionization Mass Spectrometry

ESI-MS characterization of such high nuclearity POMs is not trivial in aqueous medium because of their high molecular weights, high charge states and their limited chemical stability. Besides, ionization occurs via multiple uptake of alkali cations and protons along with solvent water molecules. Hence, very broad peaks are observed in their corresponding ESI mass spectra, which ultimately preclude accurate determination of the composition of the POMs. Cronin's group pioneered the use of ESI-MS for identification of gigantic polyanions in solution on the basis of the observation of polyanions with differing numbers of cations and water molecules existing either as monomers or oligomers of the related parent polyanion.^{19, 38-39} Molecular weights can be estimated by ESI-MS via deconvolution of multiply charged states of intact polyanion taking into consideration the spacing between the series of broad peaks in the ESI mass spectra. In this context, the ESI mass spectra of 10⁻⁴ M aqueous solutions of compounds Na-1 and Na-2 were investigated. As shown in Figure 6, the ESI-MS spectrum of Na-1 displays three broad peaks centered at m/z 1820, 2124 and 2600 encompassing 7- to 5- charge states. These peaks can be assigned to the whole cluster $[(Se_2W_{14}O_{52})_3(Mo_2O_2(S)_2(H_2O)_2)_6]^{24}$ in which some water molecules coordinated to the [Mo₂O₂S₂] linkers can be partially desolvated and for which variables amounts of protons and Na⁺ cations can be associated (see Table S1, SI). For example, the 5charged species at m/z 2600 evidences a large polyanion of a molecular weight near to 13000, fully consistent with the presence of 1. Additionally, two broad peaks at m/z 2036 and 2078 are probably due to partially dismantled POM. The ESI mass spectrum of compound Na-2 gives five broad peaks centered at m/z 2066, 2275, 2532, 2858 and 3287 encompassing different 11- to 7- charge states. These peaks can be assigned to the whole cluster $[(Se_2W_{14}O_{52})_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{13})_2(MO_2O_2S_2(H_2O)_2)_4(WO_3(H_2O))_2(W_2O_5)_2(W_4O_{13})_2(WO_2O_2S_2(H_2O)_2)_4(WO_3(H_2O))_2(W_2O_5)_2(W_4O_{13})_2(WO_2O_2S_2(H_2O)_2)_4(WO_3(H_2O))_2(W_2O_5)_2(W_4O_{13})_2(WO_2O_2S_2(H_2O)_2)_4(WO_3(H_2O))_2(W_2O_5)_2(W_4O_{13})_2(WO_2O_2S_2(H_2O))_2(W_2O_5)_2$ $Mo_2O_2S)_2(SeO_3))_4]^{40-}$ featuring different numbers of cations and water molecules. As an illustrative example, the 7- charged species at m/z 3287 strongly supports the presence of the 2 polyanion with a molecular weight of ca. 23000. Additionally, dimers derived from **2** were also observed in the gas phase at m/z 3545 and 3850 (see Table S1), as typically found in closely related gigantic POMs.^{19, 38-39} Either for Na-1 and Na-2, triply and doubly-charged species at m/z values below 1700 were observed as broad peaks (see Figure S10 and S11). It is clear that m/z values in the 1250-1450 range with 3- charges must be reasonably due to the presence of the fragments $[(Se_2W_{14}O_{52})(Mo_2O_2S_2)_n]$ with n = 1-3, associated with H⁺, Na⁺ and water molecules. The relative intensity of these species with respect to **1** (or **2**) remained largely unchanged for 30 minutes, thus suggesting that, rather than decomposition of **1** (or **2**), they are formed under the ESI conditions. Other building blocks such as the $[(Se_2W_{14}O_{52})_2(Mo_2O_2S_2)_n]$ are not observed at all.



Figure 6. Negative ESI-MS spectra of aqueous solutions (10^{-4} M) of Na-1 and Na-2 at a cone voltage of Uc = 10 V.

Conclusion

Among the experimental factors, the control of the pH is a key parameter in the formation of POMs, and thus the pH dependent synthetic approach constitutes an important research objective for the rational design of giant POM assemblies. Herein, we exemplify the feasibility of one-pot procedures to selectively isolate two original giant heteropolyoxotungstates containing a rare $\{Se_2W_{14}\}$ tetravacant selenotungstate building block. The synthetic entry proceeds under mild conditions (neither high temperature nor pressures were required) by mixing some sodium tungstate, selenium dioxide, and an [Mo₂O₂S₂(H₂O)₆]²⁺ precursor in water, at two different pH: $[(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6]^{24-}$ (1) isolated at pН 3.5 and $[(Se_2W_{14}O_{52})_4(WO_3(H_2O))_8]$ $(W_2O_5)_2(W_4O_{12})_2(Mo_2O_2(\mu-S)_2(H_2O)_2)_4(Mo_2O_2(\mu-S)_2(SeO_3))_4]^{36-1}$ (2) at pH 2. The two compounds were characterized in the solid state by single crystal X-Ray diffraction, EDX, elemental analysis, TGA, FT-IR, and ⁷⁷Se solid state NMR. Solution state NMR studies revealed however complicated spectra we were not able to analyze, probably due to some decomposition of the products at high concentration conditions. We nevertheless succeeded to evidence the presence of the intact anions 1 and 2 in water at 10^{-4} M by ESI-MS. Finally, these results probably pave the way towards a fascinating family of compounds in the ternary system WO_4^{2-} , SeO₂ or SeO₃²⁻, and $[Mo_2O_2S_2(H_2O)_6]^{2+}$ by exploring the effect of the pH and the stoichiometric ratio.

ASSOCIATED CONTENT

Supporting Information

FT-IR Spectra of **Na-1** and **Na-2** (Figures S1-S2); additional structural representation of compounds **1** and **2** (Figure S3-S7); ¹⁸³W and ⁷⁷Se NMR spectra recorded for **Na-1** and **Na-2** (Figure S8 and S9), table of ESI-MS assignments (Table S1) and additional ESI-MS spectra of **Na-1** and **Na-2** (Figures S10-S11).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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Self-assembly reactions between Na₂WO₄, SeO₃²⁻ and $[Mo_2O_2(\mu-S)_2(H_2O)_6]^{2+}$ in water give selectively two new large polyoxometalate complexes at pH = 2 and pH = 3.5, namely $[(Se_2W_{14}O_{52})_4(WO_3(H_2O))_8(W_2O_5)_2(W_4O_{12})_2(Mo_2O_2(\mu-S)_2(H_2O)_2)_4(Mo_2O_2(\mu-S)_2(SeO_3))_4]^{36-}$ and $[(W_{14}Se_2O_{52})_3(Mo_2O_2(\mu-S)_2(H_2O)_2)_6]^{24-}$, respectively for which the building units were compared and discussed.





Titre : Assemblages à base de polyoxométallates : des interactions fondamentales aux matériaux hybrides supramoléculaires.

Mots clés : Polyoxométalates, matériaux hybrides, chimie supramoléculaire

Résumé : Dans ce travail, nous présentons dans la première partie la substitution du molybdène par du tungstène dans les anions de type Keplerates, $[{Mo_6}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42-}$ (E = O or S). L'introduction du tungstène dans le milieu de synthèse a entraîné l'isolement d'une série de composés, $[\{W_xMo_{6}\}$ $_{x}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42}$, avec une teneur en métal variable dans leurs unités pentagonales $\{M_6\}$. Une observation remarquable a révélé l'occupation sélective de la position centrale dans l'unité pentagonale par les atomes W. Cette observation a été étendue à d'autres structures telles que les roues du bleu du molybdène $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ et l'anion Krebs [Mo₃₆O₁₁₂(H₂O)₁₆]⁸⁻ qui ont également montré la même occupation préférentielle des atomes W pour le site héptavalent, au centre du pentagone.

Dans la deuxième partie, nous nous concentrons sur l'élaboration d'un matériau hybride à trois composantes à base de polyoxométallates (POM), de clusters métalliques et de ycyclodextrine (γ -CD). La conception de ce matériau suivant une approche synthétique basée sur la propagation à l'infini des interactions spécifiques entre la CD et les deux types d'unités inorganiques. Dans la dernière partie, nous étendons l'étude des interactions CD-POM aux structures POMs géantes telle que l'anneau du bleu du molybdène. Une complexation non conventionnelle résulte de l'encapsulation du macrocycle organique dans la cavité centrale du l'anneau inorganique anionique. Accroître la complexité du système en introduisant une troisième espèce, conduit à la formation d'un assemblage supramoleculaire hybride par agencement hiérarchique des molécules organiques et inorganiques.

Title : Polyoxometalate-based assemblies: from primary interactions to supramolecular hybrid materials

Keywords : Polyoxometallates, hybrid materials, supramolecular chemistry

Abstract : In this work, we report in the first part the substitution of molybdenum by tungsten within Keplerate-type anions, $[\{Mo_6\}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42}$ (E = O or S). Introducing tungsten to the synthesis medium resulted in the isolation of a series of compounds, $[\{W_xMo_{6}\}$ $_{x}_{12}Mo_{30}O_{312}E_{60}(AcO)_{30}]^{42}$, with variable metal content within their pentagonal units $\{M_6\}$. An outstanding observation revealed the selective occupation of the central position in the pentagonal unit by the W atoms. This revelation was stretched to reach other historical structures as Mo-blue wheel $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ and Krebs $[Mo_{36}O_{112}(H_2O)_{16}]^{8-1}$ anions that also showed the same preferential occupation of W atoms for the heptacoordinated site.

In the second part, we focus on the fabrication of a three-component hybrid material based on polyoxometalates (POMs), metallic clusters and γ -cyclodextrin (γ -CD). Investigation of such material has been conducted using bottom-up approach by investigating the specific interactions between CD and both types of inorganic units. Finally, the three components associate together to give a well ordered polymer-like hybrid chain that is derived as hydrogel and single crystals.

In the last part, we extend the CD-POM investigation to reach giant POM structures as the Mo-blue ring. A non-conventional complexation results from this interaction explained by the encapsulation of the organic macrocycle within the inorganic torus. Increasing the complexity of the system by introducing a third species provoked the formation of a hierarchical hybrid assembly.