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Renaud Ruamps

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THÈSE

En vue de l'obtention du

DOCTORAT DE L'UNIVERSITÉ DE TOULOUSE

Délivré par : *l'Université Toulouse 3 Paul Sabatier (UT3 Paul Sabatier)*

Présentée et soutenue le *31/10/2013* **par :**

RENAUD RUAMPS

Traitement théorique de l'anisotropie magnétique

JURY

VINCENT ROBERT	Professeur d'Université	Rapporteurs
NICOLAS FERRÉ	Professeur d'Université	Rapporteurs
JEAN-PASCAL SUTTER	Directeur de Recherche	Examinateur
NATHALIE GUIHÉRY	Professeur d'Université	Directrice de thèse

École doctorale et spécialité :
Science de la Matière : Physicochimie théorique
Unité de Recherche :
Laboratoire de Chimie et de Physique Quantiques IRSAMC
Directrice de Thèse :
Pr. Nathalie Guihéry Université Toulouse 3 Paul Sabatier
Rapporteurs :
Pr. Vincent Robert Université de Strasbourg
Pr. Nicolas Ferré Université d'Aix-Marseille

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Introduction

L'étude des propriétés magnétiques des matériaux à donnée lieu à l'élaboration de complexes de métaux de transitions avec des spécificités remarquables [1], telles qu'une lente relaxation de l'aimantation engendrée par l'existence d'une barrière énergétique d'inversion du spin total d'une molécule.
Ainsi, le complexe polynucléaire $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}]\cdot 2CH_3COOH\cdot 4H_2O$ (noté ensuite Mn_{12}-acétate, voir figure 1), de spin total $S = 10$, à valence mixte formé par un anneau externe de huit Mn^{III} ($S = 2$) entourant un tétraèdre de Mn^{IV} ($S = 3/2$) [2] manifeste, d'après des mesures d'hystéresis (*cf.* figure 2), une aimantation spontanée en dessous d'une température critique, ce type de matériau est appelé aimant moléculaire ou "*Single Molecular Magnet*" (SMM). Les mesures de susceptibilité magnétique en fonction de la température démontrent un couplage ferrimagnétique entre les manganèses de degré d'oxydation différents [3], il en résulte l'apparition d'une forte anisotropie magnétique avec un axe privilégié pour l'alignement des spins dit axe de facile d'aimantation.

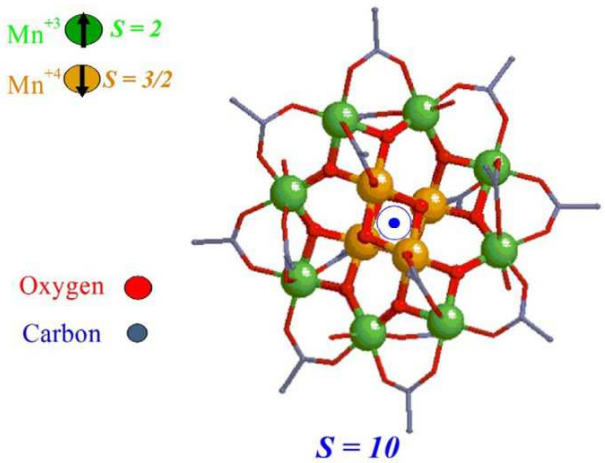

FIGURE 1 – Complexe Mn_{12}-acétate

Ce complexe possède un état fondamental de multiplicité de spin $2S + 1 = 21$, les différentes composantes du moment magnétique M_S ne sont pas dégénérées, même en l'absence de champ magnétique. Cette levée de dégénérescence est qualifiée de "*Zero-Field Splitting*" (ZFS) et est modélisée par un ensemble de paramètres dont les principaux sont les paramètres axial D et rhombique E du ZFS. Il est possible de peupler préférentiellement

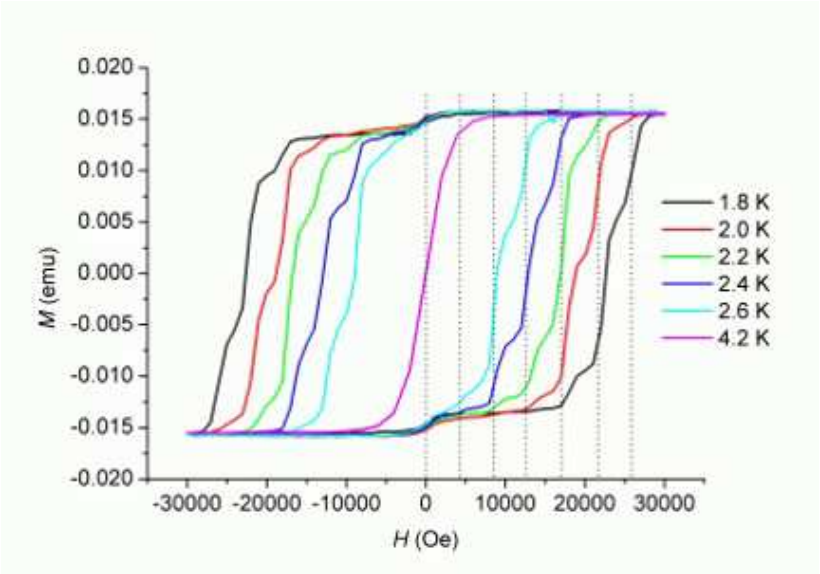

FIGURE 2 – Mesures d'aimantation en fonction du champ magnétique appliqué à différentes températures sur Mn_{12}-acétate

certaines composantes M_S en appliquant un champ magnétique et, une fois le champ interrompu, de maintenir cette population et donc l'aimantation résultante de la molécule, cependant, le phénomène de relaxation thermique tend à faire perdre cette propriété. En effet, à basse température, le moment magnétique de spin du système peut être analysé comme le cas d'une particule dans un double puits de potentiel quantique dont les différents états possibles sont d'une part les composantes avec M_S positifs, d'autre part avec M_S négatifs, et sont disposés par énergie décroissante en fonction de $|M_S|$, selon les valeurs propres de l'hamiltonien de spin $H = -|D|S_z^2$ avec S_z la composante z du moment magnétique de spin et D un paramètre négatif pour ce composé (D = -0.46 cm^{-1}). Il est alors possible de considérer que la barrière énergétique pour renverser le spin, illustrée sur la figure 3, est $U = |D|\left(M_{Smax}\right)^2$ soit 46 cm^{-1} ou exprimée comme une température 66 K [4, 5] pour ce complexe. Pour bénéficier de ces propriétés, il sera donc nécessaire de se placer à basse température ou d'accroître U. Par exemple, pour Mn_{12}-acétate, la température de blocage est approximativement de 4 K [6]. Notons, cependant, qu'un renversement du spin est aussi possible à de plus faibles énergies par effet tunnel quantique.

La relaxation magnétique à basse température laisse présager une transition magnétique à grande échelle, à l'image des aimants macroscopiques. Ainsi, à partir de poudres poly-cristallines, un phénomène d'hystéresis magnétique d'origine moléculaire est observé mais sans la formation des domaines magnétiques de Weiss de tailles variables exhibant des propriétés non uniformes comme pour les aimants traditionnels. Ainsi, un échantillon macroscopique de SMM tel qu'une poudre composée d'un ensemble de SMM préalablement alignés à l'aide d'un champ magnétique a permis l'observation d'un phénomène de marches quantifiées au sein des boucles d'hystérésis à basse température. Cela s'interprète par un effet tunnel résonnant qui peut être assisté thermiquement entre différents états de spin pour des valeurs particulières du champ magnétique, la hauteur effective de

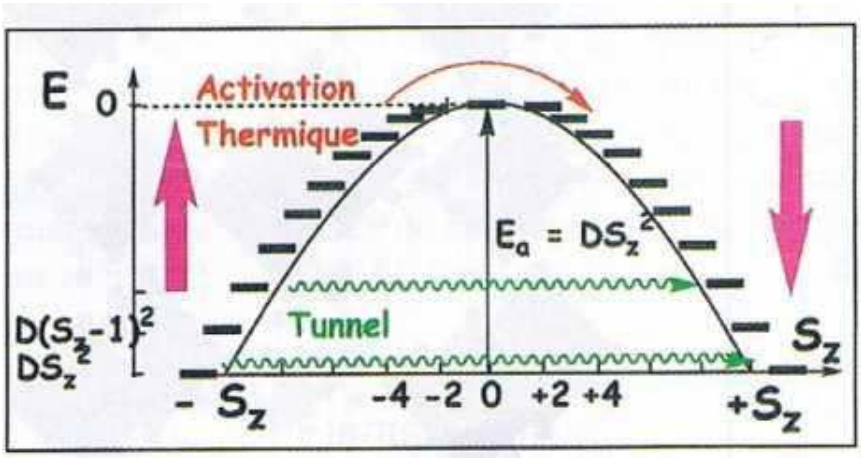

FIGURE 3 – Barrière énergétique d'inversion de spin pour une molécule à haut spin

la barrière énergétique pouvant être réduite sous l'effet du champ [7, 8]. Cette propriété peut être mise à profit pour obtenir un effet magnéto-calorique. En effet, lors d'une baisse du champ appliqué, l'entropie et la température varient fortement, un refroidissement magnétique dans des domaines comparables à l'hélium liquide semble alors possible [9].

A partir de telles observations, de nombreuses propriétés sont théoriquement possibles telles que, en profitant du blocage de l'état magnétique à basse température, le stockage d'information sous la forme d'un bit quantique associé à un SMM, ce dernier jouant le rôle d'un système bistable. Il serait ainsi possible d'élaborer un système de stockage d'information de haute densité [10] en imposant, lors d'une phase d'écriture, un état magnétique à chaque molécule si celle-ci est connectée à un conducteur électrique ces propriétés de transport seraient alors modifiées et observées lors de la phase de lecture. D'autres méthodes suggèrent une lecture et écriture par impulsion à résonance de spin. Une voie prometteuse pour l'élaboration d'ordinateur quantique utilise une superposition d'états quantiques de molécules aimants [11–13] avec des bits quantiques basés sur le spin.

Afin d'augmenter l'énergie de la barrière $U = |D| \left(M_{Smax}\right)^2$, une première piste suivie fut d'augmenter le spin de l'état fondamental du complexe, cette caractéristique étant plus facile à prédire que la valeur de D, dès lors, d'autres composés polynucléaires ont été développer tels qu'un complexe hexa-nucléaire Mn_6^{II} avec un état fondamental $S = 12$, un autre composé à valence mixte dodéca-nucléaire Mn_{12} avec $S = 14$ ou un octo-nucléaire Fe_8^{III} [1, 6] avec $S = 10$. Cependant, comme cela sera développé plus tard, le paramètre D est dépendant du spin du complexe et l'anisotropie (et donc D) tend à diminuer à proportion que le spin total augmente selon un concept de dilution anisotropique [5, 6]. En fait, $|D|$ varie en $(M_S)^{-2}$ et donc U est quasiment indépendant du spin total, en conséquence il semble préférable d'améliorer l'anisotropie locale au sein de chaque ions métalliques [5, 14] ou d'identifier plus précisément les origines de S et de D.

C'est en premier lieu, cette approche qui sera suivie afin d'augmenter l'anisotropie des SMM les plus simples : les mononucléaires, et ceux par différents moyens de sorte à obtenir une valeur de D négative et avec une amplitude maximale, donnant lieu à un système bistable comme l'exemple historique Mn_{12}-acétate et afin d'accroître la différence énergétique des composantes magnétiques $M_S = 0$ et M_{Smax} lié à la hauteur de la barrière ainsi que d'obtenir une faible valeur d'un autre paramètre du ZFS, E lié à l'effet tunnel. Ensuite, il s'agira de tester comment les anisotropies locales de deux centres magnétiques interagissent pour former une anisotropie globale d'un composé bi-nucléaire. Pour ce faire, une approche théorique sera employée à l'aide de logiciels de chimie quantique. Il est ainsi possible d'accéder précisément à la structure électronique des principaux états en prenant en compte les couplages spin-orbites (SOC) indispensables pour décrire le ZFS. Par des calculs analytiques des effets spin-orbites, des informations sur la nature ou l'origine de l'anisotropie sont obtenues et permettent de mieux comprendre les mesures expérimentales. De plus, grâce à une mise évidence de la corrélation entre la structure géométrique du complexe et ses propriétés magnétiques, une amélioration de l'anisotropie des systèmes magnétiques est envisageable. Enfin, un autre apport de la chimie théorique est la possibilité de développer des hamiltoniens modèles qui mettent en jeu, potentiellement, des paramètres utilisés pour interpréter des mesures expérimentales et qui peuvent être validés rigoureusement sur différents exemples par l'utilisation des hamiltoniens effectifs.

Cette thèse s'articule en trois chapitres. En premier lieu, au sein du premier chapitre, les outils théoriques sont présentés, en particulier, l'hamiltonien utilisé pour décrire les états énergétiques des systèmes étudiés ainsi que l'origine des paramètres magnétiques qui leur sont associés. Puis, les différentes méthodologies employées sont exposées, il s'agit de méthodes donnant accès à la fonction d'onde et aux énergies de l'état fondamental et des premiers états excités incluant les traitements des effets relativistes et de la corrélation électronique. Ensuite, la théorie permettant l'obtention d'un hamiltonien reproduisant le bas du spectre et servant à l'extraction des paramètres magnétiques est exposée, suivie d'une méthode de calcul de la densité électronique employée pour définir, si nécessaire, la structure géométrique du complexe étudié. Lors d'un second chapitre, deux voies de recherche sont proposées afin d'accroître l'anisotropie magnétique et, grâce à des collaborations avec des équipes expérimentales, appliquées à des complexes réels pour lesquels une comparaison avec des mesures magnétiques pourra être réalisée. La première voie consiste à utiliser des complexes à coordination exotique visant à engendrer une forte anisotropie et la seconde consiste à exploiter la dégénérescence orbitalaire de l'état fondamental pour obtenir une grande valeur de D. Enfin, le troisième chapitre est l'occasion d'étudier comment, en façonnant l'anisotropie locale de deux ions composant un complexe bi-nucléaire, il est possible d'accroitre ou de réduire l'anisotropie globale du complexe. En particulier, le choix d'un hamiltonien permettant de décrire les anisotropies locales et d'échange est abordé, ainsi que l'importance de la symétrie du système et la dépendance entre les paramètres de ZFS et les déformations structurales envisagées.

Chapitre 1

Théorie et Méthodes

Afin de décrire et de comprendre les propriétés magnétiques des complexes de métaux de transition de la quatrième période, nous allons définir l'hamiltonien non-relativiste de ce système à partir de l'équation de Schrödinger. Puis après l'ajout du couplage spin-orbite, principal responsable de l'anisotropie magnétique, il sera alors possible d'introduire le paramètre axial D et rhombique E, ainsi que les notions d'aimantation en fonction du champ magnétique appliqué et de susceptibilité magnétique.

1.1 Hamiltonien magnétique pour les complexes mono-nucléaires

1.1.1 Origine de l'hamiltonien des complexes mono-nucléaires en champs magnétique

Nous allons développer l'hamiltonien permettant de décrire les états d'une molécule dans un champ magnétique $\vec{B}$ en spécifiant les différentes contributions est requis [15–17]. Les différents termes vont être introduits en fonction de leur dépendance en champ et en fonction du spin. Ce dernier sera introduit de manière phénoménologique pour reproduire, au mieux, le traitement effectué dans les différents programmes de calcul de chimie quantique qui seront abordés dans la partie suivante 1.2. De même les corrections relativistes scalaires ne seront présentés que dans la partie 1.2.4.3 en fonction du programme employé.

1.1.1.1 Origine des différents termes de l'hamiltonien

Les différents moments impliqués dans les propriétés magnétiques d'une molécule sont les suivants :

- le moment angulaire électronique orbital $\vec{L} = \sum_i \vec{l}_{Gi} = \sum_i (\vec{r}_i - \vec{G}) \times \vec{p}_i$ avec un moment orbital $\vec{l}_{Gi}$ pour chaque électron, une origine de jauge $\vec{G}$, une quantité de mouvement $\vec{p}_i$ et les nombres quantiques orbitaux L, M_L. Pour simplifier les notations, la jauge ne sera pas indiquée par la suite.
- le moment magnétique de la molécule $\vec{\mu}_e$ dû au moment magnétique de spin des électrons.

- le moment magnétique permanent du noyau $\vec{\mu}_N$ dû au spin nucléaire négligé par la suite.

Dans l'approximation où l'énergie dépend seulement du champ magnétique $\vec{B}$ et de $\vec{\mu}_e$, le développement de Taylor du premier ordre autour d'un champ et moment magnétique nul de la fonction d'onde Ψ donne :

$$\Psi(\vec{B},\vec{\mu}_e) = \Psi_0 + \vec{\Psi}^{(1,0)}.\vec{B} + \vec{\Psi}^{(0,1)}.\vec{\mu}_e \tag{1.1}$$

l'ordre de dérivation par rapport, respectivement, au champ magnétique et au moment magnétique est indiqué en exposant, entre parenthèses. Au second ordre, le développement de Taylor pour l'hamiltonien est :

$$\hat{H}(\vec{B},\vec{\mu}_e) = H^{(0,0)} + \vec{H}^{(1,0)}.\vec{B} + \frac{1}{2}\vec{B}.\overline{\overline{H}}^{(2,0)}.\vec{B} + \vec{H}^{(0,1)}.\vec{\mu}_e + \vec{\mu}_e.\overline{\overline{H}}^{(1,1)}.\vec{B} + \frac{1}{2}\vec{\mu}_e.\overline{\overline{H}}^{(0,2)}.\vec{\mu}_e \tag{1.2}$$

Explicitons les termes mis en jeu :

- $H^{(0,0)}$ hamiltonien non-relativiste de la molécule en l'absence de champ magnétique
- $\vec{H}^{(1,0)}.\vec{B}$ terme Zeeman-orbital
- $\frac{1}{2}\vec{B}.\overline{\overline{H}}^{(2,0)}.\vec{B}$ terme de susceptibilité diamagnétique
- $\vec{H}^{(0,1)}.\vec{\mu}_e$ terme de couplage spin-orbite
- $\vec{\mu}_e.\overline{\overline{H}}^{(1,1)}.\vec{B}$ terme Zeeman de spin
- $\frac{1}{2}\vec{\mu}_e.\overline{\overline{H}}^{(0,2)}.\vec{\mu}_e$ terme de couplage spin-spin (il ne sera pas explicité dans cette partie car il requiert l'équation de Dirac)

De même, l'énergie peut être développée de manière perturbative en $\vec{B}$ et $\vec{\mu}_e$ au second ordre

$$\begin{aligned} \mathcal{E}(\vec{B},\vec{\mu}_e) &= \left\langle \Psi(\vec{B},\vec{\mu}_e) \middle| \hat{H}(\vec{B},\vec{\mu}_e) \middle| \Psi(\vec{B},\vec{\mu}_e) \right\rangle \\ &\approx \left\langle \Psi_0 \middle| \hat{H}(\vec{B},\vec{\mu}_e) \middle| \Psi(\vec{B},\vec{\mu}_e) \right\rangle \text{ à ce niveau de développement} \end{aligned} \tag{1.3}$$

d'où en utilisant (1.1) et (1.2), on peut séparer les différentes contributions énergétiques en fonction de leur dépendance en champ magnétique et en moment de spin, indiqué en indice :

$$\begin{aligned} \mathcal{E}(\vec{B},\vec{\mu}_e) &= \mathcal{E}_0 + \mathcal{E}_{10} + \mathcal{E}_{20} + \mathcal{E}_{01} + \mathcal{E}_{11} + \mathcal{E}_{02} \\ &= \langle \Psi_0 | \Bigg[H^{(0,0)} + \vec{H}^{(1,0)}.\vec{B} + \frac{1}{2}\vec{B}.\overline{\overline{H}}^{(2,0)}.\vec{B} \\ &\quad + \vec{H}^{(0,1)}.\vec{\mu}_e + \vec{\mu}_e.\overline{\overline{H}}^{(1,1)}.\vec{B} + \frac{1}{2}\vec{\mu}_e.\overline{\overline{H}}^{(0,2)}.\vec{\mu}_e \Bigg] \\ &\quad \left| \Psi_0 + \vec{\Psi}^{(1,0)}.\vec{B} + \vec{\Psi}^{(0,1)}.\vec{\mu}_e \right\rangle \end{aligned} \tag{1.4}$$

Tentons d'identifier ces différents éléments.

1.1.1.2 Hamiltonien non-relativiste sans spin

L'hamiltonien non-relativiste de la molécule ou de l'ion sans spin (comportant N noyaux et n électrons) présente un terme cinétique $\hat{T}$ et un terme d'énergie potentielle $\hat{V}$ selon l'équation de Schrödinger

$$\hat{H} = \hat{T} + \hat{V} = \sum_{\alpha}^{N+n} \frac{(\vec{\pi}_\alpha)^2}{2m_\alpha} + \sum_{\alpha}^{N+n} \hat{V}_\alpha + \sum_{\alpha<\beta}^{N+n} \hat{V}_{\alpha\beta} \tag{1.5}$$

avec l'impulsion $\vec{\pi}_\alpha = \vec{p}_\alpha - q_\alpha \vec{A}_\alpha$, la quantité de mouvement $\vec{p}_\alpha = -i\hbar\vec{\nabla}_\alpha$, la constant de Planck réduite $\hbar$, la charge q_α, la masse m_α, les potentiels électromagnétiques $\vec{A}_\alpha$ et Φ_α défini par $\hat{V}_\alpha = q_\alpha \Phi_\alpha$ et le potentiel d'interaction entre particule $\hat{V}_{\alpha\beta}$.

Comme $\vec{p} = -i\hbar\vec{\nabla}$, en imposant une jauge de Coulomb $\vec{\nabla}.\vec{A} = 0$, l'impulsion peut être réécrite, en l'appliquant à une fonction d'onde Ψ :

$$\begin{aligned}
(\vec{\pi})^2\Psi &= (\vec{p} - q\vec{A})^2\Psi \\
&= (\vec{p}^2 - q\vec{p}\vec{A} - q\vec{A}\vec{p} + q^2\,\vec{A}^2)\Psi \\
&= \vec{p}^2\,\Psi - q(\vec{p}\vec{A})\Psi - 2q\vec{A}(\vec{p}\Psi) + q^2\,\vec{A}^2\,\Psi
\end{aligned} \tag{1.6}$$

Le second terme disparait à cause de la jauge, l'hamiltonien s'exprime alors comme

$$\hat{H} = \sum_{\alpha}^{N+n} \left[\frac{(\vec{p}_\alpha)^2}{2m_\alpha} - \frac{q_\alpha}{m_\alpha}\vec{A}_\alpha.\vec{p}_\alpha + \frac{q_\alpha^2}{2m_\alpha}(\vec{A}_\alpha)^2 \right] + \sum_{\alpha}^{N+n} q_\alpha \Phi_\alpha + \sum_{\alpha<\beta}^{N+n} \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha\beta}} \tag{1.7}$$

où ϵ_0 est la permittivité du vide et $r_{\alpha\beta}$ est la distance entre les particules α et β. En champ nul, on a $\vec{\pi}_\alpha = \vec{p}_\alpha$, $\vec{A}_\alpha = \vec{0}$ et $V_\alpha = 0$ donc :

$$H^{(0,0)} = \sum_{\alpha}^{N+n} \frac{(\vec{p}_\alpha)^2}{2m_\alpha} + \sum_{\alpha<\beta}^{N+n} \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{\alpha\beta}} \tag{1.8}$$

En spécifiant les paramètres relatifs aux électrons, notés avec l'indice e : la charge $q_e = -e$, la masse m_e, la distance électron-électron r_{ij} d'une part, et les paramètres relatifs aux noyaux de numéro atomique Z_A : la charge $q = Z_A e$, la masse M_A, la distance noyau-électron r_{Ai}, de distance noyau-noyau r_{AB}, d'autre part, il vient :

$$\begin{aligned}
H^{(0,0)} &= \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \qquad (1.9) \\
&= -\sum_{A}^{N} \frac{(\hbar\vec{\nabla}_A)^2}{2M_A} - \sum_{i}^{n} \frac{(\hbar\vec{\nabla}_i)^2}{2m_e} + \sum_{A<B}^{N} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} - \sum_{A}^{N}\sum_{i}^{n} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{i<j}^{n} \frac{e^2}{4\pi\epsilon_0 r_{ij}}
\end{aligned}$$

On a ainsi défini l'hamiltonien de Schrödinger en champ nul, sans spin, abordons désormais les effets magnétiques d'un couplage entre un champ magnétique et le moment orbital.

1.1.1.3 Hamiltonien Zeeman-orbital et diamagnétique

Reprenons l'équation (1.7). L'induction magnétique est définie par $\vec{B} = \vec{\nabla} \times \vec{A}$, pour un champ magnétique homogène qui peut être réécrit : $\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \times \vec{r}_i$. ($\vec{r}_i$ est la position de l'électron pour une jauge donnée).
Donc, pour une géométrie donnée (noyaux fixes) et un champ magnétique uniquement statique ($\Phi_\alpha = 0$) il reste, pour les électrons (avec $q = -e$) :

$$\hat{H}_{mag} = H^{(0,0)} + \frac{e}{2m_e}\sum_i^n \left(\vec{B} \times \vec{r}_i\right).\vec{p}_i + \frac{e^2}{8m_e}\sum_i^n \left(\vec{B} \times \vec{r}_i\right)^2 \tag{1.10}$$

Le produit mixte s'exprime aussi comme $\left(\vec{B} \times \vec{r}_i\right).\vec{p}_i = \vec{B}.(\vec{r}_i \times \vec{p}_i) = \vec{B}.\vec{l}_i$ et pour le dernier terme $\left(\vec{B} \times \vec{r}_i\right)^2 = \left(\vec{B}\right)^2 (\vec{r}_i)^2 - \left(\vec{B}.\vec{r}_i\right)^2$ d'où l'hamiltonien magnétique devient

$$\hat{H}_{mag} = H^{(0,0)} + \frac{e}{2m_e}\sum_i^n \vec{B}.\vec{l}_i + \frac{e^2}{8m_e}\sum_i^n \left[\left(\vec{B}\right)^2 (\vec{r}_i)^2 - \left(\vec{B}.\vec{r}_i\right)^2\right] \tag{1.11}$$

A partir du premier terme, en introduisant le magnéton de Bohr $\mu_B = \frac{e\hbar}{2m_e}$, on peut alors définir l'hamiltonien Zeeman-orbital

$$\vec{H}^{(1,0)}_{L-B}.\vec{B} = \frac{\mu_B}{\hbar}\vec{L}.\vec{B} \tag{1.12}$$

On note ensuite la susceptibilité diamagnétique réduite (indépendante de la température) $\overline{\overline{\kappa}}^{dia}$ comme

$$\begin{aligned}
\kappa^{dia}_{ab} &= \left.\frac{\partial \mu_a}{\partial B_b}\right|_{\vec{B}=\vec{0}} = -\left.\frac{\partial^2 \mathcal{E}(\vec{B})}{\partial B_a \partial B_b}\right|_{\vec{B}=\vec{0}} && (1.13)\\
&= -\left.\frac{\partial^2 \left\langle \Psi_0 | \hat{H}_{mag} | \Psi_0 \right\rangle}{\partial B_a \partial B_b}\right|_{\vec{B}=\vec{0}} \\
&= -\frac{e^2}{8m_e}\langle \Psi_0 | \sum_i^n \left.\frac{\partial^2 (\vec{B})^2 (\vec{r}_i)^2 - (\vec{B}.\vec{r}_i)^2}{\partial B_a \partial B_b}\right|_{\vec{B}=\vec{0}} | \Psi_0 \rangle \\
&= -\frac{e^2}{4m_e}\langle \Psi_0 | \sum_i^n (\vec{r}_i)^2 \delta_{ab} - (\vec{r}_i)_a (\vec{r}_i)_b | \Psi_0 \rangle && (1.14)
\end{aligned}$$

D'où, au second ordre, pour le dernier terme de (1.11), on a $H^{(2,0)} = \overline{\overline{\kappa}}^{dia}$ et en définitive :

$$\hat{H}_{mag} = H^{(0,0)} + \frac{\mu_B}{\hbar}\vec{L}.\vec{B} + \frac{1}{2}\vec{B}.\overline{\overline{\kappa}}^{dia}.\vec{B} \tag{1.15}$$

Il reste à introduire les termes de spin pour décrire le magnétisme et retrouver l'aimantation.

1.1.1.4 Hamiltonien Zeeman de spin

Le spin de l'électron $\vec{s} = \frac{\hbar}{2}\vec{\sigma}$ (où $\vec{\sigma}$ est le vecteur des matrices de spin de Pauli) engendre un moment magnétique $\vec{\mu}_e = -\frac{g_e e}{2m_e}\vec{s} = -\frac{g_e \mu_B}{2}\vec{\sigma}$ avec g_e le facteur de Landé de l'électron. En présence d'un champ magnétique, l'énergie engendrée pour un système à n électrons est :

$$\hat{H}_{S-B} = -\vec{\mu}_e.\vec{B} = \frac{g_e e}{2m_e}\sum_i^n \vec{s}_i.\vec{B} \tag{1.16}$$

d'où, on déduit le terme Zeeman de spin (avec $\vec{S} = \sum_i^n \vec{s}_i$) :

$$\vec{\mu}_e.\hat{H}^{(1,1)}.\vec{B} = \frac{g_e \mu_B}{\hbar}\vec{S}.\vec{B} \tag{1.17}$$

1.1.1.5 Interaction spin-orbite

On peut ajouter dans l'hamiltonien magnétique le couplage spin-orbite. Commençons dans un premier temps par considérer un électron se déplaçant à une vitesse $\vec{v}_e$ en périphérie d'un noyau A. Il ressent un champ électrique $\vec{E}_A$ dû au noyau éventuellement avec un facteur d'écran dû à la présence des autres électrons. L'induction magnétique engendrée par l'électron en mouvement autour d'un noyau fixe donne :

$$\vec{B}_A = -\frac{1}{c^2}\vec{v}_e \times \vec{E}_A \tag{1.18}$$

avec c, la vitesse de la lumière dans le vide.
Si le champ électrique dérive du potentiel scalaire $\Phi_A(r)$, il vient :

$$\vec{E}_A = -\overrightarrow{grad}\ \Phi_A(r) = -\frac{\partial \Phi_A(r)}{\partial r}\frac{\vec{r}}{r} \tag{1.19}$$

et l'induction magnétique s'écrit :

$$\vec{B}_A = -\frac{1}{c^2 r}\frac{\partial \Phi_A(r)}{\partial r}\vec{r} \times \vec{v}_e \tag{1.20}$$

Ce terme est associé à la vitesse angulaire de Larmor $\omega_L = eB/m_e$ décrivant le mouvement de précession d'un moment magnétique (ici d'un électron) dans un champ magnétique. Il doit cependant être corrigé par le terme de précession de Thomas ω_T lié aux transformations relativistes pour une particule accélérée possédant un moment magnétique. Pour un électron de vitesse $\vec{v}_e$ et d'accélération $\vec{a}_e$, ce terme est donné par :

$$\vec{\omega}_T = \frac{\vec{a}_e \times \vec{v}_e}{2c^2} \tag{1.21}$$

Comme $m_e\vec{a}_e = -e\vec{E}_A$, il vient :

$$\vec{\omega}_T = \frac{e}{2c^2 m_e}\vec{v}_e \times \vec{E}_A = -\frac{e}{2m_e}\vec{B}_A = -\frac{1}{2}\vec{\omega}_L \tag{1.22}$$

En prenant en compte les deux termes, la précession devient $\omega = \omega_L + \omega_T = \omega_L/2$. L'énergie d'interaction du spin de l'électron et du champ magnétique interne prend alors un facteur 1/2 et est donnée par l'opérateur :

$$\begin{aligned} \hat{H}^{(0,1)}_{S-L}.\vec{\mu}_e &= -\frac{\vec{\mu}_e.\vec{B}_A}{2} = -\left(-\frac{eg_e}{2m_e}\vec{s}\right)\frac{1}{2}\left[-\frac{1}{c^2 r}\frac{\partial \Phi_A(r)}{\partial r}\vec{r}\times\vec{v}_e\right] \\ &= -\frac{eg_e}{4m_e^2c^2r}\frac{\partial \Phi_A(r)}{\partial r}\vec{s}.\left(\vec{r}\times\vec{p_e}\right) = \zeta_A(r)\frac{\vec{s}.\vec{l}}{\hbar^2} \end{aligned} \tag{1.23}$$

où l'on a fait apparaitre la quantité de mouvement puis le moment cinétique de l'électron. La constante de couplage spin-orbite ζ_A est alors définie par :

$$\zeta_A(r) = -\frac{eg_e\hbar^2}{4m_e^2c^2}\left(\frac{1}{r}\frac{\partial \Phi_A(r)}{\partial r}\right) \tag{1.24}$$

Évaluons la constante de couplage dans le cas de métaux de transition de type $3d$, de sorte à avoir un ordre de grandeur. Pour un potentiel coulombien engendré par un noyau de charge $Z_A e$ (éventuellement réduite par un facteur d'écran) :

$$\Phi_A(r) = \frac{Z_A e}{4\pi\epsilon_0 r} \tag{1.25}$$

on obtient, avec $\mu_0\epsilon_0 c^2 = 1$ où μ_0 est la perméabilité magnétique du vide :

$$\zeta_A(r) = \frac{e^2 g_e\hbar^2}{16\pi\epsilon_0 m_e^2 c^2}\frac{Z_A}{r^3} = \frac{\mu_0}{4\pi}\mu_B^2 g_e\frac{Z_A}{r^3} \tag{1.26}$$

Dans le cas poly-électronique, l'opérateur spin-orbite sera approché par :

$$\hat{H}^{(0,1)}_{S-L}.\vec{\mu}_e = \sum_A\sum_i \zeta_A(r_{Ai})\frac{\vec{s}_i.\vec{l}_i}{\hbar^2} \tag{1.27}$$

où r_{Ai} est la distance électron-noyau. C'est ce type d'opérateur qui est utilisé lors des calculs *ab initio*, chaque terme dépend de l'orbitale électronique considérée et donne alors un résultat précis du couplage spin-orbite.

Afin d'évaluer l'interaction spin-orbite, on va définir une constante ζ effective et on utilise l'approximation suivante pour le rayon des électrons périphériques associé à l'orbitale des nombres quantiques n et l :

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{2}{n^3(l+1)(2l+1)}\left(\frac{Z_{eff}}{a_0}\right)^3 \tag{1.28}$$

où l'on introduit la charge efficace vu par l'électron Z_{eff} autour d'un ion ou atome et le rayon de Bohr a_0 tel que :

$$a_0 = \frac{\hbar^2\epsilon_0}{\pi m_e e^2} \tag{1.29}$$

d'où pour les métaux de transition de type $3d$, pour un électron de type d ($n = 3$ et $l = 2$), on a

$$\left\langle \frac{Z_a}{r^3} \right\rangle = \frac{2}{405} \frac{Z_{eff}^4}{a_0^3} \tag{1.30}$$

D'où, avec (1.26) on peut déduire une constante spin-orbite effective :

$$\begin{aligned} \langle \zeta_{eff} \rangle &= \frac{\mu_0}{4\pi} \mu_B^2 g_e \frac{2}{405} \frac{Z_{eff}^4}{a_0^3} \\ &= 0.00289\, Z_{eff}^4 \text{ (en cm}^{-1}) \end{aligned} \tag{1.31}$$

En calculant la charge effective et le rayon moyen des électrons appartenant à chaque couche, il est possible d'estimer la constante de couplage effective. Une évaluation plus précise de cette constante est donnée dans le tableau 1.1 pour différents ions de métaux de transition.

	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
Ions (III)	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}					
ζ cm^{-1}	154	209	276	360					
Ions (II)	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
ζ cm^{-1}	79	120	168	236	335	404	528	644	829

TABLE 1.1 – Paramètre spin-orbite pour quelque ions de métaux de transition [18]

Dans les logiciels de calcul utilisés, une autre méthode de calcul du couplage spin-orbite et éventuellement spin-spin est utilisée et sera développée dans la partie 1.2 dédiée aux méthodes.

1.1.1.6 Paramètres magnétiques électroniques

Reprenons l'énergie associée à l'hamiltonien magnétique comprenant le spin de l'électron de l'équation (1.4). Son développement donne :

$$\mathcal{E}(\vec{B}, \vec{\mu}_e) = \mathcal{E}_0 - \left\langle \vec{\gamma}.\vec{B} \right\rangle_\Psi - \left\langle \frac{1}{2} \vec{B}.\overline{\overline{\kappa}}.\vec{B} \right\rangle_\Psi + \left\langle \vec{\mu}_e.\overline{\overline{\Delta g}}.\vec{B} \right\rangle_\Psi - \left\langle \frac{1}{2} \vec{\mu}_e.\overline{\overline{D}}.\vec{\mu}_e \right\rangle_\Psi \tag{1.32}$$

où le symbole $\langle\ \rangle_\Psi$ indique l'obtention de l'énergie par l'application de l'opérateur sur la fonction d'onde de l'état fondamental.

Moment magnétique permanent
Par identification, on déduit $\mathcal{E}_0 = \langle \Psi_0 | H^{(0,0)} | \Psi_0 \rangle$; ainsi que $\vec{\gamma}$, le moment magnétique permanent du système tel que :

$$\begin{aligned} \mathcal{E}_{10} + \mathcal{E}'_{11} &= \langle \Psi_0 | -\vec{\gamma}.\vec{B} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \vec{H}_{L-B}^{(1,0)}.\vec{B} + \vec{\mu}_e.\overline{\overline{H}}_{S-B}^{(1,1)}.\vec{B} | \Psi_0 \rangle \\ &= \frac{\mu_B}{\hbar} \langle \Psi_0 | \vec{L} + g_e \vec{S} | \Psi_0 \rangle .\vec{B} \end{aligned} \tag{1.33}$$

où l'énergie $\mathcal{E}'_{11}$ désigne l'une des contributions linéaire en champ et en moment magnétique de spin, l'autre contribution $\mathcal{E}''_{11}$ telle que $\mathcal{E}_{11} = \mathcal{E}'_{11} + \mathcal{E}''_{11}$ sera abordée par la suite.
On en déduit le facteur γ :

$$\vec{\gamma} = -\frac{\mu_B}{\hbar}\left(\vec{L} + g_e\vec{S}\right) \tag{1.34}$$

Susceptibilité magnétique
Pour le tenseur de susceptibilité magnétique réduite κ, il est donnée par :

$$\begin{aligned}
\mathcal{E}_{20} &= \left\langle -\frac{1}{2}\vec{B}.\overline{\overline{\kappa}}.\vec{B}\right\rangle_\Psi \\
&= \langle\Psi_0|\,\vec{B}.\overline{\overline{H}}^{(2,0)}.\vec{B}\,|\Psi_0\rangle + \langle\Psi_0|\,\vec{H}^{(1,0)}.\vec{B}\left|\vec{\Psi}^{(1,0)}.\vec{B}\right\rangle \\
&= \sum_{a,b} B_a B_b \left(\langle\Psi_0|\,H_{ab}^{(2,0)}\,|\Psi_0\rangle + \langle\Psi_0|\,H_a^{(1,0)}\left|\Psi_b^{(1,0)}\right\rangle\right)
\end{aligned} \tag{1.35}$$

L'expression des fonctions d'onde $\Psi_a^{(1,0)}$ et $\Psi_a^{(0,1)}$ suivant la théorie des perturbations (*sum over states*) pour la composante selon a est donnée, à l'aide de (1.12) et (1.27) par :

$$\begin{aligned}
\Psi_a^{(1,0)}B_a &= -\sum_{K=1}^{\infty}\frac{\langle\Psi_K|\,H_a^{(1,0)}B_a\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0}\Psi_K \\
&= -\frac{\mu_b}{\hbar}\sum_{K=1}^{\infty}\frac{\langle\Psi_K|\sum_i \hat{l}_{ia}B_a\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0}\Psi_K
\end{aligned} \tag{1.36}$$

$$\begin{aligned}
\Psi_a^{(0,1)}S_a &= -\sum_{K=1}^{\infty}\frac{\langle\Psi_K|\,H_a^{(0,1)}S_a\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0}\Psi_K \\
&= -\frac{1}{\hbar^2}\sum_{K=1}^{\infty}\frac{\langle\Psi_K|\sum_i\sum_A \zeta_A(r_{Ai})\hat{l}_{ia}\hat{s}_{ia}\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0}\Psi_K
\end{aligned} \tag{1.37}$$

où Ψ_K est la fonction d'onde du $K^{ième}$ état excité d'énergie $\mathcal{E}_K$.

On a alors, en utilisant le résultat de l'équation (1.14) :

$$\begin{aligned}
\left\langle -\frac{1}{2}\kappa_{ab}\right\rangle_\Psi &= -\frac{e^2}{4m_e}\langle\Psi_0|\sum_i^n(\vec{r}_i)^2\delta_{ab} - (\vec{r}_i)_a(\vec{r}_i)_b\,|\Psi_0\rangle \\
&\quad -\frac{\mu_b^2}{\hbar^2}\sum_{K=1}^{\infty}\frac{\langle\Psi_0|\sum_i l_{ia}\,|\Psi_K\rangle\langle\Psi_K|\sum_i l_{ib}\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0}
\end{aligned} \tag{1.38}$$

Les deux termes de l'équation (1.38) représentent respectivement les contributions diamagnétique et paramagnétique de la susceptibilité, avec :

$$\left\langle -\frac{1}{2}\kappa_{ab}^{para}\right\rangle_\Psi = -\frac{\mu_b^2}{\hbar^2}\sum_{K=1}^{\infty}\frac{\langle\Psi_0|\,L_a\,|\Psi_K\rangle\langle\Psi_K|\,L_b\,|\Psi_0\rangle}{\mathcal{E}_K - \mathcal{E}_0} \tag{1.39}$$

Le paramètre κ est directement relié à la susceptibilité molaire $\overline{\overline{\chi}}_{mol}$ (en unité SI) par :

$$\overline{\overline{\chi}}_{mol} = N_A \mu_0 \overline{\overline{\kappa}} \tag{1.40}$$

avec N_A le nombre d'Avogadro.
La susceptibilité magnétique, de même que l'aimantation sera mesurée expérimentalement et calculée numériquement par différentiation de l'aimantation en fonction du champ appliqué sur un complexe réel au cours de la partie 2.2.

Tenseur g

$\overline{\overline{\Delta g}}$ est le tenseur du rapport gyromagnétique (par effet différentiel du spin de l'électron), dénommé par la suite tenseur g, tel que $\overline{\overline{g}} = g_e + \overline{\overline{\Delta g}}$. Le terme Zeeman de spin $\overline{\overline{H}}^{(1,1)}$ ayant été inclus dans γ, par identification avec (1.32), on obtient :

$$\begin{aligned} \mathcal{E}''_{11} &= \left\langle \vec{\mu}_e . \overline{\overline{\Delta g}} \vec{B} \right\rangle_\Psi \\ &= \langle \Psi_0 | \vec{H}^{(0,1)} . \vec{\mu}_e \left| \vec{\Psi}^{(1,0)} . \vec{B} \right\rangle + \langle \Psi_0 | \vec{H}^{(1,0)} . \vec{B} \left| \vec{\Psi}^{(0,1)} . \vec{\mu}_e \right\rangle \end{aligned} \tag{1.41}$$

En utilisant l'expression du moment magnétique $\vec{\mu}_e$, on a, d'une part :

$$\mathcal{E}''_{11} = \left\langle -\frac{g_e \mu_B}{\hbar} \vec{S} . \overline{\overline{\Delta g}} . \vec{B} \right\rangle_\Psi = \left\langle -\frac{g_e \mu_B}{\hbar} \sum_{a,b} S_a \Delta g_{ab} B_b \right\rangle_\Psi \tag{1.42}$$

ainsi que son analogue en échangeant le champ et le moment magnétique, et d'autre part :

$$\begin{aligned} \mathcal{E}''_{11} &= -\frac{g_e \mu_B}{\hbar} \left[\langle \Psi_0 | \vec{H}^{(0,1)} . \vec{S} \left| \vec{\Psi}^{(1,0)} . \vec{B} \right\rangle + \langle \Psi_0 | \vec{H}^{(1,0)} . \vec{B} \left| \vec{\Psi}^{(0,1)} . \vec{S} \right\rangle \right] \qquad (1.43) \\ &= -\frac{g_e \mu_B}{\hbar} \sum_{a,b} \left[\langle \Psi_0 | \sum_i H_{ia}^{(0,1)} \hat{s}_{ia} \left| \Psi_b^{(1,0)} B_b \right\rangle + \langle \Psi_0 | H_a^{(1,0)} B_a \left| \sum_i \Psi_{i,b}^{(0,1)} \hat{s}_{ib} \right\rangle \right] \end{aligned}$$

on en déduit :

$$\langle \Delta g_{ab} \rangle_\Psi = S_a^{-1} \langle \Psi_0 | \sum_i H_{ia}^{(0,1)} \hat{s}_{ia} \left| \Psi_b^{(1,0)} \right\rangle + S_b^{-1} \langle \Psi_0 | H_a^{(1,0)} \left| \sum_i \Psi_{i,b}^{(0,1)} \hat{s}_{ib} \right\rangle \tag{1.44}$$

à l'aide de (1.37) et (1.36), il vient :

$$\begin{aligned} \langle \Delta g_{ab} \rangle_\Psi = \sum_{K=1}^{\infty} \frac{-\hbar^{-2}}{\mathcal{E}_K - \mathcal{E}_0} \Big[& S_a^{-1} \langle \Psi_0 | \textstyle\sum_i \sum_A \zeta_A(r_{Ai}) \hat{l}_{ia} \hat{s}_{ia} | \Psi_K \rangle \langle \Psi_K | \sum_i l_{ib} | \Psi_0 \rangle \\ & + S_b^{-1} \langle \Psi_0 | \textstyle\sum_i l_{ia} | \sum_i \Psi_K \rangle \langle \Psi_K | \sum_i \sum_A \zeta_A(r_{Ai}) \hat{l}_{ib} \hat{s}_{ib} | \Psi_0 \rangle \Big] \end{aligned} \tag{1.45}$$

Les valeurs propres du tenseur g seront abordées et mesurées pour différents complexes réels aux parties 2.1 et 2.2.

Tenseur de couplage spin-spin électronique

$\overline{\overline{D}}$ est le tenseur de couplage spin-spin électronique et s'écrit :

$$\begin{aligned}
\mathcal{E}_{02} = & \left\langle -\tfrac{1}{2}\vec{\mu}_e.\overline{\overline{D}}.\vec{\mu}_e \right\rangle_\Psi & = \langle \Psi_0 | \vec{H}^{(0,1)}.\vec{\mu}_e \left| \vec{\Psi}^{(0,1)}.\vec{\mu}_e \right\rangle \\
= & \left\langle -\tfrac{\mu_B^2 g_e^2}{2\hbar^2}\ \vec{S}.\overline{\overline{D}}.\vec{S} \right\rangle_\Psi & = \frac{\mu_B^2 g_e^2}{\hbar^2} \langle \Psi_0 | \vec{H}^{(0,1)}.\vec{S} \left| \vec{\Psi}^{(0,1)}.\vec{S} \right\rangle \\
= & \left\langle -\tfrac{\mu_B^2 g_e^2}{2\hbar^2} \sum_{a,b} \hat{S}_a D_{ab} \hat{S}_b \right\rangle_\Psi & = \frac{\mu_B^2 g_e^2}{\hbar^2} \sum_{a,b} \sum_{i,j} \langle \Psi_0 | \hat{H}_{ia}^{(0,1)} \hat{s}_{i,a} \left| \Psi_b^{(0,1)} \hat{s}_{jb} \right\rangle
\end{aligned} \tag{1.46}$$

Par comparaison, et avec (1.37), il vient :

$$\begin{aligned}
\left\langle -\frac{1}{2}\hat{S}_a D_{ab} \hat{S}_b \right\rangle_\Psi &= \sum_{i,j} \langle \Psi_0 | \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} | \Psi_b \hat{s}_{jb} \rangle \\
&= \frac{-\hbar^{-2}}{\mathcal{E}_K - \mathcal{E}_0} \sum_{K=1}^{\infty} \sum_{i,j} \sum_{A} \langle \Psi_0 | \zeta_A(r_{Ai}) \hat{l}_{ia} \hat{s}_{ia} | \Psi_K \rangle \langle \Psi_K | \zeta_A(r_{Aj}) \hat{l}_{jb} \hat{s}_{jb} | \Psi_0 \rangle
\end{aligned} \tag{1.47}$$

Ce dernier tenseur sera l'étude principale de cette thèse, il ne dépend pas du champ magnétique extérieur et peut entrainer une levée de dégénérescence des différents états spin-orbites. Cet effet sur la structure fine est qualifié de *Zero-Field Splitting* (ZFS) et est modélisé par un hamiltonien de spin.

Au du chapitre 3, consacré aux composés binucléaires, une distinction sera effectuée entre les termes locaux propres à un centre métallique ou d'échange, ainsi que par rapport à leur caractère isotrope ou anisotrope, symétrique ou antisymétrique. De plus, d'autres termes d'ordre plus élevé en spin pourront être introduits.

1.1.2 Hamiltonien de spin pour les systèmes mononucléaires

1.1.2.1 Tenseur D

Dans les systèmes mononucléaires, quand l'état fondamental de spin S a une multiplicité de spin supérieure à deux, il est couplé par effet spin-orbite aux états excités [19], il y a alors, si la symétrie du système n'est pas trop grande, une levée de dégénérescence des composantes M_S. Dans ce cas, l'état fondamental peut être représenté par ses composantes de spin $|S, M_S\rangle$ et l'hamiltonien décrivant ce phénomène est issu de (1.46), (après suppression des constantes) :

$$\hat{H}_{ZFS}^{(0,2)} = \frac{1}{\hbar^2} \vec{S}.\overline{\overline{D}}.\vec{S} \tag{1.48}$$

Il fait intervenir un tenseur réel de rang deux symétrique et de dimension trois soit six paramètres :

$$\hat{H}_{ZFS}^{(0,2)} = \frac{1}{\hbar^2} \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} . \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{pmatrix} . \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} \tag{1.49}$$

Par la suite, ce tenseur est diagonalisé selon $\overline{\overline{D}}^{diag} = P^{-1}.\overline{\overline{D}}.P$ où P^{-1} est formé des vecteurs propres. C'est la matrice de passage d'une base quelconque à la base dite magnétique et $\overline{\overline{D}}^{diag}$ est la matrice diagonale formée des valeurs propres D_{XX}, D_{YY}, D_{ZZ}. Par convention [16], on définit le paramètre axial D de ZFS associé à l'axe magnétique principal Z et le paramètre rhombique E tel que $|D| > 3E$ et $E \geq 0$ avec :

$$D = D_{ZZ} - \frac{1}{2}(D_{XX} + D_{YY}) \tag{1.50}$$

$$E = \frac{1}{2}(D_{XX} - D_{YY}) \tag{1.51}$$

On a alors $\hat{H}_{ZFS} = \hbar^{-2}\left\{D[\hat{S}_z^2 - S(S+1)/3] + E(\hat{S}_x^2 - \hat{S}_y^2)\right\}$.

Dans le cas d'un état fondamental triplement dégénéré pour un spin $S = 1$, tel qu'un complexe mononucléaire de nickel Ni(II), cas que nous utiliserons dans les parties 2.1 et 2.2, l'hamiltonien (1.49) devient, dans une base quelconque :

$$\begin{array}{c|ccc} H_{ZFS} & |1,-1\rangle & |1,0\rangle & |1,1\rangle \\ \hline \langle 1,-1| & \frac{1}{2}(D_{xx}+D_{yy})+D_{zz} & -\frac{\sqrt{2}}{2}(D_{xz}+iD_{yz}) & \frac{1}{2}(D_{xx}-D_{yy}+2iD_{xy}) \\ \langle 1,0| & -\frac{\sqrt{2}}{2}(D_{xz}-iD_{yz}) & D_{xx}+D_{yy} & \frac{\sqrt{2}}{2}(D_{xz}+iD_{yz}) \\ \langle 1,1| & \frac{1}{2}(D_{xx}-D_{yy}-2iD_{xy}) & \frac{\sqrt{2}}{2}(D_{xz}-iD_{yz}) & \frac{1}{2}(D_{xx}+D_{yy})+D_{zz} \end{array} \tag{1.52}$$

Cet hamiltonien s'écrit, après rotation dans le système d'axes magnétiques tel que D soit diagonal :

$$\begin{array}{c|ccc} H_{ZFS} & |1,-1\rangle & |1,0\rangle & |1,1\rangle \\ \hline \langle 1,-1| & \frac{1}{2}(D_{XX}+D_{YY})+D_{ZZ} & 0 & \frac{1}{2}(D_{XX}-D_{YY}) \\ \langle 1,0| & 0 & D_{XX}+D_{YY} & 0 \\ \langle 1,1| & \frac{1}{2}(D_{XX}-D_{YY}) & 0 & \frac{1}{2}(D_{XX}+D_{YY})+D_{ZZ} \end{array} \tag{1.53}$$

En supprimant la trace et avec les conventions et définitions (1.50) et (1.51), on a :

$$\begin{array}{c|ccc} H_{ZFS} & |1,-1\rangle & |1,0\rangle & |1,1\rangle \\ \hline \langle 1,-1| & \frac{1}{3}D & 0 & E \\ \langle 1,0| & 0 & -\frac{2}{3}D & 0 \\ \langle 1,1| & E & 0 & \frac{1}{3}D \end{array} \tag{1.54}$$

De manière analogue, pour un état fondamental de dégénérescence quadruple avec $S = 3/2$, tel qu'un mononucléaire de cobalt Co(II) que nous aborderons dans la partie 2.1, l'hamiltonien dans une base quelconque s'écrit :

$$\begin{array}{c|cccc} H_{ZFS} & \left|\frac{3}{2},-\frac{3}{2}\right\rangle & \left|\frac{3}{2},-\frac{1}{2}\right\rangle & \left|\frac{3}{2},\frac{1}{2}\right\rangle & \left|\frac{3}{2},\frac{3}{2}\right\rangle \\ \hline \left\langle\frac{3}{2},-\frac{3}{2}\right| & \frac{3}{4}(D_{xx}+D_{yy})+\frac{9}{4}D_{zz} & -\sqrt{3}(D_{xz}+iD_{yz}) & \frac{3}{2}(D_{xx}-D_{yy}+2iD_{xy}) & 0 \\ \left\langle\frac{3}{2},-\frac{1}{2}\right| & -\sqrt{3}(D_{xz}-iD_{yz}) & \frac{7}{4}(D_{xx}+D_{yy})+\frac{1}{4}D_{zz} & 0 & \frac{\sqrt{3}}{2}(D_{xx}-D_{yy}+2iD_{xy}) \\ \left\langle\frac{3}{2},\frac{1}{2}\right| & -\frac{3}{2}(D_{xx}-D_{yy}-2iD_{xy}) & 0 & \frac{7}{4}(D_{xx}+D_{yy})+\frac{1}{4}D_{zz} & \sqrt{3}(D_{xz}+iD_{yz}) \\ \left\langle\frac{3}{2},\frac{3}{2}\right| & 0 & \frac{3}{2}(D_{xx}-D_{yy}-2iD_{xy}) & \sqrt{3}(D_{xz}-iD_{yz}) & \frac{3}{4}(D_{xx}+D_{yy})+\frac{3}{4}D_{zz} \end{array} \tag{1.55}$$

et avec le système d'axe magnétique et les paramètres D et E :

$$\begin{array}{c|cccc} H_{ZFS} & \left|\frac{3}{2},-\frac{3}{2}\right\rangle & \left|\frac{3}{2},-\frac{1}{2}\right\rangle & \left|\frac{3}{2},\frac{1}{2}\right\rangle & \left|\frac{3}{2},\frac{3}{2}\right\rangle \\ \hline \left\langle\frac{3}{2},-\frac{3}{2}\right| & D & 0 & \sqrt{3}E & 0 \\ \left\langle\frac{3}{2},-\frac{1}{2}\right| & 0 & -D & 0 & \sqrt{3}E \\ \left\langle\frac{3}{2},\frac{1}{2}\right| & \sqrt{3}E & 0 & -D & 0 \\ \left\langle\frac{3}{2},\frac{3}{2}\right| & 0 & \sqrt{3}E & 0 & D \end{array} \tag{1.56}$$

1.1.2.2 Opérateurs de Stevens

Un description du ZFS pour des systèmes dont l'état fondamental a un spin de $S = 1$ ou $S = 3/2$ avec les paramètres D et E est suffisante, seulement, pour un spin supérieur, il peut être utile d'introduire des opérateurs équivalents dits de Stevens [16, 18]. Ces opérateurs $\hat{O}$, à l'origine définis pour décrire la levée de dégénérescence liée au champ cristallin, ne dépendent que d'opérateurs de moment angulaire $\hat{J}$. De manière générique, le ZFS est alors représenté par l'hamiltonien suivant :

$$\hat{H}_{Stevens} = \sum_{k=0} \sum_{n=0}^{k} B_k^n \hat{O}_k^n \tag{1.57}$$

où B_k^n sont des constantes propres à chaque système et les opérateurs $\hat{O}_k^n$ sont des tenseurs sphériques de rang k de composantes n (avec $n \leq k \leq 2S$) telles que :

$$\hat{O}_0^0 = \frac{1}{\hbar^2} \hat{\vec{J}}^2 = J(J+1) \tag{1.58}$$

$$\hat{O}_2^0 = \frac{3}{\hbar^2} \hat{J}_z^2 - J(J+1) \tag{1.59}$$

$$\hat{O}_2^2 = \frac{1}{2\hbar^2}(\hat{J}_+^2 + \hat{J}_-^2) = \frac{1}{\hbar^2}(\hat{J}_x^2 - \hat{J}_y^2) \tag{1.60}$$

Pour des raisons de symétrie, seuls les termes de rang k pair contribuent pour les complexes mono-nucléaires. L'hamiltonien ZFS de l'équation (1.48) peut se réécrire en terme d'opérateurs de Stevens de rang deux tel que :

$$\hat{H}_{ZFS} = B_0^0 \hat{O}_0^0 + B_2^0 \hat{O}_2^0 + B_2^2 \hat{O}_2^2 \tag{1.61}$$

avec $D = 3B_2^0$ et $E = B_2^2$. Il en sera aussi fait mention au chapitre 3.

1.1.3 Aimantation et susceptibilité

Reprenons le développement de Taylor de l'énergie (1.32), à l'ordre un en champ magnétique. A l'aide des relations précédentes, il vient :

$$\begin{aligned} \mathcal{E}(\vec{B}, \vec{\mu}_e) &= \mathcal{E}_0 - \left\langle \vec{\gamma}.\vec{B} \right\rangle_\Psi + \left\langle \vec{\mu}_e.\overline{\overline{\Delta g}}\vec{B} \right\rangle_\Psi - \left\langle \frac{1}{2}\vec{\mu}_e.\overline{\overline{D}}\vec{\mu}_e \right\rangle_\Psi \\ &= \mathcal{E}_0 + \frac{\mu_B}{\hbar} \left\langle \vec{L} + \overline{\overline{g}}\vec{S} \right\rangle_\Psi .\vec{B} - \frac{\mu_B^2 g_e^2}{2\hbar^2} \left\langle \vec{S}.\overline{\overline{D}}\vec{S} \right\rangle_\Psi \end{aligned} \tag{1.62}$$

De manière analogue au ZFS, la matrice Zeeman de l'état fondamental sans dégénérescence orbitalaire est donnée pour le cas d'un spin $S = 1$, dans la base diagonalisant le tenseur $\overline{\overline{D}}$ par [19] :

H_{ZFS}	$\lvert 1,-1\rangle$	$\lvert 1,0\rangle$	$\lvert 1,1\rangle$
$\langle 1,-1\rvert$	$\frac{1}{3}D + \mu_B g_z B_z$	$\frac{\mu_B}{\sqrt{2}}(g_x B_x - i g_y B_y)$	E
$\langle 1,0\rvert$	$\frac{\mu_B}{\sqrt{2}}(g_x B_x + i g_y B_y)$	$-\frac{2}{3}D$	$\frac{\mu_B}{\sqrt{2}}(g_x B_x + i g_y B_y)$
$\langle 1,1\rvert$	E	$\frac{\mu_B}{\sqrt{2}}(g_x B_x - i g_y B_y)$	$\frac{1}{3}D + \mu_B g_z B_z$

(1.63)

Les valeurs propres de cette matrice (1.63) donnent les énergies des composantes dans le cas d'un champ de direction x, y ou z, en fonction des paramètres D et E (*cf.* tableau 1.2 et figures 1.1 et 1.2).

Direction de $\vec{B}$	Pour $E \neq 0$	Pour $E = 0$
z	$D \pm \sqrt{E^2 + (\mu_B g_z B_z)^2}$ 0	$D \pm \mu_B g_z B_z$ 0
x	$D + E$ $\frac{1}{2}(D-E) \pm \sqrt{\frac{1}{4}(D-E)^2 + (\mu_B g_x B_x)^2}$	D $\frac{1}{2}D \pm \sqrt{\frac{1}{4}D^2 + (\mu_B g_x B_x)^2}$
y	$D - E$ $\frac{1}{2}(D+E) \pm \sqrt{\frac{1}{4}(D+E)^2 + (\mu_B g_y B_y)^2}$	D $\frac{1}{2}D \pm \sqrt{\frac{1}{4}D^2 + (\mu_B g_y B_y)^2}$

TABLE 1.2 – Énergies des composantes d'un état fondamental de spin $S = 1$ avec champ magnétique

Une fois les énergies des composantes obtenues, on définit la fonction de partition du système comme

$$Z_a(B,T) = \sum_i \exp\left(-\frac{\mathcal{E}_{i,a}}{kT}\right) \tag{1.64}$$

où k est la constante de Boltzman, on notera $\beta = (kT)^{-1}$ la température thermodynamique et N_A le nombre d'Avogadro. L'aimantation selon la direction $a(= x,\, y\, ou\, z)$ se calcule alors par :

$$\begin{aligned} \mathcal{M}_a(B,\beta) &= N_A \frac{\partial \ln Z_a}{\partial B_a} \\ &= \frac{N_A}{\sum_i \exp\left(-\beta \mathcal{E}_{i,a}\right)} \sum_i \left(-\frac{\partial \mathcal{E}_{i,a}}{\partial B_a}\right) \exp\left(-\beta \mathcal{E}_{i,a}\right) \end{aligned} \tag{1.65}$$

Ce type de calcul de l'aimantation en fonction de l'énergie des composantes de spin de chaque état est programmé dans les logiciels de calcul [20] et sera appliqué dans le cas d'un complexe réel dans la partie 2.2, les résultats obtenus seront comparés aux mesures expérimentales. Dès lors, pour $S = 1$, on a, en notant $G_a = \mu_B g_a B_a$, ch et sh, respectivement, le cosinus et le sinus hyperbolique :

$$\mathcal{M}_z = 2N_a \mu_B g_z \frac{G_z e^{-\beta D} sh(\beta\sqrt{E^2 + G_z^2})}{1 + 2e^{-\beta D} ch\left(\beta\sqrt{E^2 + G_z^2}\right)} \tag{1.66}$$

$$\mathcal{M}_x = 2N_a \mu_B g_x \frac{G_x e^{\frac{\beta}{2}(D-E)} sh\left(\beta\sqrt{\frac{1}{4}(D-E)^2 + G_x^2}\right)}{1 + 2e^{\frac{\beta}{2}(D-E)} ch\left(\beta\sqrt{\frac{1}{4}(D-E)^2 + G_x^2}\right)} \tag{1.67}$$

$$\mathcal{M}_y = 2N_a \mu_B g_y \frac{G_y e^{\frac{\beta}{2}(D+E)} sh\left(\beta\sqrt{\frac{1}{4}(D+E)^2 + G_y^2}\right)}{1 + 2e^{\frac{\beta}{2}(D+E)} ch\left(\beta\sqrt{\frac{1}{4}(D+E)^2 + G_y^2}\right)} \tag{1.68}$$

et dans la limite où E est nul :

$$\mathcal{M}_z = 2N_a\mu_B g_z \frac{G_z e^{-\beta D} sh(\beta G_z)}{1+2e^{-\beta D} ch(\beta G_z)} \tag{1.69}$$

$$\mathcal{M}_x = 2N_a\mu_B g_x \frac{G_x e^{\frac{\beta D}{2}} sh\left(\beta\sqrt{\frac{1}{4}D^2+G_x^2}\right)}{1+2e^{\frac{\beta D}{2}} ch\left(\beta\sqrt{\frac{1}{4}D^2+G_x^2}\right)} \tag{1.70}$$

$$\mathcal{M}_y = 2N_a\mu_B g_y \frac{G_y e^{\frac{\beta D}{2}} sh\left(\beta\sqrt{\frac{1}{4}D^2+G_y^2}\right)}{1+2e^{\frac{\beta D}{2}} ch\left(\beta\sqrt{\frac{1}{4}D^2+G_y^2}\right)} \ . \tag{1.71}$$

Enfin, pour la susceptibilité magnétique selon la direction a, on part de :

$$\chi_a = N_A kT \frac{\partial^2 lnZ_a}{\partial B_a^2} = \frac{\partial \mathcal{M}_a}{\partial B_a} \ . \tag{1.72}$$

En vue de simplifier l'aimantation (1.65), reprenons le développement de l'énergie (1.4) à l'ordre deux en fonction du champ, on a :

$$\begin{aligned} \mathcal{E}(\vec{B}) &= \mathcal{E}_0 + \mathcal{E}_{10} + \mathcal{E}_{20} + \mathcal{E}_{01} + \mathcal{E}_{11} + \mathcal{E}_{02} \\ &= \mathcal{E}^{(0)} + \mathcal{E}^{(1)}B + \mathcal{E}^{(2)}B^2 \ . \end{aligned} \tag{1.73}$$

en indiquant en exposant, entre parenthèses l'ordre de dépendance en champ magnétique. Une approximation de l'exponentielle de $\mathcal{E}(\vec{B})$ à l'ordre un donne :

$$\exp(-\beta\mathcal{E}) = \exp(-\beta\mathcal{E}^{(0)})(1-\beta\mathcal{E}^{(1)}B) \tag{1.74}$$

et pour l'ordre deux de la dérivée de $\mathcal{E}(\vec{B})$:

$$\frac{\partial \mathcal{E}}{\partial B} = \mathcal{E}^{(1)} + \mathcal{E}^{(2)}B \tag{1.75}$$

d'où (1.65) devient :

$$\mathcal{M}_a(B,\beta) = N_A \frac{\sum_i -\left(\mathcal{E}_{i,a}^{(1)} + \mathcal{E}_{i,a}^{(2)}B_a\right)(1-\beta\mathcal{E}_{i,a}^{(1)}B_a)\exp\left(-\beta\mathcal{E}_i^{(0)}\right)}{\sum_i (1-\beta\mathcal{E}_{i,a}^{(1)}B_a)\exp\left(-\beta\mathcal{E}_i^{(0)}\right)} \tag{1.76}$$

et la susceptibilité se met sous la forme de la formule de Van Vleck :

$$\chi_a = \frac{N_A \sum_i \left(\beta(\mathcal{E}_{i,a}^{(1)})^2 - 2\mathcal{E}_{i,a}^{(2)}\right)\exp\left(-\beta\mathcal{E}_i^{(0)}\right)}{\sum_i \exp\left(-\beta\mathcal{E}_i^{(0)}\right)} \tag{1.77}$$

Pour $S=1$, avec $E=0$ et $g_x=g_y$, à partir des valeurs du tableau 1.2, on a $\mathcal{E}_{ix}=\mathcal{E}_{iy}$ et on déduit le tableau (1.78).

M_s	$\mathcal{E}_i^{(0)}$	$\mathcal{E}_{ix}^{(1)}$	$\mathcal{E}_{iz}^{(1)}$	$\mathcal{E}_{ix}^{(2)}$	$\mathcal{E}_{iz}^{(2)}$
+1	D	0	$\mu_B g_z$	$\mu_B^2 g_x^2/D$	0
-1	D	0	$-\mu_B g_z$	0	0
0	0	0	0	$-\mu_B^2 g_x^2/D$	0

(1.78)

En appliquant ces énergies dans l'équation (1.77), on déduit les susceptibilités en fonction de la direction du champ :

$$\chi_z = 2N_A\beta(\mu_B g_z)^2 \frac{\exp(-\beta D)}{1+2\exp(-\beta D)} \tag{1.79}$$

$$\chi_x = \frac{2N_A(\mu_B g_x)^2}{D} \frac{1-\exp(-\beta D)}{1+2\exp(-\beta D)} \tag{1.80}$$

La variation de l'énergie des sous-niveaux $|M_S = 0, \pm 1\rangle$ de l'état fondamental en fonction d'un champ appliqué (tableau (1.78) est représentée sur les figures 1.1 et 1.2 dans le cas où D est négatif pour un champ magnétique parallèle ou perpendiculaire à l'axe principal d'aimantation.

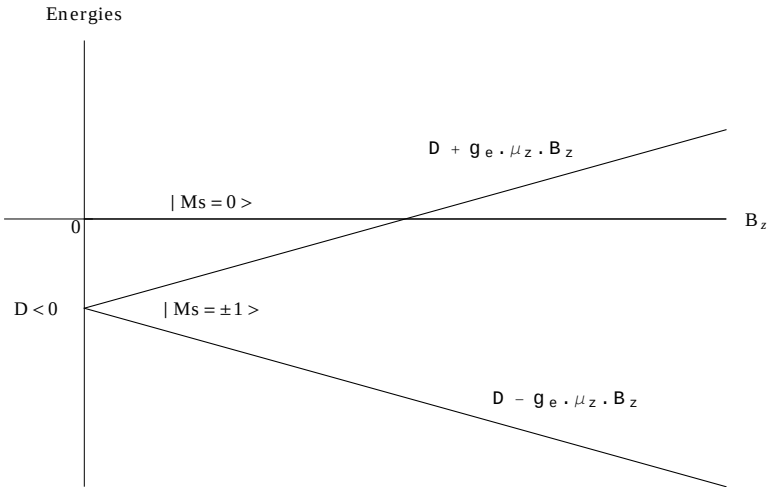

FIGURE 1.1 – Énergies des sous-niveaux $|M_S = 0, \pm 1\rangle$ de l'état fondamental en fonction d'un champ appliqué (B_z), parallèle à l'axe principal d'aimantation, pour D négatif

Les figures 1.1 et 1.2 permettent aussi de comprendre l'importance des axes magnétiques. En effet, dans le système d'axes magnétiques, pour un paramètre D négatif, le principal axe magnétique est choisi de sorte à définir D et E selon (1.50), (1.51) et $|D| > 3E > 0$ selon la direction Z par convention ; l'énergie des composantes $M_S = \pm 1$ varie linéairement en fonction de champ s'il est appliqué parallèlement à l'axe Z alors qu'elle varie de façon quadratique s'il est appliqué perpendiculaire à l'axe Z. L'axe Z est, dans ce cas, appelé "axe de facile aimantation" tandis que le plan perpendiculaire est qualifié de "plan de difficile aimantation" et contient éventuellement un "axe de difficile aimantation" si E est non nul.

Au contraire, pour D positif (figures 1.3 et 1.4), le plan perpendiculaire à l'axe Z est appelé "plan de facile aimantation" et contient éventuellement un "axe de facile aimantation" si E est non nul. Dans ce cas, pour de faibles valeurs du champ magnétique et quelque soit sa direction, l'énergie de la composante $M_S = 0$ de l'état fondamental est inférieure à celle des composantes $M_S = \pm 1$, il faut appliquer un champ intense pour qu'une des composantes $M_S = \pm 1$ soit la plus faible en énergie, en conséquence, l'axe Z est qualifié d'"axe de difficile aimantation".

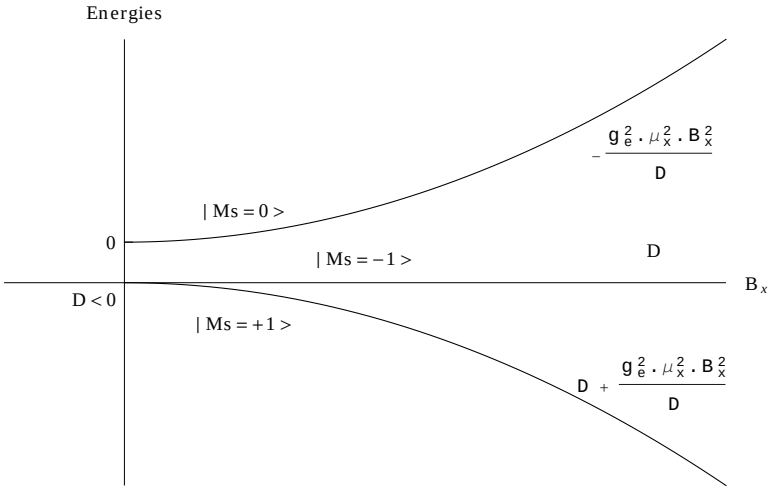

FIGURE 1.2 – Énergies des sous-niveaux $|M_S = 0, \pm 1\rangle$ de l'état fondamental en fonction d'un champ appliqué (B_x), perpendiculaire à l'axe principal d'aimantation, pour D négatif

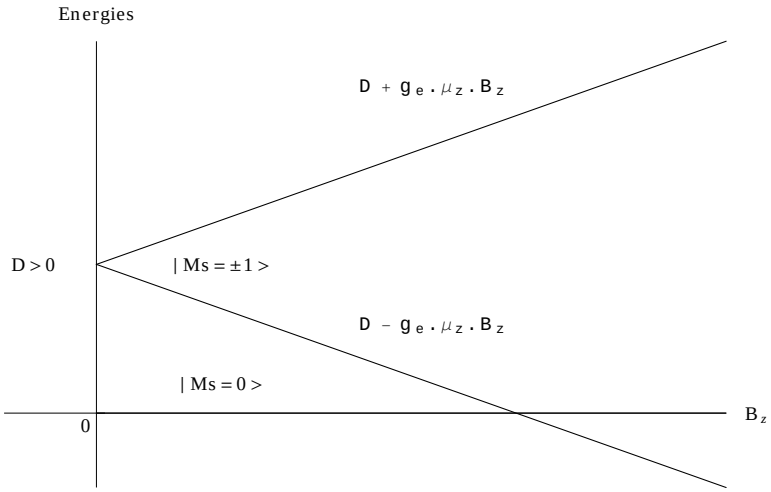

FIGURE 1.3 – Énergies des sous-niveaux $|M_S = 0, \pm 1\rangle$ de l'état fondamental en fonction d'un champ appliqué (B_z), parallèle à l'axe principal d'aimantation, pour D positif

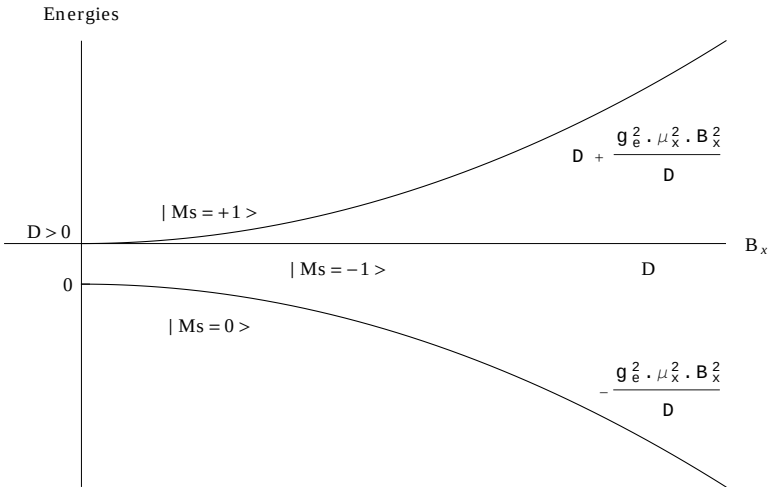

FIGURE 1.4 – Énergies des sous-niveaux $|M_S = 0, \pm 1\rangle$ de l'état fondamental en fonction d'un champ appliqué (B_x), perpendiculaire à l'axe principal d'aimantation, pour D positif

On dispose désormais des outils nécessaires pour l'étude du magnétisme moléculaire, que ce soit en champ nul, avec les paramètres de ZFS lié à $\overline{\overline{D}}$, ou en champ non nul avec l'aimantation $\vec{M}$ et la susceptibilité magnétique χ.

1.2 Méthodologie

1.2.1 Approche générale de la méthodologie employée

Pour une étude théorique du magnétisme dans les complexes mono ou poly-nucléaire, différentes approches sont possibles. De manière générale, nous partons d'une structure géométrique d'un complexe et obtenons par le calcul numérique soit la densité électronique (méthode issue de la "*Density Functionnel Theory*" : DFT), soit la fonction d'onde (méthode "*Wave Function Theory*" : WFT) [21–23] de l'état fondamental et des premiers états excités ainsi que leurs énergies. A partir de cela, les paramètres associés au ZFS, à l'aimantation, à la susceptibilité ou autres peuvent être approchés comme cela a été présenté dans la partie précédente.

Comme les propriétés magnétiques d'un complexe ont une forte sensibilité à la structure géométrique, il convient, pour obtenir des résultats théoriques en adéquation avec les mesures expérimentales, de reproduire le plus fidèlement possible cette dernière. Pour ce faire, hormis dans le cas de composés modèles tels qu'employés au chapitre 3, le point de départ est une structure cristallographique issue d'une détermination par rayon X, à l'exception du cas du complexe avec effet Jahn-Teller (*cf.* partie 2.2) où il est nécessaire de réaliser une optimisation de géométrie.

L'objet de cette thèse tient essentiellement à l'extraction des paramètres de ZFS ainsi que des axes magnétiques qui sont déterminés par une méthode de type fonction d'onde. La DFT n'est utilisée que pour obtenir une structure géométrique quand celle-ci ne peut pas être obtenue expérimentalement. La première étape de calcul donne, de manière variationnelle, les fonctions d'onde, indépendantes du couplage spin-orbite, et les énergies pour chaque état fondamental et excités. Puis, un éventuel traitement de la corrélation basé sur ces orbitales permet de corriger la valeurs des énergies. Ensuite le couplage spin-orbite (SOC) et éventuellement le couplage spin-spin (SSC) sont ajoutés et permettent de reconstruire les différents états.

1.2.2 Hartree-Fock et notion de corrélation

1.2.2.1 Méthode Hartree-Fock

Afin d'approcher les solutions de l'équation de Schrödinger $\hat{H}\Psi = \mathcal{E}\Psi$, différentes approches sont possibles et dans le cas d'une molécule comportant une cinquantaine d'atomes et les électrons associés, certaines approximations sont indispensables. A partir de l'équation (1.9), une première approximation consiste à prendre en compte le fait que le mouvement des électrons possède un temps caractéristique plus rapide que celui des noyaux à cause de leurs différences de masse. Il est alors possible de considérer que s'il y a un mouvement des noyaux, les électrons vont à chaque instant ajuster leurs positions moyennes, c'est l'approximation de Born-Oppenheimer. En conséquence, le terme cinétique nucléaire $\hat{T}_N$ de l'équation de Schrödinger peut être isolé, et la fonction d'onde peut se réécrire comme le produit d'un terme purement nucléaire et un terme dépendant de la position de toutes les charges. De plus, cette fonction d'onde Ψ peut être approximée par un produit de Hartree de fonction d'onde monoélectronique φ_i représentant les orbitales que l'on supposera orthonormées. Afin d'assurer le caractère anticommutatif de cette fonc-

tion, on utilisera un déterminant de Slater $\Psi = (Ne!)^{-1/2}\det(\varphi_1, \varphi_2, \cdots)$, on a alors une description monodéterminentale de la fonction d'onde. L'hamiltonien électronique peut désormais se décomposer en fonction du nombre d'électrons impliqués par opérateur :

$$\hat{H}_{el} = \hat{h}_0 + \sum_i \hat{h}_i + \sum_{i<j} \hat{g}_{ij} \ , \tag{1.81}$$

il contient un terme électrostatique purement nucléaire qui est constant dans le cas de noyaux fixes

$$\hat{h}_0 = \sum_{A<B}^{N} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} \ , \tag{1.82}$$

un terme mono-électronique

$$\hat{h}_i = -\frac{(\vec{\nabla}_i)^2}{2m_e} - \sum_A^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \tag{1.83}$$

et enfin un terme biélectronique

$$\hat{g}_{ij} = \frac{e^2}{4\pi\epsilon_0 r_{ij}} \ . \tag{1.84}$$

Exprimer en terme de déterminant de Slater, l'énergie des termes à un électron fait intervenir un opérateur qui ne peut affecter qu'un électron :

$$\langle\Psi| \sum_i \hat{h}_i |\Psi\rangle = \sum_i \langle\varphi_i| \hat{h} |\varphi_i\rangle \ , \tag{1.85}$$

les éléments de l'hamiltonien du terme à deux électrons sont non nuls lorsque l'opérateur ne modifie pas l'occupation des orbitales ou lorsqu'il échange deux d'entre elles, dans ce dernier cas, ce terme est alors affecté d'un signe moins pour assurer le caractère anticommutatif et justifie ainsi l'usage d'un déterminant. Il vient alors :

$$\begin{aligned}
\langle\Psi| \sum_{i<j} \hat{g}_{ij} |\Psi\rangle &= \sum_{i<j} \left(\langle\varphi_i\varphi_j| \hat{g} |\varphi_i\varphi_j\rangle - \langle\varphi_i\varphi_j| \hat{g} |\varphi_j\varphi_i\rangle\right) \\
&= \frac{1}{2}\sum_{i,j} \left(\langle\varphi_i\varphi_j| \hat{g} |\varphi_i\varphi_j\rangle - \langle\varphi_i\varphi_j| \hat{g} |\varphi_j\varphi_i\rangle\right) \\
&= \frac{1}{2}\sum_{i,j} \langle\varphi_i| \hat{J}_j - \hat{K}_j |\varphi_i\rangle
\end{aligned} \tag{1.86}$$

où $\langle\varphi_a\varphi_b| \hat{g} |\varphi_c\varphi_d\rangle$ représente l'intégrale sur les éléments de volume τ_i et τ_j relatifs aux électrons i et j

$$\langle\varphi_a\varphi_b| \hat{g} |\varphi_c\varphi_d\rangle = \int \varphi_a^*(i)\varphi_b^*(j)\frac{e^2}{4\pi\epsilon_0 r_{ij}}\varphi_c(i)\varphi_d(j)d\tau_i d\tau_j \tag{1.87}$$

On introduit les opérateurs de Coulomb $\hat{J}_j$ et d'échange $\hat{K}_j$ définis par :

$$\hat{J}_j f(1) = \left[\int \frac{e^2}{4\pi\epsilon_0 r_{ij}}\varphi_j^*(2)\varphi_j(2)d\tau_2\right] f(1) \tag{1.88}$$

$$\hat{K}_j f(1) = \left[\int \frac{e^2}{4\pi\epsilon_0 r_{ij}}\varphi_j^*(2)f(2)d\tau_2\right] \varphi_j(1) \ . \tag{1.89}$$

La fonction d'onde associée au système est obtenue en appliquant le principe variationnel à l'énergie exprimée en fonction des orbitales selon :

$$\mathcal{E}^{HF}[\Psi] = \min_{\Psi} \langle\Psi| \hat{H} |\Psi\rangle = \min_{\varphi_i} \sum_i \left(\langle\varphi_i| \hat{h} |\varphi_i\rangle + \frac{1}{2} \langle\varphi_i| \hat{J} - \hat{K} |\varphi_i\rangle \right) \ . \tag{1.90}$$

Il s'agit de minimiser l'énergie par un processus auto-cohérent (de type "Self-Consistent Field" : SCF) à l'aide d'itération sur les orbitales moléculaires définissant l'état fondamental. Considérons une variation infinitésimale en $\varphi_i + \delta\varphi_i$, au premier ordre de développement :

$$\begin{aligned} \delta^{(1)}\mathcal{E}^{HF}[\Psi] &= \sum_i \left(\langle\delta\varphi_i| \hat{h} |\varphi_i\rangle + \langle\delta\varphi_i| \hat{J} - \hat{K} |\varphi_i\rangle \right) + \text{h.c.} \\ &= \sum_i \langle\delta\varphi_i| \hat{F} |\varphi_i\rangle + \text{h.c.} \end{aligned} \tag{1.91}$$

où h.c. indique le terme hermitique conjugué, et avec l'opérateur de Fock donné par :

$$\hat{F} = \hat{h} + \hat{J} - \hat{K} \ , \tag{1.92}$$

pour avoir un minimum, il faut donc avoir $\langle\delta\varphi_i| \hat{F} |\varphi_i\rangle = 0$ et les équations d'Hartree-Fock (HF) s'écrivent pour les orbitales occupées :

$$\hat{F}\varphi_i = \epsilon_i\varphi_i \ , \tag{1.93}$$

il s'agit d'un jeu équations aux valeurs propres, comme l'équation de Schrödinger indépendante du temps mais à un seul électron, permettant de définir les orbitales moléculaires Hartree-Fock et leur énergie. Il est a noté que $\mathcal{E}^{HF} \neq \sum_i \epsilon_i$ mais

$$\mathcal{E}^{HF} = \sum_i \epsilon_i - \frac{1}{2} \sum_i \langle\varphi_i| \hat{F} |\varphi_i\rangle \ . \tag{1.94}$$

1.2.2.2 Notion de corrélation

La position d'un électron est, du fait de la répulsion électrostatique, dépendante de la position des autres électrons, on parle alors de corrélation électronique (corrélation de Coulomb) or l'utilisation du déterminant de Slater à pour conséquence l'absence de la corrélation de part l'écriture de la fonction d'onde comme produit de fonctions mono-électroniques. L'antisymétrisation de la fonction d'onde permet seulement d'assurer la corrélation de Fermi en assurant une probabilité nulle dans le cas de deux électrons de même spin de position $r_i = r_j$.
Le formalisme Hartree-Fock permet de définir l'énergie de corrélation comme la différence entre l'énergie exacte et l'énergie définie par (1.90) :

$$\mathcal{E}^{corr} = \mathcal{E}^{exact} - \mathcal{E}^{HF} \ . \tag{1.95}$$

L'erreur de corrélation ainsi définie se décompose en deux parties, la première correspond à l'approximation d'une fonction basée sur une seule configuration, dénommée corrélation

non-dynamique. En effet, une meilleure description de l'état fondamental serait obtenue en prenant en compte l'influence d'autres configurations de basses énergies qui tendent à se mélanger avec la configuration HF fondamentale. Dans le cas de molécules à couche électronique fermée, à la géométrie d'équilibre, cette approximation est justifiée mais elle engendre une erreur importante et la description du système doit être corrigée dans le cas de molécules à couche ouverte, proche d'un état de dissociation, dans un état excité et les complexes de métaux de transition qui sont justement les cas qui nous intéressent. La DFT que nous allons introduire par la suite (partie 1.2.3) souffre aussi de ces restrictions. Pour pallier à ce problème, une méthode multiconfigurationnelle est employée et décrite dans la partie ci-après (partie 1.2.4.1). La corrélation dynamique est liée à la difficulté à décrire proprement la fonction r_{ij}^{-1} quand r_{ij} tend vers zéro et à prendre en compte les effets dus à la relaxation des orbitales, à la polarisation électronique et de spin en fonction de l'occupation des orbitales environnantes. Pour corriger ces erreurs, une méthode perturbative à l'ordre deux est employée et développée dans la partie 1.2.4.2.

1.2.3 Théorie de la fonctionnelle densité DFT

La méthode de la fonctionnelle de la densité (DFT) cherche à décrire la structure électronique d'un système en utilisant la densité électronique ρ. La probabilité de trouver un électron dans un volume $d\vec{r}$ centré en $\vec{r}$ pour un système de n électrons est donnée par $\rho(\vec{r})d\vec{r}$ et la densité est définie par :

$$\rho(\vec{r}_1) = n \int |\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_n)|^2 ds_1 ds_2 d\vec{r}_2 \cdots ds_n d\vec{r}_n \tag{1.96}$$

avec la contrainte associée au fait que l'on a au total n électrons dans tout l'espace telle que :

$$\int \rho(\vec{r})d\vec{r} = n. \tag{1.97}$$

La DFT approxime la fonction d'onde par un unique produit anti-symétrisé de spin-orbitales à un électron appelé déterminant de Slater et noté $|\Psi|$.

Reprenons l'hamiltonien donné par l'équation (1.9) dans le cas électronique en séparant les potentiels d'interaction électron-électron et noyau-électron.

$$\begin{aligned} \hat{H}_e &= \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \\ &= -\sum_i^n \frac{(\hbar\vec{\nabla}_i)^2}{2m_e} - \sum_A^N \sum_i^n \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{i<j}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} \end{aligned} \tag{1.98}$$

Certains de ses termes peuvent s'exprimer en fonction de la densité électronique, sous forme de fonctionnelle, tels que l'énergie cinétique électronique $T_e[\rho]$ ou le potentiel lié aux interactions noyau-électron $V_{Ne}[\rho]$

$$T_e[\rho] = C_T \int \rho^{5/3}(\vec{r})d\vec{r}\,, \tag{1.99}$$

$$V_{Ne}[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} \tag{1.100}$$

avec

$$v(\vec{r}_i) = -\sum_{A}^{N} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \ . \tag{1.101}$$

Cependant, l'expression de $T_e[\rho]$ n'est pas toujours satisfaisante. L'énergie électronique peut alors être écrite selon l'expression de Hohenberg et Kohn (HK) [24] :

$$\mathcal{E}_{HK}[\rho] = V_{Ne}[\rho] + T_e[\rho] + V_{ee}[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + F[\rho] \tag{1.102}$$

où on introduit la fonctionnelle :

$$F[\rho] = T_e[\rho] + V_{ee}[\rho] = \langle\Psi|\,\hat{T}_e + \hat{V}_{ee}\,|\Psi\rangle \tag{1.103}$$

Une nouvelle définition de cette fonctionnelle est donnée par Kohn et Sham (KS) [25] :

$$F[\rho] = T_s[\rho] + J[\rho] + \mathcal{E}_{XC}[\rho] \ , \tag{1.104}$$

elle fait intervenir le potentiel de Hartree $J[\rho]$ qui donne la répulsion coulombienne classique entre paire d'électrons :

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \tag{1.105}$$

et l'énergie cinétique $T_s[\rho]$ d'un système d'électrons sans interaction de densité ρ. Cette énergie peut s'exprimer en terme de fonctions d'onde $\phi_i(\vec{r})$ construites de sorte à reproduire la densité $\rho(\vec{r})$ selon :

$$\rho(\vec{r}) = \sum_{i}^{n} \phi_i^2(\vec{r}) \tag{1.106}$$

par

$$T_s[\rho] = \sum_{i}^{n} \langle\phi_i(\vec{r})| - \frac{1}{2}\vec{\nabla}^2\,|\phi_i(\vec{r})\rangle \ . \tag{1.107}$$

Par identification terme à terme entre (1.103) et (1.104), on peut identifier l'énergie d'échange-corrélation :

$$\mathcal{E}_{XC}[\rho] = T_e[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \ . \tag{1.108}$$

Il s'agit de la quantité clé de la DFT, dont la définition théorique permet d'obtenir l'énergie exacte à ce niveau de théorie. Elle est cependant difficile à définir explicitement par rapport à ρ ou à ses dérivées et sa recherche a engendré le développement de nombreuses fonctionnelles.
On a désormais l'expression de l'énergie de Kohn et Sham :

$$\begin{aligned} \mathcal{E}_{KS}[\rho] &= \int \rho(\vec{r})v(\vec{r})d\vec{r} + T_s[\rho] + J[\rho] + \mathcal{E}_{XC}[\rho] \qquad (1.109) \\ &= \sum_{i}^{n} \langle\phi_i(\vec{r})| - \frac{1}{2}\vec{\nabla}^2\,|\phi_i(\vec{r})\rangle + \int \rho(\vec{r})v(\vec{r})d\vec{r} + J[\rho] + \mathcal{E}_{XC}[\rho] \ . \end{aligned}$$

La minimisation de la fonctionnelle de l'énergie avec la contrainte nombre total d'électrons $\int \rho(\vec{r})d\vec{r} = n$ peut s'exprimer à l'aide d'un multiplicateur de Lagrange μ :

$$\frac{\delta}{\delta\rho(\vec{r})}\left\{\mathcal{E}_{KS}[\rho] - \mu\left(\int \rho(\vec{r})d\vec{r} - n\right)\right\} = 0 \tag{1.110}$$

d'où :

$$\frac{\delta\mathcal{E}_{KS}[\rho]}{\delta\rho(\vec{r})} - \mu = 0 \tag{1.111}$$

et avec (1.102) ou (1.109) on déduit :

$$\mu = v(\vec{r}) + \frac{\delta F[\rho]}{\delta\rho(\vec{r})} = v_{eff}(\vec{r}) + \frac{\delta T_s[\rho]}{\delta\rho(\vec{r})} \ . \tag{1.112}$$

Il s'agit de l'équation d'Euler-Lagrange qui permet de définir le potentiel chimique μ, et le potentiel effectif :

$$v_{eff}(\vec{r}) = v(\vec{r}) + \frac{\delta J[\rho]}{\delta\rho(\vec{r})} + \frac{\delta E_{XC}[\rho]}{\delta\rho(\vec{r})} \ . \tag{1.113}$$

Cette équation (1.112) peut décrire de manière analogue un système d'électrons sans interaction entre eux dans un potentiel extérieur v_{eff}. L'hamiltonien associé à ce système est le suivant :

$$\hat{H} = \sum_i^n \left(-\frac{1}{2}\vec{\nabla}^2 + v_{eff}(\vec{r}_i)\right) \tag{1.114}$$

Comme chaque électron peut être traité indépendamment, la solution exacte de cette équation est un déterminant unique construit à partir d'orbitales ϕ_i solution de :

$$\begin{aligned} \left(-\frac{1}{2}\vec{\nabla}^2 + v_{eff}(\vec{r})\right)\phi_i &= \mathcal{E}_i\phi_i(\vec{r}) \\ \left(-\frac{1}{2}\vec{\nabla}^2 + v(\vec{r}) + \frac{\delta J[\rho]}{\delta\rho(\vec{r})} + \frac{\delta E_{XC}[\rho]}{\delta\rho(\vec{r})}\right)\phi_i &= \mathcal{E}_i\phi_i(\vec{r}) \end{aligned} \tag{1.115}$$

où l'on associe les fonctions d'onde ϕ à la densité ρ par l'équation (1.106). La théorie de Kohn-Sham consiste, dès lors, à résoudre de manière itérative l'équation aux valeurs propres (1.115) afin de construire une densité par la relation (1.106). Ensuite la fonctionnelle de l'énergie donnée par (1.109) est minimisée et permet d'obtenir un nouveau potentiel effectif qui peut être réutilisé dans (1.115). La procédure est alors répétée jusqu'à l'obtention d'un champ auto-cohérent (SCF : "*Self-Consistent Field*").

Notons que l'expression des équations de Kohn-Sham (1.109, 1.115) présente une ressemblance avec celles d'Hartree-Fock (HF) :

$$\mathcal{E}_{HF}[\rho] = \sum_i^n \langle\phi_i(\vec{r})| -\frac{1}{2}\vec{\nabla}^2 |\phi_i(\vec{r})\rangle + \int \rho(\vec{r})v(\vec{r})d\vec{r} + J[\rho] + \mathcal{E}_X^0[\rho_1] \tag{1.116}$$

$$\left(-\frac{1}{2}\vec{\nabla}^2 + v(\vec{r}_1) + \frac{\delta J[\rho]}{\delta\rho(\vec{r}_1)}\right)\phi_i(\vec{r}_1) - \frac{1}{2}\int \frac{\rho_1(\vec{r}_1,\vec{r}_2)}{r_{12}}\phi_i(\vec{r}_2)d\vec{r}_2 = \mathcal{E}_i\phi_i(\vec{r}_1) \tag{1.117}$$

où $\mathcal{E}_X^0[\rho_1]$ est l'énergie d'échange exacte donnée par :

$$\mathcal{E}_X^0[\rho_1] = -\frac{1}{4}\int\int \frac{\rho_1(\vec{r}_1,\vec{r}_2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 \tag{1.118}$$

avec $\rho_1(\vec{r}_1,\vec{r}_2)$, la matrice densité pour une particule :

$$\rho_1(\vec{r}_1,\vec{r}_2) = 2\sum_i \phi_i(\vec{r}_1)\phi_i(\vec{r}_2) \tag{1.119}$$

La DFT sera utilisée dans la partie 2.2 dans laquelle on optimise la structure géométrique d'un complexe, cette méthode s'avère très efficace pour les calcul de gradient numérique nécessaire à l'optimisation. Avec le logiciel "Gaussian" [26], une fonctionnelle de type hybride B3LYP [27,28] est utilisée. Cette fonctionnelle définie le terme d'échange-corrélation à l'aide de coefficients semi-empiriques, elle fait intervenir des quantités dépendant du gradient de la densité (de même que les fonctionnelle GGA : "*Generalised Gradient Approximations*") et introduit une part d'énergie d'échange exact. La fonctionnelle d'échange-corrélation peut être exprimée de manière générale par :

$$\mathcal{E}_{XC} = \int F(\rho,\vec{\nabla}\rho)d\vec{r} + \xi\mathcal{E}_X^0 \tag{1.120}$$

où ξ est la fraction d'échange exact incluse. Les programmes de calcul de structure électronique résolvent une version généralisée des équations de Kohn-Sham qui mêle les théories de Kohn-Sham et d'Hartree-Fock selon :

$$\left(-\frac{1}{2}\vec{\nabla}^2 + v(\vec{r}_1) + \frac{\delta J[\rho]}{\delta\rho(\vec{r}_1)} + \frac{\delta\mathcal{E}_{XC}^{GGA}[\rho,\vec{\nabla}\rho]}{\delta\rho(\vec{r}_1)}\right)\phi_i(\vec{r}_1) - \frac{\xi}{2}\int\frac{\rho_1(\vec{r}_1,\vec{r}_2)}{r_{12}}\phi_i(\vec{r}_2)d\vec{r}_2 = \mathcal{E}_i\phi_i(\vec{r}_1) \tag{1.121}$$

1.2.4 Méthode post-Hartree-Fock : CASSCF et post-CASSCF

1.2.4.1 Complete Active Space Self-Consistent Field (CASSCF)

Comme présenté précédemment, la méthode Hartree-Fock, de même que la DFT (voir partie 1.2.3), décrit la fonction d'onde par un déterminant unique [29]. Un système magnétique présente en général un ou plusieurs électrons non appariés (système à couches ouvertes) et son état fondamental, de même que ses états excités, sont donnés par un fonction d'onde comportant plusieurs déterminants. On utilise alors la méthode MC-SCF (Multi-Configurational Self Consistent Field) la plus plus célèbre : CASSCF (Complete Active Space Self-Consistent Field). Cette dernière consiste, pour toutes les configurations, à diviser l'ensemble des orbitales moléculaires en trois sous-espaces : les orbitales inactives toujours doublement occupées, les orbitales dites actives formant l'espace actif (CAS), ces orbitales pouvant être occupées par zéro, un ou deux électrons et les orbitales virtuelles toujours inoccupées. Au sein de l'espace actif (le CAS) toutes les occupations possibles des orbitales moléculaires sont autorisées permettant alors la description de systèmes à couches ouvertes ainsi que, après l'adjonction des variables de spin, la description

des différentes multiplicités de spin. L'optimisation utilisée pour cette méthode consiste à distribuer les différentes orbitales dans les trois sous-espaces afin de minimiser l'énergie des différents états demandés en respectant à la fois le spin total requis et le nombre total d'électrons du système (ou de manière équivalente sa charge globale). La difficulté principale inhérente à cette méthode tient justement au choix de la taille et de la constitution de l'espace actif. Il doit comprendre au minimum les orbitales simplement occupées de l'état fondamental (orbitales magnétiques), dans le cas des métaux de transition de la première ligne (la quatrième période), il s'agit d'orbitales $3d$ du ou des centres métalliques impliqués. Cependant pour l'obtention de paramètres magnétiques et la description des états excités, cet espace requiert aussi d'autres orbitales et, idéalement une partie des orbitales des liaisons métal-ligand. Cette méthode présente l'avantage d'être variationnelle, de respecter une stricte séparabilité par rapport à la taille du système ("*size-consistent*" : l'énergie d'un état du système $A - B$ tend vers la somme des énergies d'un état de A et d'un état de B traités indépendamment avec la même méthode quand les interactions entre A et B disparaissent) et d'être d'une grande efficacité d'un point de vue du calcul numérique. Cependant, elle exige un fort coût computationnel car l'ensemble des interactions de configurations au sein du CAS est effectué, il est donc nécessaire de limiter la taille du CAS.

1.2.4.2 Traitements Post-CASSCF

Afin d'introduire la corrélation dynamique pour obtenir une description plus précise de l'énergie des états étudiés, il a été développé, pour les méthodes basées sur un seul déterminant de référence, des correction par la théorie des perturbations à l'ordre deux ou quatre fondés sur un hamiltonien d'ordre zéro mono-électronique de type Møller-Plesset (MP2 ou MP4). Cette méthode est certes efficace mais limitée quand l'obtention d'états excités nécessite une description d'ordre zéro multi-déterminantale. Pour pallier à ce problème, d'autres méthodologies ont été adoptées utilisant comme point de départ le jeu d'orbitales moléculaires donné par un calcul CASSCF, c'est la fonction d'onde d'ordre zéro. Deux théories perturbatives à l'ordre deux d'entre elles seront utilisées par la suite par perturbation à l'ordre deux, il s'agit de la : "*Complete Active Space Perturbation Theory*" (CASPT2) [30] et la "*N-Electrons Valence Perturbation Theory*" [31].

L'objectif de ces méthodes est de corriger de manière perturbative l'énergie en prenant en compte les excitations dites simples et doubles par rapport à une référence multi-configurationnelle formée par toutes les combinaisons de déterminants selon les occupations possibles des orbitales actives (voir tableau 1.3).

Pour la méthode CASPT2, comme les états de valence atomiques ou moléculaires sont proches en énergies, une théorie des perturbations est employée. L'hamiltonien d'ordre zéro est construit de sorte que le développement perturbatif converge rapidement et qu'il soit équivalent à l'hamiltonien Møller-Plesset dans le cas d'une fonction d'onde de référence mono-déterminentale. Cet hamiltonien est basé sur un opérateur de Fock mono-électronique et implique seulement des fonctions d'ondes d'ordre un pour donner des énergies d'ordre deux. Les états excités hors du CAS pris en considération diffèrent alors seulement par une excitation (un trou ou une particule). Un problème est susceptible d'apparaitre avec cette méthode, la correction apportée à l'énergie fait intervenir des

Degré de liberté	Classe	Type d'excitation*
0	actif	$p \rightarrow q$ $pq \rightarrow rs$
1	1h	$i \rightarrow p$ $ip \rightarrow qr$
	1p	$p \rightarrow a$ $pq \rightarrow ra$
2	1h-1p	$i \rightarrow a$ $ip \rightarrow qa$
	2h	$ij \rightarrow pq$
	2p	$pq \rightarrow ab$
3	2h-1p	$ij \rightarrow pa$
	1h-2p	$ip \rightarrow ab$
4	2h-2p	$ij \rightarrow ab$

* nomenclature pour les différentes classes d'excitations

Types d'orbitales	noms	type de particule
inactive	i,j	h hole : trou
active	p,q,r,s	
virtuelle (ou secondaire)	a,b	p particule

TABLE 1.3 – Classifications des différentes excitations simples et doubles

différences d'énergie au dénominateur et celle-ci peut s'annuler ce qui produirait une correction infinie et donc une divergence du développement perturbatif. L'état impliqué dans le développement est qualifié d'état intrus. Pour traiter ce problème, il faudrait, en théorie, identifier l'état et s'il s'agit d'un véritable état, accroitre la taille de l'espace actif afin de l'inclure dans le CAS. Cependant, la taille de cet espace étant un facteur limitant pour le calcul CASSCF, de plus, comme il peut s'agir d'un état non physique, on utilise alors plutôt une technique consistant en un ajout d'un terme correctif à l'énergie du dénominateur ("*level shift*"). Il peut être réel [32] ou de préférence imaginaire [33] ; on parvient ainsi , par cette dernière méthode, à supprimer intégralement la singularité par une petite distorsion de la fonction d'énergie potentielle avec une faible incidence sur les énergies finales pour peu que l'on adopte des valeurs raisonnables du *level shift* imaginaire (0.15 hartree en général dans les calcul CASPT2).

La méthode NEVPT2 est une technique qui respecte la stricte séparabilité et ne présente pas de problème d'états intrus. Pour ce faire, elle se base sur un hamiltonien d'ordre zéro bi-électonique, développé par Dyall [34], qui utilise des projecteurs avec un hamiltonien complet dans l'espace actif et un hamiltonien d'ordre zéro de type Møller-Plesset dans les espaces inactif et secondaire. Il incorpore alors naturellement un décalage dans les dénominateurs au niveau de l'espace actif et des interactions bi-électroniques contrairement à CASPT2, qui sont ensuite corrigées par une méthode synthétisant les théories de Møller-Plesset et Epstein-Nesbet.

Les deux méthodes CASPT2 et NEVPT2, employées par la suite, sont de type "internally-contracted", c'est à dire que la fonction d'onde de référence n'est pas révisée après le calcul de la corrélation dynamique. De plus, ces méthodes sont contractées extérieurement mais une procédure permet de les décontracter intérieurement.

1.2.4.3 Ajout des effets relativistes

Pour prendre en compte les effets relativistes, dans le cadre d'une description multi-configurationnelle, une méthode en deux étapes est employée [35]. En premier lieu, un calcul de type CASSCF ou éventuellement CASPT2 ou NEVPT2 fourni pour un ensemble d'états (fondamental et excités) les énergies et les fonctions d'ondes incluant la corrélation non-dynamique et éventuellement dynamique. Par la suite, le couplage spin-orbite (SOC) est intégré au sein d'une interaction de configurations pouvant mêler plusieurs jeux d'orbitales obtenus pour des multiplicités de spin ou des groupes ponctuels de symétrie différents, et dont le mélange était jusque là interdit par symétrie. Les effets scalaires sont, dans le cas de l'utilisation de MOLCAS, rajoutés selon une méthode développé par Douglas et Kroll [36] et corrigée par Jansen et Hess [37] issue de l'hamiltonien de Dirac à quatre composantes :

$$\hat{H}_D = \hat{V} + m_e c^2 \hat{\boldsymbol{\beta}} + c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}} \tag{1.122}$$

où $\hat{V}$ est le potentiel externe, c la vitesse de la lumière, $\hat{\boldsymbol{\beta}}$ une matrice diagonale de dimension quatre avec les éléments diagonaux $\{1, 1, -1, -1\}$, $\hat{\mathbf{p}}$ est le quadri-vecteur opérateur quantité de mouvement et $\hat{\boldsymbol{\alpha}}$ est le quadri-vecteur moment de spin contenant les matrices de Pauli $\boldsymbol{\sigma}$. D'où, en notant ϕ la grande composante et χ la petite composante :

$$\Psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

on a $\hat{H}_D\Psi = \mathcal{E}\Psi$ qui s'écrit :

$$\begin{pmatrix} V & c\boldsymbol{\sigma}.\boldsymbol{p} \\ c\boldsymbol{\sigma}.\boldsymbol{p} & V - 2m_e c^2 \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = \mathcal{E} \begin{pmatrix} \phi \\ \chi \end{pmatrix} \tag{1.123}$$

L'équation de Dirac (1.123) est alors modifiée par un ensemble de transformations unitaires afin de découpler grandes et petites composantes par un développement à différents ordres du potentiel externe à un électron. A un ordre infini, on obtient ainsi un développement exact à deux composantes séparées comportant chacun une partie à énergie positive et négative. En sélectionnant seulement la partie à énergie positive de la grande composante pour un développement à l'ordre deux, on déduit une partie scalaire de correction relativiste et une partie de couplage spin-orbite.
La correction relativiste scalaire est la principale pour les atomes légers et les métaux de transition de la première ligne, elle est ajoutée à la partie mono-électronique de l'hamiltonien non relativiste et permet d'améliorer grandement les résultats. En considérant que l'erreur principale est liée à la description des états sans couplage spin-orbite, une méthode développée par Hess [38] est utilisée pour le SOC. Afin de simplifier drastiquement le calcul des éléments de matrices impliquées, les termes à deux électrons sont traités comme un facteur d'écrantage au sein des termes à un électron. On obtient ainsi des intégrales de champ moyen atomique ("*Atomic Mean Field Integral*" AMFI) en considérant l'interaction spin-orbite comme essentiellement à courte portée on obtient un traitement exact des termes à deux électrons. La méthode Douglas-Kroll-Hess est employée dans MOLCAS [39] avec un ensemble de bases dédiées ANO-RCC "*Atomic Natural Orbital with Relativistic Core Correlation*" [40].

Dans ORCA [41], une autre méthode basée sur un hamiltonien mono-électronique est employée [42–45]. En partant de l'équation de Dirac à quatre composantes (1.123), on déduit deux équations reliant grande et petite composantes :

$$V\phi + c\boldsymbol{\sigma}.\boldsymbol{p}\chi = \mathcal{E}\phi \tag{1.124}$$

$$c\boldsymbol{\sigma}.\boldsymbol{p}\phi + (V - 2m_e c^2)\chi = \mathcal{E}\chi \tag{1.125}$$

L'objectif est ensuite d'éliminer la petite composante qui s'exprime comme :

$$\chi = \frac{c\boldsymbol{\sigma}.\boldsymbol{p}}{2mc^2 + \mathcal{E} - V}\phi \equiv X\phi \tag{1.126}$$

L'équation de Dirac associée à la grande composante (1.124) donne alors :

$$H^{esc}\phi = V\phi + c\boldsymbol{\sigma}.\boldsymbol{p}\frac{c}{2mc^2 + \mathcal{E} - V}\boldsymbol{\sigma}.\boldsymbol{p}\phi = \mathcal{E}\phi \tag{1.127}$$

L'hamiltonien H^{esc} ("*eliminating the small component*") dépend de l'énergie et n'agit que sur la grande composante ϕ qui n'est pas normalisée, contrairement à Ψ. Pour pallier à ce problème, on utilise plutôt la transformation unitaire de Foldy-Wouthuysen pour découpler grande et petite composantes.

Elle est donnée par $H = UH_DU^{-1}$, avec :

$$U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}}X^\dagger \\ -\frac{1}{\sqrt{1+XX^\dagger}}X & \frac{1}{\sqrt{1+XX^\dagger}} \end{pmatrix} \tag{1.128}$$

$$U^{-1} = U^\dagger = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & -X^\dagger\frac{1}{\sqrt{1+XX^\dagger}} \\ X\frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+XX^\dagger}} \end{pmatrix} \tag{1.129}$$

De même, la fonction d'onde est transformée par U :

$$\begin{pmatrix} \Phi \\ 0 \end{pmatrix} = U \begin{pmatrix} \phi \\ \chi \end{pmatrix} \tag{1.130}$$

On en déduit :

$$\Phi = \frac{1}{\sqrt{1+X^\dagger X}}\phi + \frac{1}{\sqrt{1+X^\dagger X}}X^\dagger\chi \tag{1.131}$$

$$0 = -\frac{1}{\sqrt{1+XX^\dagger}}X\phi + \frac{1}{\sqrt{1+XX^\dagger}}\chi \tag{1.132}$$

Il faut donc avoir X tel que $\chi = X\phi$. D'après (1.126), on a l'expression de X que l'on va développer en $\mathcal{E}/(2mc^2 - V)$.

$$X = \frac{c\boldsymbol{\sigma}.\boldsymbol{p}}{2mc^2 + \mathcal{E} - V} \approx \frac{c}{2mc^2 - V}\boldsymbol{\sigma}.\boldsymbol{p} \tag{1.133}$$

d'où, on peut déduire :

$$U = \begin{pmatrix} 1 - \boldsymbol{\sigma}.\boldsymbol{p}\frac{c^2}{2(2mc^2-V)^2}\boldsymbol{\sigma}.\boldsymbol{p} & \boldsymbol{\sigma}.\boldsymbol{p}\frac{c}{2mc^2-V} \\ -\frac{c}{2mc^2-V}\boldsymbol{\sigma}.\boldsymbol{p} & 1 - \frac{1}{2}\frac{c}{2mc^2-V}p^2\frac{c}{2mc^2-V} \end{pmatrix} \tag{1.134}$$

Cette transformation donne alors le terme d'ordre zéro et d'ordre un de correction relativiste :

$$H_{ZORA} = V + \boldsymbol{\sigma}.\boldsymbol{p}\frac{c^2}{2mc^2 - V}\boldsymbol{\sigma}.\boldsymbol{p} \tag{1.135}$$

$$\begin{aligned} H_{FORA} &= H_{ZORA} - \boldsymbol{\sigma}.\boldsymbol{p}\frac{c^2}{2(2mc^2 - V)^2}\boldsymbol{\sigma}.\boldsymbol{p}.H_{ZORA} \\ &\quad + H_{ZORA}.\boldsymbol{\sigma}.\boldsymbol{p}\frac{c^2}{2(2mc^2 - V)^2}\boldsymbol{\sigma}.\boldsymbol{p} \end{aligned} \tag{1.136}$$

Cet hamiltonien d'ordre zéro ("*Zero Order Relativistic Approximation*") a l'avantage de ne pas avoir de singularité quand la distance noyau-électron tend vers zéro. Il a été obtenu en premier lieu par Chang, Pélissier et Durand [46], par une autre méthode, la théorie des hamiltonien effectif. Un développement supplémentaire fait apparaitre explicitement le terme prépondérant de couplage spin-orbite, contrairement au développement Douglas-Kroll-Hess.

$$H_{ZORA} = V + \boldsymbol{p}\frac{c^2}{2mc^2 - V}\boldsymbol{p} + \frac{c^2}{(2mc^2 - V)^2}\boldsymbol{\sigma}.\left(\boldsymbol{\nabla}V \times \mathbf{p}\right) \tag{1.137}$$

Ce dernier peut être rapproché de l'expression de la correction spin-orbite des équations (1.23, 1.24) avec $\boldsymbol{\sigma} \approx \vec{s}$ et

$$\boldsymbol{\nabla} V \approx \frac{e}{r}\frac{\partial \Phi_N(r)}{\partial r}\vec{r} \tag{1.138}$$

La correction relativiste scalaire est ajoutée par une approche analogue à la DFT (développée à la section 1.2.3) selon l'équation de Kohn-Sham en utilisant la densité non relativiste $\rho(r)$ [45]. Une fonctionnelle d'échange-corrélation est utilisée, négligeant dès lors les effets magnétiques et le phénomène de retard pour les interactions électroniques. Le potentiel $\tilde{V}$ pris en compte pour (1.137) contient désormais le potentiel d'attraction nucléaire $\tilde{V}_N$, le potentiel de Coulomb d'interaction électronique $\tilde{V}_C$ et le potentiel d'échange-corrélation $\tilde{V}_{XC}$. Ce potentiel modèle est développé de sorte qu'il ne dépende pas des orbitales Kohn-Sham mais seulement de la géométrie moléculaire, que les atomes distants ne contribuent pas et qu'il puisse être exprimé par une expression analytique dérivable à tous les ordres.

Le potentiel corrigé par une méthode Kohn-Sham est utilisé dans un calcul CASSCF et bénéficie par cette méthode de certains avantages. Les propriétés de ce potentiel permettent d'assurer la stationnarité de l'énergie totale par rapport à la variation des orbitales afin, par exemple, de ne pas avoir à recalculer les contributions relativistes à chaque itération pour un processus SCF éliminant ainsi le problème d'invariance de jauge qu'il y aurait avec le potentiel DFT traditionnel. De plus, une stricte séparabilité par rapport à la taille du système est alors conservée lors du calcul CASSCF et le calcul de gradient est facilité. Pour ce faire, la densité électronique est remplacé par une densité modèle construite par sommation de densités atomiques exprimées par des gaussiennes sur un ensemble limité d'électrons en périphérie de chaque atome. Le potentiel de Coulomb utilise cette densité, de même que le potentiel d'échange-corrélation avec une approximation d'une densité locale sans polarisation de spin. Un ensemble de bases atomiques spécialement contractées pour des calculs avec la méthode ZORA a été établi et est utilisé par la suite avec ORCA.

1.2.5 Extraction et exploitation des hamiltoniens de spin

Les diverses méthodes basées sur la fonction d'onde présentées précédemment utilisent l'hamiltonien Born-Oppenheimer exact, à un certain niveau de calcul, afin de décrire les fonctions d'onde des états du bas du spectre et leurs énergies. L'objectif étant, dans le cadre de l'étude de l'anisotropie magnétique, de modéliser cet hamiltonien par un opérateur de spin, nous allons être amené à utiliser une théorie visant à engendrer un hamiltonien reproduisant les énergies des états qui nous intéressent tout en conservant des propriétés telles que l'orthonormalité des fonctions d'ondes et le caractère hermitien de l'hamiltonien.

1.2.5.1 Théorie des hamiltoniens effectifs

Une théorie développée par Bloch [47] offre une procédure pour définir un hamiltonien effectif dans un espace modèle de faible dimension à partir des énergies et fonctions propre d'un hamiltonien exact $\hat{H}$ [46, 48, 49]. Pour un espace modèle $\mathcal{S}$ de faible dimension porté

par N_S vecteurs $|\Phi_i\rangle$, le projecteur associé est :

$$\hat{P}_S = \sum_{i \in \mathcal{S}} |\Phi_i\rangle \langle \Phi_i| \tag{1.139}$$

Supposons que l'on connaisse un ensemble d'états de fonctions d'onde $|\Psi_k\rangle$, d'énergie $\mathcal{E}_k$ associée à un Hamiltonien exact $\hat{H}$ selon l'équation de Schrödinger :

$$\hat{H} |\Psi_k\rangle = \mathcal{E}_k |\Psi_k\rangle \tag{1.140}$$

Considérons désormais les N_S vecteurs propres de $\hat{H}$ ayant la plus grande projection sur l'espace modèle $\mathcal{S}$. Ces vecteurs définissent un espace cible $\mathcal{S}c$ de même dimension que $\mathcal{S}$ et associé à un projecteur :

$$\hat{P}_{Sc} = \sum_{k \in \mathcal{S}c} |\Psi_k\rangle \langle \Psi_k| \tag{1.141}$$

On note $\widehat{\Omega}$, l'opérateur d'onde permettant le passage de $\mathcal{S}$ à $\mathcal{S}c$. On cherche désormais à définir un hamiltonien effectif $\hat{H}_{eff}$ agissant sur $\mathcal{S}$ tel qu'il reproduise fidèlement les valeurs propres de $\hat{H}$ au sein de $\mathcal{S}c$, quitte à perdre une partie de l'information sur la fonction d'onde. Il faut donc avoir :

$$\hat{H}_{eff} \left| \hat{P}_S \Psi_k \right\rangle = \mathcal{E}_k \left| \hat{P}_S \Psi_k \right\rangle \tag{1.142}$$

L'expression de l'hamiltonien effectif donné par Bloch est alors :

$$\hat{H}_{eff} = \hat{P}_S \hat{H} \widehat{\Omega} \hat{P}_S \tag{1.143}$$

Comme les opérations de projection sont susceptibles de faire perdre l'orthonormalisation des fonctions propres $|\Psi_j\rangle$ de l'hamiltonien exact, on introduit la matrice de recouvrement $\mathbf{S}$:

$$\mathbf{S}_{ij} = \langle \hat{P}_S \Psi_i | \hat{P}_S \Psi_j \rangle \tag{1.144}$$

L'hamiltonien effectif de Bloch, est alors donné par :

$$\hat{H}_{eff}^{Bloch} = \sum_k |\Psi_k\rangle \mathcal{E}_k \left\langle \mathbf{S}^{-1} \Psi_k \right| \tag{1.145}$$

D'autres méthodes d'orthonormalisation permettent de corriger ce défaut telles que la méthode de Gramm-Schmidt mais elle ne traite pas de manière équivalente les différents vecteurs, le $k^{ième}$ vecteur étant orthogonalisé par rapport au $(k-1)$ précédents et indépendamment des suivants ; on utilise donc préférentiellement la méthode de des Cloizeaux [50], pour engendrer les vecteurs propres $\left| \tilde{\Psi} \right\rangle$ de $\hat{H}_{eff}$

$$\left| \tilde{\Psi}_k \right\rangle = \left| \mathbf{S}^{-\frac{1}{2}} \Psi_k \right\rangle \tag{1.146}$$

L'hamiltonien effectif est alors hermitien. Il s'exprime alors comme :

$$\hat{H}_{eff}^{dC} = \sum_k \left| \tilde{\Psi}_k \right\rangle \mathcal{E}_k \left\langle \tilde{\Psi}_k \right| \tag{1.147}$$

et ces éléments de matrice sont donnés par :

$$\langle \Phi_i | \hat{H}_{eff}^{dC} | \Phi_j \rangle = \langle \Phi_i | \sum_k \left| \tilde{\Psi}_k \right\rangle \mathcal{E}_k \left\langle \tilde{\Psi}_k | \Phi_j \right\rangle \tag{1.148}$$

Nous allons à présent en illustrer son utilisation sur un exemple.

1.2.5.2 Exemple d'application de la théorie des hamiltoniens effectifs

Appliquons la théorie des hamiltoniens effectifs à un exemple issu de la partie 2.2. Il s'agit d'un complexe mononucléaire de $Ni^{(II)}$ avec un état fondamental triplet $S = 1$, il y a donc huit électrons à distribuer parmi les cinq orbitales $3d$ pour former jusqu'à dix états triplement dégénérés en spin et quinze états singulets (dont cinq sont à couches fermées dans la configuration d^8). On cherche à déduire les paramètres de ZFS (D et E) ainsi que les axes magnétiques du complexe en comparant les valeurs théoriques données par un hamiltonien de spin présenté dans la partie 1.1.2 et donné, pour le cas $S = 1$ par l'équation (1.52), à partir des valeurs issues d'un calcul numérique et de la théorie des hamiltoniens effectifs.

Comme abordé dans la partie 1.2.4.3, les effets spin-orbites (SO) sont rajoutés *a posteriori* après un calcul non-relativiste par diagonalisation de l'hamiltonien de couplage spin-orbite. On obtient ainsi, en fonction du remplissage de la sous-couche $3d$ du nickel, un ensemble de singulets et de triplets notés $|T_k\rangle$ pour lesquels il est désormais possible de préciser la projection des composantes magnétiques de spin $M_S = 0, \pm 1$, notées $\left|T_k^{0,\pm 1}\right\rangle$. La décomposition des états spin-orbites du bas du spectre en fonction des états indépendant de ce couplage est donnée dans le tableau 1.4.

	$\mathcal{E}$	$\left\|T_1^{-1}\right\rangle$	$\left\|T_1^{0}\right\rangle$	$\left\|T_1^{1}\right\rangle$	$\left\|T_2^{-1}\right\rangle$	$\left\|T_2^{0}\right\rangle$	$\cdots$
$\langle\Phi_1\|$	0	0.503 - 0.448i	-0.010 -0.007i	0.278-0.614 i	0.137+ 0.153i	-0.005 -0.004 i	$\cdots$
$\langle\Phi_2\|$	2.14	0.672 -0.038 i	-0.050 +0.014 i	-0.599 + 0.308 i	0.011+ 0.204i	-0.001+ 0.000i	$\cdots$
$\langle\Phi_3\|$	118.14	-0.029 -0.023 i	-0.766 -0.623 i	0.028 + 0.023 i	0.006 -0.012i	0.000 +0.000i	$\cdots$
$\langle\Phi_4\|$	1878.9	0.001 -0.001i	0.000+0.000	0.005 -0.007i	-0.045 -0.012 i	-0.934 -0.301i	$\cdots$
$\langle\Phi_5\|$	2121.9	0.185 -0.063i	0.007 -0.001i	-0.196 +0.006i	-0.216 -0.633i	0.006 -0.001i	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

TABLE 1.4 – Décomposition des états spin-orbites en fonction des états spin-free, les énergies $\mathcal{E}$ sont données en cm^{-1}

L'objectif étant de représenter la levée de dégénérescence de l'état fondamental par les paramètres ZFS, l'espace modèle est de dimension trois et composé de $|S = 1, M_S\rangle$ avec $M_S = 0, \pm 1$. Les états SO avec la plus importante projection sur l'espace modèle sont alors sélectionnés ; il s'agit des états Φ_1, Φ_2, Φ_3 de projection respective 0.953, 0.953 et 0.989. Ces trois états forment donc l'espace cible. Les fonctions d'ondes associées à ces états sont alors tronquées pour ne plus dépendre des autres états triplets et seront notées $\Phi'_1, \Phi'_2, \Phi'_3$. Cette transformation entrainant la perte de l'orthonormalisation des fonctions d'ondes, la matrice de recouvrement est alors calculée et donnée dans le tableau 1.5.

S	$\left\|\Phi'_1\right\rangle$	$\left\|\Phi'_2\right\rangle$	$\left\|\Phi'_3\right\rangle$
$\langle\Phi'_1\|$	0.908002	0.000277 + i -0.000349	0.001681 + i 0.000082
$\langle\Phi'_2\|$	0.000277 + i 0.000349	0.909004	0.002213 + i 0.003085
$\langle\Phi'_3\|$	0.001681 + i -0.000082	0.002213 + i -0.003085	0.978321

TABLE 1.5 – Matrice de recouvrement **S**

L'orthonormalisation est alors rétablie par la méthode de des Cloizeaux qui donne les

fonctions d'onde $\tilde{\Phi}_k$ grâce à l'équation (1.146), le résultat est donné dans le tableau 1.6.

	$\mathcal{E}$	$\lvert S=1, M_s=-1\rangle$	$\lvert S=1, M_s=0\rangle$	$\lvert S=1, M_s=1\rangle$
$\left\langle\tilde{\Phi}_1\right\rvert$	0	0.528 -0.471i	-0.010 -0.008 i	0.292 -0.644 i
$\left\langle\tilde{\Phi}_2\right\rvert$	2.14	0.705 -0.040i	-0.051 + 0.014 i	-0.628 + i 0.323i
$\left\langle\tilde{\Phi}_3\right\rvert$	118.14	-0.030 -0.024 i	-0.775 -0.630 i	0.029 + i 0.025

TABLE 1.6 – Projections orthonormalisées par la méthode de de Cloizeaux, les énergies $\mathcal{E}$ sont en cm^{-1}

L'hamiltonien effectif peut alors être construit en suivant l'équation (1.148) avec les énergies exactes et est présenté dans le tableau 1.7.

H^{eff}	$\lvert S=1, M_S=-1\rangle$	$\lvert S=1, M_S=0\rangle$	$\lvert S=1, M_S=1\rangle$
$\langle S=1, M_S=-1\rvert$	1.241	4.446 - 0.108i	-1.149 - 0.427 i
$\langle S=1, M_S=0\rvert$	4.446 + 0.108i	117.802	-4.446 + 0.108 i
$\langle S=1, M_S=1\rvert$	-1.149 + 0.427i	-4.446 - 0.108i	1.241

TABLE 1.7 – Hamiltonien effectif

En comparant terme à terme les éléments de l'hamiltonien effectif avec ceux de l'hamiltonien modèle de la table (1.52), on déduit les composante du tenseur $\overline{\overline{D}}$.

$$\overline{\overline{D}} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{pmatrix} = \begin{pmatrix} 57.752 & -0.427 & -6.288 \\ -0.427 & 60.049 & 0.152 \\ -6.288 & 0.152 & -57.660 \end{pmatrix} \tag{1.149}$$

Il ne reste plus qu'à diagonaliser le tenseur avec la matrice de passage P selon $\overline{\overline{D}} = P^{-1}\,\overline{\overline{D}}^{diag}\,P$ pour obtenir :

$$\overline{\overline{D}}^{diag} = \begin{pmatrix} 60.142 & 0 & 0 \\ 0 & 58.002 & 0 \\ 0 & 0 & -58.002 \end{pmatrix} \tag{1.150}$$

La trace de ce tenseur peut être choisie comme nulle car cela revient à translater le zéro en énergie des composantes de spin du triplet fondamental. Le système d'axe propre du tenseur donnent les axes magnétiques selon l'équation (1.151), qui sont représentés sur la figure 1.5.

$$\begin{pmatrix} X_{mag} \\ Y_{mag} \\ Z_{mag} \end{pmatrix} = P^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{1.151}$$

On a ainsi les paramètres D et E en respectant $|D| > 3E$ et $E \geq 0$

$$D = -117.072\ \mathrm{cm}^{-1} \quad \& \quad E = 1.070\ \mathrm{cm}^{-1}$$

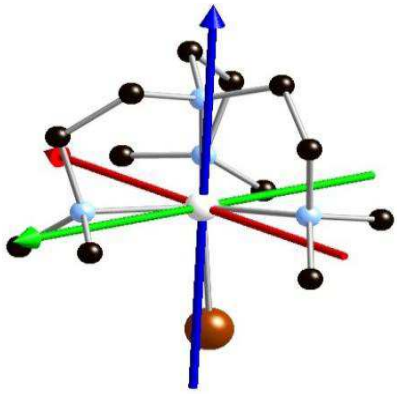

FIGURE 1.5 – Axes magnétiques du complexe $[Ni(Me_6tren)Br]^+$

Cette procédure permet donc bien de déduire les paramètres de ZFS, de retrouver les axes magnétiques et surtout ici de valider un hamiltonien effectif avec seulement un tenseur d'ordre deux et deux paramètres indépendants.

Chapitre 2

Stratégies pour accroitre l'anisotropie magnétique dans les complexes mononucléaires

De nombreux complexes mononucléaires ont été étudiés afin de recueillir leurs paramètres magnétiques [17]. La valeur du paramètre D du Zero-Field Splitting peut varier fortement en fonction du métal, de son degré d'oxydation et de son environnement (*cf.* tableau 2.1). Les différents ligands présentent différents caractères et en premier lieu le nombre de coordination ou la forme géométrique qui joue un rôle prépondérant pour l'anisotropie magnétique. Pour commencer, nous allons nous intéresser à la coordination du complexe.

2.1 Les complexes à coordinations exotiques

Afin d'accroitre les paramètres d'anisotropie magnétique et en particulier la valeur de D dans les complexes mono-métalliques de métaux de transition de la quatrième période, une voie de recherche envisagée a été de choisir des ligands de sorte à obtenir une coordination éloignée des cas octaédrique ou tétraédrique [19, 51].

En effet, dans le cas d'une géométrie octaédrique O_h pour un complexe de Ni^{II}, les huit électrons des orbitales $3d$ sont répartis comme représenté sur la figures 2.1. En représentant la fonctions d'onde pour les trous pour un système d'axes adaptés de ce complexe, il apparait que l'état fondamental est un triplet non dégénéré ($^3A_{2g}$ en notation spectroscopique) et que les trois premiers triplets excités sont dégénérés ($^3T_{2g}$, *cf.* figure 2.2).

Le calcul de l'interaction spin-orbite (*cf.* 1.27) $\hat{V}_{SO} = \sum_i \zeta \hat{l}_i.\hat{s}_i$ sur les différents états triplets est effectué et les éléments de matrices correspondant sont résumés dans le tableau 2.2. Ensuite, à l'aide de la formule définissant le tenseur D (1.48), ou plus simplement par la théorie des perturbations quasi-dégénéré (QDPT) :

$$\left\langle T_0^i \right| \hat{H}_{SO} \left| T_0^j \right\rangle = \left\langle T_0^i \right| \hat{V}_{SO} \left| T_0^j \right\rangle - \sum_\alpha \frac{\left\langle T_0^i \right| \hat{V}_{SO} \left| \Phi_\alpha \right\rangle \left\langle \Phi_\alpha \right| \hat{V}_{SO} \left| T_0^j \right\rangle}{\mathcal{E}_\alpha - \mathcal{E}_j} \tag{2.1}$$

	Composé	nc*	D (cm^{-1})
d^2	$[C(NH_2)_3]V^{III}(SO_4)_2 \cdot 6H_2O$	6	+3.74
	$Cs_3V^{III}Cl_6 \cdot 4H_2O$	6	+8.05
d^3	$[Cr^{III}(NH_3)_6](ClO_4)_2Br \cdot CsBr$	6	+0.18
	$[Cr^{III}(dedtc)_3]$[a]	6	+0.6
d^4	$[Mn^{III}(TPP)Cl(pyridine)] \cdot C_6H_6$[b]	6	-3.5
	$[Mn^{III}(acetylacetonato)_3]$	6	+3.1
d^5	$[Mn^{II}(bzimpy)Cl_2] \cdot 0.5MeOH$[c]	5	-2.73
	$[Mn^{II}(Me_6tren)Br]Br$[d]	5	+0.24
	$[Fe^{III}(Pydtc_3)]$[e]	6	-2.14
	$[Fe^{III}\{L_{NNN}\}(NO)(N_3)_2]$[f]	6	+13.6
d^6	$[Fe^{II}(2,2' - bipyridyl)Cl_2]$	5	-2
	$[Fe^{II}(phtalatocyanine)]$	4	+70
	$K[Co^{III}(3 - propyl - biuret)_2]$	4	+40.9
d^7	$[Co^{II}\{L_{NNNOO}\}]$[g]	5	-38.9
	$[Co^{II}(bzimpy)Cl_2]$[d]	5	+73.4
d^8	$[Ni^{II}(imidazole)_4(acetato)_2]$	6	-22.34
	$[Ni^{II}\{L_{NNSS}\}]$[h]	4	+53

* nc : nombre de coordination
[a] dedtc :diethyldithiocarbamato(1^-)
[b] TPP : tetraphenylporphyrinato(2^-)
[c] bzimpy : bis(benzimidazole)pyridine
[d] tren : 2,2',2"-triaminotriethylamine
[e] Pydtc :pyrrolidine-1-carbodithiolato(1^-)
[f] $\{L_{NNN}\}$: 1,4,7-trimethyl-1,4,7-triazacyclononane
[g] $\{L_{NNNOO}\}$: N,N-bis(3-tert-butyl-2-hydroxy-5-methyl-benzyliden)-1,7-diamino-4-methyl-4-azaheptane
[h] $\{L_{NNSS}\}$: 5-formylpyrazole-based thiolato Schiff base

TABLE 2.1 – Valeurs du paramètre D de ZFS pour différents complexes mononucléaires d'après des mesures de susceptibilité [17]

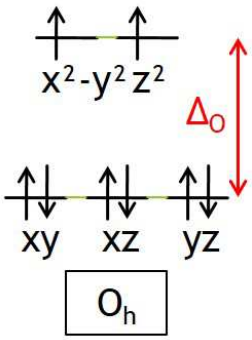

FIGURE 2.1 – Orbitales du complexe de Ni^{II} en géométrie octaédrique

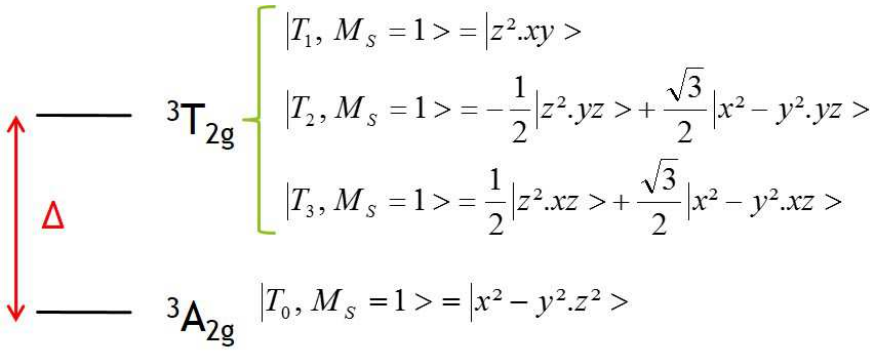

FIGURE 2.2 – État fondamental et premiers états excités dégénérés pour une symétrie octaédrique, en représentant uniquement les orbitales $3d$ du nickel simplement occupées.

$\hat{V}_{SO}$	$\left\|T_1^{+1}\right\rangle$	$\|T_1^0\rangle$	$\left\|T_1^{-}1\right\rangle$	$\left\|T_2^{+1}\right\rangle$	$\|T_2^0\rangle$	$\left\|T_2^{-}1\right\rangle$	$\left\|T_3^{+1}\right\rangle$	$\|T_3^0\rangle$	$\left\|T_3^{-}1\right\rangle$
$\left\langle T_0^{+1}\right\|$	$i\zeta$	0	0	0	$\frac{i\zeta}{\sqrt{2}}$	0	0	$-\frac{\zeta}{\sqrt{2}}$	0
$\langle T_0^0\|$	0	0	0	$\frac{i\zeta}{\sqrt{2}}$	0	$-\frac{i\zeta}{\sqrt{2}}$	$\frac{\zeta}{\sqrt{2}}$	0	$-\frac{\zeta}{\sqrt{2}}$
$\left\langle T_0^{-1}\right\|$	0	0	$-i\zeta$	0	$\frac{i\zeta}{\sqrt{2}}$	0	0	$\frac{\zeta}{\sqrt{2}}$	0

TABLE 2.2 – Éléments de matrice de l'hamiltonien spin-orbite en géométrie octaédrique

on peut déduire l'éventuelle modification du spectre en fonction de l'état de spin. On obtient la matrice suivante :

$$\hat{H}_{SO} = \begin{pmatrix} -\frac{2\zeta^2}{\Delta} & 0 & 0 \\ 0 & -\frac{2\zeta^2}{\Delta} & 0 \\ 0 & 0 & -\frac{2\zeta^2}{\Delta} \end{pmatrix} \tag{2.2}$$

Toutes les composantes M_S ont même énergie, il n'y a donc pas de ZFS.

Au contraire, dans le cas de coordination exotique, la perte de symétrie du champ cristallin permet d'obtenir une levée de dégénérescence entre les différentes orbitales $3d$ du métal autorisant, dès lors, l'obtention d'importante valeur de D.
L'objectif sera, par la suite, d'étudier sur des complexes réels, les effets de l'utilisation d'un ligand permettant de privilégier un axe magnétique pour obtenir des valeurs de D grandes et de E petites. Par une étude conjointe d'expérimentateurs et de théoriciens, il s'agira de confirmer, ou éventuellement de prévoir, par un calcul théorique à l'aide des méthodes introduites au chapitre 1, les valeurs de mesures expérimentales du ZFS déterminées à l'aide de résonances paramagnétiques électroniques à haute fréquence en champ intense, de mesures d'aimantation à basse température ou de mesures de susceptibilités magnétiques.

Cette étude portera, en premier lieu sur des complexes heptacoordonés [52] de Ni^{II} : $[Ni(H_2DAPBH)(H_2O)_2](NO_3).2H_2O$ et de Co^{II} : $[Co(H_2DAPBH)(H_2O)(NO_3)]NO_3$ puis sur des complexes pentacoordonés [53] de Ni^{II} détaillés la partie suivante 2.2. Les complexes heptacoordonnés, décrit dans l'article qui suit [54], sont formés d'un ligand pentadente de structure quasi-planaire (2,6-diacetylpyridine bis-(benzoyl hydrazone)) et deux contre-ions chlorure et/ou nitrate de part et d'autre du ligand plan afin d'obtenir une structure de bi-pyramide pentagonale. Cette géométrie permet d'observer effectivement un axe magnétique particulier pour la direction perpendiculaire au ligand plan avec un axe de facile aimantation et une valeur de D négative et relativement importante pour le complexe de nickel et, pour le complexe de cobalt, un axe de difficile aimantation selon la direction des ligands axiaux et donc un plan de facile aimantation correspondant au plan du ligand et donne une valeur positive de D. La déduction des paramètres de ZFS s'effectue par des méthodes expérimentales et théoriques, avec un bon accord, à la fois sur les signes et sur l'amplitude des valeurs. Les calculs numériques sont effectués avec le programme ORCA [41] à l'aide d'un calcul CASSCF, la corrélation dynamique est prise en

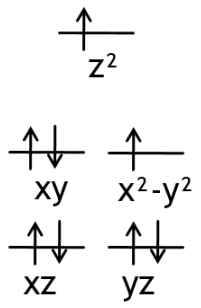

FIGURE 2.3 – Orbitales du complexe de Ni^{II} en géométrie D_{5h}

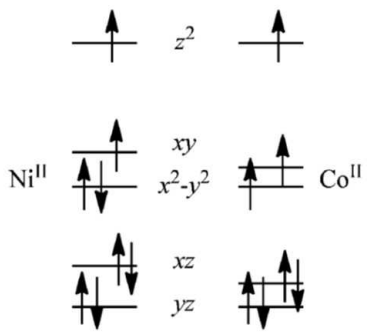

FIGURE 2.4 – Orbitales des complexes hepta-coordonés [54]

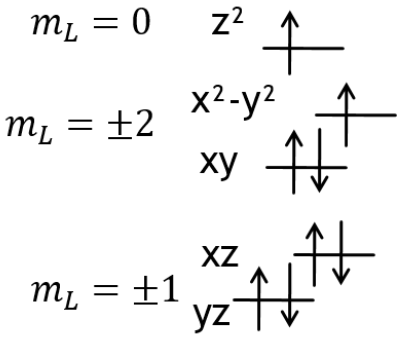

FIGURE 2.5 – Diagramme des orbitales de l'état fondamental et nombre quantique orbital associé

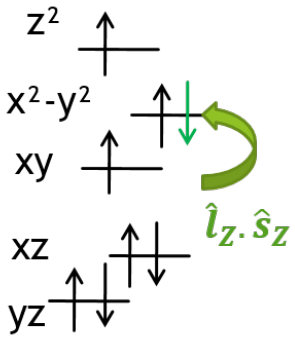

FIGURE 2.6 – Diagramme des orbitales du premier état excité et opérateur d'interaction spin-orbite permettant un couplage avec l'état fondamental

considération grâce à NEVPT2, les corrections relativistes grâce à ZORA, et aux calculs des couplages spin-orbite et spin-spin.

De plus, ces calculs donnent accès, essentiellement par l'évaluation du couplage spin-orbite entre les différentes composantes M_S de l'état fondamental et des premiers états excités, à l'origine de l'anisotropie magnétique. Par une méthode de rationalisation, les différentes contributions des états excités aux valeurs de D et E peuvent alors être analysées et interprétées en dérivant analytiquement les interactions spin-orbites entre l'état fondamental et les premiers états excités. La structure électronique de ces états s'explique grâce à la géométrie du complexe et une corrélation magnéto-structurale peut être établie. En effet, le choix du ligand permet d'obtenir une géométrie proche du D_{5h} donne lieu à la structure électronique présentée sur la figure 2.3 pour un complexe de Ni^{II}. Dans notre cas, la structure obtenue est donnée par la figure 2.4. Dès lors, pour le complexe de nickel, à partir d'un calcul de la fonction d'onde sur l'état fondamental (*cf.* figure 2.5) et les trois premiers excités (*cf.* figures 2.6 et 2.7, seuls les états de spin maximal sont représentés), il apparait que seul les deux derniers sont proches de la dégénérescence, nous les traiterons donc simultanément.

Ensuite, un calcul d'interaction spin-orbite analogue au cas octaédrique peut être

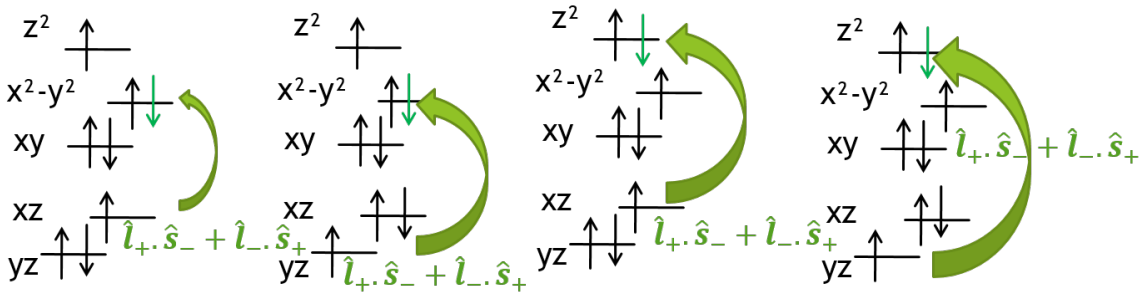

FIGURE 2.7 – Diagramme des orbitales des deuxièmes et troisièmes états excités et opérateurs d'interaction spin-orbite permettant un couplage avec l'état fondamental

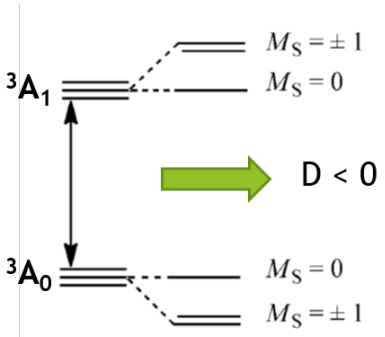

FIGURE 2.8 – Diagramme d'interaction entre l'état fondamental et le premier état triplet excité

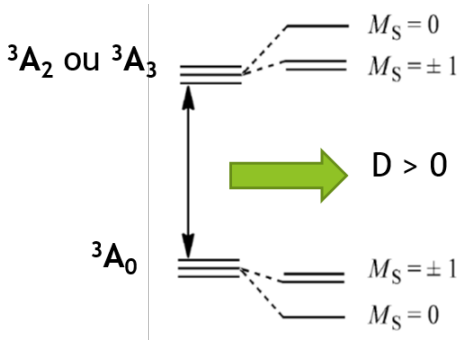

FIGURE 2.9 – Diagramme d'interaction entre l'état fondamental et le deuxième ou troisième état triplet excité

effectué afin de calculer le couplage entre chaque état excité et le fondamental. Il fait intervenir différents opérateurs orbitaux et de spin indiqués sur les figures précédentes. En notant que, pour le premier état excité, l'interaction fait passer un électron d'un orbitale de moment magnétique associé à une combinaison linéaire des valeurs ± 2 à l'orbitale présentant l'autre combinaison de ± 2, ce moment magnétique reste inchangé au cours de l'interaction et l'opérateur quantique est donc proportionnel à $\hat{l}_z.\hat{s}_z$. Dès lors, cette composante z de l'opérateur n'affecte pas le spin et donne un résultat proportionnel au carré de sa valeur (*cf.* équation 2.1), ce qui a pour conséquence de ne pas modifier l'énergie de la composante $M_S = 0$ de l'état fondamental alors que les composantes $M_S = \pm 1$ de l'état fondamental seront stabilisées (*cf.* figure 2.8) et donneront une contribution négative au paramètre D avec une amplitude importante du fait de la faible différence d'énergie entre le triplet fondamental et le premier triplet excités.

Au contraire, pour les deux triplets suivant, les interactions spin-orbite requises sont selon les composantes x et y, elles couplent des valeurs différentes du moment orbital et donc des moments de spin. De plus, comme l'amplitude des différentes interactions spin-orbite sont comparables et comme les interactions de la composante $M_S = 0$ du fondamental avec les composantes $M_S = \pm 1$ de chaque état excité sont deux fois plus nombreuses que celles faisant intervenir chacune des composantes $M_S = \pm 1$ du fondamental avec une composante $M_S = 0$ d'un état excité, il s'en suit une plus forte stabilisation de la composante de moment de spin nul que des deux autres (*cf.* figure 2.9). On a alors dans ce cas, une

contribution positive à D. Par cette procédure, on identifie l'origine des contributions aux paramètres de ZFS qui rend ainsi possible de déduire une marche à suivre pour choisir un ensemble de ligands permettant de développer les paramètres magnétiques souhaités. Dans notre cas, les principales contributions pour le complexe de nickel et, de manière analogue, pour le complexe de cobalt sont résumées dans le tableau 2.3

Complexe Ni^{II}	D (cm^{-1})	E (cm^{-1})	Complexe Co^{II}	D (cm^{-1})	E (cm^{-1})
1er triplet	-66,2	0	1er quartet	11,5	11,6
2ème triplet	22,5	12,1	2ème quartet	13,1	-13,1
3ème triplet	23,2	-13,4	1er doublet	12,6	0
Calcul complet	-16,8	1,15	Calcul complet	35,4	2,20
Expérience	-13,9	1,5	Expérience	31,0	0

TABLE 2.3 – Principales contributions des états excités aux paramètres D et E.

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Origin of the Magnetic Anisotropy in Heptacoordinate Ni^{II} and Co^{II} Complexes

Renaud Ruamps,[a] Luke J. Batchelor,[b] Rémi Maurice,[a, c, d] Nayanmoni Gogoi,[e, f] Pablo Jiménez-Lozano,[d] Nathalie Guihéry,*[a] Coen de Graaf,[d, g] Anne-Laure Barra,[h] Jean-Pascal Sutter,[e, f] and Talal Mallah*[b]

Abstract: The nature and magnitude of the magnetic anisotropy of heptacoordinate mononuclear Ni^{II} and Co^{II} complexes were investigated by a combination of experiment and ab initio calculations. The zero-field splitting (ZFS) parameters D of $[Ni(H_2DAPBH)(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**1**) and $[Co(H_2DAPBH)(H_2O)(NO_3)](NO_3)$ [**2**; H_2DAPBH = 2,6-diacetylpyridine bis(benzoyl hydrazone)] were determined by means of magnetization measurements and high-field high-frequency EPR spectroscopy. The negative D value, and hence an easy axis of magnetization, found for the Ni^{II} complex indicates stabilization of the highest M_S value of the $S=1$ ground spin state, while a large and positive D value, and hence an easy plane of magnetization, found for Co^{II} indicates stabilization of the $M_S=\pm 1/2$ sublevels of the $S=3/2$ spin state. Ab initio calculations were performed to rationalize the magnitude and the sign of D, by elucidating the chemical parameters that govern the magnitude of the anisotropy in these complexes. The negative D value for the Ni^{II} complex is due largely to a first excited triplet state that is close in energy to the ground state. This relatively small energy gap between the ground and the first excited state is the result of a small energy difference between the d_{xy} and $d_{x^2-y^2}$ orbitals owing to the pseudo-pentagonal-bipyramidal symmetry of the complex. For Co^{II}, all of the excited states contribute to a positive D value, which accounts for the large magnitude of the anisotropy for this complex.

Keywords: ab initio calculations · cobalt · heptacoordinate complexes · magnetic anisotropy · nickel

Introduction

One of the challenges in the field of molecular magnetism is the fundamental understanding of the origin of the magnetic anisotropy in mononuclear complexes that can be used as building blocks to prepare single-molecule magnets[1] and single-chain magnets.[2–4] One fruitful approach may be to combine synthetic chemistry and ab initio theoretical calculations. Such a strategy is valuable to chemists who appreciate simple rules that may direct their synthesis. Herein, we investigate the origin of the magnetic anisotropy of heptacoordinate Ni^{II} and Co^{II} complexes with pentagonal-bipyramidal geometry based on the pentadentate ligand 2,6-diacetylpyridine bis(benzoyl hydrazone), H_2DAPBH. The planarity of the pentadentate ligand ensures an axial structure and is expected to lead to large magnetic anisotropy.

[a] R. Ruamps, Dr. R. Maurice, Prof. N. Guihéry
Laboratoire de Chimie et Physique Quantiques
Université de Toulouse III
118, route de Narbonne
31062 Toulouse (France)
E-mail: nathalie.guihery@irsamc.ups-tlse.fr

[b] Dr. L. J. Batchelor, Prof. T. Mallah
Institut de Chimie Moléculaire et des Matériaux d'Orsay
CNRS, Université Paris Sud 11
91405 Orsay Cedex (France)
E-mail: talal.mallah@u-psud.fr

[c] Dr. R. Maurice
Zernike Institute for Advanced Materials
University of Groningen
9747 AG Groningen (The Netherlands)

[d] Dr. R. Maurice, P. Jiménez-Lozano, Prof. C. de Graaf
Departament de Química Física i Inorgànica
Universitat Rovira i Virgili
Marcel·li Domingo s/n
43007 Tarragona (Spain)

[e] Dr. N. Gogoi, Dr. J.-P. Sutter
CNRS; LCC (Laboratoire de Chimie de Coordination)
205, route de Narbonne
31077 Toulouse (France)

[f] Dr. N. Gogoi, Dr. J.-P. Sutter
Université de Toulouse; UPS, INPT; LCC
31077 Toulouse (France)

[g] Prof. C. de Graaf
Institució Catalana de Recerca i Estudis Avançats (ICREA)
Passeig Lluis Companys 23
08010, Barcelona (Spain)

[h] Dr. A.-L. Barra
Laboratoire National des Champs Magnétiques Intenses
UPR CNRS 3228, Université J. Fourier
25, avenue des Martyrs, B.P. 166
38042 Grenoble Cedex 9 (France)

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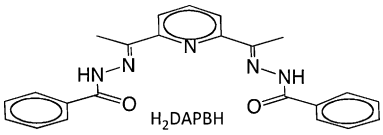

We have already combined experimental data and a semi-empirical theoretical approach to get insight into the magnetic anisotropy of hexacoordinate and pentacoordinate Ni^{II} complexes.[5–7] Theoretical studies have been already carried out on Ni^{II} and Co^{II} complexes[8–11] but, to the best of our knowledge, no reports on heptacoordinate Ni^{II} and Co^{II} complexes exist. This work aims to combine synthetic chemistry, physical studies, and ab initio calculations to unravel the effect of the different electronic parameters that govern the magnetic anisotropy in heptacoordinate complexes. Such insight aims to establish a correlation between magnetic anisotropy and parameters accessible to chemical manipulation. The approach focused here on Ni^{II} and Co^{II} heptacoordinate complexes is, of course, general and can eventually be applied to other metal ions with the same geometry and to other geometries, provided the symmetry remains very close to axial.

For mononuclear complexes having an orbitally nondegenerate electronic ground state and close-to-axial symmetry, the main contribution to magnetic anisotropy stems from the interaction between the ground and the excited electronic states coupled through the spin–orbit operator. These interactions lift the degeneracy of the $2S+1$ M_S components of the ground state, resulting in the so-called zero-field splitting (ZFS). The magnitude of the magnetic anisotropy (extent of ZFS) is therefore governed by the magnitude of the spin–orbit coupling (SOC) and by the energy difference between the ground and the excited electronic states. The smaller the energy difference between the ground and the excited states, the larger the interaction and thus the larger the magnetic anisotropy.

In this work, we investigated the magnetic anisotropy of complexes $[Ni(H_2DAPBH)(H_2O)_2](NO_3)_2{\cdot}2H_2O$ (**1**) and $[Co(H_2DAPBH)(H_2O)(NO_3)]NO_3$ (**2**) using magnetization measurements and EPR spectroscopy to estimate the ZFS parameters. Ab initio calculations were then carried out to rationalize the origin of the experimentally observed anisotropy and develop simple rules to tune the ZFS by small modifications of the complexes.

Results and Discussion

Synthesis and characterization: Complexes **1** and **2** were synthesized according to literature procedures[12,13] and characterized by mass spectrometry, elemental analysis, infrared spectroscopy, and a unit cell was collected to ensure that the structures were identical to those previously reported (see Supporting Information and Figure 1). Compound **1** contains a network of hydrogen bonds involving coordinated water and crystallization water molecules, the nitrate anions, and the oxygen atoms of the pentadentate ligand (Supporting Information Figure S1). Thermogravimetric analysis (TGA) of a freshly prepared microcrystalline powder of **1** showed steady water loss between 40 and 100 °C (Supporting Information Figure S2).

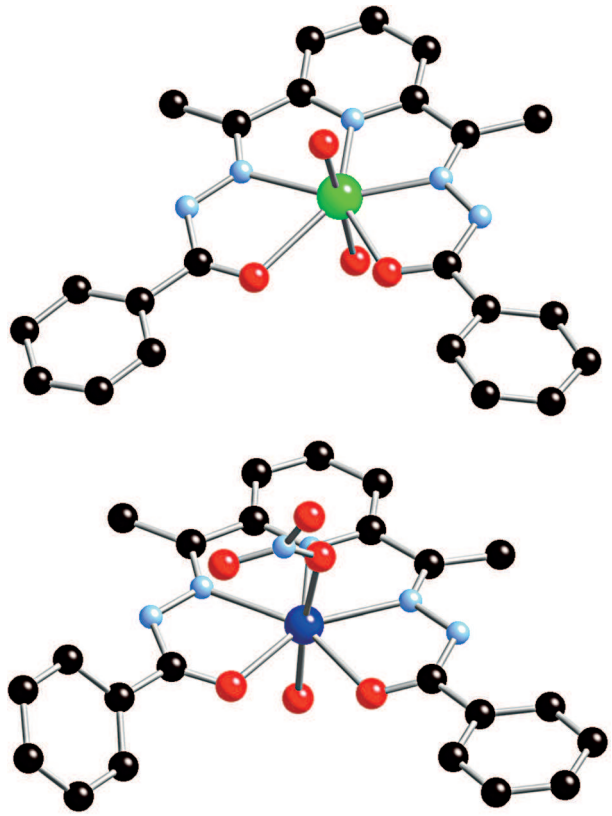

Figure 1. View of the molecular structures of **1** (top) and **2** (bottom).

Magnetic studies: Magnetization studies were carried out with a SQUID magnetometer (see Supporting Information). The temperature dependence of the magnetic susceptibility was measured at a fixed dc field of 0.1 T, and magnetization versus field was measured at 2, 4, and 6 K. Plotting $M=f(H/T)$ for **1** and **2** led to nonsuperimposable curves, which is a signature of the presence of a magnetic anisotropy (Figure 2). The data were fitted by using a home made software that diagonalizes the spin Hamiltonian with a g_{iso} value obtained from the $\chi_M T=f(T)$ curves (Supporting Information Figure S3) at high temperature to minimize the number of fitting parameters. The experimental data were fitted simultaneously for all temperatures by exact diagonalization of the energy matrices corresponding to the spin Hamiltonian $\mathbf{H}=\mu_B\mathbf{g}{\cdot}\mathbf{B}{\cdot}\mathbf{S}+D[\mathbf{S}_z^2-S(S+1)/3]+E[\mathbf{S}_x^2-\mathbf{S}_y^2]$, where D and E are the axial and rhombic anisotropy parameters, respectively) averaged over 120 orientations of the magnetic field. The best fits gave $D=-13.9\ cm^{-1}$, $E/D=0.11$, $g_{iso}=2.26$ for **1** and $D=31.0\ cm^{-1}$, $E/D=0$, $g_{iso}=2.22$ for **2**.

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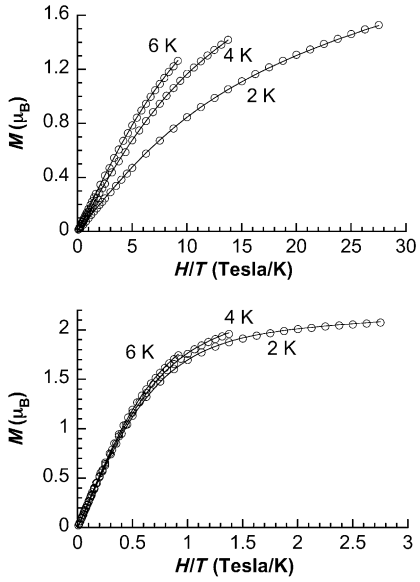

Figure 2. Reduced magnetization M versus H/T for **1** (top) and **2** (bottom) collected at 2, 4, and 6 K. Data were fitted by using homemade software described in text (solid lines); see text for parameters.

HF-HFEPR studies: We performed high-field high-frequency EPR (HF-HFEPR) studies on the two complexes. The HF-EPR powder spectra of pellet samples of complex **1** were measured at several frequencies ranging from 190 to 575 GHz. Notwithstanding the use of many different frequencies, a precise description of the magnetic anisotropy of the complex could not be obtained due to the observation of a large number of signals with respect to what is expected for a simple $S=1$ system. Hence, different samples were measured at an interval of several months. Even though the general shape of the spectra is the same, they exhibit differences in intensities, especially at 190 GHz for high field lines (Figure 3).

These two facts point towards the presence of several molecules with slightly different structural parameters within the powder, not detected by X-ray diffraction. Thus only estimates of the magnetic anisotropy parameters can be given. A first estimate comes from the spectra recorded at 380 GHz (Supporting Information Figure S4): the signal at a field very close to zero observed at this frequency indicates that an energy gap of about 12.6 cm^{-1} is present, which roughly corresponds to $|D+E|$ or $|D-E|$ for some of the molecules. The "zero-field" signal is, however, extremely large, so that slightly smaller $|D|$ values should also be present in the sample. In the spectra recorded at 190 and 285 GHz (Figure 3 and Supporting Information Figure S5), we can also recognize $\Delta M_S=1$ transitions originating from the ground M_S level and corresponding to x and y orientations of the molecules. At 190 GHz, there are four such lines (or rather groups of lines): one close to 5.5 T, another one close to 10.6 T, another one close to 13.5 T, and the last one close to 14.4 T. In the hypothesis that the lines at 5.5 and 13.5 T correspond to the x and y transitions from the same molecules, we obtain that $|E|\approx 1.6$ cm^{-1}, whereas the other two lines lead to $|E|\approx 3.3$ cm^{-1}. These values are in agreement with the large $|D|$ value obtained from magnetization measurements (-13.9 cm^{-1}) but do not allow us to establish a high-precision set of parameters.

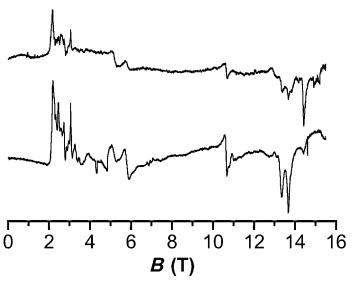

Figure 3. HF-HFEPR spectrum of **1** at 190 GHz and 5 K (bottom spectrum). The measurement was repeated several months later showing the change upon aging (top spectrum).

For Co^{II} (complex **2**), which has a half-integer spin, the D value is unfortunately too large for EPR to improve the magnetic anisotropy description as only effective spin 1/2 spectra are obtained up to the highest frequencies. Powder spectra were recorded in the frequency range from 190 to 460 GHz. All of them can be nicely reproduced by considering an $S=1/2$ spin with a rhombic effective g matrix, with $g_{eff1}=4.984$, $g_{eff2}=4.033$, and $g_{eff3}=1.996$ (Supporting Information Figure S6 and Figure 4). As the spectra at 460 GHz still only contain signals that originate from an $S=1/2$ spin, we can only deduce a lower bound for the axial anisotropy: $|D|>20$ cm^{-1}. Seemingly good fits can be obtained[14] by considering very different D values ($|D|>20$ cm^{-1}) for the $S=3/2$ spin and then adding rhombicity either on the g parameters or on the ZFS ones: if E is set to 0, then three g values are needed ($g_1=2.47$, $g_2=2.03$, and $g_3=1.99$); on the contrary, if there is no rhombicity in the g values ($g_1=g_2$), then good fits are obtained for $|E/D|=1/15$ with $g_1=g_2=2.26$ and $g_3=2.01$.

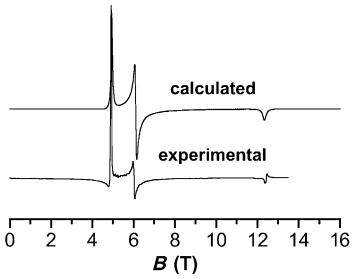

Figure 4. HF-HFEPR spectra of **2** at 345 GHz and 5 K; see text for parameters.

Theoretical calculations: To understand the difference in the sign and magnitude of D for **1** and **2**, we theoretically studied the two compounds using wave function based calculations and a procedure of extraction that has been successfully applied to other mononuclear and binuclear com-

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plexes.[15–19] We first performed complete active space self-consistent field calculations (CASSCF), which account for nondynamic electron correlation and then used the *n*-electron valence second-order perturbation theory (NEVPT2) method to describe the dynamic correlation.[20] The CASSCF wave function contains all electronic configurations that can be constructed by distributing *n* electrons over the five 3d orbitals of Ni^{II} or Co^{II} ($n=8$ and 7 for **1** and **2**, respectively). Both spin–orbit and spin–spin couplings are calculated in the complete d^n manifold.[21,22] Two procedures of extraction of the *D* and *E* parameters were used which are associated with two different kinds of ab initio calculations.[23] Similar calculations have been performed on Mn^{III} complexes.[24] Calculations were performed with the ORCA code,[25] and the values were extracted using the effective Hamiltonian theory. Further computational details are given in the Supporting Information. The results for **1** and **2** are reported in Table 1.

Table 1. NEVPT2 values of *D* and *E* for **1** and **2** extracted with the effective Hamiltonian theory.

Complex	D [cm^{-1}]	E [cm^{-1}]
1	−16.83	1.15
2	35.42	2.20

The results of the calculations are in relatively good agreement in both magnitude and sign with the experimental data for **1** and **2**. In the following, we analyze these data by considering the individual contributions of the excited states to the overall *D* values. We aim to gain insight into the chemical parameters that govern the magnitude and the sign of the magnetic anisotropy. This is reasonably easy in the present case since due to the structural axial anisotropy of the complexes; the axis frame that diagonalizes the calculated $\overline{\overline{D}}$ tensors for **1** and **2** has the *z* axis along the bonds of the metal ion and the apical oxygen atoms. In addition, despite the almost pentagonal molecular plane that contains the *x* and *y* axes, the 3d orbitals are close to the pure d_{xy}, $d_{x^2-y^2}$, d_{z^2}, d_{xz}, and d_{yz} linear combinations of spherical harmonics obtained for an octahedral symmetry. For more strongly distorted complexes the expressions of the d orbitals become more complicated, which seriously hinders the derivation of simple rules to rationalize the magnetic anisotropy. Lifting of the degeneracy of the 3d orbitals for the two complexes is shown qualitatively in Figure 5. Because of the larger distortion in the pentagonal plane for Ni^{II} than for Co^{II}, the energy difference between the d_{xy} and the $d_{x^2-y^2}$ orbitals is larger for the former.

Inspection of the contributions of all excited states shows that only a few play a role in the magnitude and sign of the *D* parameters. Since the spin–spin coupling makes a smaller contribution to the anisotropy than the spin–orbit coupling, we rationalize the values and signs of *D* using only the spin–orbit operator $\Sigma\hat{\mathbf{l}}_i\cdot\hat{\mathbf{s}}_i$. This operator couples the ground state M_S components with those of the excited states and makes

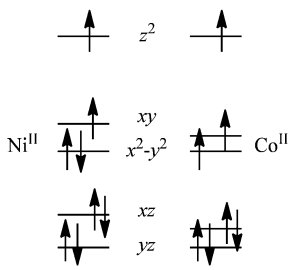

Figure 5. Orbital energy diagrams for **1** (left) and **2** (right).

the main contribution to the magnetic anisotropy. Concerning **1**, the interaction with the first three excited triplet states causes almost all of the magnetic anisotropy of the complex. To rationalize the nature and sign of the magnetic anisotropy, an estimate of the contribution of these excited states to *D* and *E* can be obtained by using perturbation theory. The perturbative calculated values are reported in Table 2.

Table 2. Main perturbative contributions of the triplet excited states to *D* and *E* for **1**.

	D [cm^{-1}]	E [cm^{-1}]
1st triplet	−66.2	0
2nd triplet	22.5	12.12
3rd triplet	23.2	−13.4

The wave function of the $M_S=1$ component of the triplet ground state is dominated by the $|d_{xy}d_{z^2}|$ determinant while the first triplet excited states is dominated by $|d_{x^2-y^2}d_{z^2}|$, corresponding to promotion of an electron from the $d_{x^2-y^2}$ to the d_{xy} orbital (see Figure 5). Since these two orbitals are both expressed as linear combinations of the d_{2+} and d_{2-} complex spherical harmonics, electron promotion does not imply changes in the m_l values. Hence, only the *z* component of the spin–orbit operator $\sum_i \hat{l}_{zi}\cdot\hat{s}_{zi}$ can couple the ground and the first excited triplet state. Because the coupling is restricted to the s_z component of the spin angular momentum, the spin–orbit operator only couples the M_S components of the ground and the excited state with the same value. The coupling between the $M_S=0$ components is zero by spin symmetry, while calculations show that the couplings between the $M_S=\pm1$ components are nonzero. This leads to stabilization of the $M_S=\pm1$ components of the ground triplet state, while the $M_S=0$ state remains unaffected. Therefore, the interaction between the ground state and the first excited triplet results in a negative contribution to *D*, as schematized in Figure 6 (top).

The second and third excited triplet state wave functions are linear combinations of determinants $|d_{xz}d_{xy}|$, $|d_{yz}d_{xy}|$, $|d_{xz}d_{z^2}|$, and $|d_{yz}d_{z^2}|$, corresponding to promotion of an electron from d_{xz} or d_{yz} to d_{xy} and d_{z^2}. These two excited triplet states couple to the ground state by the *x* and *y* components of spin–orbit operator $\sum_i \hat{l}_i^+\cdot\hat{s}_i^- + \hat{l}_i^-\cdot\hat{s}_i^+$ and not by the *z* component, at variance with the first excited state. As a con-

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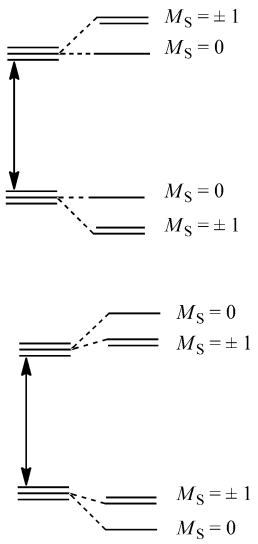

Figure 6. Interaction scheme between the ground and first triplet excited states through the z components of spin–orbit operator that couples M_S levels of the same values and stabilizes the $M_S = \pm 1$ components (top), and interaction between the ground and the second excited triplet states through the x and y components of the spin–orbit operator that couples states with different M_S values and stabilizes the $M_S = 0$ component (bottom).

sequence, the M_S components differing by ± 1 couple together, that is, $M_S = 0$ with $M_S = \pm 1$ and vice versa. The $M_S = 0$ component of the triplet ground state therefore benefits from two interactions (with the $M_S = 1$ and with the $M_S = -1$ components) of the excited states, while the two $M_S = \pm 1$ components of the ground state only benefit from the interaction with one component ($M_S = 0$) of the excited states. As a consequence, the $M_S = 0$ component of the ground triplet state is more stabilized than the $M_S = \pm 1$ components and the contribution of these two excited states to D is positive (Figure 6, bottom). However, the relative energy of the second and third excited triplets is higher than that of the first excited state, and hence this positive contribution is weaker and does not compensate the large negative contribution of the first excited triplet state. The resulting D value remains negative and is relatively large. Among the excited singlet states, six have a small but non-negligible contribution to D. Nevertheless, they all are of opposite value and almost completely compensate one another. The magnetic axes frame, which diagonalizes the computed $\overline{\overline{D}}$ tensor, has its easy axis of magnetization close to the $Ni(H_2O)_2$ bonds (Figure 7, top).

The very large positive D value of **2** results from three positive contributions (Table 3). The largest contributions arise from the interaction with two quartet and one doublet excited states. The ground-state wave function is dominated by the $|d_{xy}d_{x^2-y^2}d_{z^2}|$ determinant (see Figure 5), while the excited quartet states have a multideterminantal nature.

The determinants with the largest weights in these quartets have $|d_{xz}d_{xy}d_{x^2-y^2}|$ and $|d_{yz}d_{xy}d_{x^2-y^2}|$ character. Hence, their contribution to the axial D parameter is essentially due

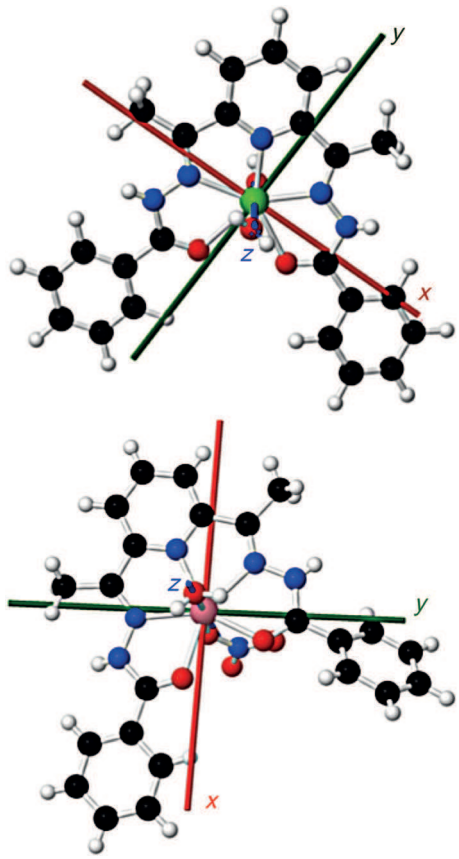

Figure 7. View of the magnetic axes obtained from ab initio calculations. For **1** (top), the magnetization is along z (negative D), and for **2** (bottom), the magnetization is in the xy plane (positive D).

Table 3. Main perturbative contributions of the excited states to the D and E values for **2**.

	D [cm^{-1}]	E [cm^{-1}]
1st quartet	11.49	11.61
2nd quartet	13.07	−13.09
1st doublet	12.58	0

to the $\sum_i \hat{l}_i^+ \cdot \hat{s}_i^- + \hat{l}_i^- \cdot \hat{s}_i^+$ operators coupling the electron that is promoted from the d_{xz} or d_{yz} orbitals to the d_{z^2} orbital. The active spin–orbit operator in the present case couples M_S components differing by a value of 1. Thus, since the $M_S = 1/2$ (respectively $M_S = -1/2$) component of the ground quartet state interacts with both the $M_S = 3/2$ and $M_S = -1/2$ components (respectively $M_S = -3/2$ and $M_S = 1/2$) of the excited states, it benefits from two interactions, while the $M_S = 3/2$ and $M_S = -3/2$ ground state components only interact with the $M_S = 1/2$ or $M_S = -1/2$ components of the excited states, respectively. As a consequence the $M_S = \pm 1/2$ components of the quartet ground state are more stabilized than the $M_S = \pm 3/2$ state, and thus these excited states give a positive contribution to D (note that a positive D value means that the lowest absolute values of M_S are stabilized). The excited doublet state wave function is dominated by the $|d_{xy}\bar{d}_{xy}d_{z^2}|$ and $|d_{x^2-y^2}\bar{d}_{x^2-y^2}d_{z^2}|$ determinants, in which an

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electron is promoted from the d_{xy} to the $d_{x^2-y^2}$ orbitals or from the $d_{x^2-y^2}$ to the d_{xy} orbital. The interactions therefore come from the $\sum_i \hat{l}_{zi} \cdot \hat{s}_{zi}$ operator and only the $M_S = \pm 1/2$ components of the ground state can be stabilized, while the $M_S = \pm 3/2$ state remains unaffected. This leads to an additional positive contribution to D. For Co^{II}, all the important contributions lead to stabilization of the $M_S = \pm 1/2$ components over the $M_S = \pm 3/2$ component, which is at the origin of the large positive D value for the Co^{II} complex. Because of the positive D value, the magnetization has an easy plane perpendicular to the $Co(H_2O)(NO_3)$ apical bonds (Figure 7, bottom).

Conclusion

The larger anisotropy found for Co^{II} in comparison to Ni^{II} is due to the fact that for the former all the excited states contribute to D in the same way (all positive), while for the latter the excited states have opposite contributions that reduce the overall D value. The difference in the sign of D stems mainly from the presence of a dominant negative contribution to D for Ni^{II}, while the contributions of all the excited states are positive for Co^{II}. It is interesting to see how the theoretical results can be used to tune and control the magnetic anisotropy in heptacoordinate Ni^{II} and Co^{II} complexes. Let us focus on Ni^{II}, which has negative and positive contributions to D. To increase the overall negative D value, one must 1) increase the effect of the coupling between the ground state and the first excited triplet by decreasing their energy difference and 2) decrease the effect of the coupling between the ground state and the higher excited triplets by increasing their energy difference. The first requirement can be achieved by reducing the energy difference between the $d_{x^2-y^2}$ and the d_{xy} orbitals by using a more symmetrical pentacoordinate ligand. The energy difference between the ground and the second and third excited triplet states can be increased by increasing the energy difference between the three sets of orbitals (d_{xz},d_{yz}), (d_{xy},$d_{x^2-y^2}$), and d_{z^2}, which will reduce the positive contribution to D and thus leads to a larger stabilization of the $M_S = \pm 1$ components. This can be achieved by substituting the axial ligands by a better σ donor to shift the d_{z^2} orbital upwards, and/or by a less effective π donor to shift the (d_{xz},d_{yz}) orbitals downwards. The same arguments hold for Co^{II}. To increase the positive D value, one must increase mainly the coupling with the first excited state by reducing its energy difference with the ground state. Replacing the apical ligands by weaker σ donors will reduce the energy difference between the (d_{xy}, $d_{x^2-y^2}$) and d_{z^2} orbitals and thus enhance the coupling and increase the positive D value.

This analysis allows a very simple qualitative evaluation tool to assess at least the sign of D for any electronic configuration of a 3d transition metal ion in a pentagonal-bipyramid surrounding to be proposed. For the high-spin d^6 configuration, the (d_{xz},d_{yz}) orbitals will have three electrons (see Figure 5). These two orbitals are both expressed as linear combinations of the d_{1+} and d_{1-} complex spherical harmonics. Electron promotion from d_{yz} to d_{xz}, which corresponds to the first excited triplet state, does not change the m_l values. Only the z component of the spin–orbit operator $\left(\sum_i \hat{l}_{zi} \cdot \hat{s}_{zi}\right)$ is therefore to be considered, as in the case of Ni^{II}, and a negative D value is expected. One of us has already reported a negative D value for a heptacoordinate pentagonal-bipyramidal high-spin Fe^{II} complex,[26] which confirms our prediction. The same kinds of arguments should allow prediction of a negative D value for the d^3 configuration (Cr^{III} and V^{II}), while a positive one is expected for the d^2 (V^{III}) and d^4 (Mn^{III}) configurations. Investigation of the magnetic anisotropy of such compounds is underway. However, when the states are strongly multiconfigurational and/or the excited states are quasidegenerate, the resulting sign of D is hard to predict from simple arguments.

Herein we have demonstrated that a combination of synthetic and theoretical approaches leads to a good understanding of the origin of the magnetic anisotropy in heptacoordinate Ni^{II} and Co^{II} complexes with a geometry close to pentagonal-bipyramidal. More importantly, it fills the gap between theory and experiment and opens the perspective of establishing a magnetostructural correlation for magnetic anisotropy that would allow chemists to tune and eventually control this important parameter in mononuclear complexes.

Experimental Section

Synthesis: Chemicals were purchased from Aldrich and used without further purification. 2,6-diacetylpyridinebis(benzoic acid hydrazone) (H_2DAPBH), $[Ni(H_2DAPBH)(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**1**) and $[Co(H_2DAPBH)(H_2O)(NO_3)](NO_3)$ (**2**) were synthesized according to literature procedures.[12] All solvents were from BDH and were used as received. All manipulations were conducted under standard benchtop conditions.

TGA of $[Ni(H_2DAPBH)(H_2O)_2](NO_3)_2 \cdot 2H_2O$: TGA was performed on a fresh crystalline sample of **1**, assumed to be $[Ni(H_2DAPBH)(H_2O)_2](NO_3)_2 \cdot 2H_2O$. The experiment was performed under a steady flow of air and the temperature increased at a rate of 5 °C min^{-1}. The sample lost mass continuously, and at constant rate, from 40 to 110 °C. At this point it had lost approximately 8% of its original mass (54 g mol^{-1}, or three molecules of water per mole). This species, postulated to be $\{Ni(H_2DAPBH)(H_2O)(NO_3)_2\}$, was stable up to 160 °C, at which point a dramatic loss of mass suggested thermolysis of the complex. The final uncharacterized material was a dark noncrystalline powder.

Magnetic measurements: Variable-temperature (300–2 K) magnetic data were measured on microcrystalline powdered samples of **1** and **2** in an eicosane matrix in 1.0 and 0.1 T fields with a Quantum Design MPMS5 SQUID magnetometer. The presence of eicosane precludes the loss of water molecules of crystallization when the sample is put under vacuum in the SQUID. The data were corrected for the diamagnetic contribution of the sample holder and eicosane and the diamagnetism of the sample estimated according to Pascal's constants. Low temperature (2, 4, and 6 K) variable-field (0–5 T) measurements were carried out in the same manner. The data were fitted by full diagonalization of the energy matrices for 120 orientations of each value of the magnetic field by means of a homemade program based on the following spin Hamiltonian: $\mathbf{H} = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + D[\mathbf{S}_z^2 - S(S+1)/3] + E[\mathbf{S}_x^2 - \mathbf{S}_y^2]$.

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HF-HFEPR: EPR experiments were performed at the High Magnetic Field Laboratory, Grenoble, France. Ground crystals (approximately 50 mg) were pressed to form a pellet to reduce torquing under high magnetic fields. The simulation program is available from Dr. H. Weihe; for more information see http://sophus.kiku.dk/software/epr/epr.html.[14]

Computations: Experimental geometries were used for the present theoretical study. Calculations were performed using the two-step approach implemented in the ORCA code, in which the SOC and SSC relativistic effects are included a posteriori. First, several solutions of the nonrelativistic Born Oppenheimer Hamiltonian are calculated by complete active space self-consistent field (CASSCF) and post-CASSCF methods. Then, the state interaction matrix of the SOC and SSC between these different solutions is calculated and diagonalized. The Breit–Pauli SSC Hamiltonian and a mean-field SOC Hamiltonian are used. Dynamic correlation is introduced by using the *n*-electron valence second-order perturbation theory (NEVPT2) correlated energies in the diagonal elements of the SOC/SSC matrix while keeping the CASSCF wave functions. Def2-tzvpp basis set was used for the Ni and Co, Def2-tzvpp(-f) basis set for the O and N of the first coordination sphere, Def2-svp basis sets for C, and Def2-sv for H.

The $\overline{\overline{D}}$ tensor was extracted by using the effective Hamiltonian theory, which enables one to calculate numerically all the matrix elements of the anisotropic spin Hamiltonian from the ab initio energies and wave functions.

For the rationalization of the magnitude and sign of the ZFS parameters the $\overline{\overline{D}}$ tensor components were calculated using the perturbative method implemented in the ORCA code. These values are slightly overestimated in comparison to those obtained by using the effective Hamiltonian theory.

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Structural description

$[Ni(H_2DABPH)(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**1**) crystallizes in the orthorhombic *pbca* space group and the structure has been fully described previously.[1,2] The neutral DABPH ligand pentacoordinates the Ni(II) ion around the equatorial plane, via the pyridyl nitrogen, both hydrazone nitrogen and both carbonyl oygen atoms. The Ni-N(pyridyl) bond is the shortest in the plane (2.019 Å), followed by the Ni-N(hydrazone) bonds (2.091 and 2.177 Å), with the longest bonds between the Ni(II) and the O(carbonyl) atoms, one of which is significantly longer than the other (2.282 and 2.477 Å). A further distortion from C_5 symmetry is observed in the equatorial plane, with angles between adjacent intra-ligand chelating atoms ranging from 66.93 – 75.92°. These features are consistent with the Jahn-Teller distortion expected for a pentagonal bi-pyramidal Ni(II) complex. Water molecules are coordinated at the axial positions (Ni-OH_2 bond lengths are 2.013 and 2.019 Å and the O–Ni-O angle is 171.76°). Charge balance is provided by the two nitrate counter ions. There is an extensive inter-molecular hydrogen-bonding network, with Ni(II) ions connected via numerous potential pathways incorporating the axial and lattice water molecules, nitrate molecules and carbonyl oxygen atoms.

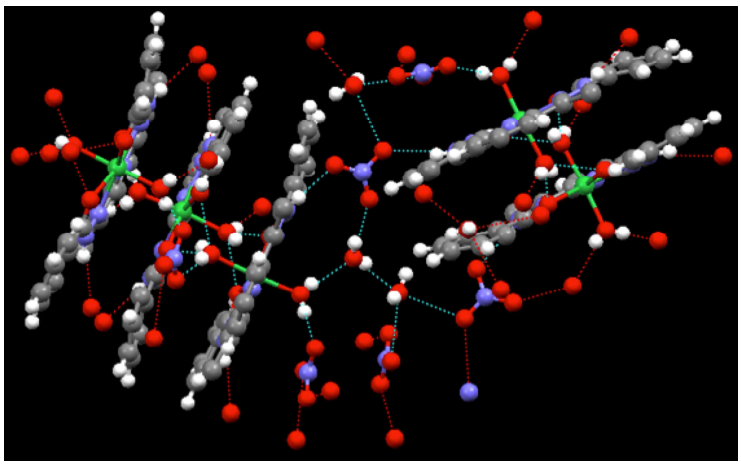

Figure S1. Extended structure of **1** showing the H-bonds network involving coordinated and crystallization water molecules, nitrate and the oxygen atoms of the pentadentate ligand.

$[Co(H_2DABPH)(H_2O)(NO_3)](NO_3)$ (**2**) crystallizes in the monoclinic *P21/c* space group and consists of a similar pentagonal bi-pyramidal mono-cationic Co(II) complex. The neutral DABPH ligand coordinates the Co(II) ion around the equatorial plane via the same atoms. In this case the bond lengths are more uniform (Co-N(pyridyl) is 2.195 Å, Co-N(hydrazone) are 2.190 and 2.203 Å,

and Co-O(carbonyl) are 2.150 and 2.229 Å), owing to the absence of Jahn-Teller effects. Similarly the range of angles between adjacent intra-ligand chelating atoms is smaller (69.54 – 72.02°). The O(carbonyl)-Co-O(carbonyl) angle is larger (78.67°) but this is merely a consequence of the non-macro-cyclic nature of the ligand. The coordination sphere is completed by one water molecule and one nitrate ligand at the axial positions (Ni-OH_2 and Ni-O_3N bond lengths are 2.135 and 2.142 Å respectively, and the O–Ni-O angle is 173.59°). Charge balance provided by the remaining nitrate counter ion.

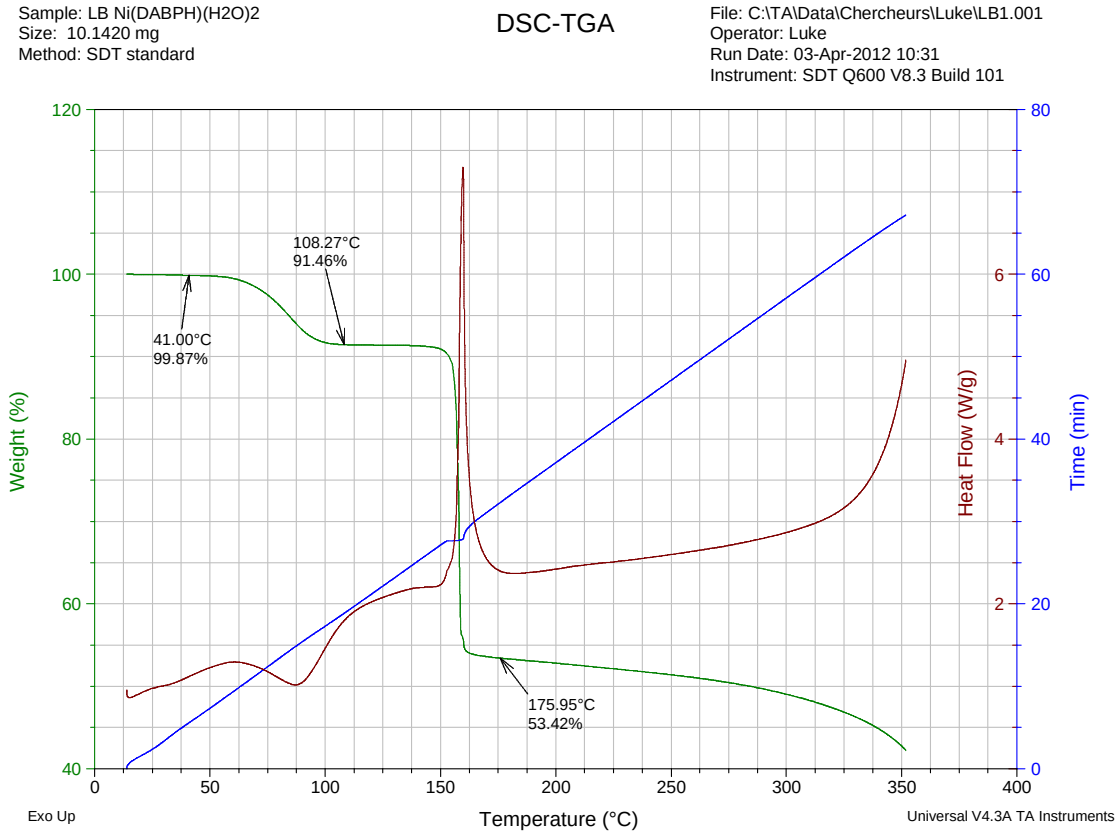

Figure S2. TGA studies for **1**.

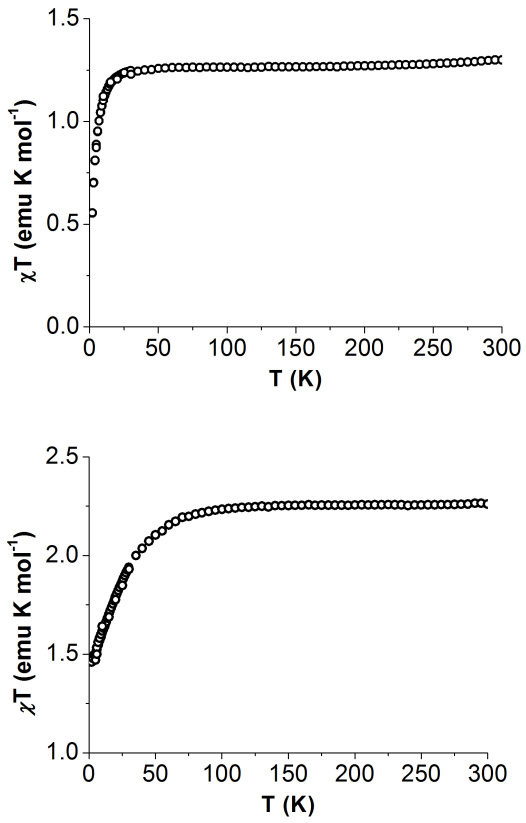

Figure S3. χT *vs.* T for **1 (**top) and **2** (bottom) in an applied field of 0.1 T

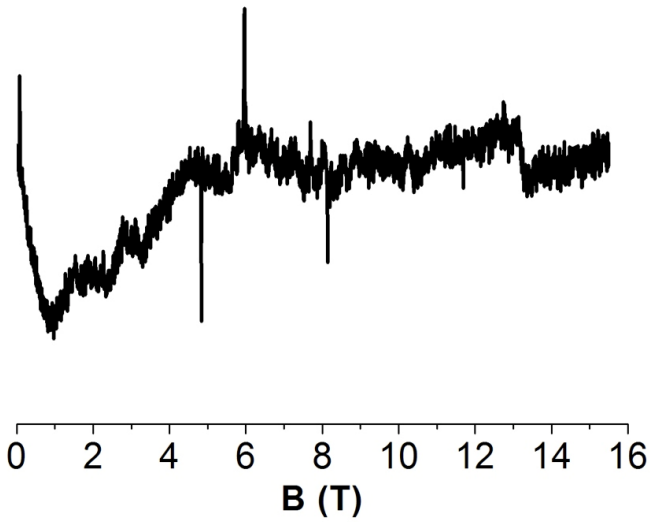

Figure S4. 380 GHz HF-HFEPR spectrum of **1** at 5 K, showing the transition at zero field.

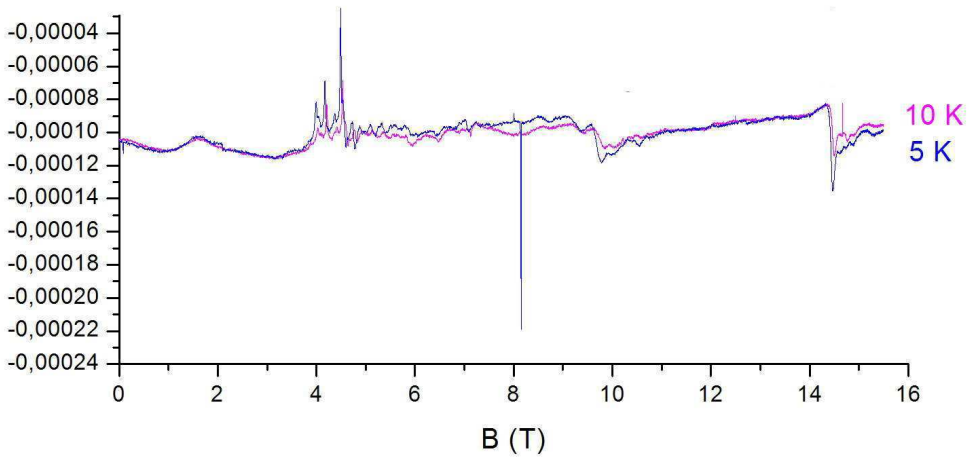

Figure S5. 285 GHz HF-HFEPR spectra of **1** at 5 and 10 K.

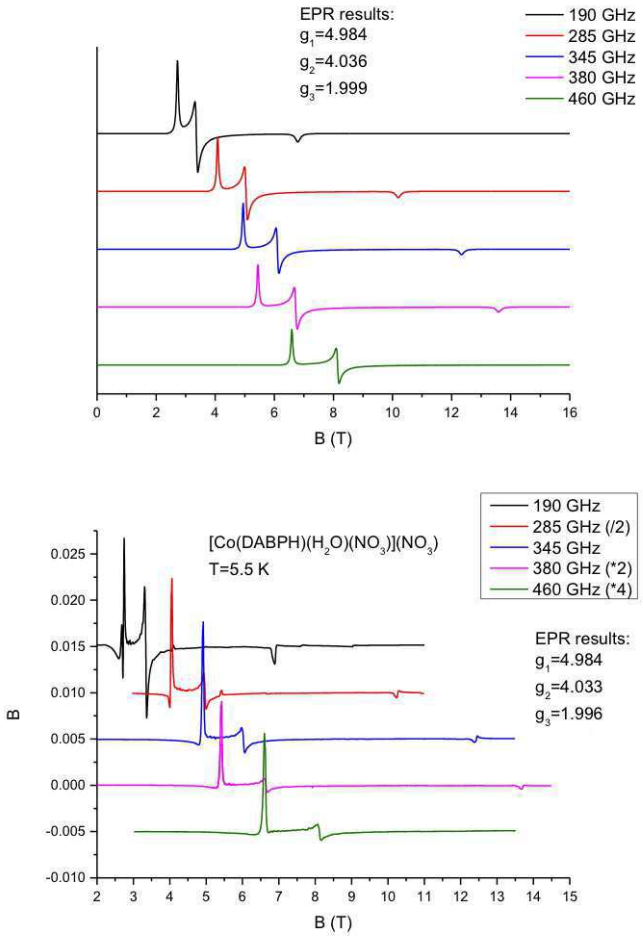

Figure S6. HF-HFEPR spectra for **2** at different frequencies and T = 5.5 K, top calculated (top) and experimental (bottom).

Only the largest contributions appear in the following tables.

Table S1: Main contributions in cm^{-1} of the excited states to the D and E values for **1.**

	D	E
1st triplet	-66.2	0
2nd triplet	22.5	12.12
3rd triplet	23.2	-13.4

Table S2: Main contributions in cm^{-1} of the excited states to the D and E values for **2.**

	D	E
1st quartet	11.49	11.61
2nd quartet	13.07	-13.09
1st doublet	12.58	0

[1] T. J. Giordano, G. J. Palenik, R. C. Palenik, D. A. Sullivan, *Inorg. Chem.* **1979**, *18*, 2445.

[2] C. Pelizzi, G. Pelizzi, S. Porretta, F. Vitali, *Acta Cryst. Sec. C* **1986**, *42*, 1131

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ARTICLE TYPE

Ising-type magnetic anisotropy and single molecule magnet behaviour in mononuclear trigonal bipyramid Co(II) complexes

Renaud Ruamps,[a] Luke J. Batchelor,[b] Régis Guillot,[b] Anne-Laure Barra,[c] W. Wernsdorfer,[d] Nathalie Guihéry,*[a] and Talal Mallah*[b]

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The magnetic anisotropy of two pentacoordinate trigonal bipyramid Co(II) complexes $[Co(Me_6tren)Cl]ClO_4$ **1** and $[Co(Me_6tren)Br]Br$ **2** was investigated and analysed by magnetic studies, high field multifrequency Electron Paramagnetic Resonance (EPR) and *ab initio* calculations. Negative *D* parameters expressing an Ising type anisotropy (easy axis of magnetization) were found experimentally for both complexes. The calculation lead to a values very close to the experimental ones, which allows a robust analysis of the origin of the anisotropy in these complexes. of the The wave functions of the ground and the first four excited states reveals that they are strongly muldeterminantal i.e. linear combinations of several determinants. It is shown that the most important contribution of the spin orbit coupling between the ground and lowest excited states stabilizes the largest $M_S = \pm 3/2$ components of the S=3/2 ground state and therefore brings a large negative contribution to *D*. The analysis of the difference between the magnitudes of the anisotropy of the two complexes leads to the conclusion that the large Ising-type anisotropy is obtained by using weak σ-donating ligands in the equatorial plane and strong π-donating ones for the axial positions, thus, giving to chemists a simple tool to predict the magnetic anisotropy in this type of complexes. The investigation of the magnetic behaviour of a single crystal of **1** by micro-squid shows, as expected, the presence of an easy axis of magnetization. Quantum tunnelling of the magnetization is observed as the result of weak intermolecular three-dimensional antiferromagnetic exchange interaction but does not disrupt the quantum nature of the individual spins. The hysteresis loops present temperature and sweep rate dependence typical of a single molecule magnet for **1**.

Introduction

The design of molecules presenting a blocking of the magnetization, called Single Molecule Magnets (SMMs), has been the subject of intense research effort since their discovery more than twenty years ago.[1-9] This is motivated, among other things, by their potential use as quantum bits.[10,11] Historically, the first SMMs based on transition metal ions were polynuclear complexes, but recently much effort has been invested in order to design mononuclear SMMs. However, very few mononuclear complexes based on transition metal ions showed a blocking of the magnetization,[12-16] and only one Co(II) complex was reported to do so in the absence of a static applied magnetic field.[17] The added value of mononuclear complexes is their chemical stability in different environments such as in solution or on surfaces allowing the manipulation and the study of the magnetic behaviour of individual molecules.[18-22]

A fundamental understanding of the origin of the magnetic anisotropy using quantum chemistry and the translation of the physics governing the anisotropy into a language useful to chemists may highly contribute to the development of new molecules. The challenge is to design stable mononuclear complexes based on transition metal ions where the slow relaxation of the magnetization occurs in the absence of a static magnetic field. This is a requirement if such molecules are to be used as single quantum bits for the design of assemblies for quantum information.[23] While preparing this manuscript, a report on tailoring the magnetic anisotropy of first row transition metal ions appeared and predicted a large axial anisotropy with an easy plane of magnetization (positive *D* parameter) for pentacoordinate trigonal bipyramid Co(II) complexes,[24] while we find a weak anisotropy with an easy axis of magnetization (negative *D* parameter) for the complexes reported here.

The prediction of the magnetic anisotropy nature of transition metal ions can be complex as i) several excited states may contribute to magnetic anisotropy and ii) the wave-functions of the ground and excited states may be formed by linear combinations of several determinants (multideterminantal). In the most interesting cases, for symmetry reasons an excited state that brings a negative contribution to *D* may be very close in energy to the ground state and thus dominates leading to an overall negative *D* value. In order to illustrate these ideas, we focus on pentacoordinate trigonal bipyramidal Co(II) complexes (C_{3v} symmetry). We study the magnetism, the Electron Paramagnetic Resonance Spectra (EPR) and perform theoretical calculations to

determine the anisotropy parameters of two complexes: $[Co(Me_6tren)Cl]ClO_4$ **1** $[Co(Me_6tren)Br]Br$ **2**. It worth noting here that the accurate determination of the spin Hamiltonian parameters using EPR and the good agreement between calculated and experimental data is crucial for a robust rationalization and prediction of the magnetic anisotropy.

Results and discussion

Syntheses and structures

The syntheses were performed as previously reported, however a structure had been obtained only for $[Co(Me_6tren)Br]Br$ **2**.[25] Single crystals suitable to structural determination with Cl as an axial ligand instead of Br were obtained upon the addition of $NaClO_4$, thus affording crystalline $[Co(Me_6tren)Cl](ClO_4)$ **1**, the first reported structure of a Me_6tren ligated penta-coordinate metal with a chloride ion in the axial position. The selection of a counter ion with potential C_3 symmetry (ClO_4) also allowed us to maintain the overall C_3 symmetry of the Co(II) complex. **1** crystallizes in the trigonal space group *R3c*. The structure of the cation consists of a Co(II) ion penta-coordinated by four amino nitrogens from the neutral Me_6tren ligand and one chloride ion. The ligands are distributed at the apices of a trigonal bipyramid with crystallographic C_3 symmetry, the three equatorial sites occupied by the terminal amines and the axial sites occupied by the central amine and the chloride ion (Figure 1). Charge balance is provided by a C_3 symmetrical perchlorate anion. The Co(II) ion lies 0.33 Å below the equatorial plane of the three nitrogen atoms with an equatorial N2-Co(II)-Cl angle of 98.75°. The Co-N1 bond length (2.176 Å) is slightly longer than the equatorial ones (2.152 Å). The Co-Cl distance is equal to 2.282 Å. The N2CoN2 and the N1CoN2 angles are equal to 117.7° and 82.5° respectively (Table S1 and S2, see ESI). Within the crystal each molecule is surrounded by other 12 molecules (Figure S1): 6 neighbours placed at the vertices of an octahedron and belonging to two adjacent (ab) planes along the c axis with Co–Co distances of 7.95 Å and 6 next neighbours forming a regular hexagon and belonging to the same plane (ab) with Co–Co distances equal to 9.89 Å. The intermolecular shortest contacts (2.747 Å) are along the c axis between the Cl and the H atoms of the Me_6tren ligand belonging to neighbour molecules.

For the structure of **2**, we carried out new measurements at T = 100 K and found the same cubic structure previously published.[25] The molecular local symmetry for **2** is C_{3v} as for **1**. (see ESI).¶

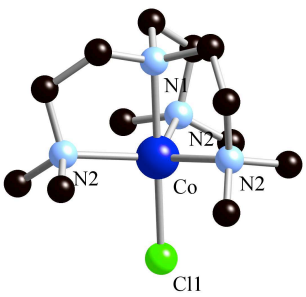

Figure 1. View of the molecular structure of the $[Co(Me_6tren)Cl]^+$ cation.

Magnetic and EPR studies

The thermal variation of the molar magnetic susceptibility, (χ) and (χT) and the magnetization *vs*. the applied magnetic field for **1** and **2** are plotted in Figure 2 and Figure S2. χT has the same behaviour for the two compounds. It is constant between room temperature and around 40 K with values close to 2.35 emu K mol^{-1}, which is expected for a S = 3/2 spin moment with a *g*-value equal to 2.24. Below 40 K, χT collapses to 1.17 and 1.51 for **1** and **2** respectively indicating the presence of magnetic anisotropy (zero-field splitting of the $M_S = \pm 1/2$ and $\pm 3/2$ sub-levels) that is larger for **1** than for **2**. The $M = f(H)$ curves confirm the presence of a magnetic anisotropy that has a larger magnitude for **1** than for **2** since the magnetization values at $\mu_0 H$ = 5.5 Tesla is weaker for the former than the latter compound. In order to quantify the magnitude of the magnetic anisotropy, we fit the magnetic data using the spin Hamiltonian $\mathcal{H} = g\beta \boldsymbol{S} \bullet \boldsymbol{B} + D[S_z^2 - S(S+1)3]$ for S = 3/2 and extract the *g*-values and the zero-field splitting parameters *D* that express the axial magnetic anisotropy. We assume that the rhombic parameter *E* is zero because of the presence of a C_3 principal symmetry axis for the complexes. The simultaneous fit of the susceptibility and the magnetization data leads to the following parameters for **1** and **2** respectively: g_{Cl} = 2.24, D_{Cl} = – 6.2 cm^{-1} and g_{Br} 2.22 = D_{Br} = – 2.5 cm^{-1}. It is not possible to obtain a better fit if the *D* parameters were constrained to be positive, which suggests that the magnetic anisotropy is of the Ising type i.e. the $M_S = \pm 3/2$ sub-levels lie lower in energy than the ±1/2 ones and there is an easy axis of magnetization.

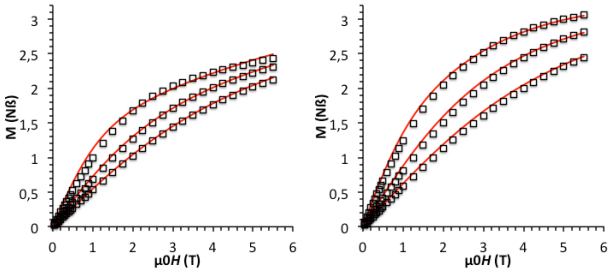

Figure 2. Experimental (□) and calculated (—) *M vs.* $\mu_0 H$ collected at 2, 4 and 6 K for **1** (left) and **2** (right). See text for the fit parameters.

In order to confirm the magnetization results and particularly the sign of *D*, we performed Electron Paramagnetic Resonance (EPR) studies up to an applied magnetic field of 16 Tesla and at different frequencies. For **1**, we found that at 475 GHz a transition near zero field is present, which indicates an energy difference between the $M_S = \pm 3/2$ and ±1/2 sublevels around 15.8 cm^{-1} (Figure S3, see ESI). Since this energy difference corresponds to 2*D* for a spin S = 3/2, we can conclude that |*D*| is very close to 8 cm^{-1}. Three other spectra were then recorded at T = 15 K and at hν = 220.8, 331.2 and 662.4 GHz (Figure 3). A good fit was obtained for the three spectra with the same set parameters $g_x = g_y$ = 2.16, g_z = 2.2 and D = – 8.12 cm^{-1}, which gives to a more accurate value for *D* and confirms its negative sign.

The EPR studies for **2** confirm the sign and the value extracted from the magnetization data. The fit of the spectra at the different frequencies gives $g_x = g_y$ = 2.1, g_z = 2.02 and D = – 2.4 cm^{-1} (see ESI, Figure S4).

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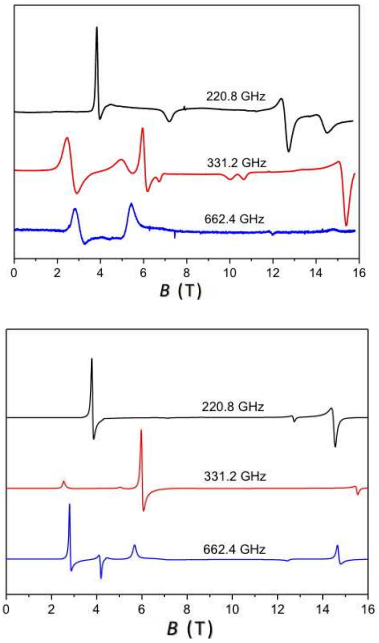

Figure 3. EPR spectra of **1** at T = 15 K at three different frequencies experimental (top) and calculated (bottom), see text for parameters.

Theoretical calculations

Experimental geometries were used for the theoretical study. The *ab initio* calculations have been performed using the two-step approach implemented in the ORCA code in which the spin-orbit coupling (SOC) and spin-spin coupling (SSC) relativistic effects are included *a posteriori*.[26-28]‡

Since the SOC contribution to the ZFS parameters is more important than the SSC one, the rationalization of the magnitude and the sign of *D* only uses the spin-orbit operator (see equation 1) that couples the ground state M_S components with those of the excited states.

$$\hat{H}_{SO} = \sum_i \xi_i \hat{l}_i.\hat{s}_i = \sum_i \xi_i \left(\hat{l}_{Z_i}.\hat{s}_{Z_i} + \frac{1}{2}\left(\hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i} \right) \right) \quad 1$$

The values of *D* are reported in Table 1, *E* was systematically found to be lower than 10^{-2} cm^{-1}. Comparing the values obtained at several levels of correlations, one may first notice that the inclusion of dynamic correlation, using the energies of the NEVPT2 method, reduces substantially the *D* values. At this level, the calculated values are in excellent agreement with the experimental data. This allows us to perform a rationalization of the origin of negative *D* value in these trigonal complexes.

Table 1. Values of *D* in cm^{-1} experimentally determined and calculated at various levels for the two complexes.

Method	[Co(Me$_6$tren)Cl](ClO$_4$)	[Co(Me$_6$tren)Br]Br
CAS(7,5)SCF (10Q-40D)	-16.47	-4.75
CAS(7,5)NEVPT$_2$ (5Q)	-10.90	-3.37
CAS(7,5)NEVPT$_2$ (10Q-40D)	-9.73	-2.12
EPR experimental values	-8.12	-2.4

The calculations show that the only first four quartet excited states noted Φ_1, Φ_2, Φ_3 and Φ_4 are close enough in energy to the ground state (see ESI, Table S3) to have a non-negligible contribution to *D*, we thus limit the rationalization to these states. As shown in Table 2 the negative *D* value is due to Φ_1, while Φ_3 and Φ_4 contribute positively and Φ_2 has zero contribution.

Table 2. Main contributions to *D* and *E* in cm^{-1} of the first excited quartet states computed at the CAS(7,5)NEVPT2 level for the two complexes.

State	Multiplicity	[Co(Me$_6$tren)Cl]ClO$_4$		[Co(Me$_6$tren)Br]Br	
		D	*E*	*D*	*E*
Φ_1	^{4}A	-27.764	0	-20.691	0
Φ_2	^{4}A	0	0	0	0
Φ_3	^{4}E	8.301	6.951	7.920	0.605
Φ_4	^{4}E	8.301	-6.951	7.920	-0.605

As we have previously explained,[29] the only way to get a negative *D* value in Co(II) mononuclear complexes is to have a low in energy excited state that is obtained from an excitation between orbitals that possess the same m_l values, for instance from d_{xy} to d_{x2-y2} ($m_l = \pm 2$) or from d_{xz} to d_{yz} ($m_l = \pm 1$), so that the $\sum_i \hat{l}_{Z_i}.\hat{s}_{Z_i}$ operator couples the two states and thus stabilizes $M_S = \pm 3/2$ components.§ This situation is, at first glance, not possible in the present case of a trigonal bipyramidal C_{3v} symmetry because, as one can see from figure 4, any excitation leading to a quartet excited state occurs between orbitals possessing different m_l values, which always stabilizes the ±1/2 components of the ground state and adds a positive contribution to *D*.§

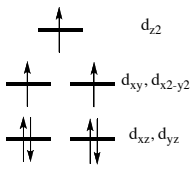

Figure 4. Lift of the degeneracy of the d orbitals in a trigonal bipyramid (C_{3v}) crystal field.

The above analysis does not take into account the symmetry of the d orbitals that turns out to be the same for d_{x2-y2}, d_{xy}, d_{xz} and d_{yz} since they all belong to the same irreducible representation E of the point group C_{3v}. Thus, except the d_{z2} orbital that is pure, the four other metallic orbitals are linear combinations of d_{xy}, d_{x2-y2}, d_{xz} and d_{yz}. Thus, the ground state is composed of several determinants when expressed in the basis of the pure d_{xy}, d_{x2-y2}, d_{xz} and d_{yz} orbitals (Figure 5, top), and the picture given by Figure 4 only gives the determinant having the largest contribution (49 %, see the composition of $^4\Phi_0$ in Figure 5) to the ground state wave function. The first excited state is also multideterminental as shown in the bottom of Figure 5.

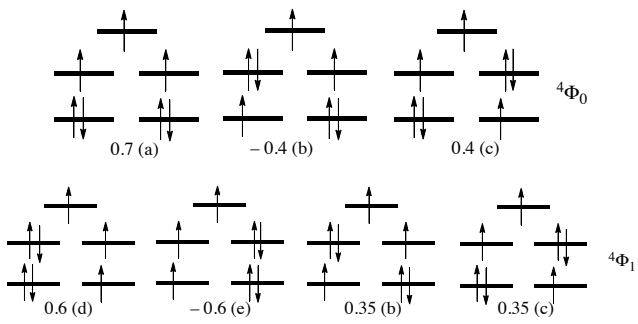

Figure 5. Composition of the wavefunctions corresponding to the ground state $^4\Phi_0$ (top) and the first excited state $^4\Phi_1$ (bottom)

The origin of the negative contribution to *D* arising from the coupling between the ground and the first excited states is thus

due to the interaction through the $\sum_i \hat{l}_{z_i}.\hat{s}_{z_i}$ operator between the (d) and (e) determinants of Φ_1 with the (b) and (c) ones belonging to Φ_0 since they involve excitations between orbitals possessing the same m_l values, which stabilize the $M_S = \pm 3/2$ ground state components more than the $\pm 1/2$ ones.[29]§ Using the same arguments, it is possible to show that all the contributions involving the determinants of Φ_2 cancel. While those belonging to Φ_3 and Φ_4 bring positive contributions to D (Table 2, Figure S5, see ESI for the detail of the determinant decomposition of each state and a detailed explanation). Since Φ_1 is much lower in energy than Φ_3 and Φ_4 (Table S1), its large negative contribution is not compensated by the positive contributions of Φ_3 and Φ_4 and the overall D value is negative.

Concerning the rhombic term E, the matrix elements affecting this parameter involve states with different M_S values and hence only the $\frac{1}{2}\sum_i \hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i}$ operator. For the same reasons as for D, the excited degenerate states Φ_3 and Φ_4 produce the principal contributions with a similar intensity but a different sign (due to imaginary part) and hence result in a zero value for the E parameter (Table 2).

While the physics that governs the ZFS values (physical content of the excited states and their spin orbit couplings) is essentially the same for **1** and **2**, the values of D are different. For **2** where Br is at the axial position, the first excited quartet state was found much higher in energy than in the case of **1** (see ESI, Table S3). As a consequence the negative contribution of this state is in absolute value larger for **1** than for **2** since, everything being equal, $|D|$ is inversely proportional to the energy difference between the ground and the excited state at hand (at the second order of perturbations).

Since the coefficients of the various determinants are similar in both compounds, electron repulsion is expected to be essentially identical. It is therefore possible to rationalize the difference in the magnitude of D between the two compounds from ligand field theory considerations i.e. considering only the energy differences between the d orbitals. The Co–Cl distance (2.282 Å) is shorter than the Co–Br one (2.451 Å) while the Co–N2 bond lengths in the equatorial plane are larger for **1** (2.152 Å) than for **2** (2.134 Å) (see ESI, Table S2). As a consequence, the σ-donor effect of the equatorial amine nitrogen atoms is larger for **2** than for **1** and the (d_{x2-y2}, d_{xy}) pair of orbitals has a higher energy in the former than in the latter. The energy difference between the (d_{xz}, d_{yz}) and (d_{x2-y2}, d_{xy}) orbital pairs is hence larger in **2**, and consequently D is expected to be weaker in this compound as found from the theoretical calculations. While less important the π-donor effect of the apical halogen atoms contributes in the same direction. Indeed, Br^- was experimentally found to have a weaker donating effect from its p orbitals than Cl^-, which destabilizes less the d_{xz},d_{yz} pair of orbitals and thus leads to a larger ((d_{xz}, d_{yz}),(d_{x2-y2}, d_{xy})) energy difference and thus to a weaker D value. In summary, since for Co(II) metal ions in a trigonal bipyramidal geometry the magnitude of $|D|$ is mainly governed by the energy difference between the (d_{xz}, d_{yz}) and (d_{x2-y2}, d_{xy}) sets of orbitals: the smaller this difference, the larger the magnitude of $|D|$. Therefore, D is large and negative in the case of a weak equatorial σ-donating and strong apical π-donating effects.

Micro-squid studies

The magnetization of compound **1** was studied by micro-SQUID measurements on a single crystal,[30] in order to assess the relaxation of its magnetization. The field was aligned with the mean easy axes of magnetization of the crystal using the transverse field method.[31] This method allowed us to confirm that indeed the crystal possess an easy axis of magnetization as the result of the negative D value determined from EPR. Magnetization *vs.* the applied magnetic field measurements were performed between 1 K and 30 mK at sweep rates ranging from 0.002 to 0.28 T/s (Figure 6 and Figure S6, see ESI). Hysteresis loops were observed below 0.2 K. As expected for SMMs, the hysteresis increases strongly with decreasing temperature and increasing scan rate. A series of steps are observed, which are typical for exchange-biased resonant quantum tunnelling.[32,33] For a S = 3/2, the steps in the $M = f(\mu_0 H)$ loop due to quantum tunnelling are expected to occur at $\mu_0 H = n|D|/g\beta$ (n = 0, 1) i.e.; at $\mu_0 H$ = 0, 8.4 T, since $|D|$ = 8.12 cm^{-1} and g_z = 2.21. Thus the absence of a step at zero field and the presence of different steps at well below 8.4 T and at small field values can indeed be attributed to the presence of very weak antiferromagnetic exchange coupling between the molecules. The examination of he structure shows that two kinds of short contacts between the molecules are present along the z axis and within the xy plane preventing a quantitative correlation between the field values at which the steps occur and the values of the exchange coupling parameters as it was done for the Mn_4 dimer.[34] Nevertheless, complex **1** behaves as a genuine single molecule magnet, where the individual S = 3/2 spins keep their quantum nature and undergo tunnelling because the three dimensional antiferromagnetic exchange coupling is not strong enough to transform the compound to an antiferromagnet.

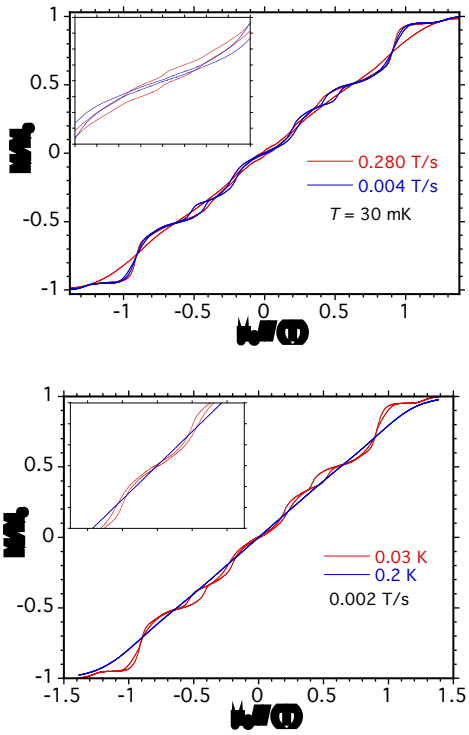

Figure 6. Magnetization *vs.* field on a single crystal of **1** with its easy axis aligned with the field at T = 30 mK and two different sweep rates (top) and at a sweep rate of 0.002 T/s and two different temperatures (bottom).

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Conclusions

The high and axial symmetry of the trigonal bipyramidal geometry of Co(II) complexes leads to a situation where the ground and the excited states wave functions cannot be expressed as single determinants. Calculations show that the wave functions are multideterminantal, and that the first excited state allows the stabilization of the largest M_S values by the action of the $\sum_i \hat{l}_{Z_i}.\hat{s}_{Z_i}$ operator. The analysis of the difference between the magnitudes of the anisotropy of the two complexes leads to the conclusion that, for pentacoordinate trigonal bipyramid symmetry (C_{3v}), a large Ising-type anisotropy is obtained by using weak σ-donating ligands in the equatorial plane and strong π-donating ones for the axial positions, thus, giving chemists a simple tool to predict the magnetic anisotropy in this type of complexes. As expected in the case of an easy axis of magnetization, single molecule magnet behaviour was demonstrated. The intermolecular 3D antiferromagnetic exchange coupling is responsible for the quantum tunnelling and can be exploited as a tool to manipulate the quantum spins providing the design of discrete assemblies with controlled interactions.

Acknowledgements

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Notes and references

[a] *Laboratoire de Chimie et Physique Quantiques, Université de Toulouse III, 118, route de Narbonne, 31062 Toulouse, France. Fax: +33 5 61556065; Tel +33 5 61556098; E-mail: nathalie.guihery@irsamc.ups-tlse.fr*

[b] *Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS, Université Paris Sud 11, 91405 Orsay Cedex, France. Fax: +33 1 69154754; Tel: +33 1 69154749; E-mail: talal.mallah@u-psud.fr*

[c] *Laboratoire National des Champs Magnétiques Intenses, UPR CNRS 3228, Université J. Fourier, 25, avenue des Martyrs, B.P. 166, 38042 Grenoble Cedex 9, France*

[d] *Institut Néel, CNRS, Université J. Fourier, BP 166 25, Avenue des Martyrs, 38405 Grenoble, France*

† Electronic Supplementary Information (ESI) available: [detailed information on the structures with distances and angles around the Co, $\chi_M T$ and $\chi_M = f(T)$ and EPR spectra at different frequencies for **1** and **2**, energy of the four first excited states for **1** and **2**, composition of the wave-functions for the ground state and the four first excited states for **1** and micro-squid data on a single crystal of **1**]. See DOI: 10.1039/b000000x/

¶ CCDC 956888-956889 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure

‡ In a first place, several solutions of the non-relativistic Born Oppenheimer Hamiltonian are calculated using complete active space self-consistent field (CASSCF) and post-CASSCF methods. Then, the effect of the SOC and SSC are taken into account using the quasi-degenerate perturbation theory. Non dynamic correlation is accounted for by the zero-order CASSCF calculation. The active spaces CAS(7,5) contains 7 electrons in the 5 essentially atomic d orbitals. Dynamic correlations are accounted for by the N-Electron Valence Perturbation Theory (NEVPT2) method (see ref. 27). Def2 split-valence Ahlrichs type basis set was used (see ref. 28). Def2-TZVPP for Co (6s5p4d2f1g), Br (6s5p4d1f) and Cl (xxxxxxxxx), Def2-TZVPP(-f) for N and O (first sphere ligand, 6s3p2d1f) and Def2-TZV for C (6s3p) and Def2-SV for H (2s).

§ The $\sum_i \hat{l}_{Z_i}.\hat{s}_{Z_i}$ operator couples the ground state and an excited state that possess the same M_S values andwhich differ by an electron excitation between two real d orbitals which are linear combinations of the spherical harmonics having the same m_l value.. This is the case for d_{xy} and d_{x2-y2} orbtials on the one hand and d_{xz} and d_{yz} on the other hand because the former two obitals are linear combinations of d_{2+} and d_{2-} and the latter of d_{1+} and d_{1-}. In such a case, all M_s components of the ground state are stabilized, but since in the lowest |Ms| values, the wave-function is decomposed on more determinants (for spin reasons), their coefficients are smaller and the effect of the SOC is reduced. As a consequence, the lowest |Ms| values are less stabilized than the largest ones and the resulting *D* value is negative. An excitation between orbitals that have different m_l values leads to a coupling through the $\frac{1}{2}\sum_i \hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i}$ operator. The $M_S = \pm 1/2$ components of the quartet excited states may be coupled with both the $M_S = \pm 3/2$ and $M_S = \pm 1/2$ components of the ground state while the $M_S = \pm 3/2$ components of the excited states may only be coupled with the $M_S = \pm 1/2$ components of the ground state. As a consequence the $M_S = \pm 1/2$ components interact with more excited components and are more stabilized, resulting in a positive contribution to *D*.

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Electronic Supporting Information

Ising-type magnetic anisotropy and single molecule magnet behaviour in mononuclear trigonal bipyramid Co(II) complexes

Renaud Ruamps,[a] Luke J. Batchelor,[b] Régis Guillot,[b] Nathalie Guihéry,*[a] Anne-Laure Barra,[c] W. Wernsdorfer,[d] Nathalie Guihéry,*[a] and Talal Mallah*[b]

Synthesis

Chemicals were purchased from Aldrich and used without further purification. Me_6tren and all cobalt complexes were synthesized according to literature procedures or minor alterations thereof. All solvents were from BDH and were used as received. All manipulations were conducted under standard benchtop conditions.

*Synthesis of [Co(Me_6tren)Cl](ClO_4) (**1**)*
$CoCl_2{\cdot}6H_2O$ (0.200 g, 0.84 mmol) was dissolved in EtOH (20 ml) at 55 °C. Me_6tren (0.214 g, 0.92 mmol) dissolved in EtOH (10 ml) was added dropwise with stirring, forming a blue solution that was stirred overnight at room temperature. $NaClO_4{\cdot}H_2O$ (0.118 g, 0.84 mmol) was added with stirring inducing precipitation of pale blue [Co(Me_6tren)Cl](ClO_4) (**1**) (0.336 g, 95%), which was isolated by filtration and dried in air. Crystals suitable for X-ray analysis were formed upon cooling a hot MeOH solution of **1**. Elemental analysis (%), observed (calculated for $CoC_{12}H_{30}N_4Cl_2O_4$) C, 33.81 (34.03) H, 7.08 (7.15) N, 13.05 (13.24). MS ESI$^+$ (MeOH): *m/z* 324.20 [Co(Me_6tren)Cl]$^+$. IR (KBr) ν/cm^{-1}: 3431 (w), 2983 (m), 2903 (m), 2852 (m), 2795 (w), 2017 (w), 1486 (s), 1475 (s), 1461 (s), 1435 (m), 1359 (w), 1300 (s), 1248 (w), 1174 (m), 1091 (s), 1053 (s), 1023 (m), 1006 (m), 938 (m), 913 (m), 807 (m), 778 (m), 742 (w), 622 (s), 602 (m), 573 (w), 486 (m), 411 (w), 382 (w).

*Synthesis of [Co(Me_6tren)Br]Br (**2**)*
$CoBr_2{\cdot}6H_2O$ (0.100 g, 0.30 mmol) was dissolved in EtOH (20 ml) at 55 °C. Me_6tren (0.077 g, 0.33 mmol) dissolved in EtOH (5 ml) was added dropwise with stirring, forming a blue solution that was stirred overnight at room temperature. This was reduced in volume to 10 ml, yielding royal blue [Co(Me_6tren)Br]Br (**2**) (0.107 g, 80%) upon addition of petroleum ether, which was isolated by filtration and dried in air. An X-ray structure has previously been reported. Elemental analysis (%), observed (calculated for $CoC_{12}H_{30}N_4Br_2$) C, 32.18 (32.21) H, 6.78 (6.76) N, 12.38 (12.53). MS ESI$^+$ (MeOH): *m/z* 368.10 [Co(Me_6tren)Br]$^+$. IR (KBr) ν/cm^{-1}: 3436 (w), 2987 (m), 2927 (m), 2873 (s), 2778 (w), 1485 (s), 1474 (s), 1456 (s), 1395 (m), 1354 (w), 1293 (s), 1275 (s), 1238 (m), 1170 (m), 1098 (s), 1061 (m), 1050 (m), 1032 (m), 1016 (s), 999 (s), 933 (s), 911 (m), 802 (m), 771 (s), 742 (w), 598 (w), 585 (w), 482 (m), 402 (w), 379 (w).

Physical measurements

IR data were measured on KBr pellets using a PerkinElmer FTIR spectrometer. Variable temperature (300 – 2 K) magnetic data were measured on powdered samples of **1** and **2** in an eicosane matrix in 1.0 and 0.1 T fields using a Quantum Design MPMS5 SQUID magnetometer. The data were corrected for the diamagnetic contribution of the sample holder and eicosane, and the diamagnetism of the sample estimated according to Pascal's constants. Low temperature (2 – 6 K) variable field (0 – 5.5 T) measurements were carried out in the same manner. Modeling of magnetic susceptibility and magnetization data was performed by matrix diagonalization methods using home made software

Structural information

X-ray diffraction data was collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

The absolute configuration was determined by refining the Flack's[4] parameter using a large number of Friedel's pairs.

The crystal data collection and refinement parameters are given in Table S1.

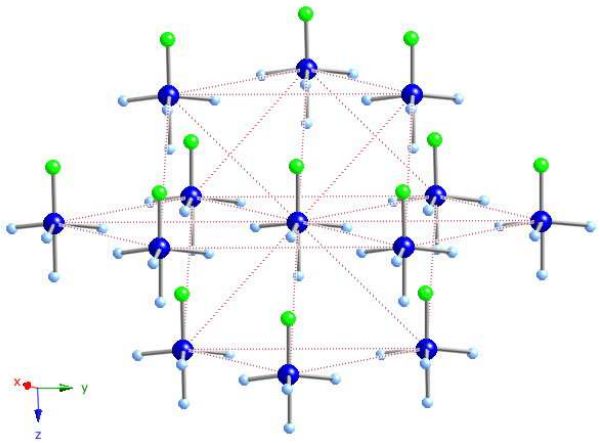

Figure S1. View of the shortest intermolecular distances. C and H atoms and ClO_4 molecules were removed for clarity. The shortest distance between molecules belonging to two different ab planes is 2.747 Å, it involves a Cl atom of one molecule and a H atom belonging to a methylene group of the Me_6tren ligand of another molecule.

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Table S1. Crystallographic data and structure refinement details for compounds

Compound	[Co(Me$_6$tren)Cl](ClO$_4$) **1**	[Co(Me$_6$tren)Br]Br **2**
Empirical formula	C_{12} H_{30} Cl_2 Co N_4 O_4	C_{12} H_{30} Br_2 Co N_4
M_r	424.23	449.15
Crystal size, mm^3	0.21 x 0.20 x 0.19	0.32 x 0.18 x 0.18
Crystal system	trigonal	cubic
Space group	*R 3c*	*P 2$_1$ 3*
a, Å	9.891(5)	12.0262(4)
b, Å	9.891(5)	12.0262(4)
c, Å	33.183(5)	12.0262(4))
α, °	90	90
β, °	90	90
γ, °	120	90
Cell volume, Å^3	2811(2)	1739.34(17)
Z ; Z'	6 ; 1/3	4 ; 1/3
T, K	100(1)	100(1)
F_{000}	1338	908
μ, mm^{-1}	1.223	5.576
θ range, °	2.68 – 37.32	2.40 – 36.28
Reflection collected	13 201	21 073
Reflections unique	2 790	2 791
R_{int}	0.0226	0.0501
GOF	1.048	0.989
Refl. obs. (I>2σ(I))	2 537	2 508
Parameters	72	549
Flack's parameter	0.031(12)	0.010(5)
wR_2 (all data)	0.0801	0.0295
R value (I>2σ(I))	0.0287	0.0212
Largest diff. peak and hole (e-.Å^{-3})	-0.423 ; 1.024	-0.531 ; 0.563

Table S2. Selected bond lengths [Å] and angles [°] for compounds (cf. Figure 1. for the labels). All esds are estimated using the value of the full covariance matrix of least square.

	[Co(Me$_6$tren)Cl](ClO$_4$) **1**	[Co(Me$_6$tren)Br]Br **2**
Co - N(1)	2.176(3)	2.2089(15)
Co – N(2)	2.1519(12)	2.1342(9)
Co – X(1)	2.2821(7)	2.4512(3)
N(2) – Co – N(2)'	117.733(19)	117.772(12)
N(1) – Co – N(2)	81.26(4)	81.34(2)
N(1) – Co – X(1)	180	180
N(2) - Co – X(1)	98.74(4)	98.66(2)
d [Co – (N(2) N(2)' N(2)''')]	0.327	0.321

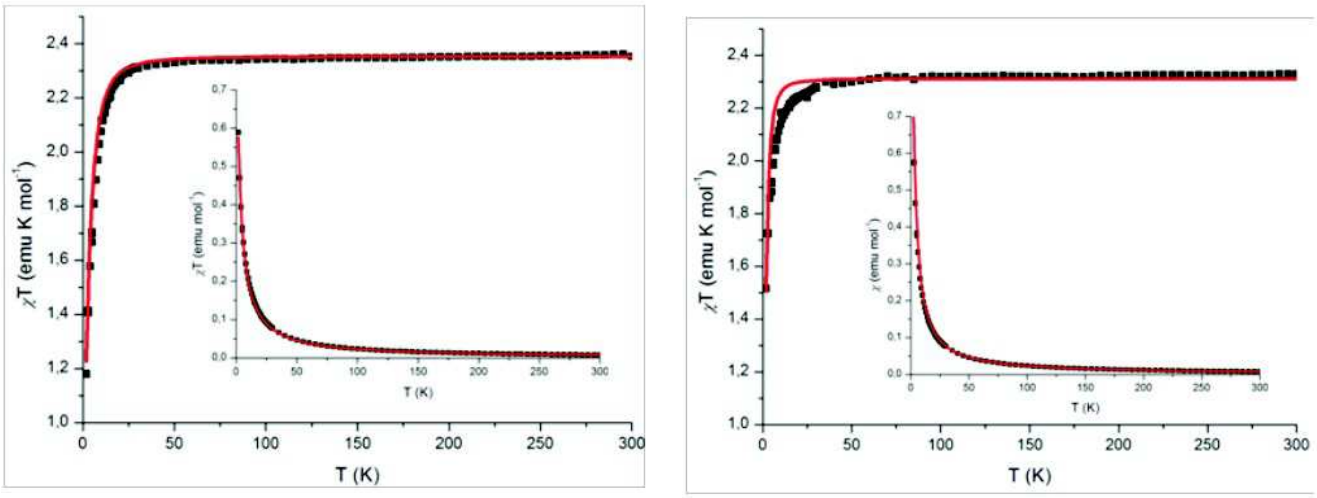

Figure S2. Experimental (■) and calculated (—) χT *vs.*T and χ vs. T (inset) for **1** (top) and 2 (bottom) in an applied field of 1.0 T. See fit parameters in the text

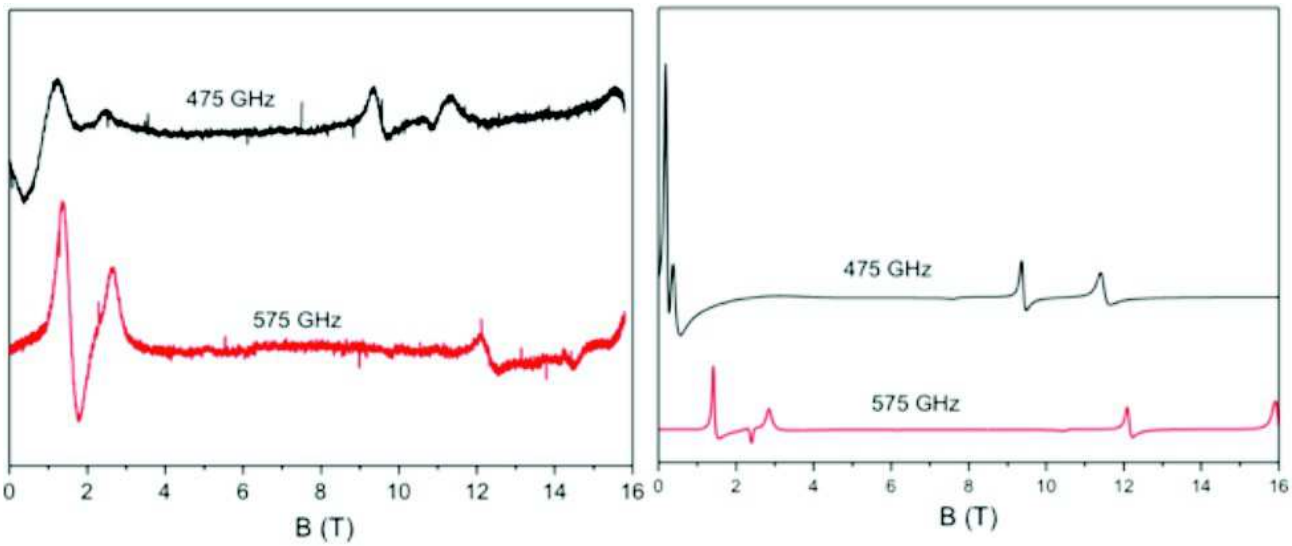

Figure S3. EPR spectra at T = 15 K for **1** at hν = 475 and 575 GHz, experimental (top) and calculated (bottom) for $g_x = g_y = 2.16$, $g_z = 2.2$ and $D = -8.12$ cm^{-1}.

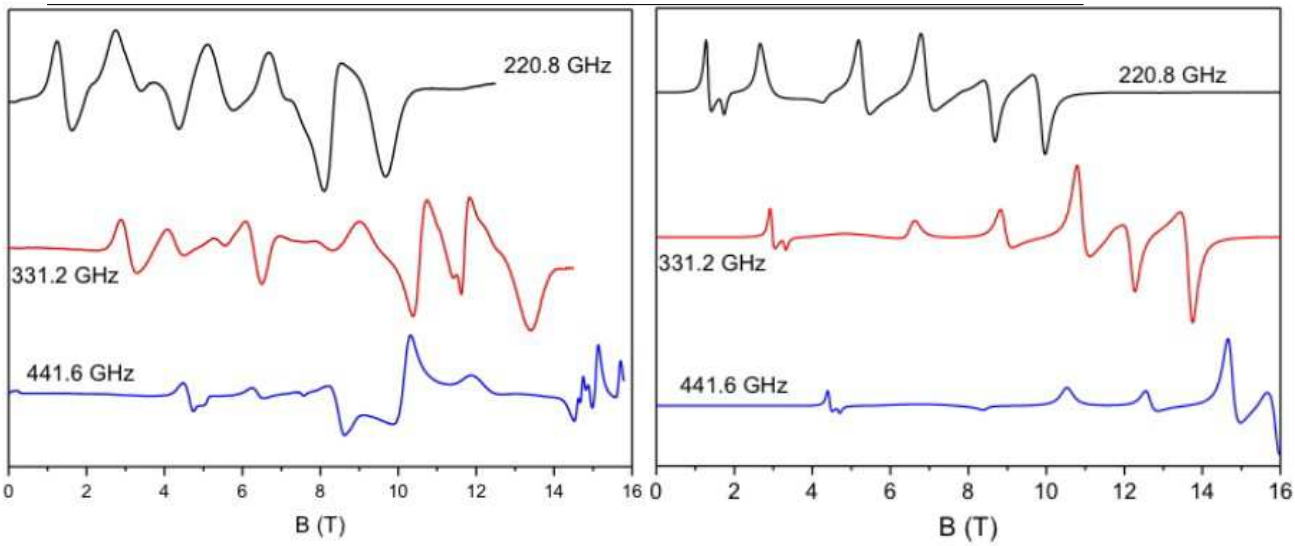

Figure S4. EPR spectra at T = 15 K for **2** at hν = GHz, experimental (top) and calculated (bottom) for $g_x = g_y =$, 2.1, g_z = 2.02 and $D = -2.4$ cm^{-1}

Table S3. Energies (cm^{-1}) of the first excited quartet states computed at the CAS(7,5)SCF and CAS(7,5)NEVPT2 level for the two complexes, notice that $^4\Phi_3$ and $^4\Phi_4$ are degenerate

	[Co(Me$_6$tren)Cl](ClO$_4$) **1**	[Co(Me$_6$tren)Cl](ClO$_4$) **1**	[Co(Me$_6$tren)Br]Br **2**	[Co(Me$_6$tren)Br]Br **2**
	CASSCF	NEVPT2	CASSCF	NEVPT2
$^4\Phi_0$	0	0	0	0
$^4\Phi_1$	2521	3861	3077	4612
$^4\Phi_2$	4118	6162	4627	6829
$^4\Phi_3$, $^4\Phi_4$	4549	6524	4947	7184

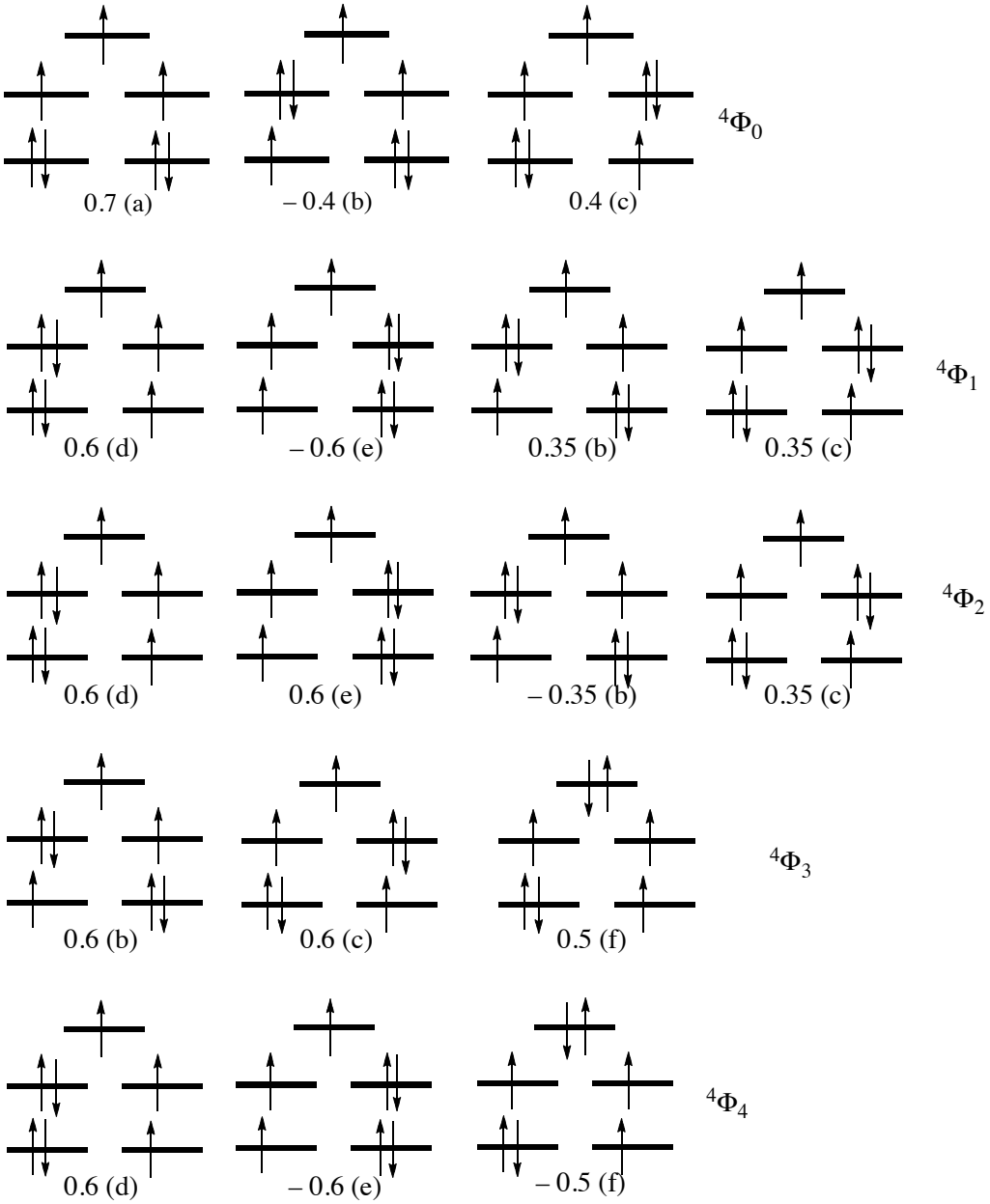

Figure S5. Main determinants and their coefficients (for **1**) in the wave functions of the ground state ($^4\Phi_0$) and in the three excited quartet states (energetically classified from lowest to highest from top to bottom) that contribute significantly to the *D* value. The composition of the orbitals is indicated in the first determinant, the coefficients of the orbitals decrease from left to right. Φ_3 and Φ_4 are degenerate so we have chosen a specific combination of the two corresponding wave functions.

The contributions of the excited states to the *D* value result from the following interactions:

(i) Two determinants (d) and (e) of the first excited state (Φ_1) interacts through $\sum_i \hat{l}_{Z_i}.\hat{s}_{Z_i}$ with the determinants (b) and (c) of (Φ_0) and contribute negatively to the *D* value. The

two contributions through $\sum_i \hat{l}_{Z_i}.\hat{s}_{Z_i}$ of the third excited state (Φ_4) which is spanned by the same determinants (d) and (e) but with opposite sign coefficients cancel.

(ii) An opposite phenomenon occurs considering the interactions through the $\frac{1}{2}\sum_i \hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i}$ operator. Indeed, the determinants (d) and (e) are coupled through $\frac{1}{2}\sum_i \hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i}$ with (a) which is the main determinant of the ground quartet state. Due to the opposite signs of these determinants in the excited (Φ_1) and (Φ_4) states, the contributions of (Φ_4) now add while that of (Φ_1) cancel.

(iii) The (Φ_3) state interacts through $\frac{1}{2}\sum_i \hat{l}_{+_i}.\hat{s}_{-_i} + \hat{l}_{-_i}.\hat{s}_{+_i}$ with (a) and contributes positively to the *D* value.

(iv) From the above cited reasons, all contributions from (Φ_2) cancel.

Since (Φ_1) is much lower in energy than (Φ_3) and (Φ_4), its large negative contribution is not compensated by the two positive contributions of (Φ_3) and (Φ_4) and the overall *D* value is negative.

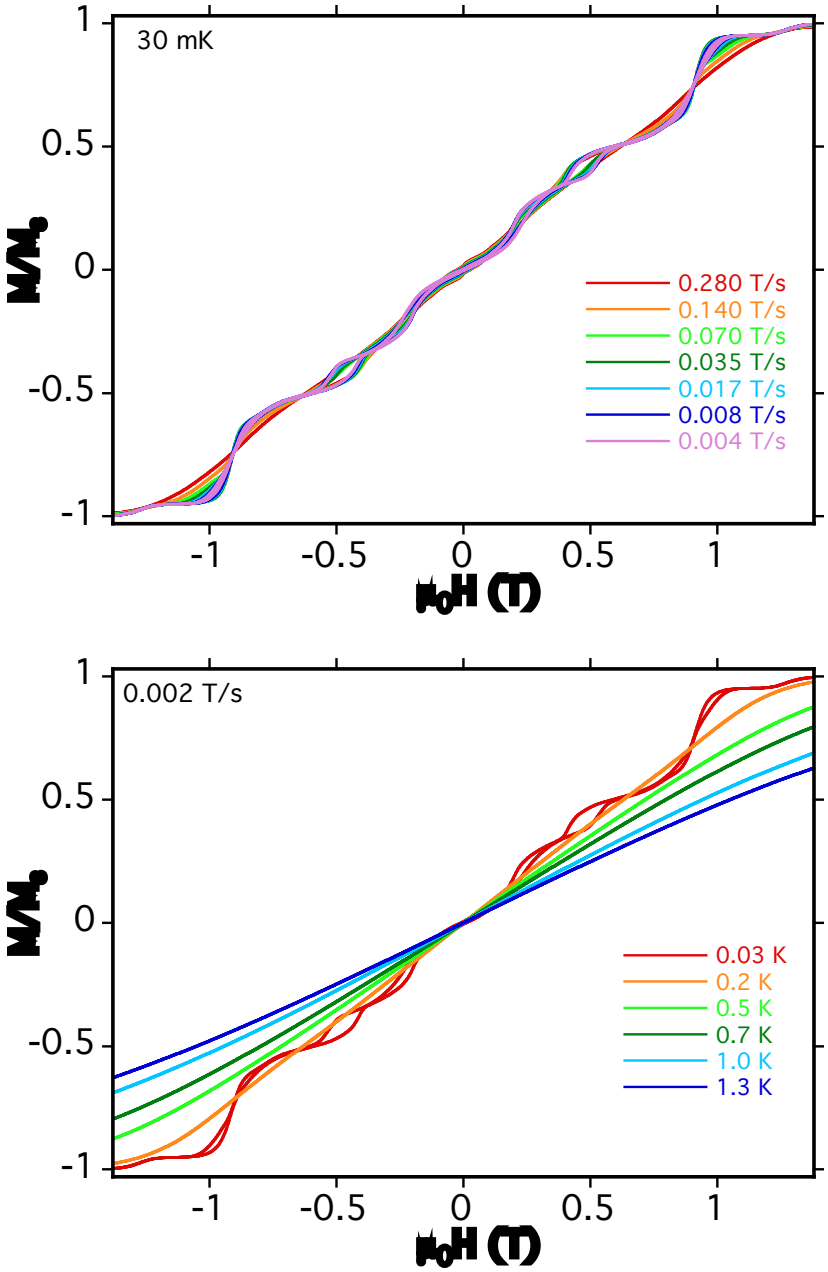

Figure S6. Magnetization *vs.* field on a single crystal of **1** with its easy axis aligned with the field at T = 30 mK and different sweep rates (top) and at a sweep rate of 0.002 T/s and temperatures from 1.3 to 0.03 K (bottom).

2.2 Quasi-dégénérescence de l'état fondamental : effets antagonistes du couplage spin-orbite et de la distorsion Jahn-Teller sur l'anisotropie magnétique

L'étude d'un autre complexe de coordination exotique a porté sur un complexe penta-coordiné de Ni^{II}. Il est formé par un ligand tétradente (hexaméthyl-2,2',2"-triamino-triethylamine) de structure trigonale rigide autorisant trois liaisons dans un plan contenant le métal et, une quatrième sur un axe perpendiculaire à ce plan. A ceci s'ajoute un ion halogène chlorure ou bromure sur le même axe, de l'autre côté du plan (*cf.* figures 2.10 pour le complexe $[Ni(Me_6tren)Cl]^+$ et 1.5 pour complexe $[Ni(Me_6tren)Br]^+$). Une forte anisotropie axiale est ainsi obtenue, comme exposée dans l'article ci-après [55].

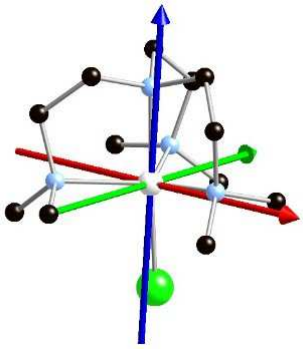

FIGURE 2.10 – Représentation schématique du complexe $[Ni(Me_6tren)Cl]^+$, le nickel est représenté en blanc, le chlore en vert, l'azote en bleu, le carbone en noir et les hydrogènes sont omis.

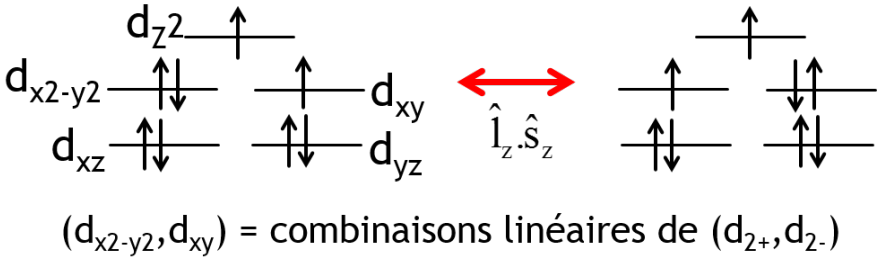

FIGURE 2.11 – Diagramme des orbitales $3d$ du complexe de nickel dans l'état fondamental doublement dégénéré

Ce cas présente un intérêt majeur en raison de la structure trigonale du ligand qui donne un groupe ponctuel de symétrie C_3 au complexe. Le champ de ligand engendre, en conséquence, une dégénérescence orbitalaire entre les orbitales $3d_{xz}$ et $3d_{yz}$ ainsi que $3d_{xy}$ et $3d_{x^2-y^2}$. L'état fondamental ^3E est alors doublement dégénéré (*cf.* figure 2.11). Il est alors possible de bénéficier d'un couplage spin-orbite du premier ordre entre les deux composantes orbitalaires de cet état, on peut dès lors attendre directement une levée de dégénérescence des composantes M_S et donc une valeur de D d'importance comparable à

la valeur de la constante spin-orbite du nickel (644 cm^{-1} voir le tableau 1.1 p. 17). Cependant, un effet antagoniste apparait alors, il s'agit de la distorsion Jahn-Teller qui tend à déformer le ligand réduisant sévèrement la valeur de D. Dans le cas d'une forte distorsion, la perte de dégénérescence structurelle n'autorise plus qu'un couplage du deuxième ordre comme dans les complexes précédemment abordés.

De manière analogue à la précédente étude, une approche mêlant théorie et expériences, vise à caractériser et rationaliser les paramètres magnétiques. Les mesures par rayons X, à une température 100 K, de la structure de ces complexes suggèrent une symétrie C_3 et ne permettent donc pas d'apprécier l'amplitude de la déformation induite par l'effet Jahn-Teller ; cet effet est pourtant attesté par la spectroscopie de résonance paramagnétique électronique et les mesures magnétiques.

Une investigation théorique, par une optimisation de géométrie à l'aide d'un calcul DFT (*cf.* partie 1.2.3), permet de prévoir la structure des trois minima C_1 équivalant par symétrie. De plus, une étude vibrationnelle permet d'en caractériser la nature (minimum) ainsi que celles des points selles, lors de transition d'un minimum vers un autre. La surface de potentiel associée aux déformations est schématisé sur la figure 2.12 et les configurations électroniques du minimum et du point selle sont illustrés par la figure 2.13. Puis les énergies des états associés à ces différentes structures, corrigées par les énergies de vibration conduisent à une estimation de la barrière énergétique entre deux minima. Quelque soit l'halogène employé, cette différence d'énergie s'avère être du même ordre de grandeur que l'énergie thermique. L'hypothèse d'une moyenne thermodynamique des trois minima par une déformation structurelle liée à un effet Jahn-Teller dynamique pourrait alors expliquer l'observation de la structure cristallographique C_3, elle n'est cependant pas attestée expérimentalement, même à basse température (10 K).

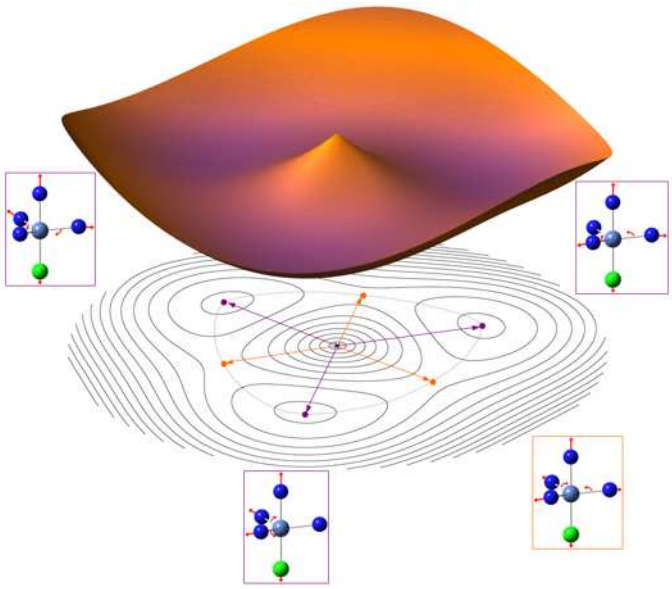

FIGURE 2.12 – Représentation schématique de la surface de potentiel autour de la structure C_3 faisant apparaitre les trois minima équivalents et les états de transition.

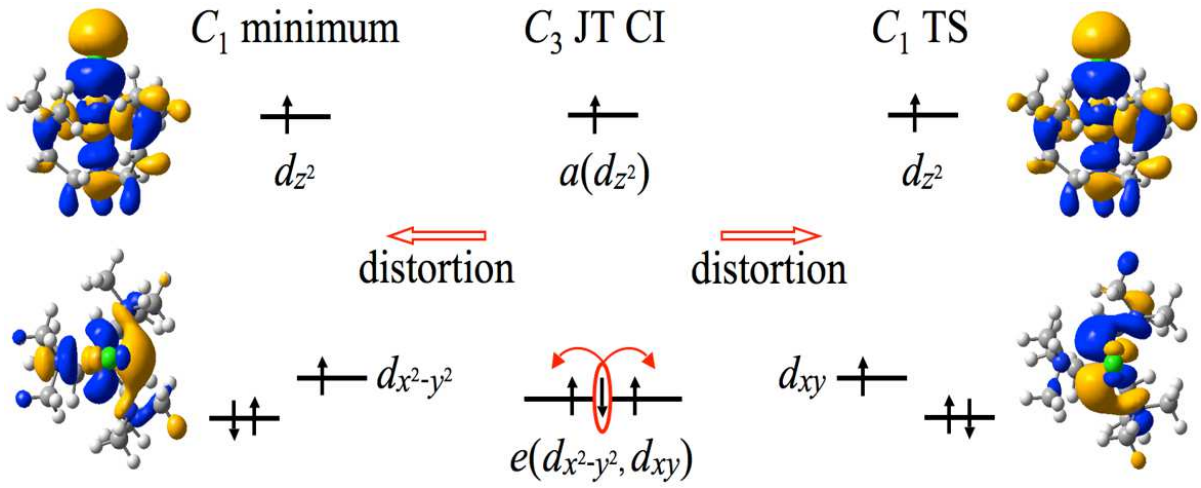

FIGURE 2.13 – Configuration électronique et orbitales simplement occupé du minimum C_1 (à gauche) et de l'état de transition (à droite).

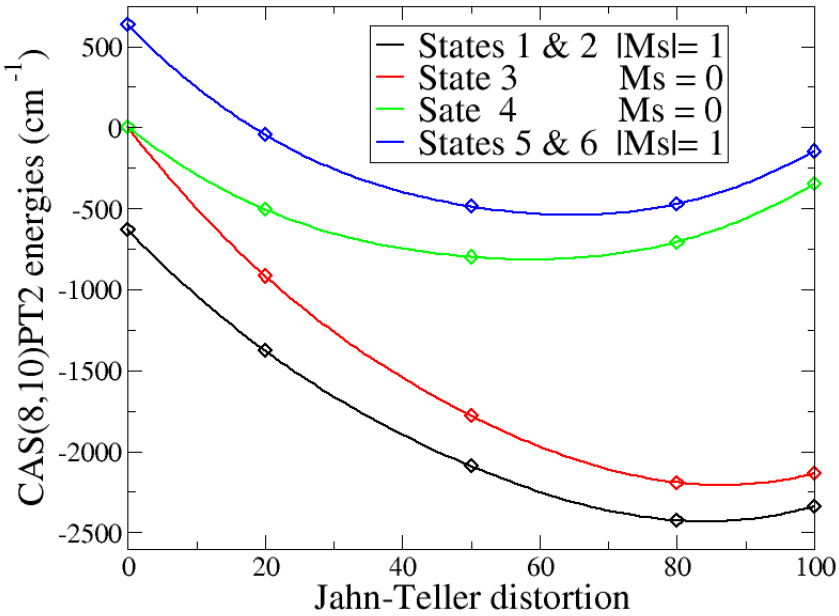

FIGURE 2.14 – Énergies des six composantes des deux triplets fondamentaux en fonction de la distorsion Jahn-Teller. L'abscisse correspond a une distorsion linéaire entre la structure C_3 et le minimum DFT C_1.

Pour étayer cette hypothèse, une analyse par une théorie de la fonction d'onde a été réalisée au moyen du logiciel MOLCAS (*cf.* partie **??**) aux géométries du minimum et du point selle. Un calcul *ab initio* de l'aimantation et de la susceptibilité magnétique, en comparaison avec les mesures analogues expérimentales, permet d'apprécier les effets de la déformation sur ces paramètres. En outre, un calcul analytique permet de modéliser le couplage spin-orbite en fonction de la déformation et de comprendre comment et avec quelle amplitude la levée de dégénérescence orbitalaire entre les deux états les plus bas en énergie affecte les valeurs de D par une atténuation des effets spin-orbite. Pour ce faire, une interpolation linéaire entre les coordonnées internes de la structure cristallographique C_3 et du minimum C_1 obtenu par DFT a permis de définir différentes géométries intermédiaires et de calculer, pour chacune d'elle, le spectre en prenant en compte le couplage spin-orbite (*cf.* figure 2.14). Cette déformation est cependant limitée par la rigidité du ligand, ces deux états restent alors proches en énergie. La valeur de D peut être évaluée au premier ordre par la différence d'énergie entre les composantes $M_S = \pm 1$ et la composante $M_S = 0$ des états de plus basses énergies, ainsi une forte diminution du paramètre D, d'environ 600 cm^{-1}pour la géométrie C_3 à environ 200 cm^{-1}pour le minimum DFT, peut donc être prédite. Cette grandeur dépend, dans le cadre d'un couplage au second ordre, de l'inverse de la différence des énergies de chaque état, une importante anisotropie axiale est, tout de même, obtenue. De plus, à ce niveau de calcul, une légère levée de dégénérescence entre les composantes $M_S = \pm 1$ est prédite, ainsi que l'attribution des différents axes magnétiques.

Les mesures par résonances paramagnétiques de l'électron en champ intense, à haute fréquence (HF-HFEPR) donne une valeur de D comprise entre -120 cm^{-1}et -180 cm^{-1}. Un bon accord entre les résultats expérimentaux et théoriques est donc atteint et permet une compréhension et une validation des causes d'une importante anisotropie avec des valeurs des paramètres du ZFS souhaitables (D négatif, de grande amplitude et E faible) pour des applications. En principales conclusions, il apparait que les ligands rigides non-planaire autorisant une coordination exotique semblent offrir une possibilité prometteuse de bénéficier d'un couplage au premier ordre à condition de contrôler la distorsion.

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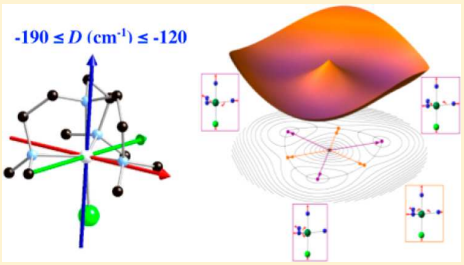
Giant Ising-Type Magnetic Anisotropy in Trigonal Bipyramidal Ni(II) Complexes: Experiment and Theory

Renaud Ruamps,[†] Rémi Maurice,[†,‡,§] Luke Batchelor,[∥] Martial Boggio-Pasqua,[†] Régis Guillot,[∥] Anne Laure Barra,[⊥] Junjie Liu,[#] El-Eulmi Bendeif,[○,◆] Sébastien Pillet,[○,◆] Stephen Hill,*[,#,▽] Talal Mallah,*[,∥] and Nathalie Guihéry*[,†]

[†]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3, 118 route de Narbonne, 31062 Toulouse cedex 06, France
[‡]Department of Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
[§]Departament de Química Física i Inorganica, Universitat Rovira i Virgili, Marcel.lí Domingo s/n, 43007 Tarragona, Spain
[∥]Université Paris Sud 11, CNRS, Institut de Chimie Moléculaire et des Matériaux d'Orsay, F-91405 Orsay, France
[⊥]Laboratoire National des Champs Magnétiques Intenses, UPR CNRS 3228, Université J. Fourier, 25, Avenue des Martyrs, B.P. 166, 38042 Grenoble Cedex 9, France
[#]National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, United States
[▽]Department of Physics, Florida State University, Tallahassee, Florida 32306, United States
[○]Université de Lorraine, CRM2, UMR 7036, Boulevard des Aiguillettes, Vandoeuvre les Nancy, F-54506, France
[◆]CNRS, CRM2, UMR 7036, Boulevard des Aiguillettes, Vandoeuvre les Nancy, F-54506, France

Supporting Information

ABSTRACT: This paper reports the experimental and theoretical investigations of two trigonal bipyramidal Ni(II) complexes, [Ni(Me$_6$tren)Cl](ClO$_4$) (**1**) and [Ni(Me$_6$tren)Br](Br) (**2**). High-field, high-frequency electron paramagnetic resonance spectroscopy performed on a single crystal of **1** shows a giant uniaxial magnetic anisotropy with an experimental D_{expt} value (energy difference between the $M_s = \pm 1$ and $M_s = 0$ components of the ground spin state S = 1) estimated to be between −120 and −180 cm^{-1}. The theoretical study shows that, for an ideally trigonal Ni(II) complex, the orbital degeneracy leads to a first-order spin−orbit coupling that results in a splitting of the $M_s = \pm 1$ and $M_s = 0$ components of approximately −600 cm^{-1}. Despite the Jahn−Teller distortion that removes the ground term degeneracy and reduces the effects of the first-order spin−orbit interaction, the D value remains very large. A good agreement between theoretical and experimental results (theoretical D_{theor} between −100 and −200 cm^{-1}) is obtained.



1. INTRODUCTION

Single molecule magnets (SMMs) exhibit a slow relaxation of their magnetization leading to a magnetic hysteresis at low temperature.[1−5] Since this bistable behavior may ultimately lead to technological applications in the domain of data storage[6] and quantum computing,[7−9] the study of these objects has generated a considerable interest. This remarkable property arises from the existence of two ground states of different magnetization $+M_s$ and $-M_s$ separated by an energy barrier. Magnetic anisotropy is responsible for both the existence of the energy barrier and the tunneling between the different M_s components. Nevertheless, the presently measured blocking temperatures of SMMs (below which the system keeps its magnetization) are still too low for daily technological applications. The magnitude of the anisotropy and its nature (either axial or rhombic) control the barrier height and the tunneling. The design of suitable SMMs therefore rests on the ability to synthesize new objects with larger and uniaxial magnetic anisotropy, characterized by a strongly negative axial anisotropy parameter D and an as small as possible rhombic parameter E. The lifting of degeneracy of the different M_s components of the high-spin ground term S originates from the spin−orbit coupling (and to a lesser extent the spin−spin coupling) combined with a low symmetry. In most of the 3d metallic complexes, magnetic anisotropy arises from the coupling between a spatially nondegenerate electronic ground state with excited states. Since these couplings are usually small in comparison with the energy difference between the electronic ground state and the excited states, the resulting anisotropy is usually weak.

Several strategies have been developed in order to enlarge the magnetic anisotropy of molecular complexes. One of them consists in replacing the d transition metals by rare earths (4f)

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or actinides (5f) in order to benefit from the large spin−orbit coupling of heavy elements.[10−14] The present work uses an alternative strategy[15] in which the complexes exhibit a nearly orbitally degenerate ground term. In such complexes, the first-order spin−orbit coupling between the spatial configurations resulting from the different orbital fillings may induce a large splitting of the M_s components of the high-spin degenerate ground term. In the recent past, several Ni(II) mononuclear complexes presenting a large Ising-type magnetic anisotropy have been proposed.[16] However, most of the Ni(II) complexes have a geometry close to octahedral in which the angular momentum is quenched. For Ni(II) complexes, one possible way to take advantage of first-order spin−orbit coupling is to design complexes with a low symmetry for which the ground term is orbitally degenerate. The main goal of this paper is to propose and study theoretically and experimentally such complexes. It is worth noting that, for the degenerate ground state, a Jahn−Teller distortion occurs. Unfortunately, this distortion that removes the orbital degeneracy tends to minimize the effect of the first-order spin−orbit coupling, thus reducing the magnetic anisotropy.[17−24]

In this paper, we report the synthesis, the characterization, and the single-crystal high-field high-frequency electron paramagnetic resonance (HF-HFEPR) study of [Ni(Me_6tren)Cl]-(ClO_4) (**1**) and [Ni(Me_6tren)Br]Br (**2**) trigonal bipyramidal complexes. In order to analyze the competition between the antagonist effects of the spin−orbit coupling and the Jahn−Teller distortion[25−28] in these two complexes, we also perform a theoretical study. Since the first attempt to calculate the anisotropic parameters in 1998,[29] in the $H_2Ti(\mu\text{-}H)_2TiH_2$ complex, several theoretical methods have been developed to calculate the zero-field splitting (ZFS) parameters. The NRLMOL code,[30,31] which constitutes one of the first density functional theory (DFT) implementations, has successfully been applied to various SMMs.[32−38] In 2003, the spin−orbit state interaction (SOSI) method,[39,40] which treats the spin−orbit coupling (SOC) in the wave function theory (WFT)-based framework, was implemented in the MOLCAS code.[41] This method has shown to provide reliable ZFS parameters of transition-metal complexes for which the ZFS is dominated by the SOC contribution,[42−51] and the present work uses this SOSI method. One should also mention that the treatment of the spin−spin coupling (SSC) in the WFT approach has been developed by Gilka et al.[52] as well as Ganyushin and Neese[53] and implemented in the ORCA program.[54] This code allows one to use either DFT or WFT methods (MRCI, CASSCF, and multireference perturbation theory NEVPT2[55]) to calculate the ZFS[56−66] and has also been successfully applied to several mononuclear inorganic complexes and organic molecules.

Section 2 is devoted to experimental results. Magnetic measurements, single-crystal X-ray diffraction, and HF-HFEPR spectroscopy were performed to experimentally characterize the studied complexes.

Section 3 is devoted to the theoretical description of two of the studied compounds. In the first place, a DFT study leads to the characterization of the main features of the potential energy surfaces. Then, the competition between spin−orbit coupling and Jahn−Teller distortion is studied using first-order spin−orbit calculations. Finally, the ZFS parameters are extracted using more sophisticated calculations accounting for both the first-order and second-order spin−orbit coupling effects.

2. MATERIALS AND METHODS

2.1. Synthesis. Chemicals were purchased from Aldrich and used without further purification. Me_6tren and [Ni(Me_6tren)Br]Br complexes were synthesized according to literature procedures or minor alterations thereof.[67] The synthesis of the [Ni(Me_6tren)(Cl)]-(ClO_4) complex is given in the Supporting Information. All solvents were from BDH and were used as received. All manipulations were conducted under standard laboratory conditions.

2.2. Magnetic Measurement. Variable temperature (300−2 K) magnetic data were measured on powdered samples of **1** and **2** in an eicosane matrix in 1.0 and 0.1 T fields using a Quantum Design MPMS5 superconducting quantum interference device (SQUID) magnetometer. The data were corrected for the diamagnetic contribution of the sample holder and eicosane, and the diamagnetism of the sample was estimated according to Pascal's constants. Low temperature (2−6 K) variable field (0−5.5 T) measurements were carried out in the same manner.

2.3. HF-HFEPR Spectroscopy. Single-crystal HF-HFEPR measurements were carried out in a 31 T resistive magnet using a cavity perturbation technique; in situ sample rotation was possible about a fixed axis.[68] A Millimeter vector network analyzer and several different multipliers were used as a microwave source and detector. Powder spectra were recorded at 5 K on powders pressed into pellets made of either pure ground polycrystalline sample or ground polycrystalline powder dispersed in eicosane. Spectra were recorded with an EPR spectrometer relying on a quasi-optical light transmission. A step-tunable frequency source was used; the final frequency was obtained by multiplying (12 times) a variable synthesizer frequency (10 and 9.58 GHz) or a PDRO source (9.2 GHz). The 220.8 GHz frequency was obtained with the help of a doubler. A Mn(II) reference (MnO diluted in MgO) added to the sample was responsible for the signal at $g = 2$.

2.4. X-ray Diffraction. Single-crystal X-ray diffraction data were measured on a Bruker APEX II CCD diffractometer with graphite−monochromated MoK radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization and absorption effects. Diffraction data were also collected at 10 K on a Supernova diffractometer equipped with an ATLAS CCD detector, MoKα radiation and a Helijet open flow cryosystem. The structures at 100 and 10 K were solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least-squares techniques using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed using the crystal structure crystallographic software package WINGX. See the Supporting Information for further details on the structural analysis.

CCDC 893397 and 912662 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.5. Calculations. DFT calculations were performed using the Gaussian 03 package.[69] The B3LYP functional was used throughout with two different basis sets. The first one is composed of the Hay−Wadt LanL2TZ(f) basis set[70,71] for the nickel metal center, including an f polarization function with an exponent of 3.13, and its corresponding relativistic effective core potential,[71,72] a Pople triple-ζ basis set (6-311G) for N, Cl, and Br atoms,[73] a Pople double-ζ plus polarization basis set (6-31G*) for C atoms,[74] and a Pople double-ζ basis set (4-31G) for H atoms.[75] This basis set (noted basis 1) was used to compute both complexes. The second basis set (basis 2) is much larger and was used to compute compound **1**. It uses a Stuttgart relativistic small-core effective potential for nickel with its associated polarized basis set[76] including two f and one g polarization functions,[77]

a correlation-consistent polarized triple-ζ basis set (cc-pVTZ) for N, and Cl atoms,[78] and a correlation-consistent polarized double-ζ basis set (cc-pVDZ) for C and H atoms.

Although the optimized geometries obtained using both basis sets compare well with the experimental ones, the distances and angles around the Ni(II) ion obtained with basis 1 are closer to the experimental ones. Since the ZFS parameters are very sensitive to the geometrical structure, the geometries of both the minimum and the transition state obtained using basis 1 were selected for the WFT of both compounds.[79]

Unrestricted DFT calculations were used to optimize minima and saddle points of the potential energy surface of the triplet ground state. Spin contamination was negligible, with $\langle S^2 \rangle$ values never exceeding 2.005. Analytical harmonic vibrational frequencies were computed to characterize the nature of the stationary points (all frequencies are positive for the minima and a single imaginary frequency appears for the saddle points) and to evaluate the zero-point vibrational kinetic energy (ZPE).

WFT-based calculations were performed using the MOLCAS 7.4 package.[80] Nondynamic correlation is accounted for by complete active space self consistent field (CASSCF) calculations. The active space is constituted of the 5d orbitals, 5d′ orbitals dedicated to correlation, and the eight d electrons. In order to take into account dynamic correlation effects, CASPT2[81] calculations were performed: (i) CAS(8,10)PT2 calculations for the lowest two triplet states; (ii) CAS(8,10)PT2 calculations for the 10 lowest triplet and 14 lowest singlet states.[82] Spin−orbit couplings are computed within the spin−orbit state interaction frame.[83] This method diagonalizes the spin−orbit matrix between well-chosen CASSCF states. For dynamically correlated calculations, the diagonal elements of the SI matrix are the CASPT2 energies of the computed states. The following ANO-RCC basis sets[84] were used: 6s5p3d1f for Br, 5s4p2d1f for Cl, 6s5p4d2f for Ni, 3s2p1d for N, 3s2p for C, and 2s for H.

3. RESULTS AND DISCUSSION

3.1. Structural Description. The cationic complex $[Ni(Me_6tren)Cl]^+$, previously unreported crystallographically, may be crystallized from a methanolic solution with a perchlorate counterion, giving $[Ni(Me_6tren)Cl](ClO_4)$, (**1**) (Figure 1). The tetrahedral anion, with four potential C_3 axes, readily forms a trigonal crystal system, *R*3*c* in the case of **1**. In accordance with the previously reported structure of $[Ni(Me_6tren)Br]Br$, **2**,[68] compound **1** consists of a Ni(II) ion penta-coordinated by four amino nitrogen atoms from the neutral Me_6tren ligand and one halide ion. The ligands are distributed at the apexes of a trigonal bipyramid with crystallographic C_3 symmetry, the three equatorial sites are occupied by the "terminal" amines, and the axial sites are occupied by the central amine and the chloride ion. The Ni(II) ion lies 0.23 Å below the equatorial plane of the three nitrogen atoms, compared to 0.22 Å in the reported structure of **2**.

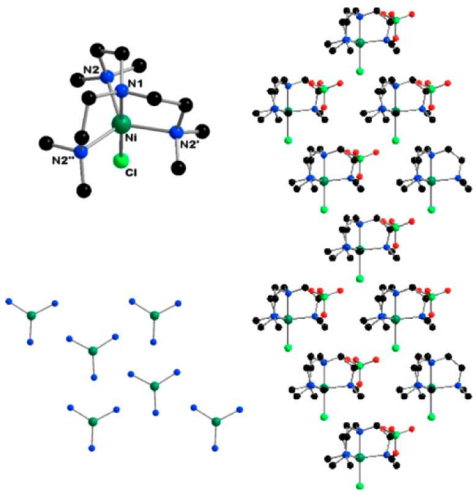

Figure 1. Structure of the cation in $[Ni(Me_6tren)Cl](ClO_4)$ (**1**) (top left) and the same complex viewed along the C_3 axis (bottom left). Packing diagram showing the parallel arrangement of molecular C_3 axes in the solid state (right). Hydrogen atoms are omitted for clarity. Color code: Ni (green), C (black), N (blue), Cl (bright green), O (red).

As highlighted by the selected bond lengths and angles in Table S1 of the Supporting Information, complexes **1** and **2** are structurally similar, and minor differences may be accounted for by greater ionic radius (Ni−X) and the trans effect (Ni−N1) of bromide. There is however a significant difference in the packing of the molecules in the solid state. Complex **2** consists of $[Ni(Me_6tren)Br]^+$ and Br^- ions, crystallized in the cubic $P2_13$ space group. This has a distorted NaCl-type arrangement of ions. As such, when viewing the unit cell along the C_3 axis of any one $[Ni(Me_6tren)Br]^+$ complex, the axes of the three remaining molecules lie pseudoperpendicular, related to one another via threefold rotational symmetry (see the Supporting Information, Figure S1). Replacement of the bromide counter-ion by the larger and nonspherical perchlorate ion results in the trigonal packing observed for **1** (Figure 1). In this case, the C_3 axes of the molecules all lay parallel and unidirectionally through the unit cell. It may thus be possible to relate molecular magnetic axes to faces and edges of the crystal, facilitating relatively simple interpretation of single-crystal spectroscopic data.

For **1**, upon temperature decrease to 10 K, no space group change associated to a symmetry breaking transition is detected; the molecular crystallographic C_3 symmetry is preserved. The absence of crystal symmetry lowering at 10 K does not rule out the presence of a molecular distortion. Indeed, a local (i.e., molecular) distortion resulting from a Jahn−Teller effect with an equal population of the three distortion modes (see the Supporting Information, Figure S2) and statistically distributed within the single-crystal sample would preserve the *R*3*c* symmetry. The structural dynamics of the $[Ni(Me_6tren)Cl]^+$ complex at 10 K has been examined by performing a TLS (rigid-body thermal motion model) analysis and indicates a possible local (i.e., molecular) structural distortion, whose spatial average maintains the crystal *R*3*c* symmetry (see the Supporting Information, Figure S3).

3.2. Magnetic Measurements. The measured molar magnetic susceptibility (χT) plot for a powdered sample of **1** has a room temperature χT value of 1.42 emu K mol^{-1}, much higher than that expected from the spin-only formula for a high-spin mononuclear Ni(II) complex (1.21 emu K mol^{-1} for g = 2.20), probably due to a large orbital contribution, and is relatively constant down to approximately 120 K. Below this temperature, it collapses, indicating significant ZFS in the S = 1 ground state. Similarly, at 2 K and 5.5 T, the observed magnetization value (1.25 μ_B) is well below the theoretical saturation for an S = 1 system (2.2 μ_B for g = 2.20) and has not reached a plateau. This, along with the fact that the reduced magnetization plots are non-superimposable, is also indicative of large magnetic anisotropy (see the Supporting Information, Figure S4). Very similar results were obtained for **2** (see the Supporting Information, Figure S5). AC susceptibility studies were performed at different frequencies of the oscillating magnetic field, but no out of phase signal was observed down to

2 K. Hysteresis studies using a microsquid array down to 50 mK did not show any hysteresis at zero field.

3.3. HF-HFEPR Spectroscopy. Given the proposed massive magnetic anisotropy of the complex, and the unreliability of inferring ZFS parameters from magnetic measurements alone, HF-HFEPR measurements were performed on a single crystal of **1**. Careful angle-dependence studies involving rotations of the crystal about a fixed axis were performed to ensure that the applied field was within 2° of the molecular hard plane (see the Supporting Information, Figure S6). Extensive frequency- and temperature-dependence studies (115−250 GHz, 1.4−10 K) were carried out at the field orientation where the EPR transition appears at the highest field, which necessarily corresponds to the field lying in the molecular hard plane (see the Supporting Information, Figure S7). It is notable that the intensities of the observed EPR transitions quickly decrease when the applied field is moved away from the molecular hard plane, which indicates that the transition matrix element vanishes when the applied field is out of the molecular hard plane. Two EPR transitions (**A** and **B**) were observed (see the Supporting Information, Figure S8) at frequencies between 115 and 240 GHz (see the Supporting Information, Figures S9 and S10). EPR experiments were repeated on several different crystals, and similar spectra were observed. For an S = 1 system, only one ground-state transition is expected; however, both of these signals were confirmed to be ground-state transitions through temperature-dependence studies (see the Supporting Information, Figure S8). We propose that the crystallographically observed molecular C_3 symmetry is broken by a Jahn−Teller-type distortion that is within the molecular triangular planes. By assuming that the easy axes of all molecules remain parallel and that the space group of the crystal remains unchanged, this yields three different molecular orientations (**A**, **B**, and **C**) that are related by a threefold rotational symmetry (see the Supporting Information, Figure S11). The molecules have equal probability ($^1/_3$) of falling in any one of these orientations. Thus, the hard axes (x axes) of the molecules are not parallel to one another giving rise to the multiple transitions that were observed experimentally. This distortion also permits the observation of a rhombic E term that is strictly forbidden if rigorous molecular C_3 symmetry is maintained. We note that the hard planes corresponding to the **A** and **B** molecules vary slightly by a few degrees (see the Supporting Information, Figure S6 inset), implying that the easy axes of the **A** and **B** molecules are not exactly parallel. Such an observation further supports our assumption that the local molecular symmetry is lowered by Jahn−Teller-type distortions at low temperatures; that is, with the presence of distortions, the anisotropy tensors of the molecules are tilted; thus, the easy axes of molecules do not coincide with the crystallographic threefold screw axes. However, the space group of **1** remains unchanged; hence, these three molecular species are related by a threefold rotation. Variable-frequency studies were performed with the field applied in the hard planes of the **A** and **B** molecules, respectively, to study the frequency dependence of these transitions (see the Supporting Information, Figures S9 and S10).

The EPR data were simulated employing the following Hamiltonian, where φ represents the angle between the field and the molecular hard axes (Figure 2):

$$\hat{H} = D\hat{S}_z^{\,2} + E(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}) + \mu_B \cdot g \cdot B(\cos(\varphi)\hat{S}_x + \sin(\varphi)\hat{S}_y) \qquad (1)$$

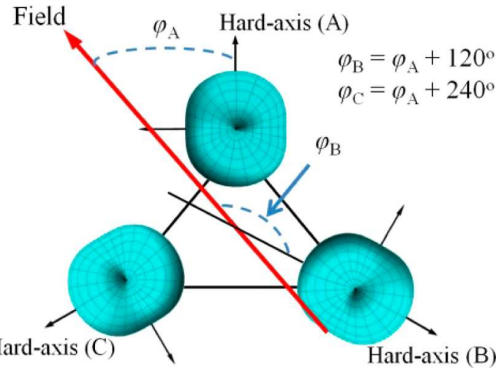

Figure 2. Origin of φ in the Hamiltonian used to fit the EPR data. The "donuts" represent the zero-field anisotropy surface of the molecules assuming the previously described Jahn−Teller distortion.

The value of g was fixed at 2.4 (extracted from the room temperature χT value) and the values of D, E, and φ were varied across a large parameter space. Due to the fact that we were only able to perform single-axis rotation, the field orientation in the molecular hard plane (φ) remains an arbitrary experimental parameter. Simulations gave the following best fit parameters: D = −179 cm^{-1}, E = 1.63 cm^{-1}, φ_A = 105.5°, and φ_B = 225.5°, as shown in Figure 3.

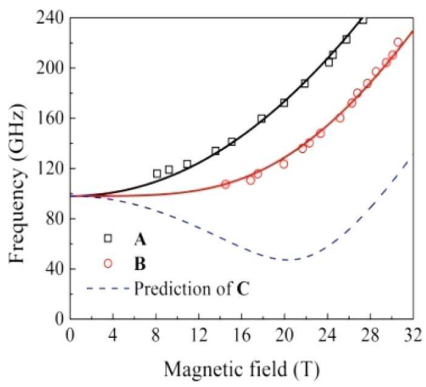

Figure 3. EPR peak positions observed for the **A** and **B** molecular transitions of a single crystal of **1**, with the field aligned in the magnetic hard plane of the **A** (black squares) and **B** (red circles) molecules, respectively. The solid lines correspond to the best fit employing the Hamiltonian (eq 1) and parameters given in the text. The dashed blue line represents the predicted positions of the EPR transitions associated with the **C** molecules.

The solid lines represent the simulations of the EPR peak positions associated with the **A** and **B** molecules. It should be noted that, for this parameter set, the predicted transitions for the **C** molecules will appear at lower frequency (Figure 3, dashed blue line) and thus were not observed experimentally. To test uncertainties associated with these parameters, each two parameters were fixed in turn, and the error associated with the simulation was calculated while the others were varied (see the Supporting Information, Figures S12−S17). These tests show a near linear dependence on D and g (see the Supporting Information, Figure S15). This is of little surprise given that it is impossible to directly measure the large ZFS of **1** (∼200 cm^{-1}) by EPR. The value of D was obtained indirectly by fitting the observed hard plane transitions (see the Supporting Informa-

tion, Figure S5), and g has the effect of scaling the Zeeman energy used to calculate the zero-field parameters. Since the field is always applied in the hard plane, the g value in the analysis corresponds to the perpendicular g value, $g_{x,y}$. It is likely that g_z is not equal to $g_{x,y}$, which should be taken into account in subsequent analysis.

The experiment does however show unambiguous evidence of the presence of a sizable E term, whose magnitude (1.6 cm^{-1}) is clearly independent of g, D, and φ (see the Supporting Information, Figures S12, S13, S16, and S17). The presence of rhombic anisotropy provides spectroscopic proof that the molecular C_3 symmetry is broken by Jahn−Teller-type distortions. In summary, the EPR measurements of **1** provide a clear determination of the magnitude of the transverse anisotropy and demonstrate the dependence of D on the g value. Even for a g value of 2.0, which would be very low given the near first-order spin−orbit coupling predicted for **1**, D is expected to be as large as −120 cm^{-1}, with a value approaching −180 cm^{-1}, more likely.

In order to check the analysis of the high-field EPR measurements performed on a single crystal, powder spectra were also recorded (on powders pressed into pellets). Indeed, with a $|D|$ value higher than 100 cm^{-1}, one cannot expect to observe the corresponding transitions even using high frequencies. Conversely, transitions associated with the E term can be observed on powder spectra at low field, that is, for frequencies only slightly larger than the energy gap. In Figure S18 (see the Supporting Information), spectra recorded at 5 K and at four different frequencies, ranging from 110 to 221 GHz, are displayed. The shift of the main line with frequency leads to the following parameters: $E = 1.56 \pm 0.05$ cm^{-1} and $g_z = 2.34 \pm 0.07$. Even if these figures are not very precise due to the limited frequency (and field) interval where they are observed, as this transition becomes weaker and weaker with the increase of the Zeeman interaction, the E and g_z values are close to the ones obtained from single-crystal measurements, thus supporting the analysis previously developed on the single crystal. It may be noticed that, for the powder measurements, more than one signal is observed except at the lowest frequency. This seems to point towards the existence of molecules with different anisotropies, which could contribute to the extra signals observed on the single-crystal spectra (especially the one appearing only slightly lower in field than the **A** signal).

Similar measurements were performed on **2**; however, multiple peaks were observed, and even the most prominent feature could be modeled with a range of parameters. The poor quality of the data reflects the difficulties associated with single-crystal measurements for **2**, where the nonparallel alignment of the molecular easy axes within the unit cell prevents the simultaneous application of the field in all of the molecular hard planes. This greatly complicates the spectra, preventing any meaningful analysis of the ZFS parameters. Future investigation may require the replacement of the bromide counterion with perchlorate, in an attempt to change the crystal system and to obtain results comparable to those for **1**. Despite the experimental difficulties associated with **2**, the ZFS parameters obtained for **1** represent a near 10-fold increase in axial anisotropy for a reported Ni(II) complex.

3.4. Theoretical Investigation. *3.4.1. Potential Energy Surface Features: a DFT Study.* Experimentally, the observed symmetry of the complexes under study is C_3. The spin multiplicity of the electronic ground state is triplet. Because of the spatial degeneracy, the ground state corresponds to a doubly degenerate ^3E state at this peculiar geometry. Due to Jahn−Teller effects, one expects the degeneracy of this state to be lifted following appropriate symmetry-breaking distortions. This gives rise to a moat surrounding a Jahn−Teller C_3 conical intersection, with three symmetry-equivalent minima and saddle points (transition states TS),[85] as shown in Figure 4.

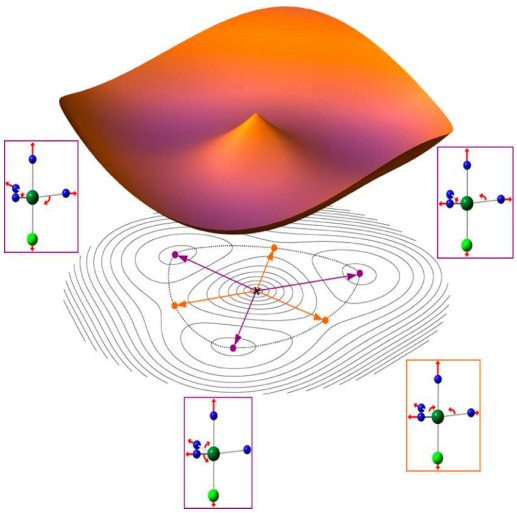

Figure 4. Schematic representation of a moat around a Jahn−Teller C_3 crossing showing the three symmetry-equivalent minima and TSs: three-dimensional representation (the tricorn, top) and equipotential contour plot (bottom). The main displacement vectors pointing to the minima (purple boxes) and to one transition state (red box) are shown.

Unrestricted DFT calculations were used to optimize these minima and saddle points allowing one to evaluate the pseudorotation barrier around the moat. Gatteschi and co-workers have already invoked a dynamic Jahn−Teller effect for these types of complexes.[86]

The degenerate ground state ^3E in the C_3 symmetry point group (SPG) is split in the C_1 SPG upon the Jahn−Teller effect in two states that differ by their electronic configuration, either $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^2 d_{xy} d_{z^2}$ or $d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{x^2-y^2} d_{z^2}$ (see Figure 5), for

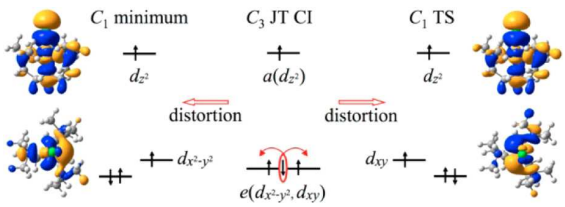

Figure 5. Electronic configuration and singly occupied molecular orbitals of the C_1 minimum state (left, $|d_{x^2-y^2}|$) and TS (right, $|d_{xy}|$). The main displacement vectors of both distortions are given in Figure 4.

which the associated determinants will be noted $|d_{xy}|$ and $|d_{x^2-y^2}|$ hereafter. One of them corresponds to a true minimum of the potential energy surface while the other one corresponds to the TS (saddle point) connecting two minima.

The main geometrical parameters of the optimized C_1 minimum, the TS, and the experimental C_3 structures are given in Table S2 of the Supporting Information for comparison. Figure S19 of the Supporting Information gives

the numbering of the atoms used in the table. In order to appreciate the magnitude of the distortion, we use the parameters δr and $\delta\alpha$ that quantify independently the distance distortion and the angular distortion (see the Supporting Information, eq S1).

The values of δr and $\delta\alpha$ are also reported in Table S2 (see the Supporting Information) showing that (i) for both compounds the angular deformation is more pronounced than the distance deformation and (ii) the Jahn−Teller distortion is almost identical for both compounds.

From the vibrational contributions, the ZPEs have been computed for the geometry of both the minima and the TSs. For compound **1**, the electronic energy barrier is 83.6 cm^{-1}. By adding the ZPE contributions to both the C_1 minimum ground state and the TS energies, the energy barrier is reduced to 75.1 cm^{-1} (108 K). For compound **2**, the energy barrier including the ZPE is 35 cm^{-1} (50 K). These very weak values rationalize the fact that the X-ray structures of both compounds determined at 100 K were found symmetric, that is, of the C_3 SPG.

3.4.2. Competition between the Antagonist Effects of the First-Order Spin−Orbit Coupling and the Jahn−Teller Distortion: a Two-State Spin−Orbit CAS(8,10)PT2 Study. In order to quantify the antagonist effects of the first-order spin−orbit coupling and the Jahn−Teller distortion, the energy of the spin−orbit states arising from the degenerate ground term (in C_3 SPG) have been calculated using the SOSI method for different geometries interpolated between the experimental geometry and the DFT minimum. Since at this stage we just want to describe the first-order effects of the SOC, only the two spin−orbit free states arising from the two spatial configurations were introduced in the SOSI matrix. Their wave functions have been optimized using minimal active space CAS(8,10)SCF calculations while their energies, used in the SOSI calculations, are the dynamically correlated CAS(8,10)-PT2 ones. The spectrum computed for **1** as a function of the distortion between the C_3 and the DFT minimum geometry is given in Figure 6.

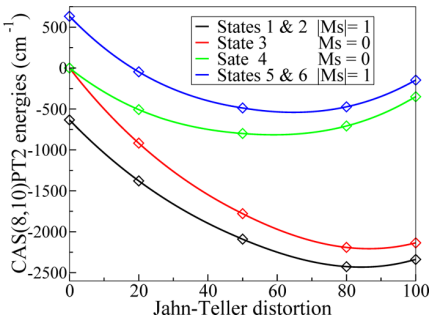

Figure 6. Low-energy spectrum of **1** computed at the two-state SOSI-CAS(8,10)PT2 level of correlation. The x axis represents a linear distortion between the C_3 (0) and the DFT C_1 minimum (100).

The geometries along the distortion are obtained by a linear interpolation between the two extreme structures. The spatial configuration in which d_{xy} is singly occupied is stabilized while the $d_{x^2-y^2}$ one is destabilized. While the $M_s = \pm 1$ components are degenerate whatever the distortion is, the $M_s = 0$ components are split by the distortion. One may notice that the SOSI-CAS(8,10)PT2 constrained minimum (along this distortion) is located at 50% between the C_3 and the C_1 DFT geometries. The geometry at this minimal energy is less distorted than the DFT one, and the energy difference between the $M_s = \pm 1$ components and the $M_s = 0$ one is therefore larger at the SOSI-CASPT2 constrained minimum than at the DFT minimum. One should mention that the SOSI-CASSCF constrained minimum is located at 75% of the C_1 structure. The spectrum of compound **2** is represented in Figure S20 of the Supporting Information. It exhibits the same features except that the SOSI-CASSCF and SOSI-CASPT2 constrained minima are both located at 80% between the C_3 and DFT C_1 geometries.

In the C_3 SPG (zero of the abscissa), the degeneracy between the $d_{x^2-y^2}$ and d_{xy} orbitals is responsible for the very important effect of the spin−orbit interaction: the spin−orbit operator directly couples the M_s components of the two spatial configurations, that is, spin−orbit interaction acts at first order. Indeed, the $d_{x^2-y^2}$ and d_{xy} orbitals are linear combinations of the complex d_{2-} and d_{2+} orbitals. The operator $\sum_i \zeta_i \hat{l}_{Zi} \cdot \hat{s}_{Zi}$ therefore couples the degenerate spatial components of the ^3E ground term, which differ by the occupation of the $d_{x^2-y^2}$ and d_{xy} orbitals. Actually only the $M_s = -1$ and $M_s = +1$ of the two spatial configurations are coupled resulting in a removal of degeneracy of the three M_s components. The usual ZFS Hamiltonian cannot model the spectrum, at this C_3 symmetry, since the ground term presents a first-order angular momentum. The values of the angular momentum components are very close to $M_l = \pm 2$. For this peculiar geometry, the spin−orbit momentum components M_J can be defined from the values of M_l and M_s. Their values are $M_J = 3, 2, 1, -1, -2$, and -3. The energy splitting between the $M_s = \pm 1$ and the $M_s = 0$ states of the ground term is around 635 cm^{-1} for both compounds, which is a value very close to the spin−orbit coupling constant of the Ni(II) ion, 644 cm^{-1}.[87]

The Jahn−Teller distortion induces a lifting of degeneracy of the $d_{x^2-y^2}$ and d_{xy} orbitals, which results in a lifting of degeneracy of the spatial configurations by the quantity $\pm\delta_1$ and therefore a reduction of the splitting due to the spin−orbit coupling. As soon as the symmetry is lowered by the distortion, the two configurations $|d_{xy}|$ and $|d_{x^2-y^2}|$ are coupled by the ligand field, by the quantity δ_2. The here-proposed model is similar to that used in similar contexts.[24,88] The representative matrix of the model Hamiltonian involving the spin−orbit coupling between the two configurations $|d_{xy}|$ and $|d_{x^2-y^2}|$ and the Jahn−Teller distortion ligand field parameters (δ_1 and δ_2) is given below (eq 2):

$$
\begin{array}{c}
 \\ \langle d_{xy}, -1| \\ \langle d_{x^2-y^2}, -1| \\ \langle d_{xy}, 0| \\ \langle d_{x^2-y^2}, 0| \\ \langle d_{xy}, 1| \\ \langle d_{x^2-y^2}, 1|
\end{array}
\begin{array}{c}
\begin{array}{cccccc} |d_{xy}, -1\rangle & |d_{x^2-y^2}, -1\rangle & |d_{xy}, 0\rangle & |d_{x^2-y^2}, 0\rangle & |d_{xy}, 1\rangle & |d_{x^2-y^2}, 1\rangle \end{array} \\
\begin{pmatrix}
-\Delta+\delta_1 & \delta_2+i\zeta & 0 & 0 & 0 & 0 \\
\delta_2-i\zeta & -\Delta-\delta_1 & 0 & 0 & 0 & 0 \\
0 & 0 & -\Delta+\delta_1 & \delta_2 & 0 & 0 \\
0 & 0 & \delta_2 & -\Delta-\delta_1 & 0 & 0 \\
0 & 0 & 0 & 0 & -\Delta+\delta_1 & \delta_2-i\zeta \\
0 & 0 & 0 & 0 & \delta_2+i\zeta & -\Delta-\delta_1
\end{pmatrix}
\end{array}
\tag{2}
$$

where ζ is the spin−orbit constant of Ni(II) reduced by the ligand field and Δ is the mean value of the eigenenergies. The values of δ_1, δ_2, and Δ depend on the geometrical structure. For the C_3 SPG, the three parameters are zero while they are maximal for the most distorted geometry of the DFT C_1 minimum. The diagonalization of this matrix gives access to

the energy of the six spin−orbit states. The general expressions of the energies are

$$E_{1,2}(M_s = \pm 1) = -\Delta - \sqrt{\delta^2 + \zeta^2}$$
$$E_{3,4}(M_s = 0) = -\Delta \pm \delta$$
$$E_{5,6}(M_s = \pm 1) = -\Delta + \sqrt{\delta^2 + \zeta^2} \quad (3)$$

where (1,2), (3,4) and (5,6) are ordered by increasing energy and $\delta^2 = \delta_1^2 + \delta_2^2$. In the C_3 geometry ($\delta = 0$, $\Delta = 0$), these energies are:

$$E_{1,2}(M_J = \pm 3) = -\zeta$$
$$E_{3,4}(M_J = \pm 2) = 0$$
$$E_{5,6}(M_J = \pm 1) = \zeta \quad (4)$$

When the distortion is dominant ($\delta^2 \gg \zeta^2$), the eigenstates are very similar to the spin−orbit free states and their energies are

$$E(^3A)_1 = -\Delta - \delta$$
$$E(^3A)_2 = -\Delta + \delta \quad (5)$$

While only values of δ and Δ are accessible from the computed energies, it is possible to determine the values of Δ, δ, δ_1, and δ_2 using both the energies and wave functions from the effective Hamiltonian theory in the formalism of des Cloizeaux.[89] This theory enables one to build a numerical effective Hamiltonian working in the model space constituted of the components of the two spatial configurations and fulfilling the following conditions:

$$H^{eff}|\tilde{\Psi}_i\rangle = E_i|\tilde{\Psi}_i\rangle \quad (6)$$

where E_i are the ab initio energies of the lowest spin−orbit states and $|\Psi\rangle$ are the orthonormalized projections onto the model space of the corresponding spin−orbit states. According to this theory, the numerical elements of the effective Hamiltonian matrix can be calculated from the spin−orbit energies and wave functions, using the spectral decomposition of the effective Hamiltonian:

$$\langle I|\hat{H}^{eff}|J\rangle = \langle I|\sum_i E_i|\tilde{\Psi}_i\rangle\langle\tilde{\Psi}_i|J\rangle \quad (7)$$

where I and J are the M_s components of the two spatial configurations, that is, the functions on which is spanned the analytical matrix (eq 2). Identifying the analytical elements and the numerical ones enables one to extract the values of all the interactions of the model. Table S3 of the Supporting Information reports the values of δ, δ_1, δ_2, Δ, and ζ (in cm^{-1}) determined for the experimental geometry, the DFT minimum, and the SOSI-CASSCF and the SOSI-CASPT2 constrained minima.

The changes of metal−ligand covalency between the different studied geometries have a negligible impact on the ζ value, since calculations show that this parameter is essentially constant. It is worth noticing that this value is far from being negligible in comparison to the value of δ, showing that (i) eq 3 should be used to reproduce the computed energies and (ii) the impact on the spectrum of the spin−orbit coupling is still very important even at the most distorted geometry (DFT minimum) justifying the terminology "first order". Of course, all the values of the introduced ligand field parameters are zero at the C_3 geometry. As expected the values of δ, δ_1 (stabilization/destabilization of the configurations), and δ_2 (mixing of the two configurations) increase with the deformation. One may also notice that the signs of δ_1 and δ_2 change between the minima and the TS, reflecting the interchange of the dominant configuration in the ground-state wave function. Finally, one may notice that Δ is positive at the SOSI-CASPT2 minimum (and for more distorted geometries) reflecting the fact that, for compound **1**, the stabilization of the ground state due to the Jahn−Teller distortion is very weak: since the excited states are destabilized by the distortion, the mean energy value is consequently positive.

3.4.3. Determination of the ZFS Parameters: a 24 State SOSI-CAS(8,10)PT2 Study. When the geometry is distorted, the impact on the spectrum of the spin−orbit coupling between the two first states decreases, and the spin−orbit effects resulting from the coupling with the other excited states may become of comparable importance. In order to better describe the lowest energy spectrum and in particular the lifting of degeneracy of the M_s components of the ground term, SOSI-CAS(8,10)PT2 calculations involving the 10 excited triplets and 14 excited singlets have been performed. The low energy spectrum reported in Figure S21 of the Supporting Information exhibits the same qualitative features as the one obtained from the two-state SOSI matrix. The main qualitative differences are (i) a slight reduction of the ζ spin−orbit coupling constant (595 versus 630 cm^{-1}) and (ii) the lifting of degeneracy of the $M_s = \pm 1$ components that results from the spin−orbit coupling with the other excited terms. For distorted structures, the energies of the three spin−orbit states arising from the ground term configuration can be described using the ZFS Hamiltonian $\hat{H}^{ZFS} = \hat{S}.\overline{\overline{\mathbf{D}}}.\hat{S}$ given by eq 1 in zero field $\mathbf{B} = 0$. Using the effective Hamiltonian theory, it is possible to extract all the components of the 2nd rank ZFS tensor $\overline{\overline{\mathbf{D}}}$. Then, its diagonalization gives access to the axial and rhombic D and E parameters and to the magnetic axes frame. The so-obtained axes of compounds **1** and **2** are represented in Figure S22 of the Supporting Information, showing that the Z axis determined theoretically is very close to the Ni−X direction.

Table 1 reports the extracted values of the D and E parameters for the four different computed geometrical structures: the C_1 DFT minimum, the constrained SOSI-CASSCF and SOSI-CASPT2 minima, and the TS geometry. It is worth noticing that, while the reduction of the values of D when introducing the spin−orbit coupling between the ground electronic term and the excited ones is non-negligible, the values are still extremely large, ranging between −100 and −200 cm^{-1}.

As shown previously,[48] the methods used here usually provide reliable values of the ZFS parameters for the experimental geometries. Since, the property is governed by both the spin−orbit coupling and the symmetry lowering (from isotropic symmetry) of the geometry, the results strongly depend on the geometrical structure. Unfortunately, the distorted experimental geometries of these compounds are not available.

In order to appreciate which of these geometries is the most reliable, we have computed both magnetization versus magnetic field $M = f(B/T)$ and susceptibility versus temperature $\chi T = f(T)$. Figures 7 and S23 (Supporting Information) show the results obtained for the SOSI-CASSCF minimum for which the

Table 1. ZFS Parameters (cm^{-1}) Computed at Several Levels of Calculations for the Geometries of the TS, the DFT Minimum, and the SOSI-CASSCF and SOSI-CAS(8,10)PT2 Constrained Minima (along the Jahn−Teller Distortion between the Experimental C_3 and the DFT Minimum)[a]

		1		2	
level of calculation	geometry	D	E	D	E
CAS(8,10)PT2 2 triplets	DFT minimum	−187	0	−202	0
	SOSI-CASSCF constrained minimum	−241	0	−234	0
	SOSI-CASPT2 constrained minimum	−299	0	−234	0
	TS minimum	−224	0	−240	0
CAS(8,10)PT2 14 singlets and 10 triplets	DFT minimum	−104	0.7	−117	1.1
	SOSI-CASSCF constrained minimum	−152	0.6	−147	1.1
	SOSI-CASPT2 constrained minimum	−205	0.8	−147	1.2
	TS minimum	−127	3.0	−146	3.1

[a]The number of states, which have been introduced in the state interaction matrix, is indicated in the left column.

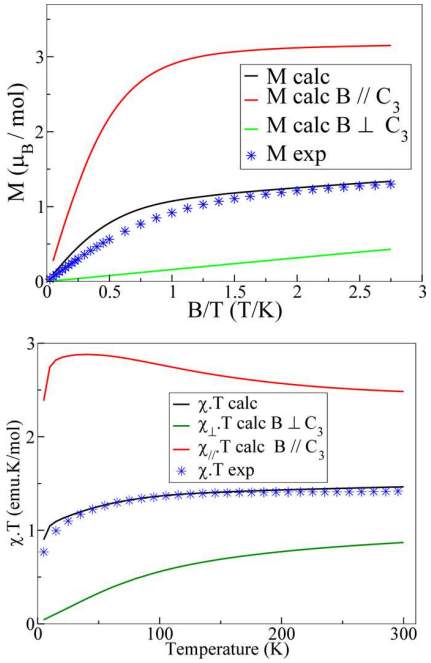

Figure 7. $M = f(B/T)$ at 2 K and $\chi T = f(T)$ curves computed from the 24 state SOSI-CASPT2 solutions at the constrained SOSI-CASSCF minimum for **1**. The experimental results are reported for comparison.

best agreement with the experiment is obtained for both $M = f(B/T)$ and $\chi T = f(T)$ (see the Supporting Information, Figures S24 and S25, for comparison with the other geometries). At the SOSI-CASSCF minimum, the value of D is −152 cm^{-1}, which is in agreement with the best estimate −180 cm^{-1} from HF-HFEPR measurements.

Looking more carefully at the SOSI matrix, one may notice that the main contributions to the ZFS are brought by the three first excited triplet states. The first excited triplet (dominated by the $|d_{x^2-y^2}|$ configuration) brings the large negative contribution. The coupling with the other excited states and in particular with the third and fourth triplet states resulting from excitations from the d_{xz} and d_{yz} orbitals to the d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ orbitals bring positive contributions that again reduce the D value. Comparing all the obtained values, one may conclude that the Jahn−Teller distortion is mainly responsible for the reduction of the D values. Indeed the lifting of degeneracy between the two spatial components of the ground term induces a reduction of the energy difference between the $M_s = \pm 1$ and $M_s = 0$ lowest components from −595 cm^{-1} (in the C_3 structure) to −241 cm^{-1} for instance at the constrained SOSI-CASSCF minimum while the total positive contribution brought by the other excited states is 85 cm^{-1}.

In summary, while the reduction of D due to the Jahn−Teller distortion is quite important, the values of D in all considered distorted structures are still extremely large in comparison to what is usually observed in mononuclear complexes. This result shows that, in the studied complexes, the Jahn−Teller distortion is not large enough to completely eliminate the large impact of the spin−orbit coupling between the two lowest states. The rigidity of the ligand preventing strong deformations is probably responsible for this result.

It was unfortunately not possible to characterize compound **2** using HF-HFEPR spectroscopy. Nevertheless, both magnetic measurements and theoretical investigations show that this compound also exhibits a giant uniaxial magnetic anisotropy with a $D = -147$ cm^{-1} value close to that of compound **1**. This result is in line with the fact that the geometrical distortion mainly due to angular contributions is similar in both compounds.

4. CONCLUDING REMARKS

Ni(II) complexes with a trigonal bipyramid symmetry, as is the case for **1** and **2**, must have a doubly degenerate ground state and thus a first-order spin−orbit coupling leading to a magnetic anisotropy of the order of the spin−orbit parameter (around 600 cm^{-1}). It is expected that, in order to gain energy, vibronic coupling lifts the degeneracy of the ground state thus drastically reducing the effect of first-order spin−orbit coupling and consequently magnetic anisotropy. In such cases, the energy difference between the M_s components of the S = 1 state is drastically reduced. In order to estimate the magnitude of the magnetic anisotropy in compound **1** that has a C_3 crystallographic axis, EPR studies were performed on a single crystal and on powder samples. These studies allowed showing that the M_s sublevels ±1 are the lowest in energy. The rhombic ZFS parameter E was determined (1.6 cm^{-1}), and the axial parameter D was estimated to be larger than 120 cm^{-1}, showing that the orbital momentum is not fully quenched. In order to rationalize the magnetic behavior and to get insight into the origin of the large Ising-type magnetic anisotropy experimentally observed, a full theoretical study was carried out. DFT calculations show that, due to Jahn−Teller effects, the potential energy surfaces of the studied complexes exhibit a moat around a conical intersection. The potential energy barrier including vibrational contributions is relatively flat.

The theoretical studies, the EPR results, and the structural analysis at 10 K of complex **1** lead to the important conclusion that the Jahn−Teller effect only weakly distorts the structure. As a consequence, a giant axial anisotropic parameter is found, resulting from a non-totally quenched orbital angular momentum. The origin of such a weak Jahn−Teller effect can be attributed to the rigidity of the Me_6tren pentadentate

ligand imposing a robust trigonal bipyramidal geometry that counterbalances the Jahn−Teller distortion. This highlights the crucial role played by the organic ligands in designing mononuclear complexes with large magnetic anisotropy. Such complexes can be used as building-block units for the elaboration of polynuclear complexes with high blocking temperatures.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data as CIF files; structural data and their analysis at 100 K for **1** and **2** and at 10 K for **1**; SQUID magnetic data on powder; angular dependence and analysis of the EPR spectra of a single crystal of **1**; powder EPR spectra of **1** at frequencies between 110 and 221 GHz; theoretical variation of the energy levels for **1** and **2** upon the magnitude of the Jahn−Teller distortion; and calculated magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*nathalie.guihery@irsamc.ups-tlse.fr; shill@magnet.fsu.edu; talal.mallah@u-psud.fr

Notes

The authors declare no competing financial interest.

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Supporting Information

Synthesis of $[Ni(Me_6tren)Cl](ClO_4)$ (**1**) $NiCl_2 \cdot 6H_2O$ (0.330 g, 1.40 mmol) was dissolved in EtOH (20 ml) at 55 °C. Me_6tren (0.322 g, 1.40 mmol) dissolved in EtOH (10 ml) was added dropwise with stirring, forming a green solution that was stirred overnight at room temperature. $NaClO_4 \cdot H_2O$ (0.196 g, 1.40 mmol) was added with stirring inducing precipitation of pale green $[Ni(Me_6tren)Cl](ClO_4)$ (2) (0.543 g, 92%), which was isolated by filtration, washed with EtOH (5 ml) and Et_2O (10 ml) and dried in air. Slow cooling a hot saturated methanolic solution of 1 yielded crystals suitable for X-ray analysis after 1 night. Elemental analysis (%), observed (calculated for $NiC_{12}H_{30}N_4Cl_2O_4$) C, 34.01 (34.11) H, 7.16 (7.16) N, 13.14 (13.27). MS ESI$^+$ (MeOH) : m/z 323.24 $[Ni(Me_6tren)Cl]^+$. IR (KBr) ν/cm^{-1} : 3437 (m), 2985 (m), 2901 (m), 2850 (m), 2793 (w), 2014 (w), 1486 (s), 1475 (s), 1462 (m), 1434 (m), 1358 (w), 1299 (m), 1248 (w), 1172 (w), 1090 (s), 1050 (s), 1023 (m), 1007 (m), 938 (s), 912 (m), 808 (m), 777 (m), 742 (w), 623 (s), 602 (w), 576 (w), 481 (w), 419 (w), 382 (w).

Physical measurements

Table S1 Details of the crystallographic analysis of **1**, and selected bond lengths and angles for **1** and **2**.

	1		
chemical formula	$C_{12}H_{30}N_4NiCl_2O_4$	$C_{12}H_{30}N_4NiCl_2O_4$	
molecular weight	423.99	423.99	
crystal dimens./mm	0.27, 0.18, 0.06	0.11, 0.23, 0.28	
crystal system	Rhombohedral	Rhombohedral	
space group	R3c	R3c	
a/Å	9.874(5)	9.8155(4)	
b/Å	9.874(5)	9.8155(4)	
c/Å	32.962(5)	32.752(2)	
$\alpha/°$	90	90	
$\beta/°$	90	90	
$\gamma/°$	120	120	
V/Å^3	2783(2)	2732.7(2)	
Z	6	6	
ρ_{calcd}	1.518	1.546	
T/K	100	10	
θ_{max}/deg	36.93	32.98	
data collected	8389	16442	
(unique)	2212	2199	
no of params	72	110	
Final $R1$, $wR2$	0.0249, 0.0609	0.0271, 0.0502	
	1 at 100 K	**1 at 10 K**	**2**
Ni – N1/Å	2.072(3)	2.064(2)	2.104(0)
Ni- N2/Å	2.143(2)	2.1303(12)	2.135(0)
Ni – X/Å	2.282(1)	2.2745(6)	2.467(0)
N1 –Ni – N2/°	83.81(5)	83.98(3)	84.22(0)
N1 – Ni – X/°	180.00	180.00	180.00
N2 – Ni – N2'/°	118.85(2)	118.913(12)	119.00(1)
N2 – Ni – X/°	96.19(5)	96.02(3)	95.78(0)

Analysis of the 10 K crystal structure.
The structural refinement of the 10K diffraction data has been conducted in the *R3c* space group, in agreement with the observed extinction conditions on the measured Bragg intensities. No symmetry breaking transition occurs with respect to the 100 K crystal structure, which could have resulted from a specific structural distortion. Attempts have been made to refine the structure in the non-isomorphic subgroup Cc, thus releasing the 3-fold symmetry passing through the [Ni(Me_6tren)Cl] complex. The resulting Ni-N2 bond distances indicate a very subtle distortion (Ni-N2 = 2.1435(16)Å, Ni-N2' = 2.1390(16)Å, Ni-N2" = 2.1394(15)Å), which is within the standard deviation ($\Delta d_{Ni-N2} \sim 3\sigma$), and therefore barely significant. The corresponding calculated distance distortion (defined by eq. 2 in the manuscript) is only 0.0063Å. Accordingly, the high symmetry *R3c* description of the structure has been considered for the discussion in the manuscript. The absence of crystal symmetry lowering at 10 K does not rule out the presence of a molecular distortion. Indeed, a local (i.e. molecular) distortion resulting from a Jahn-Teller effect with an equal population of the three distortion modes (depicted in Figure S2), and statistically distributed within the single crystal sample would preserve the *R3c* symmetry.
The atomic displacement tensors U_{ij} determined from the structural analysis of the x-ray diffraction data contain essential information on the structural dynamics of the [Ni(Me_6tren)Cl] complex, and may provide further information on the presence of a static or dynamic Jahn-Teller behavior. The U_{ij} tensors accounts at the same time for the external and internal vibration contributions, in addition to static disorder in the crystal. The structural dynamics of the [Ni(Me_6tren)Cl] complex at 10 K has been examined by performing a TLS thermal motion analysis using the THMA software. [1] The experimentally determined tensors U_{ij} have been fitted considering the complex as a rigid body, by refining the components of the translation (T), libration (L) and correlation (S, skew) tensors. This thermal motion model accounts solely for the external vibration modes. The figure S3 displays the resulting difference surfaces U_{obs}-U_{calc}(TLS). The difference surfaces of the C1, C2 and N2 atoms evidence a specific internal displacement (depicted by the black arrow), which relates to an internal libration of one fragment of the *tren* ligand. This libration is the structural signature of a Jahn-Teller effect, with a shortening of one Ni-N2 bond distance, and lengthening of the two other symmetry related Ni-N2 bonds (depicted by the red arrows in figure S3) ; this distortion mode corresponds to one of the three symmetry equivalent minima given in figure 4. Owing to the C3 symmetry, still preserved at 10 K, this internal libration occurs also for the other two similar fragments of the ligand. This libration may have here a dynamic origin (dynamic Jahn-Teller), or a static origin (static Jahn-Teller) with an equal population of the three distortion modes, and a statistical distribution within the single crystal. In this later case, the *R3c* crystal symmetry is preserved, although a local (i.e. molecular) symmetry lowering occurs with a lift of degeneracy. In conclusion, the TLS analysis of the 10 K crystal structure supports the presence of a Jahn-Teller effect, whether it is of static or dynamic origin, and agrees with the EPR findings.

$$\begin{aligned} \delta r &= \left(\sum_i \left(r_i^{C1} - r_i^{C3}\right)^2\right)^{1/2} \\ \delta\alpha &= \overline{r}\left(\sum_i \left(\alpha_i^{C1} - \alpha_i^{C3}\right)^2\right)^{1/2} \end{aligned} \quad \text{Equation S1}$$

1. V. Schomaker ; K.N.Trueblood, *Acta Cryst.* **1998**, *B54*, 507.

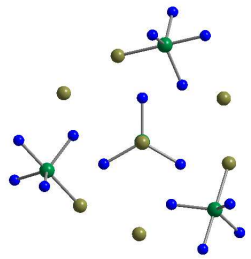

Figure S1 : Packing diagram viewed along the C_3 axis of one of the $[Ni(Me_6tren)Br]^+$ complexes in the unit cell of **2**. Carbon and hydrogen atoms have been removed for clarity.

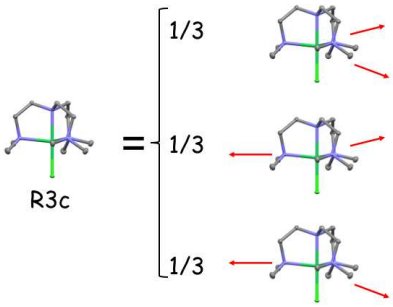

Figure S2 : Local molecular distortion resulting from a Jahn-Teller effect with an equal population of the three distortion modes

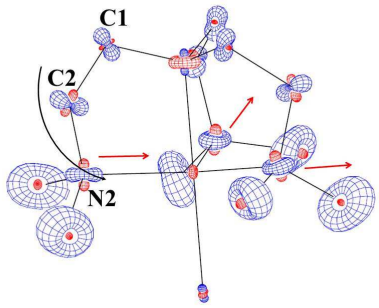

Figure S3 : Difference root mean square displacements $U_{obs} - U_{calc}$(TLS), positive in blue, negative in red.

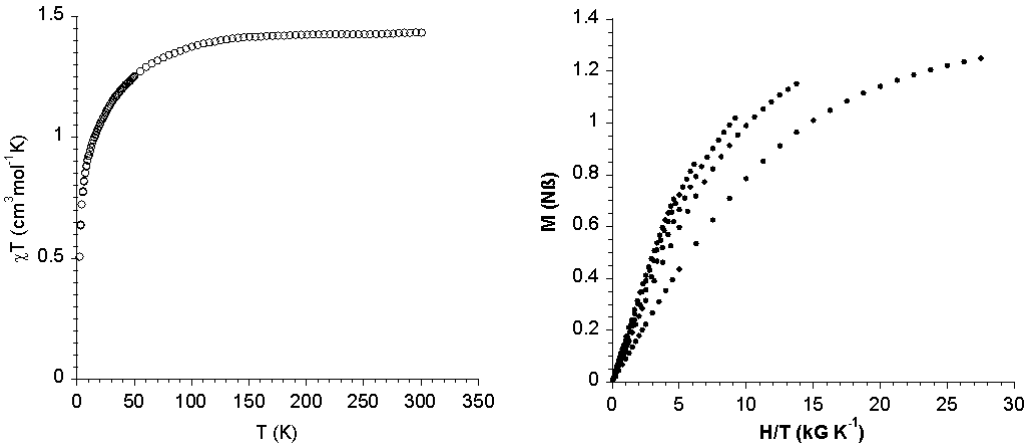

Figure S4 : χT vs. T for **1** in an applied field of 0.1 and 1.0 T (left), and reduced magnetization, M vs. HT^{-1} (right), collected at 2, 4, 6, 10 and 12 K.

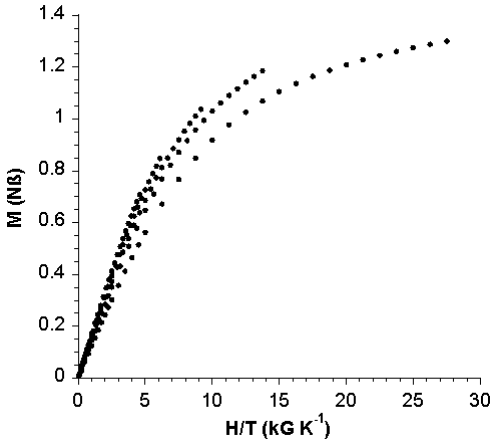

Figure S5 : χT vs. T for 2 in an applied field of 0.1 and 1.0 T (left), and reduced magnetization, M vs. HT^{-1} (right), collected at 2, 4, 6, 10 and 12 K.

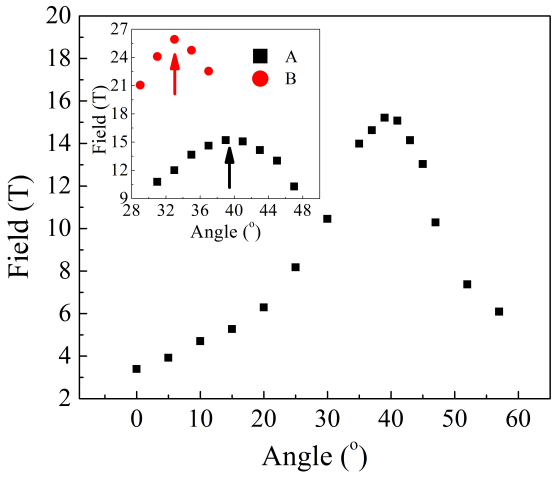

Figure S6 : (main panel) Angle dependence of the EPR peak positions of the A molecules of **1** at 161 GHz, 1.4 K. (inset) Fine angle dependence of the EPR peak positions of the A and B molecules. The experiments were performed at 161 GHz, 1.4 K. The hard planes of the A and B molecules are indicated by the black and red arrows, respectively.

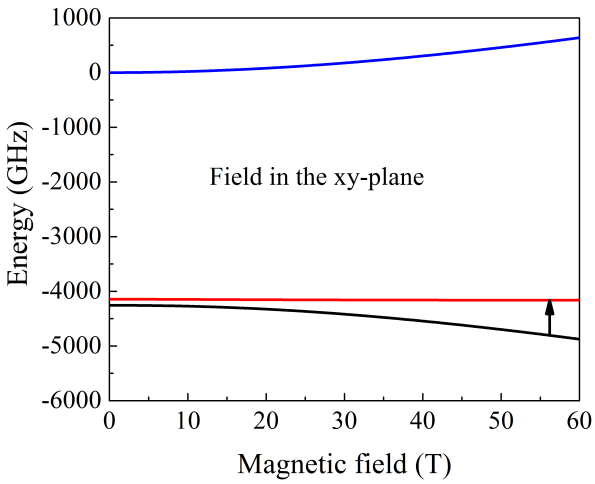

Figure S7 : Energy levels when the field is in the molecular hard plane. The black arrow corresponds to the observed EPR transition.

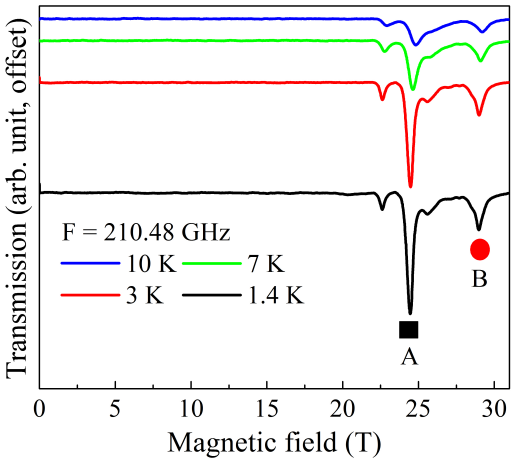

Figure S8 : Temperature dependence HFHF-EPR spectra of **1** at 210 GHz. The experiments were performed with the field applied in the hard plane of the A molecules. The two observed signals are labelled. The intensity of the signals decreases with increasing temperature confirming that they are ground state transitions. The fine structure peaks close to the A transitions are likely due to disorders and/or imperfect crystal.

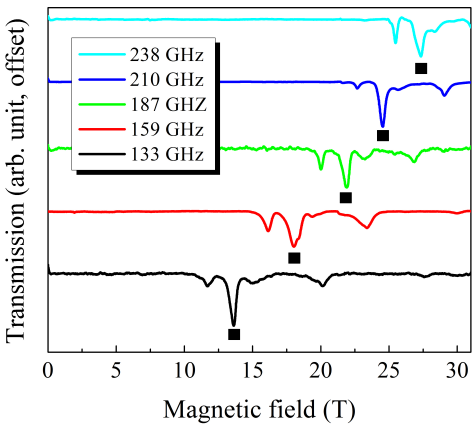

Figure S9 : Representative hard plane EPR spectra of **1** collected at 1.4 K. These experiments were performed with the field applied in the hard plane of the A molecules. The EPR transitions associated with the A molecules are labelled by the solid black squares below each spectrum.

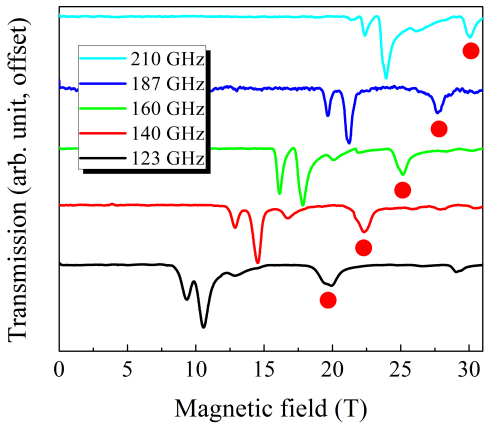

Figure S10 : Representative spectra of the frequency dependence studies of the B molecules at 1.4 K. The experiments were performed with the field applied in the hard plane of the B molecules. The EPR transitions associated with the B molecules are labelled by the solid red circles below each spectrum.

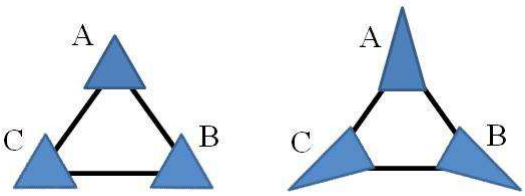

Figure S11 : Three adjacent molecules of **1** in which all molecules possess ideal C_3 symmetry (left). The proposed situation, where all molecules possess a Jahn-Teller type distortion in the trigonal plane and remain related to one another by C_3 rotations (right).

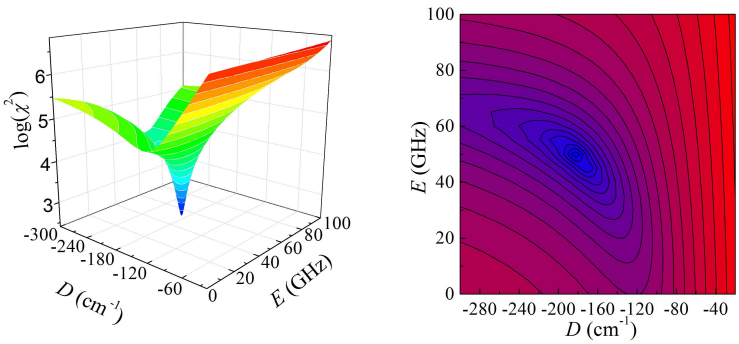

Figure S12 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case D and E are varied while g and ϕ are fixed at 2.4 and 106° respectively. N.B. The unit used for E is GHz, 30 GHz = 1 cm^{-1}.

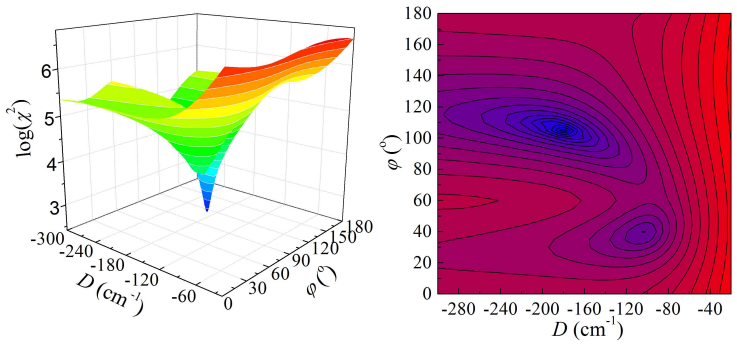

Figure S13 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case D and ϕ are varied while g and E are fixed at 2.4 and 50 GHz respectively.

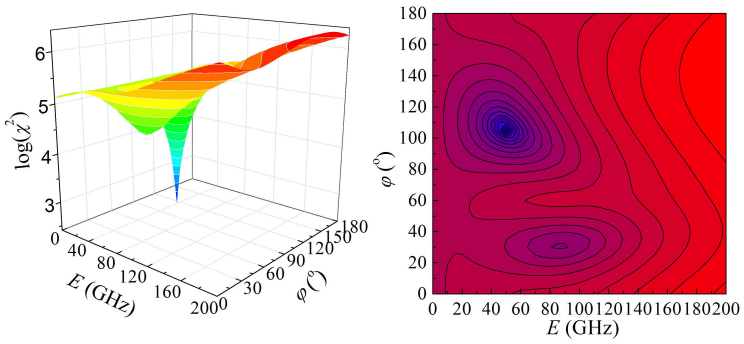

Figure S14 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case E and ϕ are varied while g and D are fixed at 2.4 and 180 cm^{-1} respectively.

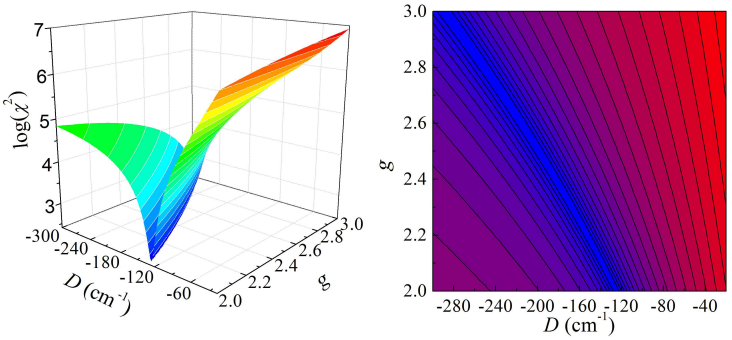

Figure S15 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case D and g are varied while E and ϕ are fixed at 50 GHz and 106° respectively

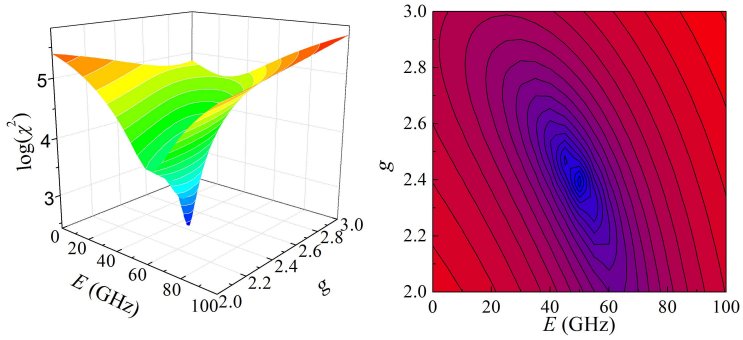

Figure S16 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case E and g are varied while D and ϕ are fixed at 182 cm^{-1} and 106° respectively

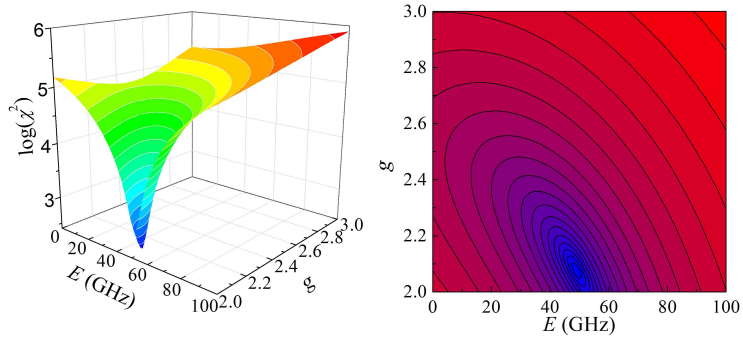

Figure S17 : 3D (left) and contour (right) plots showing the error (χ^2) associated with fitting the EPR results. In this case E and g are varied while D and ϕ are fixed at 182 cm^{-1} and 106° respectively

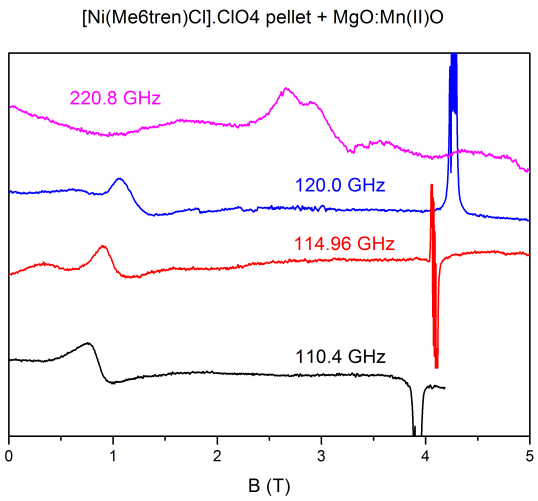

Figure S18 : Powder EPR spectra of **1** at T = 5K and four different frequencies

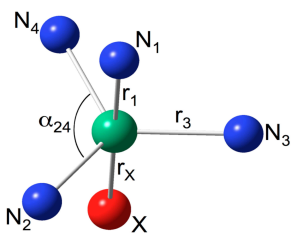

Figure S19 : Scheme depicting the first coordination sphere atoms numbering and some of the distances and angles given in Table S2.

	Ni(Me$_6$tren)Cl			Ni(Me$_6$tren)Br		
	C_3 (exp.)	C_1 (min.DFT)	C_1 (TS.DFT)	C_3 (exp.)	C_1 (min.DFT)	C_1 (TS.DFT)
r_1	2.07	2.14	2.14	2.10	2.16	2.16
r_2	2.14	2.22	2.16	2.14	2.23	2.18
r_3	2.14	2.14	2.17	2.14	2.24	2.17
r_4	2.14	2.22	2.27	2.14	2.15	2.28
r_X	2.28	2.32	2.32	2.47	2.44	2.44
α_{23}	118.9	114.0	112.9	119.0	126.5	113.2
α_{24}	118.9	127.4	121.9	119.0	114.1	122.0
α_{34}	118.9	115.2	122.8	119.0	115.2	120.7
α_{12}	83.8	83.2	84.3	84.2	83.3	83.7
α_{13}	83.8	84.8	84.0	84.2	82.4	84.1
α_{14}	83.8	83.9	83.3	84.2	84.2	82.2
α_{2X}	96.2	96.6	97.6	95.8	97.5	96.8
α_{3X}	96.2	97.2	93.8	95.8	95.2	97.8
α_{4X}	96.2	94.6	97.0	95.8	97.7	95.7
δr	0	0.14	0.16	0	0.15	0.16
$\delta\alpha$	0	0.40	0.29	0	0.39	0.28

Table S2 : Main distances (in Å) and angles (in degrees) optimized at the B3LYP DFT levels for the equilibrium and transition states geometries and of the C_3 experimental geometry.

		ζ	Δ	δ	δ_1	δ_2
1	Experimental geometry	631	0	0	0	0
	SOSI CASPT2 constrained minimum	633	87	519	186	485
	SOSI CASSCF constrained minimum	633	-86	711	299	645
	DFT minimum	635	-605	981	453	878
	Transition state geometry	635	-663	787	-634	-465
2	Experimental geometry	633	0	0	0	0
	SOSI CASSCF/PT2 constrained minimum	635	1450	742	484	562
	DFT minimum	635	1243	893	539	712
	Transition state geometry	634	1513	716	-621	-356

Table S3 : Values (in cm^{-1}) of the spin-orbit constant and of the ligand field parameters resulting from the Jahn-Teller distortion and the first-order spin-orbit coupling for different geometries. Since the SOSI-CASSCF and SOSI-CASPT2 constrained minima are both located at 80% of the distortion between the C_3 geometry and the C_1 DFT minimum, only one set of values is reported.

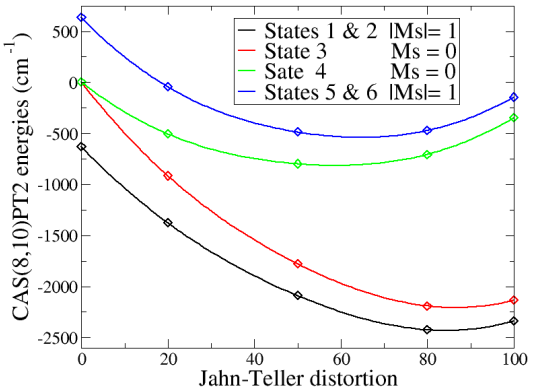

Figure S20. Low energy spectrum of **2** computed at the two states SOSI-CAS(8,10)PT2 level of correlation. The x axis represents a linear distortion between the C_3 (0) and DFT C_1 minimum (100).

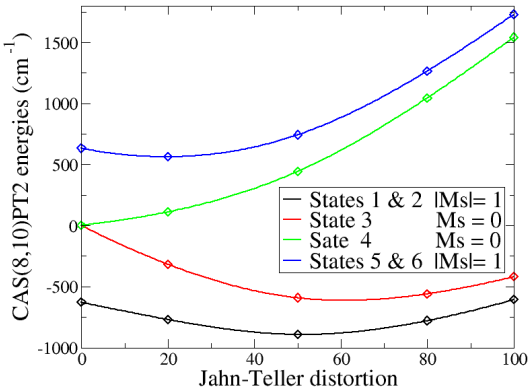

Figure S21 : Low energy spectrum of **1** computed at the two states SOSI-CAS(8,10)PT2 level of correlation. The x axis represents a linear distortion between the C_3 (0) and DFT C_1 minimum (100).

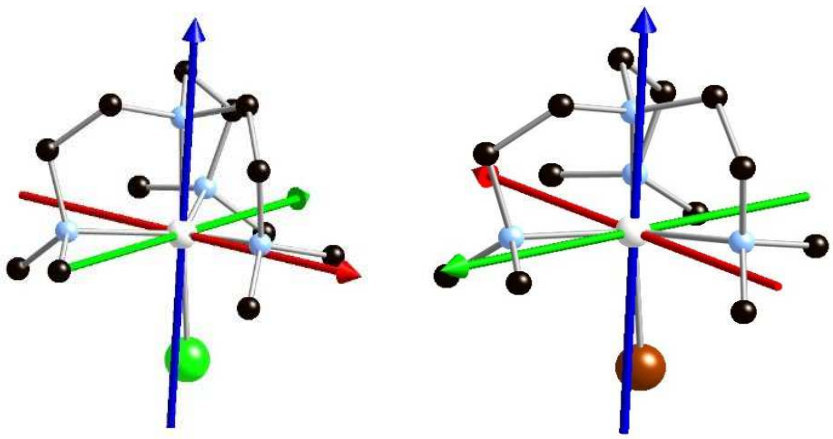

Figure S22 : Schematic representation of **1** and **2** showing the magnetic axes frame in which the 24 states SOSI-CASPT2 computed ZFS tensors are diagonal.

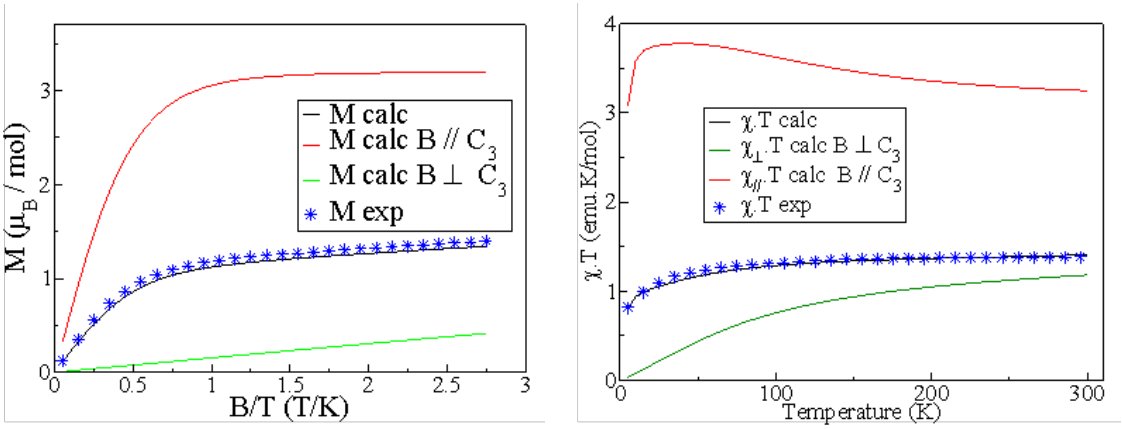

Figure S23 : $M = f(B/T)$ at 2 K (left) and $\chi T = f(T)$ (right) curves computed from the 24 state SOSI-CASPT2 solutions at the constrained SOSI-CASSCF minimum for **2**. The experimental results are reported for comparison

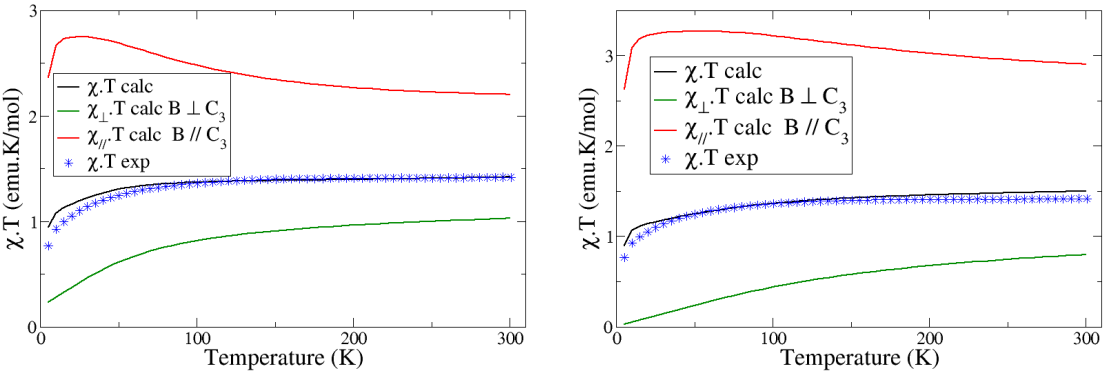

Figure S24 : χT versus T curves computed from the 24-state SOSI-CASPT2 solutions at the constrained SOSI-CASPT2 minimum (left) and DFT minimum (right) for compound **1**. The experimentally measured curve is reported for comparison.

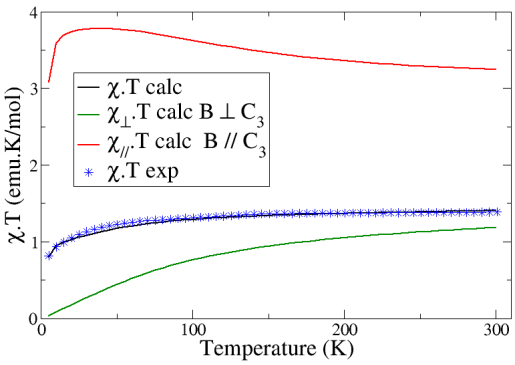

Figure S25 : χT versus T curves computed from the 24-state at the CASSCF geometry, which is identical to the CASPT2 one for compound **2**. The experimentally measured curve is reported for comparison.

Chapitre 3

Interférences et effets synergiques entre anisotropies locales dans les complexes bi-nucléaires

Après avoir étudié, dans certains complexes mononucléaires, comment améliorer l'anisotropie magnétique locale, une étude de l'interaction de deux anisotropies locales sur deux centres métalliques a été réalisée. Il s'agit d'un projet d'article concernant l'élaboration d'un hamiltonien de spin associé au bas du spectre énergétique d'un complexe modèle binucléaire comportant deux Ni^{II} pour différentes structures géométriques. Ce choix permet de définir aisément un ensemble de paramètres de ZFS associé à chaque centre métallique en modifiant les paramètres géométriques et éventuellement la nature des ligands en fonction du type d'anisotropie et de la direction des axes magnétiques souhaitée.

Afin de modéliser le spectre de ces complexes, une étude théorique est menée à l'aide d'un calcul CASSCF avec MOLCAS comportant l'ensemble des 16 électrons de la sous-couche d des deux centres métalliques dans l'espace actif. Puis, différents hamiltoniens modèles sont établis afin de modéliser l'anisotropie magnétique du quintuplet et du triplet fondamental à l'aide d'une description de type "*Giant-Spin*" [56] mais aussi une modélisation de type "*multi-spin*" [17, 19] décrivant l'ensemble des neuf états spin-orbites du spectre les plus bas en énergie issus des états singulet, triplet et quintuplet les plus bas. C'est cette dernière description qui permet de décrire l'hamiltonien en terme d'anisotropie locale et d'échange ; de plus, comme établi précédemment [57, 58], il apparait nécessaire de faire intervenir, en plus des tenseurs de rang deux, introduits lors du chapitre 1.1, un tenseur de rang quatre (*cf.* équation 3.1).

$$\hat{H}^{MS} = J\hat{S}_a \cdot \hat{S}_b + \hat{S}_a\overline{\overline{D}}_a\hat{S}_a + \hat{S}_b\overline{\overline{D}}_b\hat{S}_b + \hat{S}_a\overline{\overline{D}}_{ab}\hat{S}_b + \overline{d}_{ab}\hat{S}_a \times \hat{S}_b + \left(\hat{S}_a \otimes \hat{S}_a\right)\overline{\overline{\overline{\overline{D}}}}_{aabb}\left(\hat{S}_b \otimes \hat{S}_b\right) \tag{3.1}$$

avec

- J le paramètre d'échange isotrope
- $\overline{\overline{D}}_a$ et $\overline{\overline{D}}_b$ les tenseurs d'anisotropie locaux
- $\overline{\overline{D}}_{ab}$ le tenseur d'anisotropie d'échange symétrique

– $\overline{d}_{ab}$ le pseudo-vecteur d'anisotropie d'échange antisymétrique (pseudo-vecteur de Dzyaloshinskii-Moriya)
– $\overline{\overline{\overline{\overline{D}}}}_{aabb}$ le tenseur d'anisotropie d'échange symétrique d'ordre 4

Une extraction des tenseurs d'anisotropies liés aux états triplets de chaque centre métallique $\overline{\overline{D}}_a$ et $\overline{\overline{D}}_b$ obtenus en excluant de l'espace actif les électrons associés à l'autre Ni^{II} est aussi effectuée afin de valider la méthode de type multi-spin et de tester la transférabilité des paramètres d'anisotropie locale au complexe bi-nucléaire.

Au cours de cette étude, il apparait que le rôle de la symétrie du complexe est important et que le caractère nul de certains paramètres peut être prédit pour certaines géométries, à la fois pour les tenseurs de rang deux [59] mais aussi de rang quatre. De plus, le rôle des tenseurs locaux dans une description multi-spin est prépondérant et permet de mieux comprendre leurs influences sur les tenseurs d'échange ainsi que la nature et l'amplitude des paramètres obtenus par une approche *giant-spin*.

L'étude porte sur deux complexes modèles $O[NiCN(NCH)_4]_2$ (noté M_1) et $O[NiCl(NCH)_4]_2$ (noté M_2) soumis à différentes déformations structurales allant de géométries D_{4h} à C_1, cela permet de créer différentes anisotropies locales et de calculer les anisotropies d'interaction impliquées. Afin de représenter les ellipsoïdes associées aux anisotropies, un ensemble de conventions ont été établies en fonction de la nature et des directions du systèmes d'axes propres magnétiques qui est représenté sur la figure 3.1.

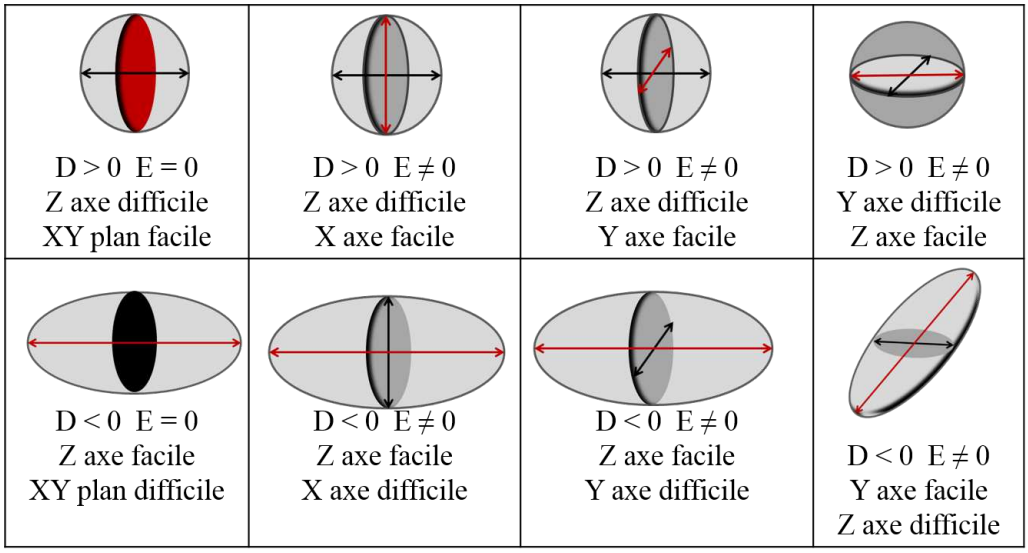

FIGURE 3.1 – Conventions pour la représentation des axes magnétiques pour le tenseur D.
Les plans de facile (resp. difficile) aimantation sont représentés en rouge (resp. noir) et les axes de facile (resp. difficile) aimantation sont symbolisés par une double flèche rouge (resp. noire).

En l'absence de déformation pour M_1 ou pour des compressions avec d'éventuelles rotations pour M_2, on obtient deux anisotropies locales axiales (*cf.* figure 3.2). Dès lors, en fonction des rotations imposées, il est possible d'orienter les axes de faciles aimantation. On constate aussi que le tenseur associé à l'état quintuplet $\overline{\overline{D}}_Q$ dans la description *giant-spin* est de même nature que les tenseurs locaux et sa direction de facile aimantation

est la moyenne de celles des tenseurs locaux à l'exception du cas **3** ou ces directions sont orthogonales auquel cas, sa nature est modifié. On a alors une anisotropie planaire mais la direction de difficile aimantation reste alignée avec celles des tenseurs locaux. De plus, il apparait que le tenseur associé à l'état triplet $\overline{\overline{D}}_T$ dans la description *giant-spin* présente une nature (axiale ou planaire) et un rôle des axes de facile ou difficile aimantation inversé par rapport au tenseur $\overline{\overline{D}}_Q$.

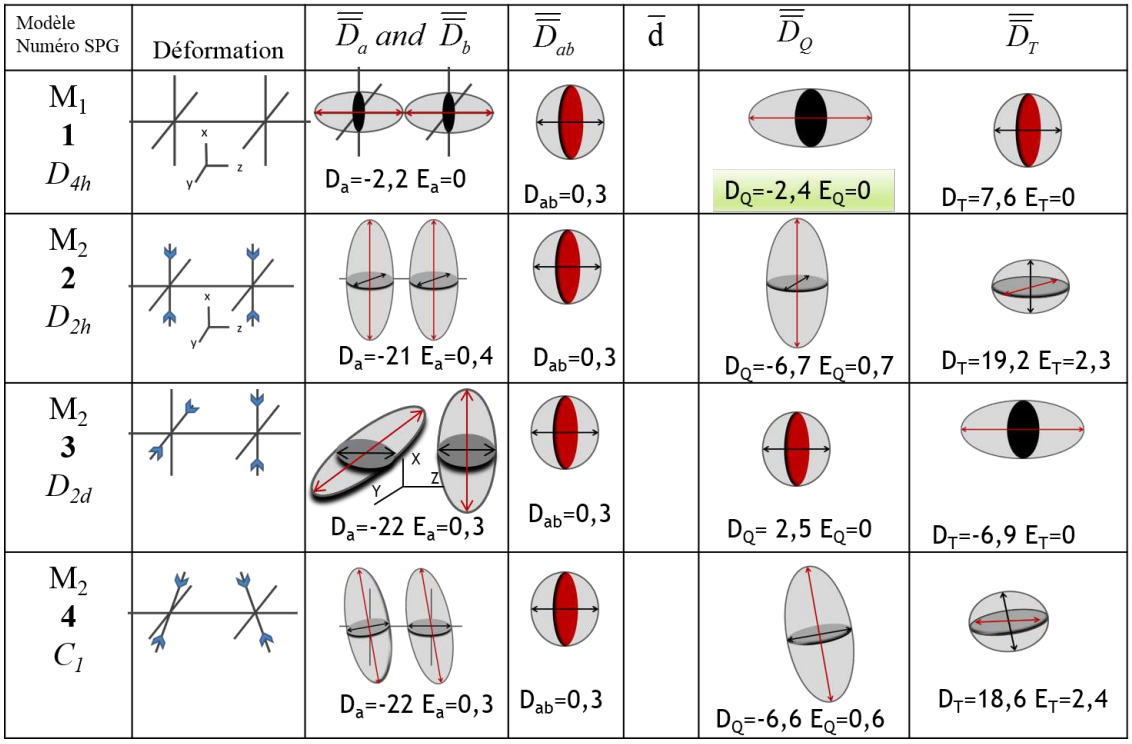

FIGURE 3.2 – Ellipsoïdes représentant l'anisotropie et les axes propres magnétiques pour les tenseurs d'anisotropie locale et globale dans le cas de deux anisotropies locales axiales. Le choix du modèle et le groupe ponctuel de symétrie (SPG) est spécifié dans la première colonne.

En l'absence de déformation pour M_2 ou pour des élongations avec d'éventuelles rotations pour M_1 ou M_2, on obtient deux anisotropies locales planaires (*cf.* figure 3.3). Là encore, le choix des déformations permet de définir, au sein du plan de facile aimantation, la direction de l'axe de facile aimantation. De plus, le tenseur $\overline{\overline{D}}_Q$ présente la même nature que les tenseurs locaux avec des axes d'aimantations bissecteurs des axes locaux, sauf dans le cas **7** d'axes locaux orthogonaux et le cas **10** pour lequel les plans d'aimantations sont orthogonaux. Il en résulte, dans ce dernier cas, une nature axiale du tenseur $\overline{\overline{D}}_Q$ avec un axe de facile orientation aligné avec ceux des tenseurs locaux malgré les valeurs des paramètres D opposées.

Enfin, à partir de déformations distinctes entre les deux centres métalliques, il est possible d'obtenir deux anisotropies locales distinctes (*cf.* figure 3.4) pouvant donner lieu à un tenseur $\overline{\overline{D}}_Q$ de nature axiale ou planaire. Ce dernier présente cependant toujours des directions d'aimantation en accord avec celles de l'anisotropie locale de plus grande amplitude. Il est même possible d'accroitre l'anisotropie globale $\overline{\overline{D}}_Q$ du composé à l'aide

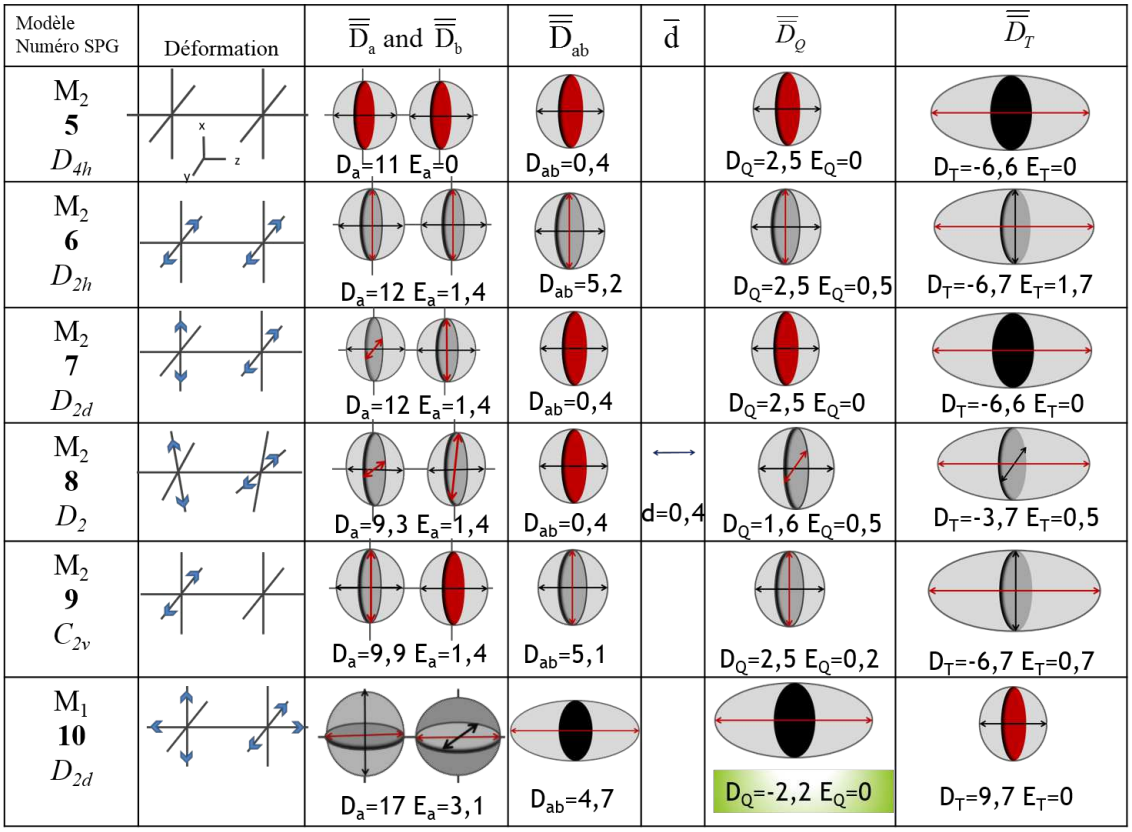

FIGURE 3.3 – Ellipsoïdes représentant l'anisotropie et les axes propres magnétiques pour les tenseurs d'anisotropie locale et globale dans le cas de deux anisotropies locales planaires.

d'une anisotropie locale planaire de même axe de facile orientation que l'anisotropie locale axiale que l'on cherche à favoriser.

Modèle Numéro SPG	Déformation	$\overline{\overline{D}}_a$ and $\overline{\overline{D}}_b$	$\overline{\overline{D}}_{ab}$	$\overline{d}$	$\overline{\overline{D}}_Q$	$\overline{\overline{D}}_T$
M_1 **11** C_{4v}		D_a=-3,6 D_b=1,1 E_a=0 E_b=0	D_{ab}=0,3		D_Q=-1,5 E_Q=0	D_T=5,2 E_T=0
M_1 **12** C_{2v}		D_a=4,6 D_b=-20,3 E_a=0 E_b=0,9	D_{ab}=0,3		D_Q=-3,6 E_Q=0,2	D_T=8,6 E_T=1,4
M_2 **13** C_{2v}		D_a=-2,1 D_b=4,2 E_a=0 E_b=0,5	D_{ab}=-4,7 E_{ab}=0,6		D_Q=-2,5 E_Q=0,3	D_T=8,0 E_T=0,9

FIGURE 3.4 – Ellipsoïdes représentant l'anisotropie et les axes propres magnétiques pour les tenseurs d'anisotropie locale et globale dans le cas de deux anisotropies locales axiale et planaire.

Finalement, nous avons réussir à obtenir une anisotropie globale axiale du quintuplet par l'association de deux anisotropies locales axiales ou, de manière plus surprenante, grâce à deux anisotropies locales planaires avec des plans orthogonaux ou par combinaison d'anisotropies locales axiale et planaire avec une direction commune de facile aimantation. Les géométries permettant d'obtenir un effet synergique entre les spins locaux pour obtenir un effet comparable au niveau du spin du quintuplet sont mises en évidence, de même que la faible dépendance des paramètres du ZFS aux distorsions angulaires des ligands. De plus, il est envisageable d'obtenir une anisotropie globale de nature différente des anisotropies locales. Il est alors possible de prédire quels types de déformations, à partir d'une structure idéale, risquent d'affecter fortement l'anisotropie globale d'un complexe poly-nucléaire.

Interferences between local anisotropies in bi-nuclear complexes

Renaud Ruamps,[1] Coen de Graaf,[2,3] and Nathalie Guihéry*[1]

[1]*Laboratoire de Chimie et de Physique Quantiques,*
IRSAMC/UMR5626, Université de Toulouse 3,
118 route de Narbonne, F-31062 Toulouse Cédex 4, France

[2]*Departament de Química Física i Inorgànica*
Universitat Rovira i Virgili, Marcel·lí Domingo s/n,
43007 Tarragona, Spain

[3]*Institució Catalana de Recerca i Estudis Avançats (ICREA)*
Passeig Lluis Companys 23, 08010, Barcelona, Spain

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Abstract

The overall magnetic anisotropy of two bi-nuclear model complexes, the local anisotropies of their two constitutive Ni(II) ions and the anisotropy of their exchange interactions are determined from correlated *ab initio* calculations. Various geometrical deformations are imposed in order to tune the local anisotropies of the Ni(II) ions and study their different combinations such as planar-planar (with same and different planes), axial-axial (with same and different axes) and axial-planar (with various orientations). The extraction of the parameters of both the giant spin and multispin Hamiltonians combined with the determination of the local and overall magnetic axes enables one to analyze the constructive and destructive interferences between local anisotropies in the resulting overall anisotropy of the complex. This study follows a previous work in which it has been shown that a four-rank tensor should be introduced in the multi-spin Hamiltonian in order to reproduce accurately the *ab initio* results. All the interactions of the revisited multi-spin Hamiltonian are extracted using the effective Hamiltonian theory.

PACS numbers: PACS

I. INTRODUCTION

Magnetic anisotropy is the origin of the single molecule magnet (SMM) behavior[1–5] which consists in a slow relaxation of the magnetization, and to a blocking of the magnetization for low enough temperatures. Since this bistable behavior may lead to possible technological applications in the domain of data storage[6] and quantum computing[7–9], the understanding of the microscopic origin of magnetic anisotropy has received a considerable interest during the last two decades. For most of the complexes based on transition metal ions, the property comes from the lift of degeneracy of the Ms components of the ground spin state S due to relativistic effects, in particular to the spin orbit coupling, and to geometrical distortions from the isotropic highly symmetric octahedron or tetrahedron. This phenomenon is called the Zero-Field Splitting (ZFS) and is characterized by two parameters, namely the axial D and the rhombic E parameters. The bistable behavior occurs when the two maximal Ms components of the ground spin state are the lowest degenerate states and is characterized by a uniaxial magnetic anisotropy, *i.e.* D is large and negative and $E = 0$. As soon as the rhombic parameter E is different from zero, the *Ms* components are coupled and the ground state is a linear combination of the Ms components while when D is positive the lowest |Ms| component(s) become(s) the ground state. The synthesis of new objects presenting the required (and improved) anisotropy characteristics rests on the ability to control the nature (uniaxial or in plane) and magnitude of the magnetic anisotropy. Several theoretical works have been devoted to the understanding of the chemical and geometrical factors which govern the magnetic anisotropy in mono-nuclear species. While due to the numerous driving factors (configurations d^n, geometries, strength of the ligand field, etc.) the conclusions of these studies are contingencies, theory allows one to understand and predict the magnetic anisotropy characteristics of mononuclear species. In poly-nuclear complexes, the situation is even more complicated since additional factors are expected to come into play:

- several and potentially of different nature local anisotropies of the constitutive ions are likely to appear. Indeed, the relativistic effects which are local effects are responsible for the lift of degeneracy of the ground spin state s_i of each ion i and these effects are very sensitive to the local environment of the ion.

- anisotropic interactions (anisotropies of exchange) between local anisotropies may oc-

cur, affecting the characteristics of the resulting overall magnetic anisotropy of the poly-nuclear complex.

The main aim of the present work is to make a first step in the understanding of synergistic effects between local anisotropies. It considers model bi-nuclear complexes constituted of two Ni(II) ions adopting various geometries for which both the nature and the magnitude of the local anisotropies may or not be different. In all cases, the parameters characterizing the local anisotropies are determined and confronted to those of the overall magnetic anisotropy of the complex. Two different anisotropic spin Hamiltonians can be used to characterize the ZFS of poly-nuclear complexes:

- The giant spin Hamiltonian only reproduces the energy levels of the ground term. When the system contains more than two unpaired electrons, and in particular in the weak exchange limit, *i.e.* when the spin mixing between the spin ground state and the excited spin state is non-negligible, the Hamiltonian contains higher than two order Stevens operators.

- The multi-spin Hamiltonian reproduces the energy levels of all spin states arising from the coupling between the local spin states of the paramagnetic ions.

In recent studies, the interactions of these two Hamiltonians have been confronted to those extracted from *ab initio* calculations performed using the all-electron exact electronic Hamiltonian. It was shown that both models are not suitable to reproduce the interactions resulting from the *ab initio* calculations of a binuclear complex constituted of two Ni(II) ions in the weak exchange limit. In the case of the Giant Spin Hamiltonian, simple additional operators were sufficient to reproduce the energy spacings between the Ms components of the ground spin state and all non-negligible interactions could be extracted.[10,11] Concerning the multi-spin Hamiltonian, it was shown that it should be extended with a bi-quadratic operator introducing a 4-rank tensor in order to reproduce accurately all non-negligible interactions.[12] Unfortunately, the number of these interactions was too large and a full extraction could not be performed. A more systematic study of all these interactions is performed here with the purpose of exploring possible relations between the various interactions in order to simplify the multi-spin Hamiltonian and determine all its non-negligible interactions.

It should be stressed that relations between the parameters of the local and overall tensors of anisotropy already exist,[13–16] it is actually possible to determine the overall tensor

of magnetic anisotropy by combining the local ones. Nevertheless these expressions are determined while neglecting the fourth-rank tensor which happens to be responsible for the largest contribution to the anisotropic interactions between the centers. The present paper quantifies and discussed the various anisotropic interactions including those of the four-rank tensor from *ab initio* calculations.

The next section briefly presents the procedure of extraction of the model interactions from the effective Hamiltonian theory and provides the computational information. Section III recalls the physics of the two considered spin Hamiltonians and presents a method for the determination of both the overall and local magnetic axis frames. Section IV discusses the magnitude and nature of the extracted anisotropic interactions of both models. It then focuses on interference effects between local anisotropies in the overall anisotropy of the bi-nuclear complex.

II. METHOD OF EXTRACTION OF THE INTERACTIONS AND COMPUTATIONAL INFORMATION

As shown in previous studies,[17–19] it is possible to establish the relevance of any model Hamiltonian and to extract its constitutive interactions using the effective Hamiltonian theory. In combination with correlated *ab initio* calculations performed using the all-electron exact electronic Hamiltonian, the effective Hamiltonian theory enables one to numerically evaluate all the matrix elements of a model Hamiltonian. This method has successfully been applied to mono- and bi-nuclear complexes in order to determine the anisotropic interactions of the Giant Spin Hamiltonian[10–12,20–24].

The effective Hamiltonian theory[25,26] enables one to extract from accurate *ab initio* calculations the most rigorous effective Hamiltonian working in the same model space as the model Hamiltonian. This effective Hamiltonian is then compared to the model one. In the des Cloizeaux formalism,[26] the general expression of the effective Hamiltonian is:

$$\hat{H}^{eff} = \sum_k |\tilde{\Psi}_k\rangle E_k \langle\tilde{\Psi}_k| \tag{1}$$

where $\tilde{\Psi}_k$ are the orthonormalized projections onto the model space of the all-electron Hamiltonian eigenvectors Ψ_k and E_k are the corresponding eigenenergies. This formulation ensures that the eigenvalues of the effective Hamiltonian are the eigenenergies of the

all-electron Hamiltonian while its eigenvectors are the projections onto the model space of the all-electron Hamiltonian eigenvectors, such that:

$$\hat{H}^{eff}|\tilde{\Psi}_k\rangle = E_k|\tilde{\Psi}_k\rangle \tag{2}$$

Since it is possible to calculate all the matrix elements of the effective Hamiltonian as:

$$\langle i|\hat{H}^{eff}|j\rangle = \langle i|\sum_k |\tilde{\Psi}_k\rangle E_k \langle\tilde{\Psi}_k|j\rangle \tag{3}$$

the method provides more information than the low energy spectrum. Values of the interactions of the model Hamiltonian can be assigned by confronting these numerical matrix elements to their analytical expression in the model Hamiltonian.

The *ab initio* calculations were performed using the Spin-Orbit State-Interaction (SO-SI) method[27] implemented in the MOLCAS package.[28] The method performs a variational treatment of the spin-orbit couplings between the lowest selected states. The preliminary spin-orbit free calculations account for non-dynamic correlation effects. The complete active space self consistent field (CASSCF) method is used to calculate non-dynamically correlated wave functions. The active space contains the 16 d electrons in the 10 d orbitals for the calculation of the magnetic anisotropy of the bi-nuclear species, *i.e.* CAS(16,10)SCF. To compute the local anisotropy tensors, the orbitals of each center were considered active alternatively while the orbitals of the other center were kept inactive, *i.e.* CAS(8,5)SCF calculations were carried out. Extended basis sets of ANO type[29] have been used namely 6s5p4d2f for Ni, 6s5p2d for Cl, 4s3p1d for O and N, 3s2p for C and 2s for H.

III. MODEL HAMILTONIANS AND PROPER MAGNETIC AXIS FRAME

A. Giant-spin Hamiltonian

The simplest description of magnetic anisotropy in polynuclear systems is provided by the giant-spin approximation.[30–33] The use of this Hamiltonian is physically based when the spin ground state of the molecule is sufficiently separated in energy from the other spin multiplets such that the magnetic properties can be described using a single spin ground state. In the considered case, since the coupling between the two Ni(II) ions is antiferromagnetic, it will be used to determine both the triplet and quintuplet excited states anisotropic parameters, in particular the D and E parameters and the corresponding magnetic axis frames.

The Hamiltonian can be expressed in terms of the standard Stevens equivalent operators $\hat{O}_k^m(\hat{S}_z, \hat{S}_\pm)$,[34] *i.e.* as linear combinations of spin operators of symmetry m ($m = 0$ is axial, $m = 2$ is rhombic, $m = 4$ is tetragonal), orders k and additional operators which were shown to be necessary in the case of a bi-nuclear complex in the weak exchange limit.

$$\hat{H}^2_{GSH} = B_2^0\hat{O}_2^0 + B_2^2\hat{O}_2^2 + B_4^4\hat{O}_4^4 + B_4^{ax}\hat{O}_4^{ax} + B_4^{ax,rh}\hat{O}_4^{ax,rh} + B_4^{rh}\hat{O}_4^{rh} \tag{4}$$

where

$$\begin{gathered}
\hat{O}_4^{ax} = \frac{1}{96}(M_S+2)(M_S+1)(M_S-1)(M_S-2)(\hat{S}_+\hat{S}_+\hat{S}_-\hat{S}_- + \hat{S}_-\hat{S}_-\hat{S}_+\hat{S}_+) \\
\hat{O}_4^{ax,rh} = \frac{1}{4\sqrt{6}}(\hat{S}_-\hat{S}_z\hat{S}_z\hat{S}_- + \hat{S}_+\hat{S}_z\hat{S}_z\hat{S}_+) \\
\hat{O}_4^{rh} = \frac{1}{24}[\hat{S}_+\hat{S}_+\hat{S}_+\hat{S}_+ + \hat{S}_-\hat{S}_-\hat{S}_-\hat{S}_- + (M_S-1)(M_S+1)(\hat{S}_z\hat{S}_+\hat{S}_z\hat{S}_- + \hat{S}_z\hat{S}_-\hat{S}_z\hat{S}_+)] \\
\hat{O}_0^0 = S(S+1) \qquad \hat{O}_2^0 = 3\hat{S}_z^2 - S(S+1) \qquad \hat{O}_2^2 = \frac{1}{2}(\hat{S}_+^2 + \hat{S}_-^2) \\
\hat{O}_4^0 = 35\hat{S}_z^4 + [25 - 30S(S+1)]\,\hat{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2 \\
\hat{O}_4^2 = \frac{1}{4}\left[(7\hat{S}_z^2 - S(S+1) - 5)(\hat{S}_+^2 + \hat{S}_-^2) + (\hat{S}_+^2 + \hat{S}_-^2)(7\hat{S}_z^2 - S(S+1) - 5)\right] \\
\hat{O}_4^4 = \frac{1}{2}(\hat{S}_+^4 + \hat{S}_-^4),
\end{gathered} \tag{5}$$

The second-order terms are related to the axial and rhombic parameters of the ZFS $\overline{\overline{D}}$ tensor such that $D = 3B_2^0$ and $E = B_2^2$. Higher than 2 order terms essentially arise from couplings between the different spin states (*i.e.* spin-mixing) and are particularly small in the considered cases since the magnetic coupling is relatively large (around 40 cm^{-1}). The values of these interactions are not reported here since the largest obtained value is $B_4^4 = 0.09\,cm^{-1}$. The determination of the proper magnetic axis frame could therefore safely be performed using only the second-order tensors $S \cdot \overline{\overline{D_2}} \cdot S$ for the quintuplet state and $S \cdot \overline{\overline{D_1}} \cdot S$ for the triplet state (*i.e.* only the B_2^0 and B_2^2 interactions for both states). For this purpose, we have artificially removed the couplings between the singlet, triplet and quintuplet M_S components to extract the tensors and consequently diagonalize them.

B. Multispin Hamiltonian

For a binuclear complex constituted of sites a and b, this model works on the basis of the $|M_{S_a}, M_{S_b}\rangle$ functions. It is designed to reproduce the energy of all the states resulting from the coupling between the ground spin states of each magnetic site. In the present study, the Hamiltonian describes the energy of all M_S components of the singlet, triplet and quintuplet states. As recently shown in a binuclear complex of Ni(II) in the weak exchange limit, it involves a biquadratic operators and a 4-rank tensor $\overline{\overline{\overline{\overline{D}}}}_{aabb}$. In the considered case, its expression is:

$$\hat{H}^{MS} = J\hat{S}_a \cdot \hat{S}_b + \hat{S}_a \overline{\overline{D}}_a \hat{S}_a + \hat{S}_b \overline{\overline{D}}_b \hat{S}_b + \hat{S}_a \overline{\overline{D}}_{ab} \hat{S}_b + \overline{d}_{ab} \hat{S}_a \times \hat{S}_b + \left(\hat{S}_a \otimes \hat{S}_a\right) \overline{\overline{\overline{\overline{D}}}}_{aabb} \left(\hat{S}_b \otimes \hat{S}_b\right) \quad (6)$$

where J is the isotropic magnetic exchange, $\overline{\overline{D}}_a$ and $\overline{\overline{D}}_b$ are local Zero Field Splitting (ZFS) tensors, $\overline{\overline{D}}_{ab}$ is the symmetric anisotropic tensor and $\overline{d}_{ab}$ is the antisymmetric anisotropic term,[13–16] known as the Dzyaloshinskii Moriya vector. The components of these two tensors read :

$$\begin{array}{ccc} \overline{\overline{D}}_{ab} & + & \overline{d}_{ab} \\ = \begin{pmatrix} D^{xx} & D^{xy} & D^{xz} \\ D^{xy} & D^{yy} & D^{yz} \\ D^{xz} & D^{yz} & D^{zz} \end{pmatrix} & + & \begin{pmatrix} 0 & d^{xy} & -d^{xz} \\ -d^{xy} & 0 & d^{yz} \\ d^{xz} & -d^{yz} & 0 \end{pmatrix} \end{array} \quad (7)$$

The analytical Hamiltonian matrix is given in reference[10] and an example of model matrix of the multispin Hamiltonian, in which the tensors are assumed to share the same axes frame is given in table I.

In order to compare the nature of the local and overall anisotropies, the proper magnetic axis frame of each Ni(II) ions of the bi-nuclear system in its triplet and quintuplet states have been determined. For this purpose, the parameters of the various tensors of both Hamiltonians (giant- and multi-spin) were extracted from the effective Hamiltonian theory, such that the model Hamiltonian matrix calculated using the extracted values of the parameters reproduces at best the numerical effective Hamiltonian matrix calculated using equation 3. Since the proper magnetic axes of each tensor may in principle be different, all tensors are computed in a single axes frame and rotations ($P = R_z(\phi).R_x(\theta).R_z(\psi)$ where R_x and R_z stand for rotation around x and z respectively and ϕ, θ, ψ are the Euler angles) between

TABLE I: Example of a multi-spin Hamiltonian matrix for a geometry in which the local tensors of the two magnetic centers share the same magnetic axes frame

	Msa,Msb>		-1,-1>		-1,0>		0,-1>		-1,1>		0,0>		1,-1>		1,0>		0,1>		1,1>
<-1,-1|	$\frac{\mathrm{Da}}{3}+\frac{2\mathrm{Dab}}{3}+\frac{\mathrm{Db}}{3}-\mathrm{Dxxzz}+3\mathrm{Dxyxy}-\mathrm{Dyyzz}+J$	$-\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Eb}$	$\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Ea}$	0	0	0
<-1,0|	$-\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{Da}}{3}-\frac{2\mathrm{Db}}{3}+\mathrm{Dxxzz}-2\mathrm{Dxyxy}+\mathrm{Dyyzz}$	$-\frac{\mathrm{Dab}}{3}+\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+i\mathrm{dz}+J$	$-\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	0	0	Ea	$-\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	0
<0,-1|	$\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	$-\frac{\mathrm{Dab}}{3}+\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}-i\mathrm{dz}+J$	$-\frac{2\mathrm{Da}}{3}+\frac{\mathrm{Db}}{3}+\mathrm{Dxxzz}-2\mathrm{Dxyxy}+\mathrm{Dyyzz}$	0	0	$\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	$-\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	Eb	0
<-1,1|	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Eb}$	$-\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	0	$\frac{\mathrm{Da}}{3}-\frac{2\mathrm{Dab}}{3}+\frac{\mathrm{Db}}{3}-\mathrm{Dxxzz}+3\mathrm{Dxyxy}-\mathrm{Dyyzz}-J$	$-\frac{\mathrm{Dab}}{3}-\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+i\mathrm{dz}+J$	2Dxyxy	0	$-\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Ea}$
<0,0|	$\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	0	0	$-\frac{\mathrm{Dab}}{3}-\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}-i\mathrm{dz}+J$	$-\frac{2\mathrm{Da}}{3}-\frac{2\mathrm{Db}}{3}-4\mathrm{Dxyxy}$	$-\frac{\mathrm{Dab}}{3}-\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+i\mathrm{dz}+J$	0	0	$\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$
<1,-1|	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Ea}$	0	$\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	2Dxyxy	$-\frac{\mathrm{Dab}}{3}-\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}-i\mathrm{dz}+J$	$\frac{\mathrm{Da}}{3}-\frac{2\mathrm{Dab}}{3}+\frac{\mathrm{Db}}{3}-\mathrm{Dxxzz}+3\mathrm{Dxyxy}-\mathrm{Dyyzz}-J$	$\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	0	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Eb}$
<1,0|	0	Ea	$-\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	0	0	$\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{Da}}{3}-\frac{2\mathrm{Db}}{3}+\mathrm{Dxxzz}-2\mathrm{Dxyxy}+\mathrm{Dyyzz}$	$-\frac{\mathrm{Dab}}{3}+\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}-i\mathrm{dz}+J$	$\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$
<0,1|	0	$-\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	Eb	$-\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	0	0	$-\frac{\mathrm{Dab}}{3}+\frac{\mathrm{Dxzxz}}{2}+\frac{\mathrm{Dyzyz}}{2}+i\mathrm{dz}+J$	$-\frac{2\mathrm{Da}}{3}+\frac{\mathrm{Db}}{3}+\mathrm{Dxxzz}-2\mathrm{Dxyxy}+\mathrm{Dyyzz}$	$-\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$
<1,1|	0	0	0	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Ea}$	$\frac{\mathrm{Dxzxz}}{2}-\frac{\mathrm{Dyzyz}}{2}+\mathrm{Eab}$	$\frac{\mathrm{Dxxzz}}{2}-\frac{\mathrm{Dyyzz}}{2}+\mathrm{Eb}$	$\frac{\mathrm{dy}}{\sqrt{2}}-\frac{i\mathrm{dx}}{\sqrt{2}}$	$-\frac{\mathrm{dy}}{\sqrt{2}}+\frac{i\mathrm{dx}}{\sqrt{2}}$	$\frac{\mathrm{Da}}{3}+\frac{2\mathrm{Dab}}{3}+\frac{\mathrm{Db}}{3}-\mathrm{Dxxzz}+3\mathrm{Dxyxy}-\mathrm{Dyyzz}+J$

the proper axes frame of each tensor and the axes frame of the calculation are introduced, enabling one to determine the axial and rhombic parameters of all magnetic anisotropy tensors. Tables II[35] and III gives the number and nature of the non-zero parameters depending on the symmetry point group for the two-rank tensor D_{ab}, the Dzyaloshinski Moriya vector and the four-rank tensor. $\kappa = \pm 1$ indicates the absence/presence of a symmetry element that interchanges the two magnetic centers. In order to simplify the extraction, we have imposed the following relation:

$$D^{xxxx} + D^{yyyy} + D^{zzzz} + 2D^{xxyy} + 2D^{xxzz} + 2D^{yyzz} = 0 \tag{8}$$

which only ensures that the anisotropic part of the Hamiltonian is traceless. In the numerical effective Hamiltonian matrix, zero (or negligible) elements appear while they correspond to the sum of various parameters in the analytical model matrix. These sums have therefore been set to zero which introduces the following additional relations:

$$D^{xxxx} = D^{yyyy} = 0 \tag{9}$$

$$D^{xxyy} = \frac{1}{2}(D^{xxxx} - D^{xyxy}) \tag{10}$$

$$D^{xzxz} - D^{yzyz} = -D^{xx}_{ab} + D^{yy}_{ab} \tag{11}$$

$$D^{xxzz} - D^{yyzz} = 2D^{xx}_{ab} - 2D^{yy}_{ab} \tag{12}$$

that are used to decrease the number of independent parameters. For all studied cases there exists an appropriate axis frame for which the 4-rank tensor reduces at most to nine independent components only (among the 81 possible *a priori*), when these relations are imposed.

TABLE II: Non-zero symmetric and anti-symmetric components of the 2 rank exchange tensors

Point group♣	$\kappa^{\heartsuit}$	Symmetric components	Antisymmetric components	Number of parameters
C_1	+1	xx,yy,zz,xy,xz,yz	xy,xz,yz	9
C_i	-1	xx,yy,zz,xy,xz,yz		6
$C_s{}^{\diamondsuit}$	-1	xx,yy,zz,xy	xz,yz	6
	+1		xy	5
C_2	-1	xx,yy,zz,xy	xz,yz	6
	+1		xy	5
D_2	-1	xx,yy,zz	xy	4
$C_{2v}{}^{\spadesuit}$	-1	xx,yy,zz	xz	4
	+1		xy	4
D_{2h}	-1	xx,yy,zz		3
D_{2d}	-1	xx=yy,zz		2
C_n	+1	xx=yy,zz	xy	3
C_{nv}	+1	xx=yy,zz		2
$D_n, S_n, C_{nh}, D_{nh}, D_{nd}$	-1	xx=yy,zz		2

♣ The higher order symmetry axis lies along z, $n \geq 3$. ♡ $\kappa = -1$ if the magnetic centers are exchanged by a symmetry operation and $\kappa = +1$ otherwise. ♢ The σ_h plane is the xy plane. ♠ The σ_v plane is the yz plane.

IV. RESULTS AND DISCUSSION

Geometrical deformations have been applied to the model complexes $O[Ni(NCH)_4CN]_2$ noted M1 (cases **1**, **10**, **11**, **13** see figure 1)and $O[Ni(NCH)_4Cl]_2$ noted M2 (cases **2-9**, **12**, see figure 2) in order to tune the characteristics of the local and overall anisotropies (see figures 4, 5, 6). Compressions, stretchings and angular distorsions generate local anisotropies with peculiar and different features.

The D_{4h} geometry (**5**) of $O[Ni(NCH)_4Cl]_2$ is such that Z is a hard axis of magnetization

TABLE III: Non-zero symmetric components of the 4th rank exchange $\overset{\equiv\equiv}{D}_{aabb}$ tensor

Point group♣	Symmetric components	Number of parameters♢
C_2, C_s, C_{2h}	xxxx,yyyy,zzzz,xxyy,xxzz,yyzz & xyxy,xzxz,yyzz,xxxy,yyxy,zzxy	14
D_2, C_{2v}, D_{2h}	xxxx,yyyy,zzzz,xxyy,xxzz,yyzz & xyxy,xzxz,yyzz	9
$C_n, C_{nv}, C_{nh}, D_n, D_{nd}, D_{nh}$	xxxx=yyyy, zzzz, xxyy, xxzz=yyzz & xyxy, xzxz=yzyz	6

♣ The higher order symmetry axis lies along z, $n \geq 3$. ♢ Reduced by potential other relation.

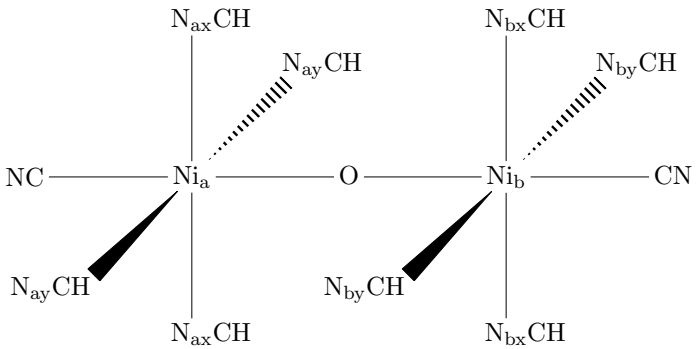


FIG. 1: Scheme of the molecular model 1 (M1)

Geometrical parameters : distances $l_{ax} = Ni_a - N_{ax}$, $l_{ay} = Ni_a - N_{ay}$, $l_{bx} = Ni_b - N_{bx}$, $l_{by} = Ni_b - N_{by}$, angles $\theta_a = (N_{ax}, Ni_a, O)$, $\theta_b = (N_{bx}, Ni_b, O)$ dihedral angles $\Phi_x = (N_{ax}, Ni_a, Ni_b, N_{bx})$, $\Phi_y = (N_{ay}, Ni_a, Ni_b, N_{by})$, $\Phi_{xy} = (N_{ax}, Ni_a, Ni_b, N_{by})$

for both centers and they do not exhibit any local rhombicity. In the D_{2h} structures (**6** and **2**) the bonds have been stretched or compressed in a single direction in order to generate respectively either two parallel easy planes (figure 5) or two collinear easy axes (figure 4) of magnetization. In the D_{2d} structures (**7** and **3**), the deformations are applied to different axes (X and Y) such that the easy planes or the easy axes are orthogonal. Angular distorsions (of 10 degrees on each sites) have been applied to both the D_{2h} geometries in order to generate the D_2 structure in which the local easy planes (**8**) are no more parallel. The C_{2v} (**9**) geometry illustrates the cases of two local planar anisotropies and only one of them is

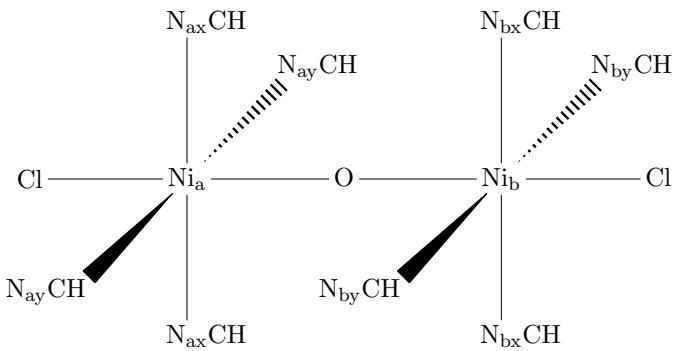
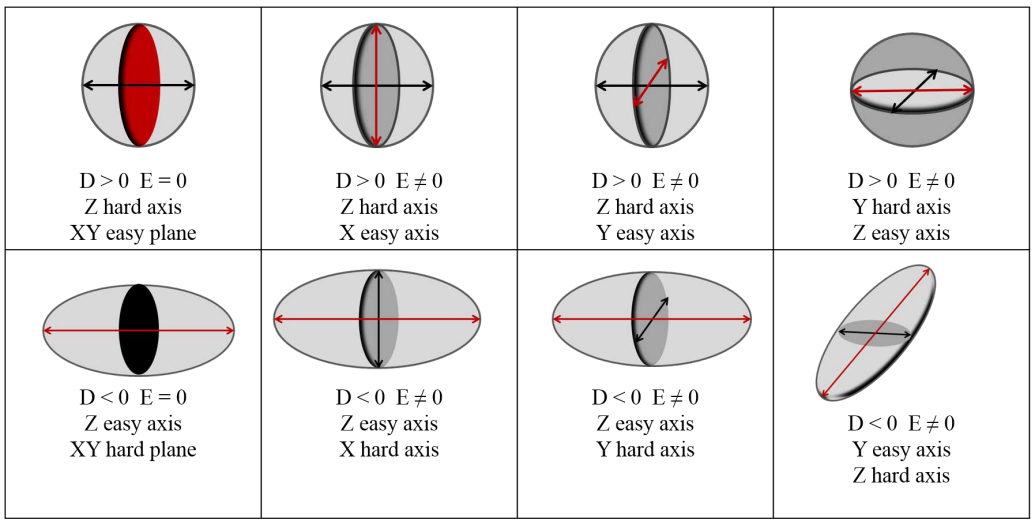


FIG. 2: Scheme of the molecular model 2 (M2)

Geometrical parameters : distances $l_{ax} = Ni_a - N_{ax}$, $l_{ay} = Ni_a - N_{ay}$, $l_{bx} = Ni_b - N_{bx}$, $l_{by} = Ni_b - N_{by}$, dihedral angles $\Phi_x = (N_{ax}, Ni_a, Ni_b, N_{bx})$, $\Phi_y = (N_{ay}, Ni_a, Ni_b, N_{by})$, $\Phi_{xy} = (N_{ax}, Ni_a, Ni_b, N_{by})$

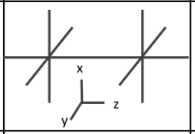
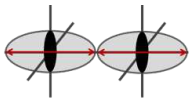
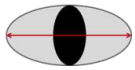
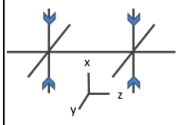
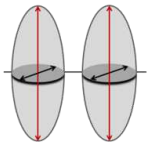
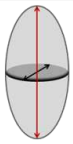
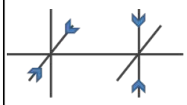
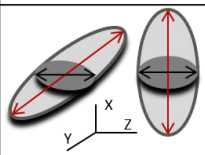
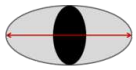
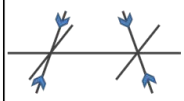
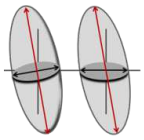
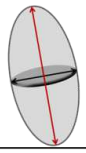
FIG. 3: Convention used to schematize the nature of the magnetic anisotropy and to show the magnetic axis frame of the D-tensors. A prolate ellipsoid indicates an axial anisotropy while an oblate ellipsoid refers to a planar anisotropy. Hard axes and hard planes are represented in black while easy axes and easy planes are in red. Plain color planes indicate the absence of rhombicity.



rhombic. In the C_{2v} (**12**) geometry, one center has a planar anisotropy while the other has an axial anisotropy and the easy axis is parallel to the easy plane. Finally the C_1 structure (**4**), the two local anisotropies are axial and one of the easy axis is in the (XY) plane and the other in the (XZ) plane.

The ligand CN^- produces a stronger ligand field which permits to study other combinations of local anisotropies. In the D_{4h} structure (**1**) of $O[Ni(NCH)_4CN]_2$, the local axial anisotropies share the same easy axis Z. The C_{4v} structure (**11**) has one axial local anisotropy

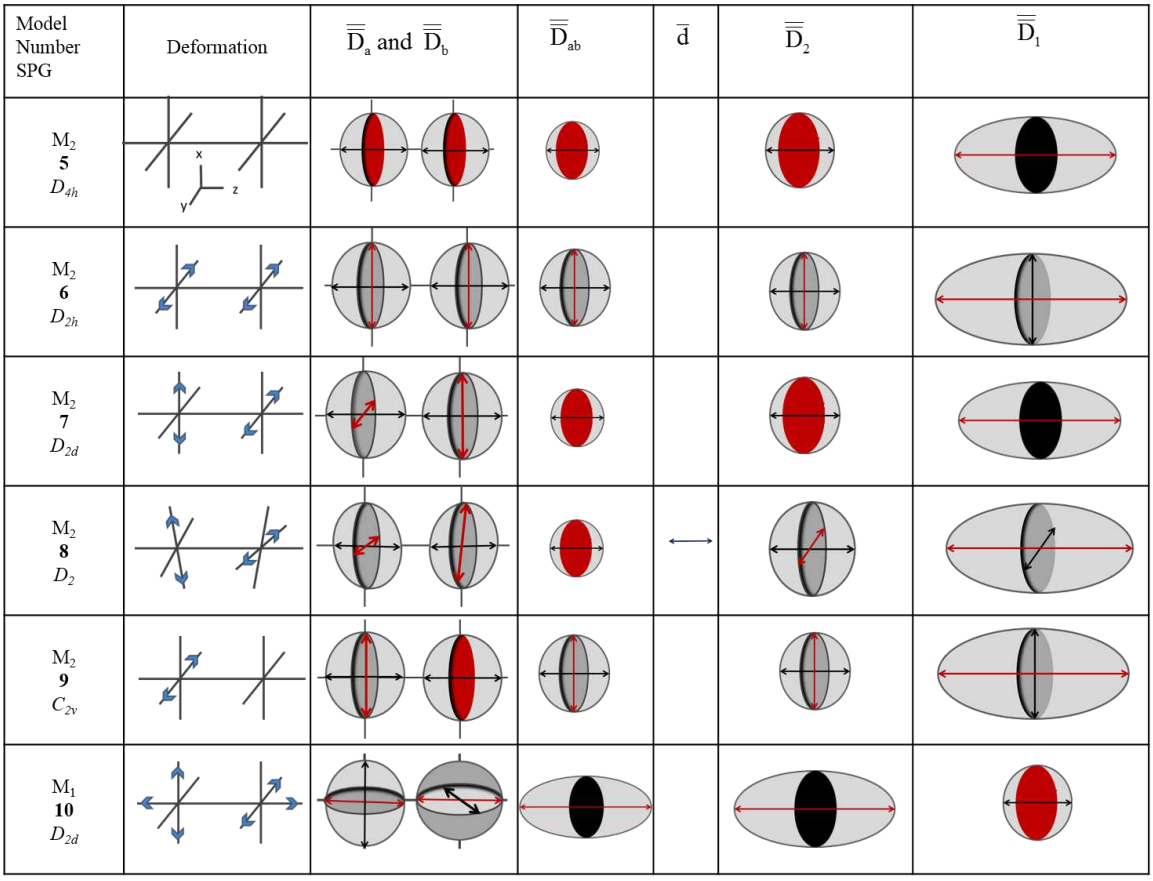
FIG. 4: Ellipsoids representing the anisotropy nature (axial or planar) and the proper magnetic axes frames of the various local and overall anisotropy tensors for different geometries in which local axial anisotropies have been imposed. The compound number and the model compound (either M1 or M2) are indicated in the left column.

Model Number SPG	Deformation	$\overline{\overline{D}}_a$ and $\overline{\overline{D}}_b$	$\overline{\overline{D}}_{ab}$	$\overline{d}$	$\overline{\overline{D}}_2$	$\overline{\overline{D}}_1$
M_1 **1** D_{4h}						
M_2 **2** D_{2h}						
M_2 **3** D_{2d}						
M_2 **4** C_1						

with the easy axis Z and a local planar anisotropy with the easy plane (XY). In the C_{2v} structure (**13**), one center has an axial anisotropy with the easy axis Z while the other has a planar anisotropy with the easy plane (YZ).

For each structure, the parameters of the three different models were extracted. The local ZFS parameters $D_a^{loc}, E_a^{loc}, D_b^{loc}, E_b^{loc}$, the Giant-Spin Hamiltonian parameters D_2, E_2 for the quintet and D_1, E_1 for the triplet and all the parameters of the multi-spin Hamiltonian can be found in table IV. The proper magnetic axis frames of all the tensors have been extracted and are represented in the figures 4 (for both axial local anisotropies), 5 (for both planar local anisotropies) and 6 (for axial and local local anisotropies) report pictures of the applied deformations and of the resulting anisotropy ellipsoids which provide a visualization of the nature of the magnetic anisotropies (both local and overall for the quintuplet and triplet states); the direction of the Dzyaloshinskii Moriya vector is also indicated when it is not

FIG. 5: Ellipsoids representing the anisotropy nature (axial or planar) and the proper magnetic axes frames of the various local and overall anisotropy tensors for different geometries in which local planar anisotropies have been imposed. The compound number and the model compound (either M1 or M2) are indicated in the left column.



zero. Note that conventions used in figures 4, 5 and 6 are given in figure 3.

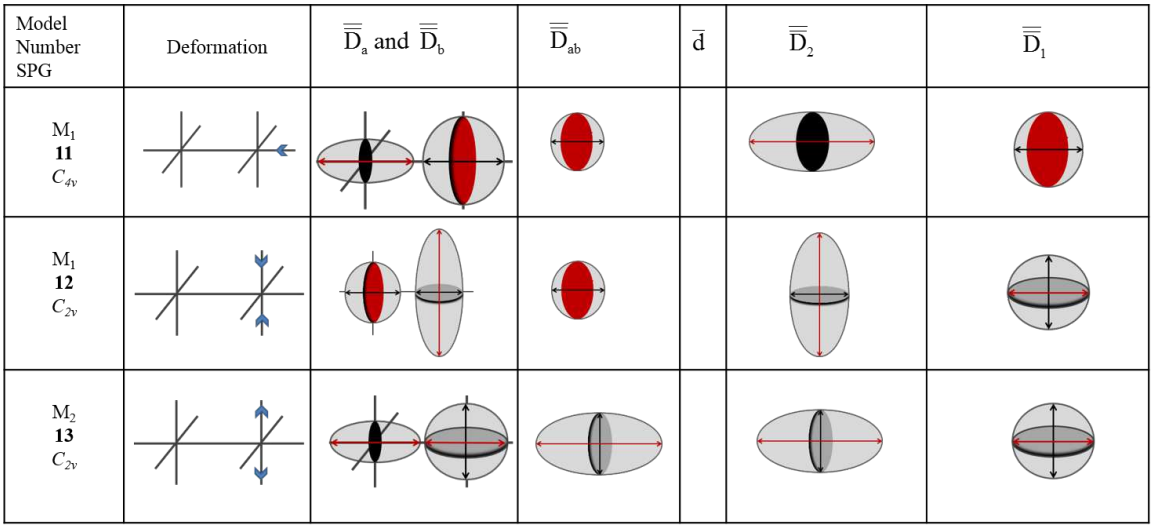
Comparing the values of the various parameters and the ellipsoids of the local and overall anisotropies deserves some general comments:

- The magnetic axes frames and local anisotropy parameters extracted from the calculations performed with one or two magnetic centers are very similar, showing the transferability of these parameters from the monomer to the dimer. The small discrepancies are due to the bias introduced in the local calculations by the closed shell character of the inactive Ni(II) center. The values of the local anisotropy parameters

TABLE IV: Values of extracted parameters in cm^{-1}

Cases	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
SPG	D_{4h}	D_{2h}	D_{2d}	C_1	D_{4h}	D_{2h}	D_{2d}	D_2	C_{2v}	D_{2d}	C_{4v}	C_{2v}	C_{2v}
D_a^{loc}	-3.1	-21.9	-19.4	-22.5	10.0	9.9	10.0	8.5	9.9	15.0	-4.3	2.2	-3.8
D_b^{loc}	-3.1	-21.9	-19.4	-24.4	10.0	9.9	10.0	8.5	9.6	15.0	2.1	-21.7	5.4
E_a^{loc}	0	3.7	2.8	0.6	0	1.6	1.5	1.8	1.5	1.3	0	0.1	1.1
E_b^{loc}	0	3.7	2.8	0.1	0	1.6	1.5	1.8	0.0	1.3	0	2.6	0.0
D_2	-2.4	-6.7	2.5	-6.6	2.5	2.5	2.5	1.6	2.5	-2.2	-1.5	-3.6	-2.5
E_2	0	0.7	0	0.6	0	0.5	0	0.2	0.2	0	0	0.2	0.3
D_1	7.6	19.2	-6.9	18.6	-6.6	-6.7	-6.6	-3.7	-6.7	9.7	5.2	8.6	8.0
E_1	0	2.3	0	2.4	0	1.4	0	0.5	0.7	0	0	1.4	0.9
J	38.9	50.3	49.7	49.8	40.9	41.1	41.1	41.0	41.8	30.6	40.3	38.6	37.2
D_a	-2.2	-21.1	-21.9	-20.7	10.9	12.0	12.1	9.3	12.0	16.6	-3.6	4.6	-2.1
D_b	-2.2	-21.1	-21.9	-21.3	10.9	12.0	12.1	9.3	12.0	16.6	1.1	-20.3	4.2
E_a	0	0.4	0.3	0.6	0	1.4	1.4	1.4	1.4	3.1	0	0.0	0.0
E_b	0	0.4	0.3	0.1	0	1.4	1.4	1.4	0.0	3.1	0	0.9	0.5
D_{ab}	0.3	0.3	0.3	0.3	0.4	5.2	0.4	0.4	5.1	-4.7	0.3	0.3	-4.7
E_{ab}	0	0.0	0	0.0	0	0.9	0	0.0	0.5	0	0	0.0	0.6
$\|\|d\|\|$	0	0	0	0.00	0	0	0	0.04	0	0.0	0	0.0	0.0
d dir								z					
D_{zzzz}	-4.9	-4.0	-5.4	-3.6	-3.8	-4.8	-4.9	-4.9	-4.9	5.5	-3.6	-3.0	-5.4
D_{xxzz}	0	0	0	0	0	-1.3	0	0	-2.2	3.3	0	0	2.2
D_{yyzz}	0	0	0	0	0	-5.0	0	0	-4.1	3.3	0	0	4.7
D_{xxyy}	2.5	2.0	2.7	1.8	1.9	8.7	2.4	2.4	8.7	-9.4	1.8	1.5	-4.2
D_{xyxy}	-1.2	-1.0	-1.4	-0.9	-0.9	-4.4	-1.2	-1.2	4.4	4.7	-0.9	-0.7	2.1
D_{xzxz}	-1.3	-1.1	-1.4	-1.3	0	-0.6	-1.2	-1.3	-0.1	-0.3	-0.9	-0.8	-2.4
D_{yzyz}	-1.3	-1.0	-1.4	-1.3	0	1.3	-1.2	-1.3	0.8	-0.3	-0.9	-0.8	-3.6

FIG. 6: Ellipsoids representing the anisotropy nature (axial or planar) and the proper magnetic axes frames of the various local and overall anisotropy tensors for different geometries in which both an axial and a planar local anisotropies have been imposed. The compound number and the model compound (either M1 or M2) are indicated in the left column.



that should be considered as the most precise are those extracted for the two magnetic centers.

- The values of D_{ab} and E_{ab} are very small and the anisotropy of the exchange is essentially brought by the four-rank tensor components. One should also note that the planar nature of the anisotropy brought by $\bar{\bar{D}}_{ab}$ seems to be unaffected by the distorsions in the considered systems, except cases **10** and **13**.

- The giant-spin 2-rank tensors $\bar{\bar{D}}_1$ and $\bar{\bar{D}}_2$ exhibit opposite anisotropic features, the axes or planes of easy or difficult magnetization are systematically opposite. For a sake of simplicity, only the values and features of $\bar{\bar{D}}_2$ will be commented hereafter. One may also note that the anisotropy parameters are larger in the triplet ($\bar{\bar{D}}_1$) than in the quintuplet ($\bar{\bar{D}}_2$), as already explained by Boca[15]. Due to the presence of the four rank tensor, the relations between the various tensors are slightly different than those already proposed[15].

- As expected, strectching and compression induce opposite local anisotropy features,

respectively planar or axial anisotropies *i.e.* positive or negative sign of the D_2 values.

- When the local anisotropies are axial (see figure 4) and the axes are collinear (cases **1** and **2**), the overall magnetic anisotropy of the highest spin state is axial and the axis is collinear to the local ones as expected. Nevertheless, the value of the axial parameter is considerably reduced unless the axes are confounded (case **1**).

- When the two axes of the local axial anisotropies are orthogonal (case **3**), the overall anisotropy of the highest spin state is planar and does not exhibit any rhombicity.

- When the local centers exhibit axial local anisotropies with non collinear and non orthogonal axes (case **4**), the resulting anisotropy of the complex is axial but again smaller and the corresponding axis bisects the two local ones. When the axes of the local axial anisotropies exhibit a weak angle, the D value of the overall anisotropy remains of the same order of magnitude whatever the direction of the deformation is.

- When the local anisotropies are planar (see figure 5) and the planes are parallel (cases **5-9**), the overall magnetic anisotropy of the highest spin state is planar and the easy plane is parallel or confounded to the local ones. When local rhombicity is present (cases **6-9**) on one or both center(s), the easy axis of anisotropy of the highest spin state is either along the same direction than the common local easy axis (case **6**) or along the easy axis of the most rhombic center. If only one center exhibit a local rhombicity, this highest spin state rhombicity is reduced (case **9**). For non parallel local rhombicity, the overall rhombicity is along the average direction (case **8**) and still reduced except if these local easy axis are orthogonal (case **7**) where no rhombicity appear for the highest spin state.

- When the nature of both local anisotropies are different (one axial and one planar, cases **11-13** see figure 6), the amplitudes of the anisotropies (D parameters) determine the nature of the resulting overall anisotropy of the highest spin state. For example, when one of the anisotropic center exhibits a weak planar anisotropy and the other one an important axial anisotropy with the axis into the plane (case **12**), the overall anisotropy of the highest spin state is axial and the axis is collinear to the axis of the local axial anisotropy with smaller parameters than both collinear local axial anisotropies. The case **13** presents one local anisotropy with an easy axis along Z perpendicular to the

hard axis of the planar anisotropy of the other center, it appears an axial exchange D_{ab} along Z that imposes it nature and magnetic axes to the overall tensor of the highest spin state.

- With two planar anisotropy with perpendicular hard axis along X and Y in D_{2d} symmetry (case **10**), an axial exchange D_{ab} along Z is obtained. The resulting overall anisotropy is axial along the common easy axes Z of the local anisotropies.

- The values of the anisotropic parameters are systematically smaller for the overall magnetic anisotropy than for the local ones except for common axial anisotropy (case **1**). Large values of the local anisotropies do not systematically induce a large anisotropy of the overall complex in its highest spin state and interferences between the local anisotropies are very important. One should also note that while in most of the cases the D_2 value has the same sign than the local ones, it is not systematic (case **3**).

- The anisotropy of exchange is more important in case of local planar anisotropies than for local axial anisotropies. The rhombic parameter of the two rank tensor $\bar{\bar{D}}_{ab}$ is always very weak or negligible in the studied cases. Finally, one should note that the most important contributions to the anisotropy of exchange are brought by the four rank tensor.

- the only synergistic cases are obtained from local planar anisotropies, either by combining one axial and one planar anisotropies with the easy axis parallel to the easy plane or two planar anisotropies exhibiting confounded easy axes (in the easy plane). In this last case (**10** since the two difficult axes are orthogonal, the resulting overall anisotropy does not exhibit any rhombicity.

V. SUMMARY AND PERSPECTIVES

Rules to predict vanishing values of symmetric and antisymmetric 2nd order exchange tensors and symmetric 4th order symmetric exchanged were presented, illustrated (see figures 4, 5 and 6) and tested on a model. It seems that the exchange ZFS parameters are essentially governed by the relative local anisotropy and are emphasised by symmetrical monomer or reduced by anti-symmetrical one.

The study leads to the conclusion that it seems possible to impose the direction of the axes of magnetization of local $\overline{\overline{D}}_a$ and $\overline{\overline{D}}_b$ tensors. A big deformation leads to an easy axis of magnetization different that the metal-metal direction despite the evident difference of environment and offer an interesting negative D-value. For weak field ligand, slight deformations let the D-value positive and the hard axis along the metal-metal direction but allow to choose the direction of the in plane easy axis of magnetization. The exchange tensor $\overline{\overline{D}}_{ab}$ present often a positive D-value and an hard axis along Z direction, except for the cases **10** and **12** where it anisotropy is axial and lead the overall anisotropy of $\overline{\overline{D}}_2$ tensor. The Dzyaloshinskii Moriya vector is governed by the symmetry of the system, it vanishes like E_{ab} in case of a rotation C_4 or improper S_4 axis of symmetry and requires a non-orthogonal disposition of the ligand to offer a non negligible value.

The giant-spin tensors appear quasi-systematically opposite in sign, with exchanged roles of easy and hard axes of magnetization. Magnetization axes of the quintet tensors $\overline{\overline{D}}_2$ are, in general, the average of the local $\overline{\overline{D}}_a$ and $\overline{\overline{D}}_b$ ones, even in both D_{2d} cases with orthogonal easy axes ; it average results in an easy plane of magnetization for $\overline{\overline{D}}_2$ tensor. It is consequently possible to produce overall $\overline{\overline{D}}_2$ planar anisotropy with two local axial anisotropies (case **3**) or overall axial anisotropy with two local planes (case **10**). In both C_{2v} cases with only a deformation on one site (cases **9** and **12**), the rombicity on one site (case **9**) produce the half value of the overall rhombicity E_2 produced with both site deformation (case **6**) and the strong axial anisotropy on one site (case **12**) is associated to half values the overall anisotropy D_2 of the highest spin state with symmetrical deformation (case **2**). Concerning the numerical giant-spin ZFS parameters, they are related to the multi-spin description (see figure IV), for example, for both local axial anisotropies (cases **2-4**), the $3|D_2|$ and $|D_1|$ parameters or, for both planar local anisotropies (cases **6-9**) $3E_2$ and E_1 parameters are around the average of the equivalent ZFS parameters of each local tensors.

The role of the relative symmetry of each monomer should be a guideline to obtain important D-value of higher multiplicity giant-spin. Consequently, chain of metallic compounds connected by inorganic bridge with inorganic ligands compress along a nearly parallel direction is expected to give interesting ZFS magnetic properties.

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Appendix A: Analytical matrix elements of the multi-spin Hamiltonian expressed in the $|S, M_s\rangle$ basis of the quintet and singlet components, in the proper magnetic axes frame.

$$\langle 2,-2|\hat{H}|2,-2\rangle = (1) + \tfrac{2}{3}[D_a + D_{ab}] + J$$

$$\langle 2,-2|\hat{H}|2,-1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,0\rangle = \sqrt{\tfrac{2}{3}}[(2) + (3) + E_a + E_{ab}]$$

$$\langle 2,-2|\hat{H}|2,1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,2\rangle = (4)$$

$$\langle 2,-2|\hat{H}|0,0\rangle = \tfrac{1}{\sqrt{3}}[2(2) - (3) + 2E_a - E_{ab}]$$

$$\langle 2,-1|\hat{H}|2,-1\rangle = -\tfrac{D_a}{3} - \tfrac{D_{ab}}{3} + (5) + (6) + J$$

$$\langle 2,-1|\hat{H}|2,0\rangle = 0$$

$$\langle 2,-1|\hat{H}|2,1\rangle = -(3) + E_a + E_{ab} + (7)$$

$$\langle 2,-1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,-1|\hat{H}|0,0\rangle = 0$$

$$\langle 2,0|\hat{H}|2,0\rangle = \tfrac{1}{3}[(1) - 2D_a - 2D_{ab} - 4(6) + (8) + 2(9)] + J$$

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$$\langle 2,0|\hat{H}|2,1\rangle = 0$$

$$\langle 2,0|\hat{H}|2,2\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}]$$

$$\langle 2,0|\hat{H}|0,0\rangle = \tfrac{\sqrt{2}}{3}[(1)+2D_a-D_{ab}-(6)+(8)-(9)]$$

$$\langle 2,1|\hat{H}|2,1\rangle = -\tfrac{D_a}{3}-\tfrac{D_{ab}}{3}+(5)+(6)+J$$

$$\langle 2,1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,1|\hat{H}|0,0\rangle = 0$$

$$\langle 2,2|\hat{H}|2,2\rangle = (1)+\tfrac{2}{3}[D_a+D_{ab}]+J$$

$$\langle 2,2|\hat{H}|0,0\rangle = \tfrac{1}{\sqrt{3}}[2(2)-(3)+2E_a-E_{ab}]$$

$$\langle 0,0|\hat{H}|0,0\rangle = \tfrac{1}{3}[2(1)+4(6)+2(8)+(9)]-2J$$

$$(1) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) + \frac{1}{2}D_{xxyy} + D_{xxzz} + D_{yyzz} + D_{zzzz}$$

$$(2) = \frac{1}{4}(D_{xxxx} - D_{yyyy}) + \frac{1}{2}(D_{xxzz} - D_{yyzz})$$

$$(3) = \frac{1}{2}(D_{xzxz} - D_{yzyz})$$

$$(4) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) - \frac{1}{2}D_{xxyy} - D_{xyxy}$$

$$(5) = \frac{1}{2}(D_{xxxx} + D_{yyyy}) + D_{xxyy} + D_{xxzz} + D_{yyzz}$$

$$(6) = \frac{1}{2}(D_{xzxz} + D_{yzyz})$$

$$(7) = \frac{1}{2}(D_{xxxx} - D_{yyyy})$$

$$(8) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) + D_{xyxy} - \frac{1}{2}D_{xxyy}$$

$$(9) = D_{xxxx} + D_{yyyy} + 2D_{xxyy}$$

Appendix B: Analytical matrix of the $S \cdot \overline{\overline{D}} \cdot S$ Hamiltonian, expressed in an arbitrary axes frame.

$\|S, M_S\rangle$	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$
$\langle 2,-2\|$	$D_{11}+D_{22}+4D_{33}$	$-3D_{13}-3iD_{23}$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}+2iD_{12})$
$\langle 2,-1\|$	$-3D_{13}+3iD_{23}$	$\frac{5}{2}(D_{11}+D_{22})+D_{33}$	$-\frac{\sqrt{6}}{2}(D_{13}+iD_{23})$
$\langle 2,0\|$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}-2iD_{12})$	$-\frac{\sqrt{6}}{2}(D_{13}-iD_{23})$	$3(D_{11}+D_{22})$
$\langle 2,1\|$	0	$\frac{3}{2}(D_{11}-D_{22}-2iD_{12})$	$\frac{\sqrt{6}}{2}(D_{13}-iD_{23})$
$\langle 2,2\|$	0	0	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}-2iD_{12})$

$\|S, M_S\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	0	0
$\langle 2,-1\|$	$\frac{3}{2}(D_{11}-D_{22}+2iD_{12})$	0
$\langle 2,0\|$	$\frac{\sqrt{6}}{2}(D_{13}+iD_{23})$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}+2iD_{12})$
$\langle 2,1\|$	$\frac{5}{2}(D_{11}+D_{22})+D_{33}$	$3D_{13}+3iD_{23}$
$\langle 2,2\|$	$3D_{13}-3iD_{23}$	$D_{11}+D_{22}+4D_{33}$

Appendix C: Analytical matrix of the $S_a \cdot \overline{\overline{D}}_a \cdot S_a + S_b \cdot \overline{\overline{D}}_b \cdot S_b$ Hamiltonian expressed in an arbitrary axes frame; $\overline{\overline{D}}_a = \overline{\overline{D}}_b$ are the local ZFS tensors of the multi-spin Hamiltonian.

$\|S, M_S\rangle$	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$
$\langle 2,-2\|$	$D_{a11}+D_{a22}+2D_{a33}$	$-D_{a13}-iD_{a23}$	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}+2iD_{12})$
$\langle 2,-1\|$	$-D_{a13}+iD_{a23}$	$\frac{1}{2}(3D_{a11}+3D_{a22}+2D_{a33})$	$-\frac{1}{\sqrt{6}}(D_{a13}+iD_{a23})$
$\langle 2,0\|$	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}-2iD_{a12})$	$-\frac{1}{\sqrt{6}}(D_{a13}-iD_{a23})$	$\frac{1}{3}(5D_{a11}+5D_{a22}+2D_{a33})$
$\langle 2,1\|$	0	$\frac{1}{2}(D_{a11}-D_{a22}-2iD_{a12})$	$\frac{1}{\sqrt{6}}(D_{a13}-iD_{a23})$
$\langle 2,2\|$	0	0	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}-2iD_{a12})$

$\|S, M_S\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	0	0
$\langle 2,-1\|$	$\frac{1}{2}(D_{a11} - D_{a22} + 2iD_{a12})$	0
$\langle 2,0\|$	$\frac{1}{\sqrt{6}}(D_{a13} + iD_{a23})$	$\frac{1}{\sqrt{6}}(D_{a11} - D_{a22} + 2iD_{a12})$
$\langle 2,1\|$	$\frac{1}{2}(3D_{a11} + 3D_{a22} + 2D_{a33})$	$D_{a13} + iD_{a23}$
$\langle 2,2\|$	$D_{a13} - iD_{a23}$	$D_{a11} + D_{a22} + 2D_{a33}$

Appendix D: Analytical matrix elements of the giant-spin Hamiltonian derived from the multi-spin Hamiltonian at the second-order of perturbation.

$$\langle 2,-2|\hat{H}|2,-2\rangle = (1) + \tfrac{2}{3}[D_a + D_{ab}] + J + \tfrac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,-2|\hat{H}|2,-1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,0\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \tfrac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,-2|\hat{H}|2,1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,2\rangle = (4) + \tfrac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,-1|\hat{H}|2,-2\rangle = 0$$

$$\langle 2,-1|\hat{H}|2,-1\rangle = -\tfrac{D_a}{3} - \tfrac{D_{ab}}{3} + (5) + (6) + J$$

$$\langle 2,-1|\hat{H}|2,0\rangle = 0$$

$$\langle 2,-1|\hat{H}|2,1\rangle = -(3) + E_a + E_{ab} + (7)$$

$$\langle 2,-1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,0|\hat{H}|2,-2\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \tfrac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,0|\hat{H}|2,1\rangle = 0$$

$$\langle 2,0|\hat{H}|2,0\rangle = \frac{1}{3}[(1) - 2D_a - 2D_{ab} - 4(6) + (8) + 2(9)] + J + \frac{2[(1)+2D_a-D_{ab}-(6)+(8)-(9)]^2}{27J}$$

$$\langle 2,0|\hat{H}|2,1\rangle = 0$$

$$\langle 2,0|\hat{H}|2,2\rangle = \sqrt{\frac{2}{3}}[(2) + (3) + E_a + E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,1|\hat{H}|2,-2\rangle = 0$$

$$\langle 2,1|\hat{H}|2,-1\rangle = -(3) + E_a + E_{ab} + (7)$$

$$\langle 2,1|\hat{H}|2,0\rangle = 0$$

$$\langle 2,1|\hat{H}|2,1\rangle = -\frac{D_a}{3} - \frac{D_{ab}}{3} + (5) + (6) + J$$

$$\langle 2,1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,2|\hat{H}|2,-2\rangle = (4) + \frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,2|\hat{H}|2,-1\rangle = 0$$

$$\langle 2,2|\hat{H}|2,0\rangle = \sqrt{\frac{2}{3}}[(2) + (3) + E_a + E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,2|\hat{H}|2,1\rangle = 0$$

$$\langle 2,2|\hat{H}|2,2\rangle = (1) + \frac{2}{3}[D_a + D_{ab}] + J + \frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

TABLE V: Matrix elements of the Giant Spin Hamiltonian for the quintuplet state in the proper magnetic axes frame

$\|S, M_S\rangle$	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	$9B_2^0 + B_4^{rh}$	0	$\sqrt{6}B_2^2 + B_4^{ax,rh}$	0	$12B_4^4 + B_4^{rh}$
$\langle 2,-1\|$	0	0	0	$3B_2^2$	0
$\langle 2,0\|$	$\sqrt{6}B_2^2 + B_4^{ax,rh}$	0	-$3B_2^0 + B_4^{ax}$	0	$\sqrt{6}B_2^2 + B_4^{ax,rh}$
$\langle 2,1\|$	0	$3B_2^2$	0	0	0
$\langle 2,2\|$	$12B_4^4 + B_4^{rh}$	0	$\sqrt{6}B_2^2$	0	$9B_2^0 + B_4^{rh}$

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Conclusion et perspectives

Au cours de cette thèse, une étude de l'anisotropie magnétique de différents complexes mono- et bi-nucléaires a été menée afin de déterminer les paramètres permettant de caractériser la structure électronique et les états spin-orbites en l'absence de champ magnétique.

Pour ce faire, un ensemble de calculs théoriques *ab initio*, réalisés si possible sur les structures cristallographiques issues de mesure par rayons X, est mené. Ces calculs prennent en compte, dans une certaine mesure, les phénomènes relativistes ou de corrélation afin de décrire, le plus précisément possible, la fonction d'onde et l'énergie des états spectraux nécessaire à l'évaluation du ZFS. Par la suite, une procédure d'extraction d'un hamiltonien effectif est utilisée et permet, par comparaison avec un hamiltonien modèle, d'obtenir les axes magnétiques et les valeurs des paramètres de ZFS afin de les comparer aux valeurs spectroscopiques et magnétiques obtenues expérimentalement.

Dans le cas des complexes mono-nucléaires étudiés, des rationalisations permettant de comprendre comment accroître ces paramètres ont été réalisées, il est alors possible d'identifier les principaux états excités responsables de l'anisotropie magnétique par effet spin-orbite ou spin-spin, en utilisant, par exemple, des complexes à coordination exotique afin d'obtenir une forte anisotropie. De plus, il a été observé qu'en utilisant un ligand à haute symétrie structurelle, dans le cas d'un complexe de $Ni^{(II)}$, il est possible d'obtenir un état fondamental à haut spin quasi-dégénéré. Le couplage spin-orbite, principal responsable du ZFS, est alors important, de l'ordre de la constante de couplage spin-orbite.

Cependant, une distorsion de la géométrie du ligand par effet Jahn-Teller tend à lever cette dégénérescence et, en conséquence, à réduire le ZFS. Ce phénomène est corroboré par les mesures expérimentales motivant ainsi les collaborations entre expérimentateurs et théoriciens. De même, les mesures et calculs théoriques d'aimantation et de susceptibilité magnétique en fonction de la température et du champ magnétique appliqué permettent de vérifier la validité des structures.

Il semble donc intéressant, d'utiliser des ligands polydentes rigides qui imposent une structure géométrique proche d'une haute symétrie mais légèrement déformée afin d'obtenir des orbitales moléculaires majoritairement métalliques proche de la dégénérescence. Le bénéfice du couplage spin-orbite est alors partiellement maintenu car la distorsion est limitée, ainsi, les premiers états excités pouvant potentiellement contribuer à un D négatif sont proches en énergie et donnent une valeur importante de D et faible de E.

Dans le cas des complexes poly-nucléaires, l'étude s'est restreinte à des composés bi-nucléaires de $Ni^{(II)}$ afin de pouvoir définir des paramètres et axes magnétiques locaux sur chaque centre métallique, de manière analogue aux composés mono-nucléaires présentant plus de deux électrons célibataires, ainsi que des paramètres d'anisotropie d'échange. Notons que ce type de composés requiert un important coût de calcul.

Différents hamiltoniens effectifs et modèles ont été déterminés, dans le cadre d'une description "giant-spin", pour le quintuplet et le triplet fondamental afin de déduire un lot de paramètres d'anisotropie globale ; puis dans le cadre d'une description "multi-spin", pour l'ensemble des états les plus bas du spectre. Dans cette dernière, l'ajout d'un terme d'échange nécessitant un tenseur d'ordre quatre à été confirmé. Enfin, une modélisation de l'anisotropie de chaque centre métallique indépendamment de l'autre a été effectuée.

Ces composés bi-nucléaires ont été analysés avec différentes déformations structurales afin de présenter différents cas d'anisotropies planaires ou axiales, il apparait alors que certains groupes ponctuels de symétrie impliquent une annulation de paramètres d'échanges. Le seul moyen d'obtenir un effet synergique entre les anisotropies locales est d'aligner des anisotropies axiales locales, l'anisotropie globales du quintuplet fondamental est alors accrue. Dans le cas d'anisotropies locales parallèles, l'effet global est réduit, mais de même nature et direction ; dans le cas de faibles variations angulaires entre les axes magnétiques locaux, l'effet global est encore réduit et la direction obtenue est une moyenne de celle des axes locaux. Dans le cas d'anisotropies axiales de directions orthogonales, par contre, l'anisotropie globale est planaire.

Des résultats analogues sont obtenus dans le cas d'anisotropies planaires locales et l'anisotropie globale apparait, en général, comme une moyenne des anisotropies locales. Il est cependant possible d'obtenir dans certaines configurations une anisotropie globale planaire avec deux anisotropies locales axiales, ou, au contraire, une anisotropie globale axiale avec deux anisotropies locales planaires.

Il semble donc possible, dans le cas de composés poly-nucléaires, de contrôler le spin global du complexe en modifiant l'environnement de chaque centre métallique tout en respectant quelques règles de symétrie afin d'accroitre ou de réduire les paramètres de ZFS selon l'objectif recherché. Cependant, une parfaite compréhension des phénomènes mis en jeu n'est pas à l'ordre du jour et nécessiterait une analyse plus détaillée avec, en particulier, les mécanismes électroniques impliqués dans l'anisotropie et comment les modéliser par les différents tenseurs. Il serait ainsi possible d'assurer une maîtrise de l'anisotropie locale et de la transposabilité vers une anisotropie globale du complexe.

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