Pressure-Induced Conversion of Paramagnetic Fe2Co2 Square Complexes into Molecular Switches
 Buqin Xu

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Pressure-induced conversion of paramagnetic Fe$_2$Co$_2$ square complexes

into molecular switches

Par Buqin Xu

Thèse de doctorat de Chimie Moléculaire

Dirigée par Dr. Yanling Zheng et Prof. Rodrigue Lescouëzec

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Chapter 1

P1: the complexes can switch reversibly between two ground states with distinguished electronic configurations: $t_{2g}^6e_g^0$ ($S = 0$) and $t_{2g}^2e_g^2$ ($S = 2$), as shown by the figure 1. This spin crossover (SCO) is also called spin transition.

Correction: P1: the complexes can switch reversibly between two spin states with distinguished electronic configurations: $t_{2g}^6e_g^0$ ($S = 0$) and $t_{2g}^4e_g^2$ ($S = 2$), as shown in figure 1. This phenomenon is also called spin crossover (SCO).

P2: This can be reflected in the distortion parameter noted $\Sigma$ Fe(II), which is the sum of the deviation of the twelve pseudo-orthogonal N-Fe(II)-N of an octahedral $\{N_6\}$ coordination sphere.

Correction: This can be reflected in the distortion parameter noted $\Sigma$ Fe(II), which is the sum of the deviation of the twelve pseudo-orthogonal N-Fe(II)-L(L means coordination ligand) of an octahedral $\{N_6\}$ coordination sphere.

P2: One example of the spin-crossover system with the most available crystallographic data is $[\text{Fe}(1\text{-bpp})_2][\text{BF}_4]_2$ compound (bpp = 2,6-di(pyrazol-1-yl)pyridine).

Correction: One example of the spin-crossover systems with the most available crystallographic data is $[\text{Fe}(1\text{-bpp})_2][\text{BF}_4]_2$ compound (bpp = 2,6-di(pyrazol-1-yl)pyridine).

P3: The most commonly studied bistable system among them is cyanido-bridged Fe-Co complexes.

Correction: The most commonly studied bistable systems among them are cyanido-bridged Fe-Co complexes.

P4: Adding more reference studies.

Then, Michel Verdaguer et al. deeper studied the efficiency of the photoinduced process through this series of thermally induced electron transfer already observed by Hashimoto. They observed that the amount of $[\text{Fe(CN)}_6]$ vacancies also controls a thermally induced electron transfer, for high alkali cations insertion rates, $\Delta_{\text{Co}}$ ligand field is the strongest, and the Co atoms remain essentially low spin at the +III oxidation state, whatever the temperature, on the contrary, $\Delta_{\text{Co}}$ is weak, and the Co$^{II}$ ions remain essentially high spin.

P5: The first two bistable Fe$_2$Co$_2$ square complexes have been reported by two French teams in 2010: $\{[[\text{Tp}^*\text{Fe}^{III}(\text{CN})_3]_2[\text{Co}^{II}(\text{bpy})_2]_2][\text{OTf}]_2\cdot4\text{DMF}\cdot2\text{H}_2\text{O}$ (Tp$^* = \text{tris}(3,5$-dimethyl)pyrazolyl borate, bpy = 2,2'-bipyridine, and OTf = trifluoromethanesulfonate) published by Clérac and Mathonière’s group.

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P7: The SCO and ETCST share a lot of similarity, and they are all entropy-driven process. For example,
during a thermally induced SCO or ETCST of a diluted system, the free energy of the system, $\Delta G$, is decomposed into entropy ($\Delta S$) and enthalpy ($\Delta H$) terms:

Correction: The SCO and ETCST share a lot of similarities, and they are all entropy-driven processes. For example, during a thermally induced SCO or ETCST of a diluted system, the free energy of the system, $\Delta G$, is decomposed into entropy ($\Delta S$) and enthalpy ($\Delta H$) terms:

P8: The magnitude of the volume change between the two magnetic state of a compound determines the importance of the pressure effects

Correction: The magnitude of the volume change between the two magnetic states of a compound determines the importance of the pressure effects

P10: Slichter and Dickamer have introduced a non-linear phenomenological term, $G_{nHS}$ ($1 - n_{HS}$), into the equation 3 to take into account of the solid-state interactions.

Correction: Slichter and Dickamer have introduced a non-linear phenomenological term, $G_{nHS}$ ($1 - n_{HS}$), into equation 3 to take into account the solid-state interactions.

P11: The compound containing Cl and Br exhibit complete, gradual, and slightly irreversible spin crossover behavior in the temperature range of 300 - 500 K with equilibrium temperatures ($T_{1/2}$) 375 K (Cl) and 380 K (Br), separately. The loss of the water molecule loss in the compound with $X = CH_3$ leads to a complete and non-cooperative spin crossover with some unusual irreversible features between 300 K and 475 K.$^1$

Correction: The compound containing Cl exhibits complete, gradual, and slightly irreversible spin crossover behavior with equilibrium temperatures ($T_{1/2}$) 375 K (Cl), and that containing Br shows the same SCO phenomenon around 380 K. The loss of the water molecule in the compound with $X = CH_3$ leads to a complete and non-cooperative spin crossover with some unusual irreversible features between 300 K and 475 K.$^1$

P13: $\{[Fe(pzTp)(CN)_3][Co(dpq)_2]_2\cdot2A$ (pzTp = tetrakis(pyrazolyl)borate, dpq = dipyrido[3,2-d:2',3'-f]quinoxaline; A = BF$_4^-$, PF$_6^-$, OTf and $[Fe(pzTp)(CN)_3]^-$)

Correction: $\{[Fe(pzTp)(CN)_3][Co(dpq)_2]_2\cdot2A$ (core structure $\{[Fe(pzTp)(CN)_3][Co(dpq)_2]_2 = 1$, pzTp = tetrakis(pyrazolyl)borate, dpq = dipyrido[3,2-d:2',3'-f]quinoxaline; A = BF$_4^-$, PF$_6^-$, OTf and $[Fe(pzTp)(CN)_3]^-$)

P26: Reference correction.

Chapter 2

P35: Unlike light and temperature which normally favors the paramagnetic state, pressure stabilizes the diamagnetic state at which the complexes have shorter metal-ligand length and smaller molecular volume.

Correction: Unlike light and temperature which normally favors the paramagnetic state, pressure stabilizes the diamagnetic state at which the complexes have shorter metal-ligand bond length and smaller molecular volume.

P35: Furthermore, pressure could also, modify the core structure
Correction: Furthermore, pressure could also modify the core structure

P37:

![Graph](image1)

Figure 1. The thermal variation of the product of $\chi\text{M}T$ in solid state in the temperature range of 2 - 400 K for 1 and 2 (a), the green crystals of 2 (b) and red crystals of 1 (c).

Correction:

![Graph](image2)

Figure 1. The thermal variation of the product of $\chi\text{M}T$ in solid state in the temperature range of 2 - 400 K for 1 and 2 (a), the green crystals of 2 (b) and red crystals of 1 (c).

P37: The IR spectra of compound 1 and 2 are presented in figure 2. The typical cyanide stretching vibration peaks are observed at 2135 cm$^{-1}$ (ascribed to Fe$^{III}$-CN moieties) and 2155 cm$^{-1}$

Correction: The IR spectra of compounds 1 and 2 are presented in figure 2. The typical cyanide stretching vibration peaks are observed at 2135 cm$^{-1}$ (ascribed to Fe$^{III}$-CN moieties) and 2155 cm$^{-1}$

P38: we measured its thermal relaxation of the magnetization at three different temperatures from 120 to 135 K to estimate its activation energy ($E_a$).

Correction: we measured its thermal relaxation of the magnetization at three different temperatures from 120 to 135 K to estimate its activation energy ($E_a$).

P47: The relationship formula can help to approximately predict the pressure value $p_{\text{1/2 up}} = 0.55$ GPa and $p_{\text{1/2 down}} = 0.50$ GPa

Correction: The relationship formula can help to approximately predict the pressure value $p_{\text{1/2 up}} = 0.55$ GPa and $p_{\text{1/2 down}} = 0.50$ GPa.

P48: As depicted above, the increase of the thermal hysteresis loop under pressure, ca. 15 K per GPa, indicates an enhancement of the cooperative elastic interactions with pressure.
Correction: As depicted above, the increase of the thermal hysteresis loop under pressure, ca. 15 K per GPa, indicates an enhancement of cooperativity (hysteresis) with increasing pressure.

P48: \( g_{\text{dia}} \) and \( g_{\text{para}} \) with as \( g_{\text{para}} \gg g_{\text{dia}} \)

Correction: \( g_{\text{dia}} \) and \( g_{\text{para}} \) with \( g_{\text{para}} \gg g_{\text{dia}} \)

P58: Finally, the original spectrum can be recovered when releasing pressure to ambient pressure, showing a good reversibility of the electronic/structural/interaction changes.

Correction: Finally, the original spectrum can be recovered when releasing pressure to ambient pressure, showing a good responsibility of the electronic/structural/interaction changes.

P59: 1D show partial para-to-dia conversion with 10 K hysteresis width at, ca. 0.15 GPa.

Correction: 1D shows partial para-to-dia conversion with 10 K hysteresis width at, ca. 0.15 GPa.

P59: the para-dia conversion is more progressive and the thermal hysteresis width decreases with increasing pressure, which is a “normal” ETCST behavior.

Correction: the para-dia conversion is more progressive and the thermal hysteresis width decreases with increasing pressure, which is a “normal” ETCST behavior as we depicted in the introduction.

P62 reference correction.

Chapter 3

P68: The peaks near 3138 cm\(^{-1}\) comes from the C-H stretching vibration and the overlapping peak around 1648 cm\(^{-1}\) covers the contribution from four functional groups

Correction: The peak near 3138 cm\(^{-1}\) comes from the C-H stretching vibration and the overlapping peak around 1648 cm\(^{-1}\) covers the contribution from four functional groups

P68: These peaks are similar to those obtained in a previously reported diamagnetic square complex, and are respectively assigned to Fe\(^{II}\)-CN-Co\(^{III}\) linkages and to a nonbridging Fe\(^{II}\)-CN linkage for the lowest vibration.

Correction: These peaks are similar to those obtained in a previously reported diamagnetic square complex, and are respectively assigned to Fe\(^{II}\)-CN-Co\(^{III}\) linkages and to a nonbridging Fe\(^{II}\)-CN linkage for the lowest vibration.\(^2\)

P68: Figure 3. ATR spectrum of compound \( \text{3} \) (left); FT-IR compound \( \text{4} \) (right)

Correction: Figure 3. FTIR spectrum of compound \( \text{3} \) (left) and compound \( \text{4} \) (right)

P69: To check this hypothesis, a sample of \( \text{4} \) was desolvated in SQUID.

Correction: To check this hypothesis, a sample of \( \text{4} \) was desolvated in the magnetism device when measuring.

P72: The bond lengths between the Fe ion and the Tp ligand are close in compound \( \text{4} \) and \( \text{3} \).

Correction: The bond lengths between the Fe ion and the Tp ligand are close in compounds \( \text{4} \) and \( \text{3} \).
P75: close to that observed in solution is also coherent with the moderate impact of the weak intermolecular interaction on the ETCST process in 2 and 4.

Correction: close to that observed in solution is also coherent with the moderate impact of the weak intermolecular interaction on the ETCST process in 2 and 4.

P77: The stabilization of paramagnetic state in phase 3 is thus clearly due to solid-state interactions.

Correction: The stabilization of paramagnetic state in compound 3 is thus clearly due to solid-state interactions.

P77: In any cases, the occurrence of ETCST in the solution and the solid-state compound 4 indicates that the paramagnetic 3 may have similar energy level than the diamagnetic 4.

Correction: In any cases, the occurrence of ETCST in the solution and the solid-state compound 4 indicates that the energy gap between diamagnetic and paramagnetic state is small in this system.

P84: Moreover, as shown in figure 13, these all values return to the vicinity of their original positions (ambient pressure) in the process of decreasing pressure to ambient pressure.

Correction: Moreover, as shown in figure 13, all values return to the vicinity of their original positions (ambient pressure) in the process of decreasing pressure to ambient pressure.

P87: Even before the ETCST happen in 3

Correction: Even before the ETCST happens in 3

P95: reference correction.

Chapter 4

P101: A plateau (of 97%) is observed between 73 and 215 °C. Then, a sudden weight drop of 39% occurs in the temperature range of 215 °C to 304°C followed by a further slower weight reduction of 30% from 304 to 394 °C. The important weight drops after 215 °C indicate the compound decomposition.

Correction: A plateau (of 97%) is observed between 73 and 215 °C. Then, a sudden weight drop of 39% (the decomposition of Mebik ligands) occurs in the temperature range of 215 °C to 304°C followed by a further slower weight reduction of 30% (the decomposition of Tp* ligands) from 304 to 394 °C. The important weight drops after 215 °C indicate the compound decomposition.

P111: The figure 10 shows the orientations of the two types intermolecular interactions (CH- π and O-HC) versus that of the Co-NC-Fe linkages of 5. This might help us to understand why the pressure is---

Correction: The figure 10 shows the orientations of the two types of intermolecular interactions (CH- π and O-HC) versus that of the Co-NC-Fe linkages of 5. This might help us to understand why the pressure is---

P118: this is probably due to the pressure measurement difference (pressure is slightly overestimated for HP-Raman measurements) and the different experimental set-up.

Correction: this is probably due to the pressure measurement difference (pressure is slightly
overestimated for XRD measurements) and the different experimental set-up between HP-Raman and XRD. XRD experiments are carried out after HP-Raman (the pressure value is detected in HP-Raman experiments and will increase with time in a fixed temperature)

P119: Here, even at low scan rate, it was not possible to reveal any ETCST at low temperature in $5$.
Correction: Here, even at low scan rate of 0.01 K/min, it was not possible to reveal any ETCST at low temperature in $5$.

P122: reference correction.

Chapter 5

P129: The conformation of two vbik ligands evolve also: the dihedral angles of vbik1 (13.79 °) and of vbik2 (21.52 °) at 240 K decrease to 10.78 ° and 17.56 ° respectively at 270 K, while the average Co-C-O(c=o) angle remains unchanged.

Correction: The conformation of two vbik ligands evolves also: the dihedral angles of vbik1 (13.79 °) and of vbik2 (21.52 °) at 240 K decrease to 10.78 ° and 17.56 ° respectively at 270 K, while the average Co-C-O(c=o) angle remains unchanged.

P128: When heated slowly (0.4 K/min), the $\chi_M$T shows a sharp decrease from 80 to 100 K. The relaxation temperature determined as the inflection point is ca. 90 K as shown in the figure 3(c).

Correction: When heated slowly (0.4 K/min), the $\chi_M$T shows a sharp decrease from 80 ( $\chi_M$T : ca. 5.67 mol$^{-1}$ cm$^3$ K) to 100 K ( $\chi_M$T : ca. 0.01 mol$^{-1}$ cm$^3$ K). The relaxation temperature determined as the inflection point is ca. 90 K as shown in the figure 3(c).

P128-P134, Figures of 1-6 order change.

P138: The figure 8 shows the images of the crystal at paramagnetic and diamagnetic states at 280 K and 230 K respectively.

Correction: The figure 8 shows the images of the crystal at paramagnetic and diamagnetic states at 280 K and 230 K respectively, which also shows a responsibility of the magnetic propertis and XRD measurements.

P143: reference correction.

P156- P160: Adding more support information (High-pressure cell user illustration for preparing sample)
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Abbreviations

SQUID  Super-Conducting-Quantum-Interference-Device
NMR   Nuclear Magnetic Resonance
FT    Fourier Transformed
IR    Infra-Red
UV    Ultra-violet
XRD   X-Ray Diffraction
HP – XRD High pressure X-Ray Diffraction
TGA   Thermal-Gravimetry-Analysis
CV    Cyclic voltammetry
SCE   Saturated Calomel Electrode
DCM   Dichloromethane
THF   Tetrahydrofuran
Et2O  Diethyl ether
NBu4  Tetra(butyl)ammonium
PBA   Prussian Blue Analogues
Pz    Pyrazole
Tp    Hydrotris(1-pyrazolyl) borate
pzTp  Tetra-pyrazolylborate
Tp*   Tris(3,5-dimethyl)pyrazolyl borate
Vbik  Bis(1-vinylimidazol-2-yl) ketone
Mebik Bis(1-methylimidazol-2-yl) ketone
Bpy   2,2'-bipyridine
OTf   Trifluoromethanesulfonate
ETCST Electron-Transfer Coupled Spin-Transition
HS    High-Spin
LS    Low-Spin
SCO   Spin-Crossover
ST    Spin-Transition
ET    Electron-Transfer
T_{1/2} Transition temperature
Squares: complexes

General abbreviation: $\{[\text{Fe}(L1)(CN)_3][\text{Co}(L2)_2]\}_{2}(A)_2 \cdot S$

**CN**  Cyanide ion  
**L1**  Ligand (Tp, PzTp, Tp*)  
**L2**  Ligand (vbik, Mebik)  
**A**  Counterion (BF$_4^-$, PF$_6^-$, ClO$_4^-$)  
**S**  Solvent

**Chapter 1**

$\{[\text{Fe}(L1)(CN)_3][\text{Co}(L2)_2]\}_{2}(A)_2 \cdot S$  
$L1 = \text{Tp}, \text{PzTp}, \text{Tp*}; L2 = \text{bik}, \text{bpy}; S = \text{H}_2\text{O}, \text{MeOH}, \text{DMF}$

**Chapter 2**

**Compound 1**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik})_2]\}_{2}(\text{BF}_4)_2 \cdot 2\text{CH}_3\text{OH} \ (1)$

**Compound 1D**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik}_2)]_{2}(\text{BF}_4)_2 \cdot 2\text{CD}_3\text{OD} \ (1D)$

**Compound 2**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik})_2]\}_{2}(\text{BF}_4)_2 \cdot \text{MeOH} \cdot 10\text{H}_2\text{O} \ (2)$

**Chapter 3**

**Compound 3**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik})_2]\}_{2}(\text{PF}_6)_2 \cdot 2\text{CH}_3\text{OH} \ (3)$

**Compound 4**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik})_2]\}_{2}(\text{PF}_6)_2 \cdot 17\text{CH}_3\text{OH} \ ($or $31\text{H}_2\text{O}$) \ (4)$

**Chapter 4**

**Compound 5**  
$\{[\text{Fe}(\text{Tp}^*)](CN)_3][\text{Co}(\text{Mebik})_2]\}_{2}(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O} \ (5)$

**Chapter 5**

**Compound 6**  
$\{[\text{Fe}(\text{Tp})(CN)_3][\text{Co}(\text{vbik})_2]\}_{2}(\text{ClO}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2 \ (6)$
2.3.4 H-bond between the terminal cyanide and the protic solvent in 1 and 2 at ambient pressure

3. Thermal ETCST of 1 under various pressures – HP magnetic measurements

3.1 Results of HP-magnetic measurements

4. p-induced ETCST studied by HP-X-Ray Diffraction measurements on single crystals (HP-SC-XRD)

4.1 The core structure modification of 1 by pressure

4.2 Molecular geometry anisotropic deformation

4.3 Evolution of the intermolecular interactions upon pressure increase

4.3.1 Pseudo π-π interactions vs pressure

4.4 The role of H-bond formed between terminal CN and MeOH solvent

4.4.1 The variation of the interatomic distance O···N against pressure

4.4.2 Raman spectra of compound 1 at different pressures

4.4.3 Thermal ETCST behaviors of 1 with deuterated methanol (1D) under pressure

5. Conclusion

Reference

Chapter 3 Partial thermal ETCST under pressure and pressure-induced phase transition of a paramagnetic square \{[Fe(Tp)(CN)3]2[Co(vbik)2]2](PF6)2·2CH3OH (3)

1 Introduction

2 Syntheses, structural and spectroscopic characterizations of the compounds

2.1 Preparation of \{[Fe(Tp)(CN)3]2[Co(vbik)2]2](PF6)2·2CH3OH (3)

2.2 Preparation of \{[Fe(Tp)(CN)3]2[Co(vbik)2]2](PF6)2·MeOH·15H2O (4)

2.3 TGA of compound 3 and 4

3 Magnetic properties at ambient pressure of the compound 3 and 4

4 Description of the crystal structures at ambient pressure

5 Partial thermal ETCST under pressure and pressure-induced phase transition in solid-state

5.1 Phase transition revealed by HP-XRD at ambient temperature
5.2 Pressure-induced paramagnetic to diamagnetic ETCST in 3 probed by HP-μ Raman spectroscopy

6 Conclusion

Reference

Chapter 4 Pressure-induced conversion of a paramagnetic square \{[Fe(Tp*)(CN)3]2[Co(Mebik)2]2\}(BF4)2·2H2O (5) into a molecular switch

1 Introduction

2 Syntheses, spectroscopic and structural characterizations

2.1 Synthesis, FT-IR spectrum and TGA of \{[Fe(Tp*)(CN)3]2[Co(Mebik)2]2\}(BF4)2·2H2O (5)

2.2 Structure and intermolecular interactions of 5 at ambient pressure

3 Thermal ETCST under different pressures: results of High-Pressure (HP) magnetic measurements

4 Pressure-induced ETCST identification by X-ray diffraction at 300 K

4.1 Changes of the core structure and interactions of 5 induced by pressure

4.2 Variation of the unit cell parameters of 5 versus pressure

4.3 Modification of the intermolecular interactions in 5 upon pressure

4.4 The influence of the H bond in the ETCST behaviors of 5

5 Pressure-induced paramagnetic to diamagnetic ETCST transition in 3 probed by HP-μ Raman spectroscopy

6. Conclusion

Reference

Chapter 5 Thermal ETCST of \{[Fe(Tp)(CN)3]2[Co(vbik)2]2\}(ClO4)2·2CH2Cl2 (6) at ambient pressure and direct observation of its ETCST propagation by optical microscopy

1 Introduction

2 Syntheses, structural and spectroscopic characterizations

2.1 Preparation of \{[Fe(Tp)(CN)3]2[Co(vbik)2]2\}(ClO4)2·2CH2Cl2 (6)

2.3 Thermal ETCST by magnetic measurements
2.3 Determination of the structures of 6 at diamagnetic (240 K) and paramagnetic (270 K) state by XRD measurements ................................................................. 128

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2.5 Structure-property relationship of Fe₂Co₂ squares having general formula \([\text{Fe(Tp)CN}_3\text{]}_2\text{[Co(vbik)]}_2\cdot\text{(A)}\cdot\text{S}\) ........................................................................................................................ 136

3 Thermal ETCST of 6 on single crystal – Nucleation and Propagation of the transition observed by optical microscopy ........................................................................................................................... 137

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Chapter 1

Introduction to SCO and ETCST phenomena and pressure studies

on SCO and ETCST compounds
1 Introduction of SCO and ETCST phenomena and pressure studies on SCO and ETCST compounds

1.1 SCO transition of Fe(II)-based complexes

Molecular magnetic switches are able to reversibly change their physical (optical, magnetic, dielectric, etc.) properties under external stimuli such as light irradiation, temperature, magnetic or electric fields, and pressure. The research interest for these systems is essentially fundamental up to now, but the perspective of their future applications is very promising. The molecular switches could be used as molecular memory devices, pressure sensors, actuators, and so on.

The SCO phenomena have been discovered in the 1930’s and widely studied since the 1950’s. The most thoroughly studied molecular magnetic switches are Fe(II) based systems which are mono- or polynuclear complexes containing up to eight Fe(II) in these complexes, Fe(II) have generally an octahedral N6 coordination environment where the ligand field splitting between t2g and eg is in the same order of magnitude than the energy caused by environmental variation. Under an external stimulus, such as temperature (T), pressure (P), and light..., the complexes can switch reversibly between two spin states with distinguished electronic configurations: t2g6eg0 (S = 0) and t2g4eg2 (S = 2), as shown in figure 1. This phenomenon is also called spin crossover (SCO).

[Figure 1. Spin-Crossover (SCO) or spin transition in Fe(II) complexes.]

SCO is responsible for the change of the magnetic properties, as well as all other physical properties that are correlated to the electronic state: optical, dielectric etc..., it is worth noticing that a spin-state change is also accompanied by structural changes. From low-spin (LS) to high-spin (HS) state, an elongation of Fe(II)-N bonds of 0.2 Å (10%) is generally observed because of the change in the population of the antibonding eg orbitals: two electrons are moving from slightly-bonding t2g orbitals (LS state) to the anti-bonding eg orbitals (HS state) during the SCO process. It’s well known that the coordination sphere of the HS Fe(II) is often more distorted than the LS one, because the absence...
of the antibonding $e_g$ electrons at LS state results in a stronger Fe(II)-N bonding and thus a less deformable coordination sphere. Hence the complexes of Fe(II) in low-spin states generally adopt more regular coordination geometries than their high-spin counterparts. This can be reflected in the distortion parameter noted $\Sigma_{\text{Fe(II)}}$, which is the sum of the deviation of the twelve pseudo-orthogonal N-Fe(II)-L(L means coordination ligand) of an octahedral $\{N_6\}$ coordination sphere. $\Sigma_{\text{Fe(II)}}$ is substantially lower at LS state than at HS one. The HS Fe(II) with higher $\Sigma_{\text{Fe(II)}}$ usually exhibit greater structural flexibility, than their low-spin states. The difference of $\Sigma_{\text{Fe(II)}}$ value, $\Delta \Sigma_{\text{Fe(II)}} = \Sigma_{\text{Fe(II)}}_{\text{HS}} - \Sigma_{\text{Fe(II)}}_{\text{LS}}$ reflects generally the magnitude of the structural re-arrangement taking place during SCO process. In some cases where the $\Delta \Sigma_{\text{Fe(II)}}$ values are too large, the compounds may not undergo spin-crossover on cooling. The structural change that would be required is too great to be accommodated by the rigid solid lattices, and such compounds tend to remain trapped in their high-spin state.

Figure 2. The structure of $[\text{Fe(1-bpp)}_2][\text{BF}_4]_2$ with bpp = 2,6-di(pyrazol-1-yl)pyridine (Left); The plot of $\chi_M T$ vs. $T$ for the polycrystalline $[\text{Fe(1-bpp)}_2][\text{BF}_4]_2$ in cooling (•) and warming (◆) modes (Right).

One example of the spin-crossover systems with the most available crystallographic data is $[\text{Fe(1-bpp)}_2][\text{BF}_4]_2$ compound (bpp = 2,6-di(pyrazol-1-yl)pyridine), which shows a thermal spin transition centered at 259 K ($\chi_M T \leq 0.3$ cm$^3$ K mol$^{-1}$ for the low-spin state, $\chi_M T = 3.6 - 3.7$ cm$^3$ K mol$^{-1}$ for the high-spin state) and with a 3 K hysteresis loop width (see the figure 2). This compound has an approximate local $D_{2d}$ symmetry. The Fe-N bond lengths in its crystal at 290 K (2.1248 - 2.185 Å) are consistent with a high-spin Fe(II) ion. In contrast, at 240 K, the Fe-N bond lengths have shortened to 1.893(3)-1.981(4) Å, which are characteristic of a low-spin Fe(II) center. The difference between the
average Fe-N distances at 290 and 240 K in this compound is 0.215(10) Å, which is a typical value for a spin-state transition involving a Fe(II) complex with [N6] coordination environment.\textsuperscript{19}

\textbf{1.2 Bistable charge-transfer systems - from Prussian Blue Analogues (PBAs) to Molecular Analogues of Prussian Blues (mPBAs)}

The common feature of PBAs and mPBAs is that they are both heterobimetallic systems where the metallic pairs are linked by the cyanide bridges. However, the former are 3D coordination polymers and the second, discrete bi-metallic coordination clusters. The most commonly studied bistable systems among them are cyanido-bridged Fe-Co complexes.\textsuperscript{20} In these Fe-Co compounds, an external stimulus (T, P or light...) can trigger an intramolecular electron transfer from one metal site to another, which is accompanied by a spin state change on the Co site, as shown in figure 3. These systems can therefore exhibit the interconversion between two electronic structures: $\text{Fe}^{II}_{LS}-\text{CN}-\text{Co}^{III}_{LS}$ and $\text{Fe}^{III}_{LS}-\text{CN}-\text{Co}^{II}_{HS}$. The former is diamagnetic, and the second, paramagnetic.\textsuperscript{[20-22]} This phenomenon is called electron-transfer coupled spin-transition (ETCST).

![Figure 3. Electron Transfer Coupled Spin Transition (ETCST) in Fe-Co system.](image)

The occurrence of reversible ETCST requires that the two valence states involved in the equilibrium are close in energy, or that the redox potentials of the two metal-based subcomponents are close enough in energy. This can be achieved by tuning the stoichiometry of PBAs or by selecting the suitable ligands on Fe and Co sites in mPBAs.

The first report on bistable PBAs and mPBAs have appeared much later in the literature than for SCO complexes. Hashimoto and his collaborators have discovered the occurrence of photo-induced ETCST in a CoFe PBAs, $K_{0.2}Co_{1.4}-[\text{Fe(CN)}_6]-6.9\text{H}_2\text{O}$, in 1996.\textsuperscript{24a} They demonstrated an increase of the magnetization of the Co-Fe PBAs after the filtered red light (660 nm with 50 nm half-width, 3.5
mW/cm²) at low temperature. Meanwhile, the Curie temperature of the PBAs rose up from 16 K to 19 K (Figure 4). Then, Michel Verdaguer et al. also deeply studied the efficiency of the photoinduced process through this series of thermally induced electron transfer phenomena already observed by Hashimoto. They observed that the amount of [Fe(CN)₆] vacancies also controls a thermally induced electron transfer, for high alkali cations insertion rates, ∆Co ligand field is the strongest, and the Co atoms remain essentially low spin at the Co(III) oxidation state, whatever the temperature, on the contrary, ∆Co is weak, and the CoII ions remain essentially high spin.²⁴b

In 2004, Curtis P. Berlinguette et al. (Dunbar’s group) have observed for the first time the thermally activated ETCST in a pentanuclear Fe₂Co₃ complex: the discrete cyanide-bridged complex of formula {[Co(tmphen)₂]₃[Fe(CN)₆]₂} (tmphen = 3,4,7,8-tetramethyl-1,10 phenanthroline).²⁵ This compound can switch between two magnetic states when the temperature varies, to which the corresponding electronic configurations are [(CoIIHS)₃(FeIIILS)₂] and [(CoIIHS)₂CoIIILSFeIIILSFeIIILS] respectively. The figure 5 shows the structure of the pentanuclear cluster and thermal variations of its χMT for the three isomeric forms ([CoIIICoIIIFeII2], [CoIIICoIIIFeIIILS], and [CoIIICoIIILSFeIIILS]). The magnetic properties of this complex, which can exist in three electronic isomeric forms are very sensitive to interstitial solvent content as well as temperature. Additionally, when the compound is exposed to humidity, it shows modest photomagnetic activity with a partial transition from the [(CoIIHS)₂CoIIILSFeIIILSFeIIILS] state to the [(CoIIHS)₃(FeIIILS)₂] state.

Figure 4. Photoinduced magnetization enhancement in K₀.₂Ca₁.₄[Fe(CN)₆]·6.9H₂O as observed in the increase of the ferrimagnetic ordering temperature Tᵣ.
The work of Berlinguette et al. has incited several research groups (for example, Clerac and Mathonière’s team, and Lescouëzec’s team in France, Stephen M. Holmes’s team in America, Oshio and Nihei’s team in Japan) to “extract” molecular units from 3D PBAs by using the capping ligands on metal sites during the synthesis process. They foreseed many advantages of these mPBAs compared with 3D PBAs: with well-defined stoichiometry, good solubility, and crystallization, the mPBAs are very attractive for the fundamental comprehension of ETCST as well as for the applicative aspects. In 2008, D. F. Li et al. have reported the first bistable octa-nuclear Fe$_4$Co$_4$ cluster, \{[(pzTp)Fe$^{III}$\(\text{CN}\)$_3$]$_4$[Co$^{II}$\(pz\)$_3$CCH$_2$OH]$_4$ \} [ClO$_4$]$_4$·13DMF·4H$_2$O, which truly represents the elementary unit of Co-Fe PBAs.$^{26}$

The first two bistable Fe$_2$Co$_2$ square complexes have been reported by two French teams in 2010: \{[(Tp*)$\text{Fe}^{III}$\(\text{CN}\)$_3$]$_2$[Co$^{II}$\(bpy\)$_2$]$_2$\} [OTf]$_2$·4DMF·2H$_2$O (Tp* = tris(3,5-dimethyl)pyrazolyl borate, bpy = 2,2'-bipyridine, and OTf = trifluoromethanesulfonate) published by Clérac and Mathonière’s groups.$^{27}$ and \{[(pzTp)Fe$^{III}$\(\text{CN}\)$_3$]$_2$[Co$^{II}$\(bik\)$_2$]$_2$\} [ClO$_4$]$_2$·3H$_2$O (pzTp = tetra-pyrazolylborate, bik = bis(1-methylimidazol-2-yl)ketone) published by Lescouëzec’s group. $^{28}$ Actually, the Fe$_2$Co$_2$ square complexes are attracting more and more attention. They are the most studied mPBAs complexes, as they can accommodate a variety of blocking ligands on Fe and Co sites, different counter-anions and co-crystallized solvents. They are used often in the investigation of different factors influencing ETCST, such as ligand substituents, crystal packings, or intermolecular interactions.$^{29}$ These cyanide-bridged Fe$_2$Co$_2$ square molecules are generally obtained by reacting derivative of the fac-[Fe$^{III}$\(L_1\)(CN)$_3$]$^+$ metalloligand with [Co$^{II}$\(L_2\)$_2$(S$_2$)]$^{2+}$ complexes (\(L_1\): tris(pyrazoyl)borate derivatives and \(L_2\): α- or β-diimine). M. Nihei et al. have demonstrated that the Fe$_2$Co$_2$ square complexes could be bistable if the redox potential difference between the two building blocks, $\Delta E_{1/2} = E_{1/2} (\text{Fe}^{III/II}) - E_{1/2}$
(Co$^{III/II}$), is about - 0.8 V. A smaller or greater $\Delta E_{1/2}$ values lead respectively to a diamagnetic or paramagnetic square.$^{29}$

Like SCO, the ETCST in FeCo PBAs and mPBAs is associated with the significant modification of their magnetic, optical, and mechanic properties as well. The anti-bonding $e_g^*$ orbitals of Co site populated by two unpaired electrons at paramagnetic state is empty at diamagnetic one. The Co-N bond lengths vary typically from 2.1 to 1.9 Å (about 10%) during ETCST. Similar to Fe(II), the distortion of the Co site pseudo-octahedral coordination sphere ($\Sigma Co$) is much higher at HS state than at LS one. In contrast, the change occurring in the low-spin iron coordination sphere remains much more moderated upon redox state change. The following paragraphs will quote the examples of temperature - and photo - induced ETCST in the first two Fe$_2$Co$_2$ squares complexes at solid state published in 2010.

The first square complex reported in 2010, $\{[(Tp^*)Fe^{III}(CN)_{3}]_{2}[Co^{II}(bpy)_{2}]_{2}]$OTf$_2$·4DMF·2H$_2$O crystallizes in triclinic space group.$^{30}$ It exhibits a complete thermal ETCST of first order with $T_{1/2}^{\uparrow} = 190$ K and $T_{1/2}^{\downarrow} = 169$ K, as showed by figure 6. Its thermal hysteresis width, $\Delta T_{1/2} = 23$ K, is still the highest among all the Co-Fe mPBAs studied until to now. The square shows also a complete photo-induced ETCST at 10 K when irradiated by white light. The structure of the square at diamagnetic state is rather regular with two Co-N≡C-Fe linkages almost linear ($\angle Co$-N≡C: 173.7\degree /177.5 $\degree$, the value of $\Sigma Co$ = 42.3 $\degree$, and the average Co-N length is 1.955 Å). After the thermal ETCST, the $\angle Co$-N≡C values change hardly ($\angle Co$-N≡C: 174.9 \degree /177.7 $\degree$), whereas the average Co-N length increases to 2.113 Å and the $\Sigma Co$ value, to 58.6 $\degree$. The intermolecular interactions of the square are characterized by the $\pi$ - $\pi$ stacking of bpy ligands belonging to two adjacent squares. The DSC measurements have allowed the determination of the enthalpy change associated to the thermal ETCST: $\Delta H \approx 20$ KJ/mol with a temperature scanning rate of 2 K/min. The thermal relaxation of the thermally quenched and photo-excited paramagnetic state has been also investigated, allowing the estimation of the activation energy, $E_a = 2854$ K. This $E_a$ value is very high compared with that for Fe(II) based SCO compounds (< 110 K).$^{31}$
After the report of the thermal and photo-induced ETCST of \([([pzTp]Fe^{III}(CN)_3)_2[Co^{II}(bik)_2]_2)[ClO_4]_2\cdot3H_2O\) in 2010\(^{32}\), the On-Off process of this square implying the photo-excitation by irradiation at 808 nm and magnetization reversal by subsequent irradiation at 532 nm is the subject of a second publication in 2013\(^{33}\). In this study, the On-Off process of a molecular switch was followed for the first time by cryo-XRD measurements on single crystal, the photo-excited paramagnetic structure of the square was obtained. Under irradiation at 808 nm (at 15 K), the diamagnetic green square shows a complete photo-induced ETCST and reaches the photo-excited metastable state which is paramagnetic. The subsequent irradiation at 532 nm converts partially the metastable paramagnetic state to the initial diamagnetic state. Figure 7 shows the schema of this On-Off process and the corresponding temporal variation of the square’s \(\chi MT\). The average Co-N bond is 1.914 Å at diamagnetic state, 2.086 Å at paramagnetic metastable state, and 1.950 Å after the irradiation at 532 nm, and the corresponding \(\sum\text{Co}\) values are 20 °, 41 °, and 19 ° respectively. The cryo-XRD data are in agreement with the results of photomagnetic measurements.
1.3 Thermodynamics of SCO and ETCST

The SCO and ETCST share a lot of similarities, and they are all entropy-driven processes. For example, during a thermally induced SCO or ETCST of a diluted system, the free energy of the system, $\Delta G$, is decomposed into entropy ($\Delta S$) and enthalpy ($\Delta H$) terms:

$$\Delta G = \Delta H - T\Delta S$$

where $\Delta H$ and $\Delta S$ are respectively the enthalpy and entropy differences between HS/paramagnetic state and LS/diamagnetic state: $\Delta H = H_{HS/para.} - H_{LS/dia.} > 0$, and $\Delta S = S_{HS/para.} - S_{LS/dia.} > 0$.

The figure 8 illustrates the evolution of the energy gap between two magnetic states, $\Delta G$ at three different temperatures for an ETCST compound. At low temperature, $\Delta G$ is positive, the low-spin/diamagnetic state is more stable. At high temperature, the HS/paramagnetic state is more stable, as the entropy increases at this state from both higher vibrational and electronic contributions. The thermally-induced switching from the diamagnetic to the paramagnetic state can thus occur upon increasing temperature, if $T\Delta S$ overcomes $\Delta H$. At equilibrium, the HS/paramagnetic fraction is equal to the LS/diamagnetic one, and $\Delta G = 0$, the transition temperature $T_{ETCST}$ is thus the ratio $\Delta H/\Delta S$. For those compounds, whose $\Delta H$ value is very large, $T_{ETCST}$ will be “out of reach” and the compounds will remain in the diamagnetic state. On the contrary, when the $\Delta H$ value is very small, $\Delta G$ is always negative, the compound will be HS/paramagnetic in all temperature range. In solution or in diluted system, the variation of the HS/paramagnetic species fraction, $\gamma_{HS}$ or $\gamma_{para}$ versus temperature is gradual, and follows the prediction of a Boltzmann distribution between the two vibronic manifolds.34
When pressure (P) is used as external stimulus in addition of temperature, a third term is added to the equation 1:

$$\Delta G = \Delta H - T\Delta S + P\Delta V$$  \hspace{1cm} (2)

where $\Delta V$ is the volume variation between HS/paramagnetic and LS/diamagnetic states, and $\Delta V > 0$. Unlike the increase of temperature, which tends to stabilize HS/paramagnetic state, the pressure increase tends to stabilize the LS/diamagnetic state. This is related to the shortening of metal-ligand bonds which decreases the complex’s volume at LS/diamagnetic state. The magnitude of the volume change between the two magnetic states of a compound determines the importance of the pressure effects, which are expected to be higher for those complexes showing the larger volume change. This principle applies to both SCO and ETCST systems. Therefore, the application of pressure will tend to increase the energy gap, $\Delta G$, between the two magnetic states and shift the transition temperature upward for an ETCST compound, as showed in figure 9. Meanwhile a larger energy gap decreases the activation energy, $E_a$, for a paramagnetic species to relax thermally to the diamagnetic one. When the pressure exceeds a certain threshold, $E_a = 0$, the HS/paramagnetic species becomes LS/diamagnetic.
Figure 9. Effect of pressure on ETCST process: pressure increases the energy gap between paramagnetic and diamagnetic states. $\Delta G$ is the energy gap between the two states, $E_a$ is the activation energy for the ETCST compound to relax thermally from paramagnetic state to diamagnetic one.

For SCO compounds at solid state, the situation is more complex, since intermolecular interactions may lead to cooperative effects, which give steep and hysteretic transitions. They may also affect the geometry (e.g., coordination sphere distortion) of the molecule and thus impact the $\Delta H$ and $\Delta S$ values and thus the transition temperature. In 1972, Slichter and Drickamer have proposed the first thermodynamic model for spin transition at solid state.\textsuperscript{35} W. Nicolazzi and A. Bousseksou have given a modern lecture of this macroscopic model in a recent review article.\textsuperscript{36} The model was based on the regular solid solution theory, that considers a mixture of $N$ noninteracting HS and LS molecules. The Gibbs energy of such a system is expressed by the equation 3.

$$G = n_{HS} G_{HS} + (1 - n_{HS}) G_{LS} - T S_{mix}$$

Where $n_{HS}$ is the molar fraction of HS species and the mixing entropy $S_{mix}$ is given by the equation 4.

$$S_{mix} = - K_B N \left[ n_{HS} \ln(n_{HS}) + (1 - n_{HS}) \ln(1 - n_{HS}) \right]$$

Where $K_B =$ Boltzmann constant and $N =$ Avogadro’s constant.

Slichter and Dickamer have introduced a non-linear phenomenological term, $\Gamma n_{HS} (1 - n_{HS})$, into equation 3 to take into account the solid-state interactions. Therefore the equation of the free energy of the whole system could be described as follow:\textsuperscript{37}

$$G = n_{HS} G_{HS} + (1 - n_{HS}) G_{LS} + \Gamma n_{HS} (1 - n_{HS}) - T S_{mix}$$

The interaction parameter, $G$, is related to the strength of intermolecular interactions in a solid state. Initially, Slichter and Dickamer considered it as dependent on $T$ and $P$. As the $P$- and $T$- dependences are difficult to find, $G$ is often kept constant in the later application of the model.
At equilibrium state, \((\partial G/\partial n_{HS})_{T,P} = 0\), then

\[ T = \frac{\Delta H + \Gamma (1 - 2n_{HS})}{R \ln[(1-n_{HS})/n_{HS}] + \Delta S} \] (6)

Where \(R\) is the constant of perfect gas \((R = K_B N)\). With \(n_{HS} = 0.5\) and \(\Delta G = 0\), the transition temperature remains unchanged: \(T_{1/2} = \Delta H/\Delta S\).

Sometimes, the \(n_{HS}\) values can give the same temperature, they are related to the existence of stable, metastable and instable states. To verify the stability of the extrema of \(G\), it’s interesting to examine the sign of the second derivative of \(G\) around equilibrium temperature:

\[ (\partial^2 G/\partial n_{HS}^2)_{T,P,n_{HS}=0.5} = -2 \Gamma + 4 R T_{1/2} \] (7)

The magnitude of \(\Gamma\) compared with \(R T_{1/2}\) determines the three types of SCO transition: (1) In case of weak interactions, \(\Gamma < RT_{1/2}\), the second derivative is positive and \(n_{HS} = 0.5\) corresponds to the \(G\) minimum, the SCO transition is gradual. (2) For strong interactions, \(\Gamma > RT_{1/2}\), the second derivative of \(G\) is negative, \(n_{HS} = 0.5\) corresponds to the \(G\) maximum. Then, the transition is abrupt and hysteretic with two transition temperatures: \(T_{1/2}\) cooling and \(T_{1/2}\) heating. The phase between the two transition temperatures is metastable. (3) When \(T_{1/2} = \Gamma < 2R\), the transition is abrupt, but without hysteresis.

When taking into account the pressure effect, the free energy change, \(\Delta G\), was denoted as:

\[ \Delta G = \Delta G(0) + P \Delta V + \frac{P^2}{2} \Delta \frac{v(0)}{B} \] (8)

Where \(V\) is the volume and \(B\) is the bulk modulus at ambient pressure. The first term of the equation (8) is the free energy variation at room pressure, the second term, the contribution of the pressure due to the fact that the volumes of the HS and LS components are different. The third term reflects the fact that the two phases have different bulk moduli. The last term is generally neglected, as the pressure used is small compared to \(B\). With the third term removed, the equation (8) becomes:

\[ \Delta G = \Delta G(0) + P \Delta V \] (9)

Based on the Slichter-Dickamer’s model, many others macroscopic models have been developed to describe the mechanism of more complicated spin transitions, such as incomplete and multistep transitions. But Slichter-Dickamer’s model is still used to extract the thermodynamical parameters from the experimental measurements of one step, gradual, or hysteretic SCO.
1.4 Structure-properties relationship for SCO and ETCST complexes

The structure-properties relationship (SPR) for SCO has been thoroughly investigated in SCO complexes, and continues to be a topic attracting large-scale interests in the world. In 2011, M. A. Halcrow has remarkably described how the temperature and the cooperativity of spin transition are related to structural data of different types of SCO compounds in a critical review article.⁴⁰ Many recent reports can be find in the literature handling each time the structure-property relationships of the SCO compounds with identical or similar ligands, such as polymorph Fe(II) polymorphs⁴¹ and Fe(II) complexes with thio-pybox ligands.⁴² Generally speaking, increasing the spatial crowding around the ligand donor atoms tends to favor high-spin state, thereby decreasing $T_{1/2}$. Under the same other conditions, functionalizing a ligand with attractive or donor groups allows modulating the $T_{1/2}$. These effects can be directly correlated to the ligand field, which is the critical parameter to adjust for controlling SCO properties. There are also numerous other factors affecting $T_{1/2}$, such as coordination geometry, counterion nature and size, and lattice solvent and so on. For example, Guionneau et al. have surveyed a family of cis-[Fe(NCS)$_2$L$_2$] complexes (L is a bidentate N-donor chelate). It is noteworthy that they observed a reasonable negative correlation between $T_{1/2}$ and the coordination geometry of the complexes. This is a remarkable observation, since the compounds surveyed contain different N-donor types with different basicities and steric requirements, and few of them are isostructural. However, there was no obvious relationship between $T_{1/2}$ and other measures of the coordination sphere of the iron atoms in the high-spin state (the average Fe-N distance, the Fe-N-C angles to the isothiocyanate ligands, or distortion parameter $\Sigma$).

Another family containing bidentate ligand (containing N-donor Schiff base) are the complexes of cis-[Fe$^{n}$X-PPMA]$_2$(NCS)$_2$·H$_2$O (X-PPMA = 4-X-N-(phenyl(pyridin-2-yl)methylene)aniline, X = Cl$^-$, Br$^-$, CH$_3$), which is involved in 2-benzoylpyridine and 4-chloroaniline/4-bromoaniline/4-methylaniline. These family compounds are studied by G.Chastanet’s team at present. The compound containing Cl$^-$ exhibits complete, gradual, and slightly irreversible spin crossover behavior with equilibrium temperatures ($T_{1/2}$) 375 K (Cl$^-$), and that containing Br$^-$ shows the same SCO phenomenon around 380 K. The loss of the water molecule in the compound with $X = \text{CH}_3$ leads to a complete and non-cooperative spin crossover with some unusual irreversible features between 300 K and 475 K.⁵⁵

Besides $T_{1/2}$, the shape of the transition is also correlated to the solid-state structure of the complex. In neat spin-crossover compounds, cooperative interactions of elastic origin due to the large
differences in metal-ligand bond lengths $\Delta r_{HL} = r_{HS} - r_{LS}$ of $\sim 0.16 - 0.21$ Å$^{[54-59]}$ and the simultaneous differences in crystal volumes $\Delta V_{HL} = V_{HS} - V_{LS}$ of $\sim 20 - 30$ Å$^3$ $^{[41-43]}$ per molecular unit between the two states, result in generally much steeper transition curves and thermal hysteresis with and without accompanying crystallographic phase transition.$^{[63-69]}$

The abrupt spin transition with hysteresis is considered to reflect the intensity of the interaction between the spin centers in the material. It can be expected that strong cooperative transitions are common in metal organic frameworks and coordination polymers, where the spin centers are covalently linked. Polymeric structures with iron centers bridged by rigid linkers often show strong cooperativity,$^{[70-73]}$ but the reality is that the most strongly cooperative spin-crossover materials are in fact mononuclear complexes: the family compounds of formula $[\text{Fe}(\text{HIm})_2(L_1)]$ ($\text{HIm} = \text{imidazole}, L_1 = \text{diethyl(E,E)-2,2'-[1,2-phenylenebis (iminoethylidyne)]-bis[3-oxobutanoate]}$)$^{[76]}$ show a $70$ K wide hysteresis.$^{75}$ The exceptional cooperativity exhibited by those compounds cannot be explained in detail, since most of the structural data in both spin states are not available in SCO complexes.

Although mechano-elastic theoretical models have been developed in the last decades to rationalize the different spin-transition shape,$^{77}$ the real systems are much more complex, and the rationalizing of solid-state properties remains quite challenging.

In addition, it has been proposed that hydration play an important role in influencing the spin behavior in the last twenty years. The hydrogen bond favors to stabilize the LS state through hydrogen bonding of the water molecule with ligands.$^{78}$ It indeed seems to be the case for most hydrates, but in the cationic SCO system, the ligand only bonded to the relevant anion, which in turn is bonded to the water molecule. The effect may be opposite, that is, the loss of water will also lead to the stabilization of LS state. For example, the compound of $[\text{FeL}_2][\text{NO}_3]_2\cdot4\text{H}_2\text{O}$ ($\text{L}_2$ is the substituted derivatives: 2,6-bis(1,2,4-triazol-3-yl)pyridine) studied by Harold A. Goodwin in 1993, shows an extensive hydrogen-bonded network involving the N-H group, the anions, and the water molecules. With the loss of one water molecule, the compound of $[\text{FeL}_2]\text{Cl}_2\cdot3\text{H}_2\text{O}$ is high-spin and undergoes a partial transition to low-spin at low temperature. Conversion to low-spin is complete when the complex is dehydrated. The author declares that this change is associated with the effects of the hydrogen bonding. In their case, the loss of water molecules eliminates the hydrogen bonds and stabilize LS state.$^{79}$

The presence or absence of thermal hysteresis of a spin transition is closely related to the crystal packing and to the intermolecular interactions.$^{80}$ A gradual spin transition is often attributed to the
weakness of intermolecular interactions.\textsuperscript{81,82} On the contrary, an abrupt spin transition is generally associated with intermolecular H-bonds\textsuperscript{83,84} and the intermolecular $\pi - \pi$ stackings.\textsuperscript{82,85,86} Nowadays, it’s commonly admitted that an important hysteresis is promoted by large structural rearrangement in spin transition and to the strong intermolecular interactions implying rigid ligand groups.\textsuperscript{87}

There are much less magneto-structural investigations on discrete FeCo ETCST compounds (mPBAs) than on Fe(II) SCO complexes, due to their recent appearance. However, ETCST of FeCo mPBAs at solid-state shares many similarities with the spin transition of SCO compounds. Therefore, many structure-property correlations for SCO compounds are also valid for ETCST ones. According to M. Nihei\textsuperscript{88}, the ETCST behaviors of mPBAs depend at first on the nature of the blocking ligands on the Fe and Co sites,\textsuperscript{89} which determine the redox potentials of the Fe and Co building blocks $[E_{1/2}(M), M = Fe^{II/II} \text{ or } Co^{II/II}]$. If the redox potential difference, $\Delta E_{1/2} = E_{1/2}(Fe^{II/II})- E_{1/2}(Co^{II/II}) = - 0.80$ V, the Fe$_2$Co$_2$ square compound is likely magnetically bistable. The complex tends to be paramagnetic for lower $\Delta E_{1/2}$, and diamagnetic for higher $\Delta E_{1/2}$. H. Oshio and M. Nihei have also demonstrated that the transition temperatures, $T_{1/2}$, of thermal ETCST in solution of a series of four Fe$_2$Co$_2$ complexes are correlated to the $\Delta E_{1/2}$ values: greater $\Delta E_{1/2}$ value leads to lower $T_{1/2}$.\textsuperscript{90}

Depending on the strength of intermolecular interactions, three other parameters of the core structure are often considered for the ETCST of Fe$_2$Co$_2$ squares: the distortion of the coordination environment of Co site, $\Sigma Co$, the distortion of the Co-N≡C-Fe linkage represented by the two angles of Co-N≡C or their average value (N≡C-Fe moiety is considered more rigid), and the H-bond formed between the terminal cyanide and the co-crystallized protic solvent. By analogy with Fe(II) SCO complexes, a large $\Sigma Co$ value stabilizes the paramagnetic state and lowers the ETCST temperature, but a too large $\Sigma Co$ value can block the complexes at its paramagnetic state. For example, Tao Liu’s team has studied the impact of intermolecular interaction on the transition temperature $T_{1/2}$ in five square compounds of $[[[Fe(pzTp)(CN)_3]_2[Co(dpq)_2]_2\cdot2A$ (core structure $[[Fe(pzTp)(CN)_3]_2[Co(dpq)_2]_2$ $= 1$, pzTp = tetrakis(pyrazolyl)borate, dpq = dipyrido[3,2-d:2′,3′-f]quinoxaline; A = BF$_4^-$, PF$_6^-$, OTf$^-$ and $[Fe(pzTp)(CN)_3]$), as show in figure 10. They showed that $\pi - \pi$ intermolecular interactions between dpq ligands in the neighboring $[[Fe(PzTp)(CN)_3]_2[Co(dpq)_2]_2]^{2+}$ moieties could be affected by varying the size of the counter anions. The intensity of the $\pi - \pi$ interactions impacts the coordination sphere and results in different bend angles of the Co-N≡C bonds, and octahedral distortions around the Co center. The stronger $\pi - \pi$ interactions lead to the stronger distortion of the cobalt
coordination spheres and stabilize paramagnetic \{Fe^{III}_{ls}(\mu-CN) \text{Co}^{II}_{hs}\} state as confirmed by DFT calculation. 

![Graph showing plots of χT vs temperature for different compounds](image)

**Figure 10.** Plots of χT vs temperature for $1 \cdot BF_4$, $1 \cdot PF_6-\alpha$, $1 \cdot PF_6-\beta$, $1 \cdot OTf$, and $1 \cdot Fe(PzTp)(CN)_3$

<table>
<thead>
<tr>
<th>Compounds (LT state)</th>
<th>$\angle \text{Co-N≡C}$ (°)</th>
<th>Av. $\pi-\pi$ distance [Å]</th>
<th>$\sum \text{Co}^{a)}$ (*)</th>
<th>CshMCo$^{b)}$</th>
<th>$T_{1/2}$ (K) of the ET or magnetic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \cdot BF_4$</td>
<td>164.2(3)/165.8(3)</td>
<td>3.559(4)</td>
<td>37.7</td>
<td>0.276</td>
<td>333.0/337.6</td>
</tr>
<tr>
<td>$1 \cdot PF_6-\alpha$</td>
<td>163.6(4)/170.5(3)</td>
<td>3.526(1)</td>
<td>63.2</td>
<td>1.082</td>
<td>paramagnetic</td>
</tr>
<tr>
<td>$1 \cdot PF_6-\beta$</td>
<td>159.6(8)/159.7(8)</td>
<td>3.569(8)</td>
<td>47.1</td>
<td>0.409</td>
<td>275.7/277.8</td>
</tr>
<tr>
<td>$1 \cdot OTf$</td>
<td>162.0(5)/171.6(5)</td>
<td>3.576(1)</td>
<td>62.1</td>
<td>1.085</td>
<td>paramagnetic</td>
</tr>
<tr>
<td>$1 \cdot Fe(PzTp)(CN)_3$</td>
<td>161.6(4)/166.7(4)</td>
<td>3.670(3)</td>
<td>36.6</td>
<td>0.271</td>
<td>429.0</td>
</tr>
</tbody>
</table>

(a)$\sum \text{Co}$: the sum of $|90-\alpha|$ for the 12 cis- N-Co-N angles around the cobalt atom;

(b)CshMCo: the continuous shape measurements relative to ideal octahedron of the Co center.

As shown in table 1, two of the square complexes $1 \cdot OTf$ and $1 \cdot PF_6-\alpha$ are paramagnetic in all the studied temperature range because of their too large $\sum \text{Co}$. The chapters 2 - 4 of this PhD thesis will show three other $\text{Fe}_2\text{Co}_2$ compounds trapped at their paramagnetic state by solid phase interactions as well.

The Co-N≡C angles are the specific feature for Fe-Co PBAs and mPBAs. It has been demonstrated that in Fe-Co PBAs, more straight is the Co-N≡C angle, stronger is the ligand field of -N≡C ligand. A smaller Co-N≡C angle stabilizes the paramagnetic state. Then Li D.F. is the first to point out the
effects of the distortion of Co-N≡C-Fe linkage on the magnetic properties of the Fe₂Co₂ square compounds. A too bent Co-N≡C angle will lead to the weakening of the N≡C bond and lower the redox potential on Fe site. This will favor the paramagnetic state and lower the ETCST transition temperature. However, the Co-N≡C angles change are probably correlated to ∑Co for the Fe₂Co₂ square complexes: smaller are the Co-N≡C angles, greater is ∑Co value.⁹²

Figure 11. Plots of χ₁ vs. temperature for {[Fe(Tp*)CN₃]₂[Co(bpy*)₂]₂·(PF₆)₂·2CP·8BN (Left); X-ray crystal structure (Right), Red dotted lines represent HB interactions between terminal cyanide nitrogen atoms N(CN) and phenol oxygen atoms O(CP).

Regarding the H-bond between the terminal CN group and the protic solvent, the protonation of the terminal cyanide nitrogen atoms withdraws electron density from the iron center, leading to stabilization of the iron(II) state. H. Oshio and M. Nihei et al. reported in 2017 a remarkable study demonstrating the H-bond effect on the ETCST behaviors of a Fe₂Co₂ square compound. The tetranuclear complex {[Fe(Tp*)CN₃]₂[Co(bpy*)₂]₂·(PF₆)₂·2CP·8BN (CP), with bpy* = 4,4’-diméthyl-2,2’-bipyridine, and BN = butyronitrile, was co-crystallized with 4-cyanophenol (CP). The H-bond was formed between CN group and CP molecule, and its strength was represented by the interatomic distance between N(CN) and O(CP), dNO, as shown in figure 11. By using variable temperature XRD measurements on single crystal, the authors demonstrated that the electronic configuration of each square in the unit cell depends closely on dNO. The square is diamagnetic with dNO ≤ 2.655 Å and paramagnetic with dNO ≥ 2.70 Å. The compound displays a three-step ETCST, resulting from the thermal evolution of dNO of the two squares in the same unit cell combined with a phase transition.⁹⁴-⁹⁶
Similar to spin transition, the thermal hysteresis of ETCST is often related to the existence of $\pi - \pi$ stacking between the ligands on adjacent metal sites in Fe$_2$Co$_2$ molecular complexes. The long-range interactions are indispensable to ensure the communication between squares and thus the cooperativity of ETCST. As mentioned above, the $\pi - \pi$ stacking of bpy ligands is responsible for the large ETCST hysteresis of 23 K of the first reported Fe$_2$Co$_2$ complexes, $\{([Tp^*]{\text{Fe}^{III}}\text{(CN)}_3]_2 \text{[Co}^{II}\text{(bpy)}_2]_2\cdot\text{[OTf]}_2\cdot\text{4DMF}\cdot\text{2H}_2\text{O}. Another example is given by the ETCST behaviors of a series of four square complexes prepared by Yuan-Zhu Zhang’s group. Their general formula is $\{([Tp^*]{\text{Fe(CN)}_3}\text{Co(bpyC=N(CH}_2\text{)}_7\text{N=Cbpy})]_2[X]_2\cdot\text{sol}$, where the counter-anions, X, is respectively ClO$_4^-(1)$, PF$_6^-$ (2) and OTf$^-$ (3) with sol = 6DMF, and BPh$_4^-$ with sol = 2DMF (4). The peculiarity of these square complexes is that the bpy ligands on the Co ions were connected by the flexible length heptyl chains to form a capsule around the Fe$_2$Co$_2$ squares. Three complexes of the family show interesting complete thermo- ($T_{1/2}^\uparrow = 237$ K, and $T_{1/2}^\downarrow = 233$ K) and photo-induced ETCST, and the fourth is paramagnetic. The bi-stability of the first three complexes were attributed to the existence of the long-range intermolecular interactions of $\pi - \pi$ type, which are absent in 4 due to the steric effect of BPh$_4^-$. Furthermore, the $T_{1/2}$ values are tentatively correlated to the effects of counter-anion, as the H···O and H···F interactions between the solvent, bpy ligand and anions depend on anion’s type.

2 Pressure study of Fe SCO complexes

The application of pressure allows to investigate the thermodynamics and the mechanism of spin transition in solid state in an original way. Under pressure a wide range of spin-crossover behaviors can be observed, from incomplete to complete, gradual to abrupt transitions with and without thermal hysteresis. A general review of the pressure effects on spin transition is out of the scope of this first chapter. Here we would like to introduce at first the notions of “normal” and “abnormal” spin transitions, after giving an example of the pressure-induced phase transition of a SCO complex. Then, we will gives the examples of pressure-induced spin transition of several paramagnetic complexes of Fe(II).

2.1 Pressure-induced phase transition of a SCO complex of Fe(II)

Numerous pressure studies on the thermally and photo-induced spin transition have been reported for the SCO complexes of Fe(II) coordinated by pseudo-halide ligands.$^{98-102}$ One of the studies has
been carried out on [Fe(PM-Bia)₂(NCS)₂] (PM-Bia=(N-(2′-pyridylmethylene)-4-aminobiphenyl)) complex by V. Ksenofontov in 1998. At atmospheric pressure, a complete and abrupt thermal spin transition is observed with a hysteresis of 5 K width as shown in figure 12. When the pressure is increased up to ca. 0.60 GPa, the width of the hysteresis loop is reduced. At higher pressures (0.73 GPa - 0.79 GPa) the hysteresis width is enlarged to approximately 25 K. Above 1.0 GPa, the spin transition becomes more gradual and the hysteresis width diminishes slightly. Further increase of pressure has no additional effect (almost the same at 1.14 GPa and 1.26 GPa). The obviously different hysteresis loop shape (open squares: below 0.61 GPa; filled circles: above 0.73 GPa) suggests a phase transition between 0.61 and 0.73 GPa, and both phases exhibit first-order spin transition with thermal hysteresis.

![Figure 12. Plot of the high-spin molar fraction, γ_{HS}, vs. T at different pressures for [Fe(PM-Bia)₂(NCS)₂]](image)

2.2 “Normal” and “abnormal” spin transitions under pressure

If a thermal spin transition becomes more gradual under pressure or if the thermal hysteresis narrows or disappears when the pressure is increased, the spin transition is called a normal spin transition. The complexes of Fe(phen)₂(NCX)₂ (phen = phenanthroline; X = S, Se) are among the most extensively studied SCO system complexes of iron (II). At ambient pressure, the transition curve is extremely steep with T_{1/2} = 177 K with a narrow thermal hysteresis. The hysteresis disappears upon the application of a pressure of 0.17 GPa, and the transition temperature shifts upward when the pressure increases. Furthermore, the shape of the spin-transition curve become more and more gradual with pressure increasing, as shown in the figure 13. Many compounds with abrupt spin transitions at ambient pressure show such typical pressure-induced SCO behavior.
The compounds of $[\text{Fe(2-pic)}_3]\text{Cl}_2\cdot\text{EtOH}$\textsuperscript{108} and $[\text{Fe(bt)}_2(\text{NCS})_2]$\textsuperscript{109} (pic = 2-picolyamine, bt = 2, 2'-bi-2-thiazoline) are other typical examples, where the transition temperature increases and the hysteresis and the slope of the transition curve diminish as pressure increases. Their pressure-induced magnetic behaviors are thus said “normal”, the hysteresis vanishes at a critical pressure, and at even higher pressures the transition transforms to the more gradual type.\textsuperscript{110}

Figure 13. Molecular structure (a) and the $\chi_M T$ vs $T$ curves at different pressures for $[\text{Fe(phen)}_2(\text{NCS})_2]$ polymorph II (b).

Beside the “normal” behaviors of spin-transition complexes under pressure, a particularly interesting “abnormal” behavior has been described for few spin-transition complexes. If a spin transition shows a pressure - enhanced cooperativity whose hysteresis width increases under increasing pressure, such behaviors is considered as a kind of “abnormal” spin transition behavior. For example, the mononuclear compound of $[\text{Fe(bapbpy)}(\text{NCS})_2]$ (bapbpy = 6,6’-bis(amino-2-pyridyl)-2,2′-bpyridine) studied by Gabor Molnár et al., displays a two-step spin transition with thermal hysteresis at ambient pressure as shown in figure 14 for powder and slowly crystalized samples. The low-temperature transition of the powder sample becomes very distorted and nontrivial to rationalize. However, in contrast with most of the other spin transition compounds, pressure dependence of $\chi_M T$ versus $T$ curves clearly shows abnormal behavior for both powder and crystallized sample: the transitions shift to higher temperature and the hysteresis width increases as pressure goes up.\textsuperscript{111}
Another example of abnormal SCO behavior under pressure was discovered for the complex [Fe(phy)$_2$](BF$_4$)$_2$ (phy = 1,10 phenanthroline-2-carbaldehyde phenyl hydrazone) studied by V. Ksenofontov in 1999.\textsuperscript{112} This compound shows an abrupt spin transition with thermal hysteresis under room pressure. Upon the application of pressure up to 0.58 GPa, the hysteresis width increases regularly, as depicted in figure 15. In addition, in this specific case a nonlinear response of $T_{1/2}$ as a function of pressure has been reported. This singular behavior was explained by using the mean field theory by introducing the dependence of the bulk modulus (K) under pressure. Unfortunately, the structural data at high pressure are not available to further probe this unexpected behavior. It is clear that the obtention of the crystal structures under hydrostatic pressure is crucial for establishing relevant magneto-structural, not only for spin transition complexes but also for ETCST ones.
2.2.1 Pressure-induced spin transitions of paramagnetic compounds of Fe(II)

In the literature, few examples of pressure-induced spin transition of the paramagnetic Fe(II) complexes have been reported. In a recent review articles, Ana B. Gaspar and coworkers have given three examples: the mononuclear complexes $[\text{Fe(abpt)}_2(\text{NCS})_2]$ (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) polymorph B$^{114}$ and $[\text{Fe(stpy)}_4(\text{NCBH}_3)_2]_{\text{cis}}$ (stpy = styrylpyridine),$^{115}$ and the di-nuclear compound, $\{[\text{Fe(bpm})(\text{NCS})_2]_2(\text{bpym})\}$ (bpm = 2,2'-bipyrimidine).$^{116}$ All the three compounds are paramagnetic at atmospheric pressure as shown in figure 16 (a, b and c). The two Fe(II) ions are anti-ferromagnetically coupled in the dimer. The pressure-induced spin transitions of the three complexes share some common features: the HS to LS conversion by pressure is partial at low pressure at room temperature, the conversion is complete at 0.86 GPa for $[\text{Fe(abpt)}_2(\text{NCS})_2]$ and almost complete for $[\text{Fe(stpy)}_4(\text{NCBH}_3)_2]_{\text{cis}}$ at 0.50 GPa, and it reaches only 55% for $\{[\text{Fe(bpm})(\text{NCS})_2]_2(\text{bpym})\}$ at 0.89 GPa; All spin transitions are normal SCO process without thermal hysteresis; The transition temperature $T_{1/2}$ increases with increasing pressure and a linear dependence of $T_{1/2}$ on pressure is revealed for these complexes.

Figure 15. The HS fraction versus temperature under applied pressures up to 5.8 kbar for $[\text{Fe(phy)}_2](\text{BF}_4)_2$. 
In 2016 M. Neville and coworkers have reported the pressure-induced spin transition of a 2D Hoffmann-type coordination polymer, [FePd(CN)₄(thiome)₂]·2H₂O [thiome = 4-[(E)-2-(5-methyl2-thienyl)vinyl]-1,2,4-triazole]. The compound is paramagnetic under room pressure, and the structural and magnetic investigations reveal that the spin transition is inhibited by the combined effects of the steric hindrance and quest molecule (H₂O). Upon pressure application, a partial one-step spin transition appears which becomes a more complete two-step one when the pressure is greater than 0.42 GPa (figure 17). The first step is more abrupt and occurs within 30 K whereas the second one is more gradual but with thermal hysteresis. The structural results under pressure suggest that the polymer layers distort to accommodate the volume change from the HS to the LS state. Moreover, the application of pressure strengthens the intermolecular interactions leading to a cooperative spin transition.
3. Pressure effects on the ETCST of Co-Fe systems

3.1 Pressure study on PBAs

The magnetic Prussian blue analogues (PBAs) are an interesting class of cyanide-based coordination polymers with a diverse range of properties, including spin-crossover, ETCST, and photo-induced bistability. The varied functionality of this material can be attributed to the compositional and structural versatility. PBAs have similar structures than double perovskites, and their general formula is \( \text{AxBy[B'(CN)\_6]z} \), where A, which is not always present, is an alkali metal and B and B' are transition metal ions. The pressure application can modify the structures and a number of physical properties of PBAs, such as magnetic ordering temperature, phase transition, SCO transition, and ETCST. Pressure can also trigger the cyanide linkage isomerization of PBAs. However, among so many pressure studies of PBAs, few reports concern the pressure effects on the ETCST of Co-Fe PBAs.

In 2003, in order to provide a deeper understanding of the charge transfer process in Co-Fe Prussian blue analogs, Vadim Ksenofontov et al. have studied the magnetic properties of three FeCo PBAs under several hydrostatic pressures: \( \text{K\_0.1Co\_4Fe(CN)\_2.7\_18H\_2O} \), \( \text{K\_0.28Co\_4[Fe(CN)\_6]2.76\_18H\_2O} \), and \( \text{Cs\_0.7Co\_4[Fe(CN)\_6]2.9\_16H\_2O} \). In these three compounds, the Co/Fe ratios are 1.48, 1.45, and 1.38. As shown in figure 18(a), the \( \chi_M T \) vs T plots of \( \text{K\_0.1Co\_4Fe(CN)\_2.7} \) measured at ambient pressure indicate an antiferromagnetic interaction and a ferrimagnetic ordering below ca. \( T_C \approx 16 \) K. Upon the application of a pressure of 0.4 GPa, the \( \chi_M T \) values decrease strongly, indicating a pressure-induced conversion of paramagnetic Fe-Co pair into diamagnetic one. These pressure-induced diamagnetic pairs show a thermally-induced ETCSTs observable between 200 - 300 K for pressure between 0.4 - 0.73 GPa. The transition is shifted to higher temperature as the pressure increases.

In the case of \( \text{Cs\_0.7Co\_4Fe\_2.9\_16H\_2O} \) (Figure 18b), the compound shows an ETCST near 200 K at ambient pressure. In this case, the application of small pressure of 0.07 GPa causes a significant shift of the transition toward higher temperature and a decrease of the residual \( \chi_M T \) value at low-temperature. Further increase of pressure not only shifts the transition in the \( \chi_M T \) vs T curve to higher temperatures, but monotonically decreases the residual low temperature baseline. For \( \text{K\_0.28Co\_4[Fe(CN)\_6]2.76\_18H\_2O} \) (Figure 18c), a pressure-induced transition appears as the pressure increases. As expected, it is again shifted to higher temperature range upon pressure increase. The joint study of the magnetic properties and hyperfine interactions by Mössbauer spectroscopy in
these three PBAs compounds under pressure provides the clear evidence of pressure-induced electron transfer $\text{Co}^{2+}(S = 3/2) - \text{NC-Fe}^{3+}(S = 1/2) \rightarrow \text{Co}^{3+}(S = 0) - \text{NC-Fe}^{2+}(S = 0)$.

Figure 18. Temperature dependence of $\chi_M T$ for $\text{K}_{0.1}\text{Co}_4\text{Fe(CN)}_{6}\cdot 18\text{H}_{2}\text{O}$ (a); $\text{Cs}_{0.7}\text{Co}_4[\text{Fe(CN)}_6]_2\cdot 16\text{H}_{2}\text{O}$ (b) and $\text{K}_{0.28}\text{Co}_4[\text{Fe(CN)}_6]_2\cdot 18\text{H}_{2}\text{O}$ (c) at different pressures. Measurements at 1 bar after release of pressure reveal a reversible behavior in the samples.

The pressure-induced ETCST of $\text{K}_{0.1}\text{Co}_4\text{Fe(CN)}_{6}\cdot 18\text{H}_{2}\text{O}$, abbreviated as $c_0$, has been later investigated again at room temperature by A. Bleuzen et al., using energy dispersive X-ray diffraction and X-ray adsorption spectra in an extended pressure range ($0 - 6$ GPa). This investigation has evidenced the complicated interplay of structural and electronic events in $c_0$ under pressure. At room pressure, $c_0$, essentially composed of $\text{Co}^{II}(\text{HS})$ and $\text{Fe}^{III}(\text{LS})$, has a faced-centered cubic structure. The rigid entity $[\text{Fe}^{III}(\text{CN})_6]$ is highly stabilized in its octahedral symmetry with short $\text{Fe}-\text{C}$ distances ($\approx 1.92$ Å) and quasi-linear FeCN angles. The $\text{Co}^{II}$ ions coordinated with $\text{H}_2\text{O}$ molecules and $[\text{Fe}^{III}(\text{CN})_6]$ have longer Co-ligand distances and therefore weak Co-ligand interactions. The weak point of the structure under pressure is the articulation between $\text{Co}^{II}$-$\text{N}$ and NCFe$^{III}$. The tilt of the rigid $[\text{Fe}^{III}(\text{CN})_6]$ entity induced by pressure leads to the decreasing of the $\text{Co}^{II}$-$\text{NC}-\text{Fe}^{III}$ angle and the shortening of the $\text{Co} - \text{Fe}$ distance. The phase transition of $c_0$ from cubic structure to rhombohedral structure occurs before 1 GPa. Above 1 GPa, the important tilt of $[\text{Fe}^{III}(\text{CN})_6]$ triggers the conversion of $c_0$ from paramagnetic to diamagnetic state accompanied by the linearization of $\text{Co}^{III}$-$\text{NC-Fe}^{II}$. At $P = 2$ GPa, the pressure-induced ETCST is complete, and $c_0$ is mainly composed of $\text{Co}^{III}(\text{LS})$ and $\text{Fe}^{II}(\text{LS})$.

More recently, the pressure-induced ETCST of $c_0$ has been studied again besides Mn-Fe PBAs. The pressure has completely opposite effects on the low temperature ordering of the two PBAs: the
maximum $\chi_m T$ of $c_0$ decreases and then disappears with increasing pressure, whereas that of Mn-Fe PBAs increases. The two phenomena have the same origin: the pressure-induced charge transfer.

### 3.2 Pressure effects on a cyanide-bridged Fe$_2$Co$_2$ square compound

To our knowledge, there was only one study about pressure-induced ETCST in Fe$_2$Co$_2$ discrete compounds when we initiated this work (from Li Don Feng’s group). In this study, Cao et al. investigated the piezo-chromic property of the square complex $\{[\text{Fe(Tp})(\text{CN})_3]_2[\text{Co(4,4’-bcbpy)}_2]_2\}\text{(ClO}_4\text{)}_2$ which exits a reversible, gradual and partial ETCST around room temperature. This compound was obtained by the desorption of MeOH and a single crystal-to-single crystal (SC-SC) transformation from $\{[\text{Fe(Tp})(\text{CN})_3][\text{Co(4,4’-bcbpy)}_2]_2\}\text{(ClO}_4\text{)}_2\cdot 2\text{MeOH}$. The compound shows a normal pressure-induced magnetic behavior: no cooperativity (hysteresis) was observed, and the transition becomes more gradual with increasing pressure, as shown in figure 19.

![Figure 19. Crystal structure of $\{([\text{Tp})\text{Fe(CN)}_3]_2[\text{Co(4,4’-bcbpy)}_2]_2\}\text{(ClO}_4\text{)}_2$ (Left) and $\chi_m T$ vs. T plots of the complex under different hydrostatic pressures (H = 5000 Oe) (Right).](image)

Due to the lack of pressure study of those cyanide Fe$_2$Co$_2$ molecular complexes, we decided to explore further this rare and interesting research field. Our laboratory has been investigating the Fe$_2$Co$_2$ square compounds since 2009 by using the ligands of Tp family (Tp = hydrotris (pyrazol-1-yl)borate) on Fe building bloc and the ligands of bik family (bik = bis(imidazolyl)ketone) on the Co one.
In chapter 2, we investigated the conversion by pressure for our first paramagnetic Fe$_2$Co$_2$ square, \{[Fe(Tp)(CN)$_3$)$_2$[Co(vbik)$_2$]$_2$)(BF$_4$)$_2$·2MeOH (1), into a bistable complex [vbik = bis(1-vinylimidazol-2-yl)ketone]. The HP-magnetic and HP-Raman measurements reveal the reversible and complete conversion of the Fe$^{III}$Co$^{II}$ paramagnetic state into a Fe$^{II}$Co$^{III}$ diamagnetic state of 1 by pressure. More importantly, the compound displays an abnormal ETCST behavior: its thermal hysteresis broadens with increasing pressure. We have carried out the HP-XRD measurements on single crystal of 1 in order to find the molecular origin of this unusual phenomenon.

In chapter 3, the BF$_4^-$ counter ion of compound 1 has been replaced by a PF$_6^-$ counterion. We thus kept the same core complex: a red crystal phase of \{[Fe(Tp)(CN)$_3$)$_2$[Co(vbik)$_2$]$_2$)(PF$_6$)$_2$·2MeOH (compound 3) obtained by controlling the crystallization temperature, which maintains the transition temperature in solution close to room temperature. The paramagnetic compound 3 shows different magnetic properties under pressure compared with compound 1, helping us to understand the impact of structural change and supramolecular interaction on the pressure-induced behavior of these compounds.

In chapter 4, we continue our efforts to study the pressure-induced ETCST by changing not only the counter ion but also the blocking ligands on Fe and Co sites. The compound \{[Fe(Tp*)(CN)$_3$)$_2$[Co(Mebik)$_2$]$_2$)(BF$_4$)$_2$·2H$_2$O (5) (Mebik = bis(1-methyl imidazole-2-yl)ketone)) shows a two-step transition under pressure. The XRD structural analyses showed a completely different crystal packing in 5, with intermolecular interactions that seem weaker (e.g., pseudo-H-bonds). We have demonstrated that the H-bond involving the terminal cyanide and the solvent molecule might play an important role in the paramagnetic to diamagnetic transition. Probably due to the weaker intermolecular interactions, the para to dia conversion of 5 by pressure is much more gradual.

In chapter 5, we successfully isolated a new compound \{[Fe(Tp)(CN)$_3$)$_2$[Co(vbik)$_2$]$_2$·2ClO$_4$·2CH$_2$Cl$_2$ (6) which shows a complete thermally-induced ETCST with a reversible hysteresis loop of 18 K at ambient pressure. In continuation to the works mentioned in previous chapters, we have drawn possible structure-properties correlation, and tried to demonstrate that the geometrical parameter, metal distortion, and intermolecular interactions (pseudo-π-π intermolecular interactions) in the supramolecular structures of Fe$_2$Co$_2$ square compounds could influence their ETCST properties.
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Chapter 2

Pressure-induced conversion of a paramagnetic square

\{[\text{Fe(Tp)(CN)}_3]_2[\text{Co(vbk)}_2]_2\text{(BF}_4)_2\cdot2\text{MeOH (1)}\} \text{ into a molecular magnetic switch}
1. Introduction

The first bistable cyanide-bridge FeCo tetranuclear complexes, which can be seen as a molecular model of the well-known FeCo Prussian blue analogues (PBAs), have been published in 2010.\(^1,^2\) Since then, the electron transfer coupled spin transition (ETCST) which occurs in these complexes has been intensively studied by several research groups in the world, both in solution\(^5^-^7\) and in the solid states.\(^6\) Actually, light irradiation, temperature, and pressure changes were proven to be efficient means to adjust the energy gap between two electronic states (or valence tautomeric forms) of square-like compounds \([\text{diamagnetic Fe}^{II} \text{LS} \text{Co}^{II} \text{LS} \text{and paramagnetic Fe}^{III} \text{LS} \text{Co}^{II} \text{HS}]\). However, most of the published studies focus almost exclusively on the light-induced and thermally activated ETCST process and deal rarely with pressure-induced one. Actually to our knowledge, there was only one reported pressure study on charge-transfer FeCo molecular complex before we started this work.\(^7\) As described in the general introduction, most of the knowledge on the impact of pressure on switchable magnetic systems comes from the studies on spin-transition compounds and Fe-Co PBA inorganic polymers.

Unlike light and temperature which normally favors the paramagnetic state, pressure stabilizes the diamagnetic state at which the complexes have shorter metal-ligand bond length and smaller molecular volume. Therefore, the application of pressure is expected to shift the transition temperature of a bistable compound, \(T_{1/2}\), upward, as it was observed in spin-transition complexes or FeCo PBAs. Furthermore, pressure could also modify the core structure (for example, the distortion of the coordination sphere), which may influence the diamagnetic-paramagnetic energy difference.\(^8\) Pressure is also expected to impact the crystal packing (intra- and intermolecular interactions of the bistable compounds), which should influence the ETCST dynamics and hence the cooperativity of the systems. Such effect has been observed in SCO compounds.\(^9\) Most of these compounds display a so-called normal behavior\(^10\) which has two following features: (i) their spin transition becomes more gradual upon pressure increase; (ii) if there thermal hysteresis exists, it gets narrower or is even suppressed with increasing pressure. However, several spin transition compounds have shown abnormal behavior under pressure: their thermal hysteresis becomes larger when pressure increases.\(^11\) The abnormal behavior is rare and far more interesting than the normal one, since it leads to bi-stability domain and memory effect, but its origin is not well-understood. By analogy with spin transition compounds, the de-solvated Fe\(_2\)Co\(_2\) square reported by
Li D. F. et al in 2014 displayed a normal behavior: its initially gradual and partial ETCST transition becomes more gradual upon the application of pressure.

This chapter describes the conversion by pressure of the paramagnetic Fe$_2$Co$_2$ square of formula \([\text{[Fe(Tp)(CN)$_3$]$_2$[Co(vbik)$_2$]$_2$}(\text{BF}_4)_2\cdot2\text{MeOH}} (1)\), into a bistable complex. The study of the thermally activated ETCST transition of 1 under different pressures was carried out by HP magnetic measurements. The pressure-induced ETCST transition at room temperature was probed by high-pressure X-ray diffraction measurements on single crystal (HP-SC-XRD) and HP-micro-Raman measurements. The square compound 1 is in fact an ETCST compound trapped in paramagnetic state at low temperature in the solid state. As reported before this work, during its synthesis, 1 undergoes an ETCST transition in MeOH solution at room temperature. The paramagnetic form is in equilibrium with the diamagnetic form. The crystallization of the mother solution can therefore yields two different compounds according to the crystallization temperature: a red-colored paramagnetic compound 1 is obtained at high temperature (ca. 35 - 40 °C), a green-colored diamagnetic compound \([\text{[Fe(Tp)(CN)$_3$]$_2$[Co(vbik)$_2$]$_2$}\cdot\text{MeOH}\cdot10\text{H}_2\text{O}} (2)\), at low temperature (ca 5 °C). The figure 1 recalls the thermal variation of the $\chi_M T$ product for the two compounds in solid state in the temperature range of 2 - 400 K ($\chi_M$ being the molar susceptibility). The compound 2 exhibits an irreversible ETCST transition at about 325 K, whereas 1 seems to be completely paramagnetic in the whole temperature range with standard conditions of magnetic measurements (temperature scanning rate = 2 K/min). The shape of $\chi_M T$ versus T curve for 1 is due to the combined effects of spin-orbit couplings (SO) on the high-spin Co$^{II}$ and low-spin Fe$^{III}$ ions, weak magnetic exchange interactions between metal ions and antiferromagnetic intermolecular interactions at low temperature (<10K). The equilibrium of the two tautomeric forms of the Fe$_2$Co$_2$ square in solution and the occurrence of an ETCST behavior near room temperature in 2 indicate that the diamagnetic and paramagnetic states have similar potential energy. We can thus expect to convert the paramagnetic compound 1 into a diamagnetic one by application of pressure. We could also expect to observe a thermally induced ETCST in the pressure-induced diamagnetic state.
2. Syntheses and magnetic characterizations of the two compounds

2.1 Syntheses and IR spectra of 1 and 2

The synthesis, XRD measurements at ambient pressure and IR analysis of compounds 1 and 2 have been described in a previous publication. In order to underscore the role of the H-bond between the terminal CN group and the solvent (MeOH) of compound 1, we have also synthesized the compound 1D by replacing CH$_3$OH by CD$_3$OD in 1. The magnetic measurements of compound 1D have been accomplished and the HP-SC-XRD analysis are planned this year.

The IR spectra of compounds 1 and 2 are presented in figure 2. The typical cyanide stretching vibration peaks are observed at 2135 cm$^{-1}$ (ascribed to Fe$^{III}$-CN moieties) and 2155 cm$^{-1}$ (ascribed to...
Fe\textsuperscript{III}-CN-Co\textsuperscript{II} bridging cyanide link) in compound 1 whereas characteristic peaks at 2058 cm\textsuperscript{-1} (non-bridging Fe\textsuperscript{II}-CN), 2109 cm\textsuperscript{-1} and 2126 cm\textsuperscript{-1} (due to Fe\textsuperscript{II}-CN-Co\textsuperscript{III} bridges) are observed in compound 2. A remarkable difference between the two IR spectra also occurs for the carbonyl vibration, which is shifted toward lower wavenumbers position in 2.

### 2.2 Study of kinetically trapped ETCST and thermal relaxation of 1 in solid-state

#### 2.2.1 Kinetically trapped ETCST in 1

The fresh sample of 1 was at first measured in the temperature range of 2 - 300 K at 2 K/min. No obvious ETCST transition was observed in the whole temperature range. However, by slowing down the scan rate of temperature (ST) to 0.1 K and 0.01 K / min, a partial ETCST transition appears around 140 K when ST = 0.1 K/min, and the ETCST becomes more complete when S = 0.01 K/min. At 110 K, the $\chi_{M}T$ value is 6.80, 6.53 and 6.15 cm\textsuperscript{3}mol\textsuperscript{-1}K respectively for ST = 2.0, 0.1 and 0.01 K/min. When calculated the proportion difference with the $\chi_{M}T$ value at ST = 2 K/min, about 3.97% proportion of the compound shows a partial transition at ST = 0.1 K/min in the temperature range of 110 - 160 K, and the proportion of transition compound increases to 9.55% with decreasing the scan rate to 0.01 K/min. This result reveals a kinetically inhibited ETCST of 1 with a much lower transition-temperature than the one observed in solution or in phase 2 (325 K). This downward shift of the transition temperature is likely related to solid-state effects that impact the molecular structure of 2, which on its turn influences the electronic-state energy in 1, and stabilizes the paramagnetic state.

![Figure 3. Plots of $\chi_{M}T$ vs T at three different variation rates of temperature for compound 1: 2 K/min (red circle), 0.1 K/min (magenta circle) and 0.01 K/min (olive circle).](image)

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2.2.2 Thermal relaxation of compound 1

Thermal relaxation is a method often used to measure the lifetime of the high-spin state in spin transition complexes, obtained either by photoexcitation or quenching of the compounds at high-spin state. Since compound 1 shows an apparent kinetic trapping of the paramagnetic state, we measured its thermal relaxation of the magnetization at three different temperatures from 120 to 135 K to estimate its activation energy \((E_a)\).

The relaxation from HS to LS has been well studied in the spin transition compound systems, we will use here the same formalism as that used for spin transition complexes. For the compounds with non-cooperative behavior, the thermal relaxation obeys to the two following laws:

\[
\gamma_{\text{HS}}(t) = \exp\left[-K_{\text{HL}}(T)t\right] \quad (1)
\]

\[
K_{\text{HL}} = K_{\text{HL}}^0 \exp\left(-E_a / k_B T\right) \quad (2)
\]

Where \(E_a\) is the activation energy associated with the HS-LS (para-dia) relaxation, \(\gamma_{\text{HS}}(t)\), the high spin fraction (paramagnetic fraction in our case) of the compounds at time \(t\). \(k_{\text{HL}}(T)\) stands for the relaxation rate at \(T\), \(k_{\text{HL}}^0\) is the pre-exponential factor.\(^{13,14}\)

As \(\gamma_{\text{HS}} \propto (\chi_T - \chi_\infty T) \propto [M(t) - M_\infty]\) with \(T\) constant, the equation 1 becomes:

\[
\chi_T = \chi_0 T \exp\left[-(t/\tau)^\beta\right] + \chi_\infty T \quad (3)
\]

where the \(\chi_T\) is product of temperature and the molar susceptibility, and \(\chi_\infty T\) \((M_\infty)\) is the value of \(\chi_T\) (magnetic moment) when relaxation time is approaching to infinity. In order to take into consideration of the inhomogeneity of the system, which gives rise to a distribution of \(E_a\) value, a stretched exponential constant \(\beta\) value is sometime used. Thus, the eq (4) derived from eq (3) is written as:

\[
M(t) = M_0 \exp\left[-(t/\tau)^\beta\right] + M_\infty \quad (4)
\]

Besides, the relationship between \(\tau\) and \(T\) can be written as eq (5) when replacing \(K_{\text{HL}}\) by \(\tau = 1/K_{\text{HL}}\) and \(\tau_0 = 1/K_{\text{HL}}^0\):

\[
\ln(\tau) = E_a/k_B T + \ln(\tau_0) \quad (5)
\]

Here, \(\tau\) is the relaxation time at \(T\), and \(\beta\) is a constant at a given temperature.
Figure 4 shows the isothermal relaxation curves of 1 at three temperatures. In a typical experiment, 1 is directly introduced into SQUID magnetometer at 150 K and the temperature is then quickly reduced to the temperature of relaxation. 1 is thus quenched in its metastable state by rapid cooling, and the measurements of magnetic moment versus time are started when the temperature is stabilized at 120 K, 130 K and 135 K. Above 140 K, the relaxation is so rapid that the relaxation process cannot be recorded. The magnetization versus time curves shows an exponential decreasing following eq (4). The simulation of these curves leads to the values listed in the table 1. The $M_\infty$ values are obtained by the fitting of the experimental $M(t)$ data according to the eq (4). By drawing the relationship of $\beta$ value and $M_0$, $\tau$ value, we can find the optimum $\beta$ value for the smallest fitting residual parameter of $R$ ($R = \sum_n(M_{\text{calc}}-M_{\text{exp}})^2/ \sum_n M_{\text{exp}}^2$, $n$ is the number of data, $M_{\text{calc}}$ and $M_{\text{exp}}$ are calculated and experimental magnetic moments respectively).

<table>
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<tr>
<th>$\beta$</th>
<th>$R \times 10^{-6}$</th>
<th>$\tau \text{ (min)}$</th>
<th>$M_0$</th>
<th>$M_\infty$</th>
</tr>
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<td>Relaxation temperature: 120 K</td>
<td></td>
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<td></td>
<td></td>
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<tr>
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<tr>
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<td>1505.50</td>
<td>0.00102918</td>
<td>0.000967805</td>
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</tbody>
</table>

Table 1. Simulation value of relaxation process at low temperature
As shown in figure 5(a), the optimal $\beta$ value is 0.8 (corresponding to the lowest $R$ values for the three temperatures). We have plotted $\ln(\tau)$ versus $1/T$, as shown in figure 5(b). The linear regression of the straight line, $\ln(\tau)$ versus $1/T$, ($R = 0.98977$) gives $\ln(\tau_0) = -8.2540$, and $E_a/\hbar = 1855.27$ K, which correspond to $\tau_0 = 0.1262$ s, and an activation energy $E_a = 1289.41$ cm$^{-1}$.

There are only very few relaxation studies on molecular FeCo charge transfer systems, generally on photo-induced metastable state. In 2010, Clerac’s group has investigated the thermal relaxation of a quenched paramagnetic Fe$_2$Co$_2$ square $\{[\text{Fe}^{III}(\text{Tp}^*)(\text{CN})_3]_2[\text{Co}^{II}(\text{DMF})_4]_2(\text{OTf})_2\cdot2\text{DMF}\}$ in the temperature range of 100 - 124 K. They have found the following relationship between the relaxation time and the temperature: $\tau = 9.1 \times 10^{-9} \exp (2854/T)$, which can also be expressed as $\ln(\tau) = 2854/T - 18.51$ ($\tau_0 = 0.0001238$ s, $E_a = 2854$ K = 1983.5 cm$^{-1}$). The compound 1 has lower activation energy and higher $\tau_0$ value compared with the compound of $\{[\text{Fe}^{III}(\text{Tp}^*)(\text{CN})_3]_2[\text{Co}^{II}(\text{DMF})_4]_2(\text{OTf})_2\cdot2\text{DMF}\}$. The activation energy of these two squares $\{[\text{Fe}^{III}(\text{Tp}^*)(\text{CN})_3]_2[\text{Co}^{II}(\text{DMF})_4]_2(\text{OTf})_2\cdot2\text{DMF}\}$ are much higher than these $A \subset [\text{Fe}_4-\text{Co}_4]$ cyanido cubes ($A = K, \text{Rb, and Cs}$) $(E_a$ is in the range of 150 – 200 cm$^{-1}$).
2.3 Structural characterizations of the two compounds at ambient pressure

2.3.1 Crystal structure and crystal packing of 1 and 2 at ambient pressure

We remind here that the description of the crystal structure of 1 [{Fe(Tp)(CN)₃}₂{Co(vbik)₂}₂(BF₄)₂·2MeOH and 2 [{Fe(Tp)(CN)₃}₂{Co(vbik)₂}₂(BF₄)₂·MeOH·10H₂O, has been published before this Ph.D. work. Both compounds crystallize in P1 space group. The cobalt-cyanide bond length, ca. 2.1 Å in 1 and 1.9 Å in 2, are characteristic of Co(II) and Co(III) respectively. They are also coherent with the cyanide stretching vibrations observed in the IR spectra of 1 and 2.

It is worth noticing that there are two square molecule motifs in one molecular crystal unit cell of compound 2 (noted a and b) with almost linear Co-N-C-Fe moieties (⟨∠Co-N-C⟩av = 173.70° for a and 172.96° for b), while the compound 1 has more twisted Co-N-C angles (⟨∠Co-N-C⟩av = 161.62°).
The figure 7 shows the perspective views of 1 (7a) and 2 (7b) from a direction. The two crystal packings are quite different. In 1, cationic sheets of square complexes are formed by the intermolecular interactions involving the vbik ligands parallel to the (a, b–c) plane and separated from each other by BF₄⁻ counterions. In 2 the square a is oriented parallel to b and the square b, parallel to c, and two squares a and two squares b form a large cavity alongside a direction. The two typical distances between the two Co sites are 22.354 Å respectively. The cavity is filled with solvent molecules (H₂O and MeOH).

Figure 7. Perspective views from a direction of the crystal packing in 1 (left) and 2 (right) (Co: violet, Fe: green, C: gray, N: light blue, O: red, F: yellow, B: pink. H atoms have been removed for clarity, and the counter-anions have been omitted for 2).

2.3.2 Intermolecular interactions of 1 at ambient pressure

The two vbiks ligands on Co site are crystallographically nonequivalent, and they are named vbik1 and vbik2 respectively according to the libeling of their oxygen. The figure 8 shows the two types of pseudo π-π stackings between the vbik ligands that connect each square to four other neighboring squares. The π-π stacking of vbik1 pair includes two C-C short contacts (C18-C21), two C-O short contacts (C17-O1) and an antiparallel arrangement of two carbonyl groups with a distance of 3.162 Å. The energy of this dipolar interaction can be of the same order as a hydrogen bond of mean intensity. The π-π stacking of vbik2 pair involves only four C-C short contacts (double C27-C31, double C28-C32), and the strength of these nondirectional interaction is much weaker. Overall, the interactions involving vbik1 and vbik2 put a strain on the Co coordination sphere. In contrast, there are not strong intermolecular interactions involving the {Fe(Tp)(CN)₃} subunits.
Figure 8. View of two pseudo π-π stackings organizing the squares of 1 into a 2D layer parallel to the (a, b–c) plane.

Figure 9a. The short contacts of counter-anion BF$_4^-$ in compound 1 at ambient pressure

The counter-anions BF$_4^-$ ensure the cohesion of the square layers by forming F-C and F-H shorts contacts with Tp and vbik ligands belonging to two adjacent layers. These indirect contacts link the squares into 1D chain parallel to c direction, as showed by the figure 9a. The Tp ligand presents also an interlayer π-π stacking (C4-C5) and C-C short contacts (C7-C21), as showed by the figure 9b. The distances are 3.108 Å for C4-C5 and 3.327 Å for C7-C21.
2.3.3 Intermolecular interactions of 2 at ambient pressure

There are no π-π stackings in 2. We can distinguish two types of intermolecular interactions in this compound: the interactions by direct short contacts of the adjacent ligands and that mediated via the counter-anion BF$_4^-$ as showed by figure 10. The direct short contacts include, C-H /C-C contacts, and the indirect short contacts are those between fluorine atoms and the C, H and N atoms of the vbik ligands. The distances of the short contacts are 2.795 Å for C25-H67 and 2.745 Å, for C26-H67.

Figure 10. The direct short contacts between ligands (above) and indirect short contacts via BF$_4^-$ counter-anion (bottom) in compound 2.
2.3.4 H-bond between the terminal cyanide and the protic solvent in 1 and 2 at ambient pressure

The hydrogen bond involving the nitrogen of the terminal cyanide occurs in almost all of the studied square complexes in this thesis when protic solvents such as water or alcohol are used for the crystallization. The hydrogen bond energies cover more than two orders of magnitude, about 0.2 to -40 kcal mol$^{-1}$, on a logarithmic scale, but the bond energy of the N···H-O is roughly in the middle above 20 kcal mol$^{-1}$. The H-bond strength depends greatly on the distances N(CN)···H(solvent) and N(CH)···O(solvent) as well as on the angle N-H-O.

The H-bond was proved to influence greatly the ETCST properties of the switchable square complexes. Indeed, the occurrence of an interaction between an H-donor (H$_2$O, MeOH, etc.) and the nitrogen of the terminal cyanide decreases the electronic density on the cyanide ligand. This is expected to lead to an increase of the oxidation potential of Fe site and a stabilization of diamagnetic state, as shown in Masayuki Nihei’s research work.$^{21}$

Figure 11. View of the hydrogen bonds in compound 1 (left) and 2 (right) at ambient pressure

Here we will consider the distance between the oxygen atom of the methanol solvent and the nitrogen atom belonging to the terminal cyanide ligand to evaluate the hydrogen bond since no accurate location of hydrogen atoms can be found from XRD. We will consider also the angle between the C35···O7···N3 that should be roughly 109° if the H is located close to the O···N axis.$^{21–23}$ As shown in figure 11, in 1, the H-bond distance associated with N3 (free terminal CN of Fe subunit)···O7 (methanol solvent) is 2.844 Å at ambient pressure, and the angle of C35···O7···N3 is 118.04° is close to 109° (H atom is located close to the O···N axis).
In compound 2, we observed two H-bonds involving in terminal CN and methanol solvent, and an important H-bond network formed by water molecules. The two interatomic distances N6-O are 2.591 and 2.885 Å in the two H-bonds. This should favor the diamagnetic state in compound 2, which is coherent with the results in Masayuki Nihei’s work.

3. Thermal ETCST of 1 under various pressures – HP magnetic measurements

3.1 Results of HP-magnetic measurements

The figure 12 illustrates the pressure-driven conversion of 1 (under six different pressure values) from paramagnetic state at ambient pressure to diamagnetic one (para to dia conversion). The pressure-induced diamagnetic state can be subsequently converted into a paramagnetic state by increasing temperature (thermal ETCST transition). The ETCST properties of 1 have two outstanding features: firstly, the para to dia conversion of 1 is complete and starts at a small pressure value of 0.11GPa, as shown in figure 12. Secondly, an interesting and unusual behavior occurs: a hysteresis appears upon pressure, whose width becomes wider as the pressure increases: from 2 to 15 K when raising pressure up to 0.84 GPa. This behavior has been rarely observed in few spin-transition complexes and was named as “anomalous behavior”, in contrast with the usual transitions, which widths decrease or vanish as the pressure increases. Importantly, in the present case a magnetic bistability can be created near room temperature upon pressure application.

Figure 12. Thermal variation of the paramagnetic $\{\text{Fe}^{III}_{2}\text{Co}^{II}_{2}\}$ molar fraction $\gamma_{\text{para}}$ in 1 under various hydrostatic pressures.
This abnormal behavior is reproducible and repeatable. The hysteresis loops can be cycled several times (e.g., 7 times at 0.11 GPa). This phenomenon has occurred in some other cyanide-bridge inorganic polymers and Prussian blue Analogues (PBA). However, it is the second study about pressure-induced ETCST in a discrete FeCo switchable complex, and the first time, an abnormal behavior is observed.

The figure 13 (left) shows a linear relationship between the transition temperatures measured upon heating and cooling process, \( T_{\frac{1}{2}}^{\pm} \) and \( T_{1/2} \) versus pressure. We calculated the formula based on the Clapeyron’s law as observed in spin transition complexes, which was shown as follow:

\[
T_{\frac{1}{2}}(p) = T_{\frac{1}{2}}(0) - (p - p_0) \frac{\Delta V}{\Delta s}
\]

where \( \Delta V \) (negative) is the volume change between diamagnetic and paramagnetic states, and \( T_{\frac{1}{2}}(0) \) is the transition temperature corresponding to the threshold pressure value, \( p_0 \), beyond which ETCST transition takes place. Interestingly, the measured shift rates of \( T_{1/2}^{\pm} \) and \( T_{1/2} \) down (228.4 K GPa\(^{-1}\) and 213.6 K GPa\(^{-1}\), respectively) are larger than those measured in related FeCo PBA, \( K_{0.1}\text{Co}_4[\text{Fe(CN)}_6]_{2.7}\cdot18\text{H}_2\text{O} \) (170 K GPa\(^{-1}\)) and other spin transition solids complexes (190 K GPa\(^{-1}\) - 200 K GPa\(^{-1}\)). The relationship formula can help to approximately predict the pressure value \( p_{1/2}^{\pm} = 0.55 \) GPa and \( p_{1/2} \) down = 0.50 GPa, at which could occur the transition near ambient temperature under isothermal condition. These value can be confronted to those measured by Raman spectroscopy and advanced XRD experiments under pressure.

As depicted above, the increase of the thermal hysteresis loop under pressure, ca. 15 K per GPa, indicates an enhancement of the cooperativity (hysteresis) with increasing pressure. Considering the similarity between SCO and ETCST systems, this abnormal ETCST transition was rationalized in a phenomenological approach by using a microscopic Ising-like mechano-elastic model, which has been successfully used to model various types of spin transition systems but never used yet for ETCST as shown in figure 13 (right). This simple model is based on the description of the Fe\(_2\)Co\(_2\) square by a two-state fictitious spin, \( s \), whose eigenvalues - 1 and + 1 are associated with the diamagnetic \([\text{Fe}^{\text{III}}_{\text{LS}}-\text{Co}^{\text{III}}_{\text{LS}}]\), and the paramagnetic \([\text{Fe}^{\text{II}}_{\text{LS}}-\text{Co}^{\text{II}}_{\text{HS}}]\) states, respectively. These states have different degeneracies, respectively denoted, \( g_{\text{dia}} \) and \( g_{\text{para}} \) with \( g_{\text{para}} >> g_{\text{dia}} \), due to the significant difference of their electronic (spin state) and vibrational (density of states) properties. At 0 K, the fundamental diamagnetic state and the excited paramagnetic state are separated by the energy barrier, \( \Delta E = E_{\text{para}} - E_{\text{dia}} \). In practice, this energy difference is correlated to the differences of redox
potential between the Fe$^{\text{III/II}}$ and Co$^{\text{II/II}}$ couples. The diamagnetic/paramagnetic transition can thus be described using an Ising-like model, whose Hamiltonian is:

$$H = -J_0 \sum_i s_i s_j + \Delta_{\text{eff}} \sum_i s_i$$  \hspace{1cm} (7)$$

Where $J_0 > 0$ stands for the ferro-elastic interaction and the effective energy gap, $\Delta_{\text{eff}} = \Delta_0 - k_B T \ln(g)$, (with $g = g_{\text{para}} / g_{\text{dia}}$) contains enthalpic ($\Delta_0$) and entropic contribution, $k_B \ln(g)$. In this model, the expression of the transition temperature is easily obtained as: $T_{1/2}^0 = \Delta_0 / [k_B \ln(g)]$.

Figure 13. Pressure dependence of the ETCST transition temperatures, heating and cooling $T_{1/2}$ (left); Thermal dependence of the paramagnetic fraction under pressure showing a transformation from a strict paramagnetic state to first-order spin transition as the pressure increases from 0 to 20 kbar in line with the experimental results. The model parameter values are: $g^{0.5} = 150$, $\Delta_0 = 400 \text{K}$, $zJ_0 = 120 \text{K}$, $\alpha = 200 \text{K GPa}^{-1}$, $\gamma = 80 \text{K GPa}^{-1}$ (right).

The phase diagram of the present model is simple: (i) a first-order spin transition with a thermal hysteresis is obtained when $T_C^0 > T_{1/2}^0$, where $T_C^0 = zJ_0 / k_B$, $T_{1/2}^0 = \Delta / k_B \ln(g)$: $z$ is the lattice coordination number; while (ii) a gradual dia/para conversion takes place otherwise. The application of an external pressure, $p$, on the lattice affects both the energy barrier, $\Delta_0$, and the elastic interaction $J_0$, whose expressions become:

$$\Delta = \Delta_0 + \alpha P \text{ and } J = zJ + \gamma P$$ \hspace{1cm} (8)$$

Following the standard resolution of Ising-like models in mean-field approximation, it is possible to express the fraction of paramagnetic state as a function of temperature. According to $\alpha$, $\gamma$, $T_{01/2}$ and $T_{0C}$ values, several behaviors are possible, among them, the present experimental case showing an increase of the thermal hysteresis width (cooperativity) as well as the transition temperature under
pressure. This occurs when \( \alpha \) and \( \gamma \) are taken strictly positive, which means that the pressure strengthens both the energy difference, \( \Delta = E_{\text{para}} - E_{\text{dia}} \) (stabilizing the diamagnetic one with a smaller volume) and the long-range elastic interactions (\( J \)) in the system.

4. P-induced ETCST studied by HP-X-Ray Diffraction measurements on single crystals (HP-SC-XRD)

To further understand the abnormal magnetic behavior in 1, we carried out advanced single – crystal XRD experiments at 300 K under various pressures at Synchrotron Soleil, in collaboration with Lise Marie Chamoreau and Benoit Baptiste.

4.1 The core structure modification of 1 by pressure

The figure 14 shows the change of four types of averaged metal-ligand bond lengths with increasing pressure at 300 K. A clear ETCST occurs in the pressure range of 0.56 GPa to 0.73 GPa. As expected, the average length of the Co-N\(_{CN}\) bridging coordination bonds is above 2.1 Å before the P-induced ETCST range, but it sharply drops from 2.1 to 1.9 Å between 0.56 - 0.7 GPa. Then it remains almost constant even upon further pressure increase. The average bond length of Co-N\(_{vbik}\) ligands also shows the same change behavior. These changes are typical of a high-spin Co(II) and low-spin Co(III) conversion. In contrast, the Fe coordination sphere shows moderate change in ETCST region. The average Fe-C bridging coordination bonds slightly reduce from 1.91 Å below 0.60 GPa to 1.88 Å above 0.73 GPa, and the average Fe-N\(_{Tp}\) bonds increase from 1.98 to 2.0 Å during the ETCST. It is known that iron metal-ligand bonds show weaker changes during ETCST in FeCo charge transfer system.31

Figure 14. Average metal-ligand bond change with increasing pressure (red dots: Co-N (vbik ligand); black dots: Co-N\(_{CN}\) (cyanide bridge); grey green dots: Fe-N\(_{Tp}\) (Tp ligand); blue dots: Fe-C\(_{CN}\) (cyanide bridge), the corresponding lines are for guide eyes)
As usual, the change in the Co-Ligand bond distance is accompanied by a distortion decrease of Co metal sphere as shown in figure 15(a), which shows the pressure dependence of the distortion, ΣCo and ΣFe. The distortion, ΣM, is defined as the sum of the deviation from orthogonality of 12 pseudo-orthogonal angles in the octahedral coordination sphere of the M center (M = Co, Fe). The distortion of Co coordination sphere is indicative of the Co redox state. Here, the total deviation from orthogonality of the twelve N-Co-N angles varies slightly around 35 ° in the pressure range 0 - 0.56 GPa. This agrees with the occurrence of a high-spin Co(II). The drop to 16 ° - 20 ° at higher pressures agrees with the occurrence of a low-spin Co(III). In contrast, the situation is greatly different for the [Fe(Tp)(CN)₃] subunit. There is no significant difference in the distortion between the low-spin Fe⁵C₃N₃ and high-spin Fe⁷C₃N₃ coordination sphere: it only slightly increases from 26 ° to 30 ° in the pressure range of 0 - 1.2 GPa.

The Co-N1-C1 angle does not show large variation that could be clearly ascribed to the ETCST while the Co1-N2-C2 angle decreases with pressure between 0 - 0.3 GPa, remains stable between 0.3 - 0.56 GPa before increasing above 0.56 GPa (figure 15 b). Regarding the conformation of the vbik ligands, the dihedral angle between two imidazole rings and the angle of Co-C-O also did not vary significatively with pressure as shown in figure 15 c and d.

![Figure 15. The molecular distortion of 1 under various pressures](image-url)
4.2 Molecular geometry anisotropic deformation

The local change in the coordination sphere of the metal ions is accompanied by an anisotropic change in the geometry of the square complex: the diagonal distance in Fe···Fe direction notably decreases during ETCST but the one in the Co···Co direction is steadier. As shown in figure 16, firstly, the diagonal distance between Fe···Fe keeps steady at 7.4 Å in the pressure range of 0 - 0.45 GPa, then sharply decreases to 6.8 Å above 0.76 GPa. However, the Co···Co distance direction which slightly decrease from 7.0 Å to 6.8 Å above 0.76 GPa does not show distinct variation when increasing the pressure value (figure 16a). One side keeps almost stationary, and another one is oriented in a preferred direction, it is reminiscent of physical characteristics of anisotropy existing in many materials. This anisotropic deformation of molecular geometry occurring in compound 1 might be related to intermolecular interaction change.

As for the square side distance, both of the Fe···Co distance follow the same trend as shown in figure 16b: they abruptly decrease from ca. 5.1 Å to ca. 4.9 Å between 0.56 GPa and 0.85 GPa. The sudden variation observed in the ETCST range are not transferred to the crystal cell, which show a more regular variation as the pressure increases. As shown in Figure 17, the unit cell parameters, a, b and c, and the crystal cell volume, V, decrease almost linearly as reported in many pressure-induced spin-transition complexes.32

Figure 16. Fe···Fe (Co···Co) diagonal distance vs P(a); Fe···Co side distance vs P (b); scheme of the core structure distance(c).
4.3 Evolution of the intermolecular interactions upon pressure increase

4.3.1 Pseudo π-π interactions vs pressure

The supramolecular organization of the square molecules in the crystal lattice is not greatly changed with pressure variation. However, as mentioned above, an anisotropic deformation of the square core results from the increase of pressure. It might be related to intermolecular interactions change, this change is linked to the shortening of Co-ligand coordination bonds and thus the shortening of the Fe-Co distance but its anisotropic character is to be related to the intermolecular interactions change under pressure. For better understanding how the intermolecular interactions evolve under pressure, and the possible origin of this anisotropic distortion, the number of short contacts between adjacent neighboring molecules has been studied at distinct pressure and the results are shown in table 2.

As mentioned previously, the short contacts between the neighboring square complexes mainly involved the vbik ligands which interact through π-π like interaction. This leads to 2D supramolecular layers that are separated by the BF₄⁻ counterions. The number of contacts between the square complexes and the BF₄⁻ counter-anions ensure a great cohesion of the squares alongside the c direction, so that the shrinkage of the unit cell parameter c under pressure is the smallest: Δa = -4.23%, Δb = -4.80% and Δc = -1.40% for pressure varying from 0 to 1.05 GPa. As shown in figure 9a above, the contacts between these supramolecular 2D layer can be considered as indirect, mediated by the BF₄⁻ counterions.

Besides, the number of short contacts involving the Tp⁻ ligands coordinated to iron does not change a lot with increasing pressure. These short contact distances are also longer than those involving vbik ligands. In the paramagnetic state, almost all contacts between the vbik1···vbik1, vbik2···vbik2 and vbik1···vbik2 are intralayer while the contacts involving Tp ligands are exclusively between the...
supramolecular square’s layer as shown above in Figure 7. In summary, the highest quantity of short contacts observed arises from the vbik1 and vibk2 ligands stackings and their numbers greatly change between $10^{-5}$ GPa and 0.85 GPa as shown in table 2.

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As we depicted at ambient pressure for compound 1, there exists pseudo π-π interactions between vbik1 pair with anti-parallel C=O pair and vbik2 pair without anti-parallel C=O pair. The figure 18 shows contact distance change with increasing pressure. The contact distance of C16-O1 (the C=O-C=O distance in vbik1 pair) displays a sudden decrease from 3.138 Å (para) to 3.027 Å (dia) between 0.56 – 0.73 GPa (P-induced ETCST range). While the contact distances of C27-C31 and C28-C32 in vbik2 pair vary smoothly in all the pressure range studied.

![Figure 18](image.jpg)

Figure 18. The variation of four short contacts distances versus pressure in two vbik pairs: C16-O1 (black, vbik1), C17-O1 (red, vbik1), C27-C31 (blue, vbik2), C28-C32 (green, vbik2). The solid lines are eye-guides.
Furthermore, the angle $O_{1}C_{16}O_{1}$ in vbik1 pair also drops around 0.56 GPa as shown in figure 19, but on the contrary, that angles $C_{28}C_{27}C_{31}$ and $C_{28}C_{32}C_{31}$ in vbik2 pair slightly increase. As the same as the contact distance change situation in vbik1 and vbik2 ligands, the angle associated with vbik1 also take an obvious decrease, but that of vbik2 did not decrease, even increase slightly.

Figure 19. The contact angle among vbik1 and vbik2 change vs P

The π-π interactions of vbik1 pair are stronger than that in vbik2 pair. As the former includes an antiparallel arrangement of two C=O groups, and this build an additional dipolar interaction whose energy values are similar to those of H-bonds ($ca. 10 - 20$ kcal mol$^{-1}$). We believe the stronger intermolecular interactions between vbik ligands in the supramolecular layers put some strain on the cobalt coordination sphere so that these metal site cannot move as much as the iron site under pressure. As mentioned above, the intermolecular interactions involving $Tp^\prime$ ligands are weaker so that the Fe sites could be more mobile with increasing pressure. This is likely responsible for the anisotropic deformation of the square core under pressure. At this stage it is not clear if such anisotropic deformation might be correlated to the abnormal behavior (increase of hysteresis under pressure increase).

4.4 The role of H-bond formed between terminal CN and MeOH solvent

4.4.1 The variation of the interatomic distance O···N against pressure

The application of pressure does not significantly change the methanol solvent position in the crystal structure of compound 1. However, the distance between the O (of the methanol) and the N$_{CN}$ (of
the terminal cyanide bond) noted $d_{(CN-O\text{Me})}$ clearly evolves at various pressure values (as the exact position of the proton involved in the H-bond with the terminal cyanide cannot be determined, we discuss here the $d_{(CN-O\text{Me})}$ distance).

The bond distance $d_{(CN-O\text{Me})}$ is ca. 2.84 Å at ambient pressure. It is notably reduced to ca. 2.71 - 2.74 Å between 0.11 - 0.73 GPa. The change from the paramagnetic to the diamagnetic state is thus accompanied by a shortening of the cyanide-methanol distance. A second decrease of $d_{(CN-O\text{Me})}$ occurs when the pressure reaches 0.90 GPa, after the ETCST, the $d_{(CN-O\text{Me})}$ value decreases to ca. 2.66 Å as shown in figure 20 (left). The decrease of $d_{(CN-O\text{Me})}$ means that the strength of the H-bond increases. Moreover, the $\angle N3O3C35$ is 110.84° at ambient pressure, and keeps small variation with increasing pressure. Before ETCST, the $\angle N3O3C35$ is 108° plus 3°, then 108° minus 3° after ETCST as shown in figure 20 (right). In general, the compound 1 shows approximate 0.2 Å difference of $d_{(CN-O\text{Me})}$ between paramagnetic and diamagnetic state with a small angle variation of $\angle N3O3C35$ (±3° before and after ETCST).

![Figure 20](image)

**Figure 20.** The interatomic distance of terminal CN···O Me (MeOH) vs pressure (left) and the change of $\angle N3O3C35$ vs pressure (right)

### 4.4.2 Raman spectra of compound 1 at different pressures

We have performed the micro-Raman spectrum experiments (300 K) on the single crystal of 1 at different pressures in the Raman shift range of 1400 - 2300 cm$^{-1}$ by using an exciting laser light at 514.5 nm. The figure 21 shows the micro-Raman spectra on single crystal of 1 at room temperature and under various pressures. The stretching cyanide vibration are observed at 2164 cm$^{-1}$ for the
cyanide bridge, \([\text{Fe}^{III}\text{L}_{5}\text{-CN-Co}^{II}\text{H}_{5}]\), and 2132 cm\(^{-1}\) for the terminal \(\text{Fe}^{III} - \text{CN} \) cyanide group. The characteristic \(\text{C=O}\), \(\text{C=N}\), and \(\text{C=C}\) stretching vibrations of vinyl/pyrazole/imidazole/carbonyl are in the range from 1648 to 1655 cm\(^{-1}\). In the “fingerprint” region, pyrazole and imidazole rings give overlapping bands at 1409, 1421, 1455 and 1502 cm\(^{-1}\).

We can monitor the electronic state of the molecule by the Raman shifts variation of the cyanide stretching frequencies, \(v_{\text{CN}}\) bond, and as well as solvent C-H bond change.\(^{36–40}\) As we can see, increase of pressure compresses the intensity of shift at 2164 cm\(^{-1}\) and 2132 cm\(^{-1}\), which belongs to \([\text{Fe}^{III}\text{-CN-Co}^{II}]\) and \([\text{Fe}^{III}\text{-CN}]\) group. The intensity peak of 2164 cm\(^{-1}\) and 2132 cm\(^{-1}\) becomes weak at 0.47 GPa and even invisible at 0.76 GPa.

Besides, the new peak of 2073 cm\(^{-1}\) associated with \([\text{Fe}^{II}\text{-CN-Co}^{III}]\) occurs at 0.47 GPa, but its intensity is weak with further increasing pressure to 0.76 GPa. It is worth noting that there is no obvious intensity increase of diamagnetic states (identified as \([\text{Fe}^{II}\text{-CN-Co}^{III}]\)) with an increase of pressure. The high-pressure micro-Raman results thus indicate that the conversion of \(1\) at room temperature is well advanced at 0.47 GPa and complete before reaching 0.76 GPa, which keeps consistency with the results magnetism and HP-SC-XRD experiments.

Furthermore, the peak at 1502 cm\(^{-1}\) which may arise from H-bonded MeOH molecule shows a sudden blue shift to 1538 cm\(^{-1}\) at 0.47 GPa. This peak is further shifted to 1542 cm\(^{-1}\) when pressure is increased to 1.14 GPa.\(^{41}\) The blue shift of this peak might be related to the enhancement of the H-bond of the terminal CN group, which is reflected by the decrease of the inter-atomic distance between N(CN) and O(MeOH).

Finally, the original spectrum can be recovered when releasing pressure to ambient pressure, showing a good responsibility of the electronic/structural/interaction changes. In order to verify this hypothesis, we further carried out the HP - magnetism measurements on the compound \(1\text{D}\), which can be considered as \(1\) whose MeOH is replaced by CD\(_3\)OD.
4.4.3 Thermal ETCST behaviors of 1 with deuterated methanol (1D) under pressure

In order to further probe the influence of the H-bond on the switchable properties, we replaced CH₃OH solvent by the deuterated CD₃OD to synthesize the analogous, red-colored crystal compound 1-CD₃OD (1D). X-ray diffraction study revealed that 1D shows the same crystal structure as 1 at ambient pressure. The magnetic measurements (see figure 22a) also reveal that the sample shows a paramagnetic state at ambient pressure when measured in standard conditions (2 K/min).

Interestingly, the magnetic behavior of 1D displays obviously different ETCST behaviors compared to 1 (CH₃OH) upon pressure application. 1D shows partial para-to-dia conversion with 10 K hysteresis width at, ca. 0.15 GPa. At higher pressure (> ca. 0.21 GPa), 1D is fully converted to the diamagnetic state, and the subsequent thermal hysteresis width decreases to ca. 8 K. At 0.420 GPa the hysteresis width decreases further to 4 K. Each thermal cycle has been repeated twice, and the χₘT value returns to its initial value when the pressure is released completely in the pressure cell. The relationship between the transition temperatures and the pressure values is also characterized based on the three pressure-induced thermal dependence curves as shown in figure 22b.
In summary, when replacing CH$_3$OH by CD$_3$OD, the pressure-induced ETCST phenomenon has been greatly changed: the para-dia conversion is more progressive and the thermal hysteresis width decreases with increasing pressure, which is a “normal” ETCST behavior as we depicted in the introduction. From these results, it is clear that the H-bond plays a role on the switchable magnetic properties in compound 1.

The influence of the deuteration of the conversion rate at low pressure is coherent with our hypothesis concerning the role of the H-bond in the stabilization of the diamagnetic state. The replacement of CH$_3$OH by CD$_3$OD lead to a weaker methanol – CN bond which does not favor so efficiently the diamagnetic state.

5. Conclusion

In conclusion, we showed that the application of pressure makes it possible to recover the thermally induced charge transfer in a Fe$_2$Co$_2$ complex that shows ETCST in solution but which is kinetically trapped in its paramagnetic state in the solid state. Remarkably, the pressure-induced Fe$^{III}$Co$^{II}$-Fe$^{II}$Co$^{III}$ conversion is reversible and complete even at a small pressure threshold of 0.11 GPa for paramagnetic compound 1. More importantly, the complex displays an abnormal behavior for charge transfer switchable complexes: a hysteresis broadening upon increasing pressure. A theoretical Ising model directly inspired by work on spin transition complexes is used to rationalize
this phenomenon and suggests an enhancement of both the elastic interactions and the $E_{\text{para}} - E_{\text{dia}}$
energy difference.

The abundant XRD structure data of the crystal under various pressures allow the determination of
the p-induced transition region as 0.56 GPa - 0.73 GPa. It also provides us with structural data that
could help figuring out the origin of the abnormal magnetic behavior in 1. The crystal packing is not
significantly affected by the applied pressure. The square molecules show an anisotropic
deformation (contraction and elongation are observed along one diagonal direction). This feature
can be related to the supramolecular organization. The Co sites are strained by the intermolecular
interaction involving peripheral vbik ligands, especially the π-π stacking of vbik1 ligands. The
shortening of the contact distance between the vbik1 might be responsible for the pressure
enhanced cooperativity.

The efficiency of paramagnetic to diamagnetic state conversion in 1 at low pressure seems to be
enhanced by the shortening of the interatomic distance N(CN)···O(MeOH). This is coherent with the
fact that the H-bond strengthening stabilizes the diamagnetic state. The HP-magnetic
measurements on 1D confirm the role of the H-bond on the p-induced para-to-dia conversion and
the thermal ETCST transition.

For further understanding pressure induced ETCST with abnormal magnetic behavior in compound
1, we tried to obtain other square compounds with similar core structure by slightly adjusting the
synthesis condition and then to study their magnetic and structural properties in the following
chapters.
Reference


(5) De, S., Jiménez, J. R., Li, Y., Chamoreau, L. M., Flambard, A., Journaux, Y., ... & Lescouëzec, R. One synthesis: two redox states. Temperature-oriented crystallization of a charge transfer \([\text{Fe2Co2}]\) square complex in a \([\text{FeIIILSCoIIILS}]_2\) diamagnetic or \([\text{FeIIILSCoIIHS}]_2\) paramagnetic state. RSC advances. 2016, 6(21), 17456-17459.


(10) Pressure-Induced High Spin State in \([\text{Fe(Btr)}_2(\text{NCS})_2] \cdot \text{H}_2\text{O}\) (Btr ) 4,4¢-Bis-1,2,4-Triazole)†.Pdf.


Chapter 3
Partial thermal ETCST under pressure and pressure-induced phase transition of a paramagnetic square \{[\text{Fe(Tp)(CN)₃}]₂[\text{Co(vbik)₂}]₂\}(\text{PF₆})₂·2\text{CH}_3\text{OH} (3)
1 Introduction

In this chapter, we continue the investigations of the pressure-induced para-to-dia conversion and of thermally and pressure-induced ETCST transitions of Fe₂Co₂ square compounds. Here we chose to study the compound \([\text{Fe(Tp)(CN)}_3\text{2[Co(vbik)}_2\text{]}_2\text{]}\) \((\text{PF}_6)_2 \cdot 2\text{MeOH}\), which can be considered as square complex 1 whose BF₄⁻ counter-anion is replaced by counterion of PF₆⁻. The change of the counter-anion here aims at varying slightly the intermolecular interactions. A comparative magnetostructural study on a slightly different square may help in understanding the impact of supramolecular interaction on the ETCST behavior of these compounds. We thus keep the same core structure of the complex, which allows for maintaining the transition temperature in solution close to room temperature. By controlling the crystallization temperature, we then expect to isolate different crystal phases at relative different temperatures, and possibly a phase where the complex could be trapped in the paramagnetic state as compound 1.

As expected, we obtained two crystal phases of \([\text{Fe(Tp)(CN)}_3\text{2[Co(vbik)}_2\text{]}_2\text{]}\) \((\text{PF}_6)_2\) : a green phase (4) crystallized at 5 °C and a red phase (3) at 50 °C. As expected, the PF₆⁻ complex exhibits the same optical signature in solution in the UV-vis region. The solution UV-Vis spectra obtained at variable temperature on redissolved crystals of 3 and 4 or directly on the mother solution are all the same, as shown in figure 1 (left). The spectra recorded at different temperatures on re-dissolved red crystals of 3 in the temperature range (0 °C - 40°C) show a significant increase of the broad absorption centered at 750 nm (MMCT band) and a decrease of the absorption between 400 and
500 nm as the temperature is decreased. An isosbestic point is also observed at 500 nm. These features indicate the occurrence of an electron transfer equilibrium in solution between the diamagnetic and paramagnetic states, as the same as previously observed in square 1. Actually, all of our diamagnetic Fe$_2$Co$_2$ square compounds exhibit a MMCT near 750 nm.$^{3-5}$

2 Syntheses, structural and spectroscopic characterizations of the compounds

2.1 Preparation of [{Fe(Tp)(CN)$_3$)$_2$[Co(vbik)$_2$]$_2$}(PF$_6$)$_2$·2CH$_3$OH (3)

A mixture of CoCl$_2$·6H$_2$O (23.7 mg, 0.1 mmol) and vbik (42.4 mg, 0.2 mmol) was dissolved in a 10 ml methanolic solution. Then a 15 ml methanolic solution containing the complex NBu$_4$[Fe$^{III}$(Tp)(CN)$_3$] (59 mg, 0.1 mmol) and a methanolic solution of NBu$_4$PF$_6$ (77 mg, 0.2 mmol) were added subsequently to the previous solution at 50 °C. The resulting orange-red solution was stirred at this temperature in the water bath for 20 minutes, then filtered. Red square-like crystals were obtained in a few days with a yield of 50 % by slow evaporating the solution at 45°C on a sand bath. Elemental analysis calcd (%) for C$_{68}$H$_{60}$B$_2$Co$_2$Fe$_2$N$_{34}$O$_4$F$_{12}$P$_2$ (characterized solvent: 2H$_2$O and MeOH) is that C: 40.89; H: 3.38; N: 23.50; Found: C: 40.26; H: 3.27; N: 23.37. FTIR (KBr, cm$^{-1}$): several characteristic peaks are observed at 2508 cm$^{-1}$ ($v_{B-H}$), 2166 cm$^{-1}$ ($v_{C-N}$), 2126 cm$^{-1}$ ($v_{C-N}$), 2077 cm$^{-1}$ ($v_{C-N}$), 1648 cm$^{-1}$ ($v_{C-O}$), 896 cm$^{-1}$ ($v_{PF_6}$).

2.2 Preparation of [{Fe(Tp)(CN)$_3$)$_2$[Co(vbik)$_2$]$_2$}(PF$_6$)$_2$·MeOH·15H$_2$O (4)

A mixture of CoCl$_2$·6H$_2$O (23.7 mg, 0.1 mmol) and vbik (42.4 mg, 0.2 mmol) was dissolved in a 10 ml methanolic solution. Then a 15 ml methanolic solution containing the complex NBu$_4$[Fe$^{III}$(Tp)(CN)$_3$] (59 mg, 0.1 mmol) and a 5 ml methanolic solution of NBu$_4$PF$_6$ (77 mg, 0.2 mmol) were added subsequently to the previous solution. The resulting orange-red solution was stirred at 50 °C in the water bath for 20 minutes, then filtered. The green square-like crystals were obtained in a few days in a yield of 50 % by slow evaporation of the solution at 5 °C in the fridge. Elemental analysis calcd (%) for C$_{68}$H$_{60}$B$_2$Co$_2$Fe$_2$N$_{34}$O$_4$F$_{12}$P$_2$ (extra characterized solvent: one MeOH and 15H$_2$O) is that C: 36.64; H: 4.07; N: 21.37; Found: C: 36.66; H: 4.19; N: 21.06. FTIR (KBr, cm$^{-1}$): several characteristic peaks are observed at 2502 cm$^{-1}$ ($v_{B-H}$), 2166 cm$^{-1}$ ($v_{C-N}$), 2126 cm$^{-1}$ ($v_{C-N}$), 2077 cm$^{-1}$ ($v_{C-N}$), 1648 cm$^{-1}$ ($v_{C-O}$), 896 cm$^{-1}$ ($v_{PF_6}$).
The crystal of compound 3 lost its shiny color after being left in the air for half hour, but that of compound 4 still keeps green shiny color for one day. In order to prevent solvent loss, 3 and 4 are kept in their mother solutions, like all others solvated square complexes. Depending on the sample preparation prior to each physical measurements (XRD, element analysis, and TGA, etc.), the amount of solvent molecules may vary.

2.3 Thermogravimetric analysis (TGA) of compound 3 and 4

Figure 2 shows the thermal stability of compounds 3 and 4 analyzed by TGA. The crystals of both 3 and 4 were put into TGA device immediately after filtrating from mother liquid, and the TGA curves were recorded under N₂ flow. The compound 3 undergoes a first weight loss between 20°C and 92°C (ca. 3.8%), then a pseudo plateau from 92 °C to 230 °C (with a slight weight loss of ca. 1.3 %), before decomposing above ca. 230 °C. The first weight loss could be associated to the removal of methanol solvent molecules. The TGA results show that the fresh crystals of 3 likely contain more than 2 MeOH molecules in the crystal lattice detected by XRD analysis (described below), because a very little amount of methanol solvent was loaded together with the fresh crystal from the mother liquid when measuring as fast as possible.

The TGA curve of 4 shows a sudden and sharp weight loss (ca. 26.99%) below 100°C, which could be related to the loss of solvent molecules. Actually, as shown below, the crystal packing of 4 consists of the stacking of the two-dimensional supramolecular layers of square complexes that are separated by a lot of solvent molecules. A pseudo plateau is then observed from 100 °C - 230 °C because the sample becomes a solvent-free dry phase. Above 230 °C, the compound starts to decompose at the third stage.
2.4 FT-IR spectra of 3 and 4

As shown in figure 3, the cyanide stretching vibrations observed in FT-IR spectroscopy provide information on the bridging mode of the cyanide ligand and the redox states of the metal ions. For compound 3, typical cyanide stretching vibrations of the Fe$$^{III}$$-CN-Co$$^{II}$$ linkage are observed at 2163 cm$$^{-1}$$ whereas a characteristic band of the nonbridging Fe$$^{III}$$-CN is located at 2133 cm$$^{-1}$$. The small peak at 2078 cm$$^{-1}$$ is typical of the Fe$$^{II}$$-CN-Co$$^{III}$$ linkage and indicates that the paramagnetic red complex can partially evolve during the preparation of the sample (grinding and application of a 10 Kbar pressure for the KBr pellet preparation). The peak near 3138 cm$$^{-1}$$ comes from the C-H stretching vibration and the overlapping peak around 1648 cm$$^{-1}$$ covers the contribution from four functional groups: the carbonyl, vinyl and imidazole rings of vbik ligand, as well as the pyrazole rings of Tp$$^{-}$$ ligand. The broad band of 3430 cm$$^{-1}$$ observed at higher energy position can be ascribed to water molecules involved in hydrogen bonds ($$\nu_{OH}$$). The absorption bands at 1480 cm$$^{-1}$$, 1426 cm$$^{-1}$$, 1310 cm$$^{-1}$$, and 1283 cm$$^{-1}$$ are characteristic of the Tp$$^{-}$$ ligand. The two consecutive bands at 896 and 841 cm$$^{-1}$$ are typical features of PF$$^{6-}$$ ions.

The FTIR spectrum of compound 4 shows similar features as that of 3 (the same peaks are observed for the vbik and Tp$$^{-}$$ ligands) but there are some differences in the position of cyanide vibrations. In the FTIR spectrum of compound 4, the typical cyanide stretching vibrations are observed at 2129 cm$$^{-1}$$, 2113 cm$$^{-1}$$, and 2085 cm$$^{-1}$$. These peaks are similar to those obtained in a previously reported diamagnetic square complex, are respectively assigned to Fe$$^{II}$$-CN-Co$$^{III}$$ linkages and to a nonbridging Fe$$^{II}$$-CN linkage for the lowest vibration.$^{3}$
To sum up, the infrared spectra of compounds 3 and 4 are coherent with the occurrence of paramagnetic and diamagnetic states respectively at room temperature, but traces of diamagnetic contribution appear in 3 that can be related to the sample preparation (grinding and application of pressure).

![Figure 3. FTIR spectrum of compound 3 (left) and compound 4 (right)](image)

3 Magnetic properties at ambient pressure of the compound 3 and 4

The magnetic susceptibility measurements were performed on fresh crystals of compounds 3 and 4 from 2 K - 350 K. Compound 4 shows a full irreversible ETCST transition near ambient temperature (ca. $T_{1/2} = 315$ K) upon heating. The $\chi_M T$ value measured below ambient temperature is around $ca$ 0.0 cm$^3$ mol$^{-1}$K, increasing to $ca$ 7.00 cm$^3$ mol$^{-1}$K at 340 K. The variation of the $\chi_M T$ value corresponds to the changeover of the diamagnetic states (two Co$^{II}_{LS}$ ($S = 0$), and two Fe$^{II}_{LS}$ ($S = 0$) ions for $T < 300$ K) to a paramagnetic state with magnetically isolated two Co$^{II}_{HS}$ ($S = 3/2$, $g = 2.4$), and two Fe$^{III}_{LS}$ ($S = 1/2$, $g = 2.6$) ions, both of the iron and cobalt sites showing significant orbital contributions at 340 K. After heating the sample to 340 K, the compound 4 is trapped in the paramagnetic state. As previously observed in similar [Fe$_2$Co$_2$] square complexes, the thermally-induced ETCST is not reversible upon cooling. This is often associated to the solvent loss leading to the alteration of the ETCST properties. To check this hypothesis, a sample of 4 was desolvated in magnetism device when measuring. As expected, it remains the paramagnetic state in the temperature range of 240 - 350 K.

As shown in figure 4 (left), the compound 3 exhibits a typical paramagnetic behavior due to the occurrence of [Fe$^{III}_{HS}$Co$^{II}_{LS}$] pairs in the temperature range of 2 - 330 K. The $\chi_M T$ value measured at
300 K, ca. 7.50 cm$^3$ mol$^{-1}$K, is close to the expected value (see above). The nonlinear variation of $\chi MT$ product upon cooling is due to the spin-orbit coupling of both ions.\textsuperscript{11} The sharp decrease below 20 K is possibly due to the intermolecular antiferromagnetic coupling or the effect of the magnetic anisotropy.

As described in the previous chapter, magnetic measurements for the compound \textbf{1} at very low temperature scan rates (ca 0.01 K/min) have been carried out to probe for a small partial ETCST occurring below 140 K. Actually, when the $T_{1/2}$ is low (typically below 150-100 K), a kinetic trapping of the paramagnetic state can be responsible for the lack of observed ETCST at “high” temperature scan rate (2K/min). However, in contrast with compound \textbf{1}, no transition is observed in \textbf{3} even at low temperature scan rate (0.01 K/min). This suggests that the paramagnetic state in \textbf{3} is better stabilized than that in \textbf{1}.

In summary, in contrast with the transition observed in solution, the compound \textbf{3} is trapped in the paramagnetic state in the solid-state between 2 and 330 K. The different magnetic properties of \textbf{3} and \textbf{4}, and the impact of the de-solvation show how critical are the solid-state interactions on the switchable properties of these square molecules. For instance, it is known that structural parameters, such as the distortion of the Co coordination sphere (which can be impacted by intermolecular interactions) can play a crucial role on the switchable properties.\textsuperscript{12} In order to better understand the magnetic properties and establish structure-properties correlation, single crystal XRD analyses have been carried out.

Figure 4. Plots of $\chi M T$ vs temperature for compound \textbf{3} (left), and compound \textbf{4} (right)
4 Description of the crystal structures at ambient pressure

The single-crystal X-ray structural analyses of 3 and 4 were performed at 200 K. The selected crystal parameters and the core structure features are listed in the tables 1 and 2 for the two compounds.

3 crystallizes in the triclinic space group P1(2) and the single crystal is orange-red and square-like. Its structure consists of a centrosymmetric cyanide-bridged \( \text{Fe}_2\text{Co}_2 \) square, hexafluorophosphate counter-ions, and co-crystallized MeOH solvent. The Fe site is in \( N_3C_3 \) coordination environment. Each Fe ion is coordinated by a tridentate \( \text{Tp}^- \) ligand with a facial configuration and the remaining coordination sites are occupied by three cyanide carbon atoms. Two out of the three cyanide groups act as bridging ligands between the iron and cobalt atoms. The cobalt site has an \( N_6 \) coordination sphere: two bidentate vbik ligands are coordinated to each cobalt metal ion in cis position, and two cyanide bridges occupy the remaining cis coordination sites. The figure 5 shows the molecular structures of 3 and 4 whose unit cell contains two distinguished squares. For 3, the Fe-CN-Co edges are quasi-identical [5.077 Å and 5.109 Å] and the angles at the corners of the metallic square are close to orthogonality [Co-Fe-Co = 85.67 ° and Fe-Co-Fe = 94.33 °]. The cyanide bridges are notably bent on the cobalt side [Co1-N1-C1 = 159.31 ° and Co1-N2-C2 = 167.12 °], while they remain close to linearity on the iron metal one [Fe1-C1-N1 = 176.55 ° and Fe1-C2-N2 = 172.25 °]. The non-bridging cyanide is connected to the Fe atom in an approximately linear mode \([\text{Fe1-C3-N3} = 176.92 \text{ Å}]\). The Fe-C\text{cyano} bond distances vary in the range 1.918 Å - 1.927 Å which is similar to the value measured in the related high-spin \([\text{Fe}^{III}(\text{Tp})(\text{CN})_3]^-\) complex [1.910 Å - 1.929 Å].\(^6\)\(^8\)\(^13\)\(^15\) The angles subtended by the tripodal ligand on the iron atom slightly deviate from orthogonality (from 88.0 ° to 89.0 °).

The Co site presents a distorted octahedral coordination environment, and the degree of the distortion is represented by \( \Sigma \text{Co} \), which is defined as the sum of deviation from 90 ° of the twelve cis-N-Co-N angles around the Co center. The \( \Sigma \text{Co} \) value is 38.06 ° for 3, greater than that for 1 (\( \Sigma \text{Co} = 35.08 \) °). More quantitative data can be obtained through continuous shape calculation. The parameter \( \text{CSh}_{\text{MCo}} \) quantifies the deviation of the actual coordination sphere from an ideal octahedral geometry. The \( \text{CSh}_{\text{MCo}} \) value of 3 is 0.295, which is also higher than that of 1 (\( \text{CSh}_{\text{MCo}} = 0.223 \)). Furthermore, the interplanar dihedral angles on the vbik ligands amount to 8.83 ° and 11.69 °, these are comparable than those found in compound 1 (9.71 ° and 11.8 °).

The Co-NNC bond lengths [Co-NNC = 2.109 Å and 2.114 Å] are slightly inferior to that of Co–Nvbik ones (Co–Nvbik values range from 2.117 Å to 2.153 Å), these metal ligands bond length value and local distortion parameters are coherent with the existence of a high-spin Co(II) electronic state.\(^13\)\(^14\)
The compound 4 crystallizes in the P1(2) space group as well. Its structure is made of square-like complexes, counter ion and solvent molecules, like in compound 3. The crystal unit cell contains two square molecules 4a and 4b, which have almost the same metal-ligand bond distances (4a: Co-N1C1 = 1.876 Å, Co-N2C2 = 1.875 Å; 4b: Co-N4C4 = 1.879 Å, Co-N5C5 = 1.873 Å). The crystal lattice also contains a lot of solvent molecules which are not well identified because of the structural disorder. As the exact solvent content of the compound cannot be determined by X-ray diffraction, an estimation of the amount of solvent can be obtained based on the molecular size from X-ray diffraction data. The volume is around 622 Å³ per square and the estimated number of remaining electrons (not localized on well identified atoms) is 313. Considering 18 Å³ per non-hydrogen atom, the volume can contain up to 34 solvent atoms. This can be considered an upper limit since the value of 18 Å³ is a good estimation for a well-ordered crystal. The real amount must be lower, so the number of electrons can be assigned to roughly 17 methanol or 31 water molecules.

For 4, the Co-N_{CN} average length of 1.875 Å and the Co-N(vbik) average length of 1.922 Å, are shorter than in 3 and they correspond to the occurrence of a low-spin Co(III) ion. The distortion parameter, ΣCo, is much lower in 4 and in agreement with a LS Co(III) ion (ca. 16.21 °). Furthermore, the interplanar dihedral angles on the vbik ligands amount to 23.32 ° and 24.90 ° separately, much greater than in the compound 3.

The bond lengths between the Fe ion and the Tp ligand are close in compounds 4 and 3. The Fe-C_{CN} bond lengths are below 1.90 Å in 4 and a little above that value in 3. This differences has been
previously observed in [Fe(Tp)CN₃]⁻ based complexes and is indicative of low-spin Fe(II) and Fe(III) redox states, respectively.

Table 1. Crystal unit cell parameters of 3 and 4

<table>
<thead>
<tr>
<th>Formula</th>
<th>(\text{C}<em>{68}\text{H}</em>{60}\text{B}<em>{2}\text{Co}</em>{2}\text{Fe}<em>{2}\text{N}</em>{34}\text{O}<em>{4}, 2(\text{F}</em>{6}\text{P}), 2(\text{CH}_{4}\text{O})) (3)</th>
<th>(\text{C}<em>{68}\text{H}</em>{60}\text{B}<em>{2}\text{Co}</em>{2}\text{Fe}<em>{2}\text{N}</em>{34}\text{O}<em>{4}, 2(\text{F}</em>{6}\text{P})) (4)</th>
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<td>200</td>
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<td>2082.43</td>
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<td>Triclinic P-1</td>
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<tr>
<td>α (°)</td>
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<td>80.292(2)</td>
</tr>
<tr>
<td>β (°)</td>
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<td>79.298(2)</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>84.572(2)</td>
</tr>
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<td>V [Å³]</td>
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<td>Z: 2; Z’:0</td>
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<td>Independent reflections</td>
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<td>10811</td>
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<td>(R1 [I\geq2o(I)])</td>
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<td>0.0619</td>
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<tr>
<td>(R2 [I\geq2o(I)])</td>
<td>0.1085</td>
<td>0.1748</td>
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Table 2. Core structure parameters of 3 and 4

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<th>(4)</th>
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</thead>
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<tr>
<td>$d_{[\text{Fe-(CN)}\text{bridging}]}\text{av (Å)}$</td>
<td>1.918(3)</td>
<td>1.857(5)</td>
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<td>$d_{[\text{Fe-N(Tp)}]}\text{av (Å)}$</td>
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<td>2.001(6)</td>
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<td>$d_{[\text{Co-(NC)}\text{bridging}]}\text{av (Å)}$</td>
<td>2.112(3)</td>
<td>1.872(5)</td>
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<td>$d_{[\text{Co-N(vbik)}]}\text{av (Å)}$</td>
<td>2.137(0)</td>
<td>1.922(0)</td>
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<td>(N-Co-N) av bridging angle (°)</td>
<td>90.03(4)</td>
<td>90.02(0)</td>
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<td>$\Sigma\text{Fe} (^\circ)$</td>
<td>23.00</td>
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<td>$\Sigma\text{Co} (^\circ)$</td>
<td>38.06</td>
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<td>[Co-C-O(c=o)] av angle (°)</td>
<td>173.9(7)</td>
<td>161.7(3)</td>
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<td>[(NC-Fe-CN) bridging] av angle (°)</td>
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<tr>
<td>[(CN-Co-NC) bridging] av angle (°)</td>
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<td>[(N-C-Fe) bridging] av angle (°)</td>
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<td>[(C-N-Co) bridging] av angle (°)</td>
<td>163.21(5)</td>
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<td>[Fe···Co distance] av (Å)</td>
<td>5.093(0)</td>
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Figure 6. Perspective view of the supramolecular square sheets in 3 (left) and cavities in 4 (right)

Compound 3 and 4 show very different supramolecular organizations. As the intermolecular interaction are known to play an important role in switchable magnetic molecules, we have investigated in depth these interactions. Figure 6 shows perspective view of the supramolecular
sheet of compound 3 (left) and 4 (right). Like 1, the supramolecular square layers of 3, parallel to bc plan are separated by counterion PF$_6^\text{−}$. As for compound 4, which contains two molecule motifs 4a and 4b, they form a large cavity (18.581 Å x 24.046 Å based diagonal Co sites) alongside a axis direction. There are a lot of solvent molecules existing in these large cavity as presented in figure 6 (right). We also distinguish two kinds of intermolecular interactions in these molecular sheets as for compounds 1 and 2: (i) direct intermolecular interactions involving the vbik ligands between neighboring squares in compound 3 as shown in figure 7; (ii) indirect intermolecular interactions that involve the counterion PF$_6^\text{−}$ as shown in figure 8.

Figure 7. View of the pseudo π-π contact between two neighboring square molecules (left) and supermolecule frame linked by intermolecular interaction (right) in 3 at ambient pressure.

Similar to the compound 1, there are two pseudo π-π stackings between the neighboring vbik ligands in the compound 3. The distances of some O-C short contacts are: $d_{O1\cdots C16} = 3.039$ Å and $d_{O1\cdots C18} = 3.175$ Å for vbik1 pair, and $d_{O2\cdots C25} = 3.114$ Å for vbik2 pair. One of two π-π stackings (vbik1 pair) includes an antiparallel C=O/O=C arrangement. It is worth noticing that the distance between the antiparallel C=O pair is much shorter in 3 than that in 1 ($d_{O1\cdots C16} = 3.162$ Å) at ambient pressure, leading to a higher interaction energy of the C···O pair in 3. Besides, there are 9 short contacts between C···C and C···O types in vbik1 pair for 3 but only 6 in vbik1 pair for 1. These two factors likely contribute to higher energy of intermolecular interactions in 3 compared to 1. It seems that the stronger intermolecular interactions might go along with a higher distortion of cobalt sites ($\Sigma\text{Co} = 38.06^\circ$ for 3 and $\Sigma\text{Co} = 35.08^\circ$ for 1) without affecting significantly the average value of the (C-N-
Co) bridging angle (163.21° for 3 and 161.62° for 1). A higher ∑Co value would thus better stabilize the square in the paramagnetic state. Moreover, the counterion PF$_6^-$ also creates indirect contacts between two adjacent neighboring square molecules, each fluorine element of the counterion has F···C or F···H contacts as shown in figure 8, and there are more contacts in 3 than 1 as well.

![Figure 8. The indirect contacts via PF$_6^-$ in 3.](image)

In contrast, few direct short contacts of CH···O and C···H types exist between vbik ligands in the diamagnetic compound 4, leading to weak intermolecular interactions, as shown in figure 9. Most of the indirect contacts are associated with the counterions PF$_6^-$ similarly to compound 2 which has been described in chapter 2. The absence of strong intermolecular interactions seems to result in a much more regular square core structure of 4. The transition temperature, $T_{1/2}$, of 4, close to that observed in solution is also coherent with the moderate impact of the weak intermolecular interaction on the ETCST process in 2 and 4.

The structural analysis suggests that the strong pseudo π-π intermolecular interactions between the neighboring square complexes lead to a distortion of the Co coordination sphere and a stabilization of the Co(II) state. This implies that the transition temperature should be moved to lower temperature. Then the thermal bath energy may not be strong enough near $T_{1/2}$ to overcome the energy barrier associated to the structural reorganization of the local coordination sphere.
5 Partial thermal ETCST under pressure and pressure-induced phase transition in solid-state

5.1 Partial thermal ETCST unveiled by magnetic measurements

As depicted above, compound 3 (red phase) is paramagnetic from 2 - 300 K at ambient pressure, while the compound 4 (green phase) with a same square complex maintains an ETCST near room temperature. The stabilization of paramagnetic state in compound 3 is thus clearly due to solid-state interactions. In any cases, the occurrence of ETCST in the solution and the solid-state compound 4 indicates that the energy gap between diamagnetic and paramagnetic state is small in this system. Similar to compound 1 in the previous chapter, the application of hydrostatic pressure on the paramagnetic compound 3 also should lead to a stabilization of the diamagnetic state, which has a smaller volume compared to the paramagnetic state. Besides, the stronger intermolecular interactions make 3 better stabilized at paramagnetic state without kinetic trapping, so that it might need higher pressure to convert 3 to diamagnetic state compared to 1.
The figure 10 shows the $\chi_{MT}$ versus $T$ curves under six hydrostatic pressures for compound 3. At ambient pressure, in the pressure cell, the compound 3 is paramagnetic over the whole temperature range from 2 K to 300 K, which is consistent with the magnetic properties measured on the bulk in standard conditions as depicted above. Upon pressure application, two distinct pressure regimes can be distinguished in the magnetic behavior of 3. When the pressure increases from ambient pressure to ca. 0.53 GPa, the paramagnetic pairs are converted into diamagnetic ones at low temperature (below 270 K). Approximately up to 47% of the pairs can be converted at ca. 0.53 GPa (the percentage is calculated by measuring the $\chi_{MT}$ values difference of HT and LT at 0.53 GPa: 7.35 – 3.90) X 100 /7.35). Interestingly, the new diamagnetic pairs show a thermally induced ETCST transition with large hysteresis opening, whose width decreases with increasing pressure. For example, a thermal hysteresis of ca. 50 K and centered at ca 200 K is observed at 0.42 GPa (42 K of hysteresis loop at 0.45 GPa). It is worth noticing that the hysteresis loops are repeatable and can be cycled at least three times (after cycling we checked that they were no pressure reduction by measuring the lead critical temperature around 6 - 7 K).

Surprisingly, there is a second regime with upon further increase of the pressure, above 0.58 GPa, the magnetic behavior changes: the transition temperature is still shifted to higher temperature as expected but the $\gamma$ value before ETCST markedly increases to 92% at 250 K. The thermal hysteresis width keeps diminishing with pressure: at 0.69 GPa the hysteresis width goes down to 16 K. In other word, above a threshold pressure value, part of the diamagnetic pairs is back converted into paramagnetic ones. The phenomenon was shown to be reversible as a decrease of pressure (e.g. at 0.42 GPa) allows finding back the prior behavior. Three different batches samples have been measured to check the reproducibility of this unusual magnetic behaviors under pressure.

Figure 10. Temperature dependence of $\chi_{MT}$ value in 3 under various hydrostatic pressures.
Actually, our lowest applied pressure is 0.1 GPa, at which no para to dia conversion is observed. At 0.39 GPa, 10% of 3 is converted into diamagnetic state which undergoes thermal ETCST around 220 K. Therefore we deduced that the pressure threshold, \( p_0 \), for para- to dia-magnetic conversion of 3 is between 0.1-0.39 GPa. The figure 11 shows the paramagnetic molar fraction, \( \gamma_{\text{para}} \), versus T for 3, and \( \gamma_{\text{para}} \) is calculated from \( \chi_{\text{MT}} \) values: \( \gamma_{\text{para}} = (\chi_{\text{MT HT}} - \chi_{\text{MT LT}})/\chi_{\text{MT HT}} \). By polynomial fitting of \( \gamma_{\text{para}} \) versus pressure in the pressure range of 0.39 - 0.59 GPa, we obtain the relation of \( \gamma_{\text{para}} \) against pressure in the low pressure phase: \( \gamma_{\text{para}} = 2.461 - 6.064 P + 4.748 P^2 \). The pressure corresponding to \( \gamma_{\text{para}} = 1 \) is the pressure threshold \( p_0 \) (0.32 GPa). It is important here to point out that the pressure in magnetic measurements was determined between 6 - 7 K by using supracritical Pb as manometer.

The real pressure in HP cell increases with increasing temperature, especially after the melting of daphne oil 7373, and it can exceed the pressure value at low temperature by 0.1 - 0.2 GPa at 300 K.16–21

![Figure 11. The relationship of \( \gamma_{\text{para}} \) vs \( p \) (\( p < 0.63 \) GPa) for 3. The solid line results from the simulation of the \( \gamma_{\text{para}} \) versus \( P \) data by a polynomial equation: \( \gamma_{\text{para}} = 2.461 - 6.064 P + 4.748 P^2 \)](image)

Figure 12 shows the linear relationship between the transition temperatures measured upon heating ad cooling, \( T_{1/2 \text{ up}} \) and \( T_{1/2 \text{ down}} \) versus pressure. As for compound 1, the transition temperature of 3 also obeys to the Clapeyron’s law (even including data from both regimes, below and above 0.6 GPa)

\[
T_{1/2} (p) = T_{1/2} (0) - (p - p_0) \frac{AV}{AS}
\]
where ΔV (negative) is the volume change between diamagnetic and paramagnetic states, T_{1/2} (0) is the transition temperature corresponding to the threshold pressure value, p_0, beyond which ETCST transition takes place. Interestingly, the measured shift rates of T_{1/2 up} and T_{1/2 down}, 247 K GPa^{-1} and 306 K GPa^{-1}, respectively, are larger than those measured in related compound 1 (the slope of T_{1/2 up} = 228 K GPa^{-1}; the slope of T_{1/2 down} = 213 K GPa^{-1} for compound 1).

Figure 12. The calculated relationship between transition temperature (left); hysteresis width (right) with increasing pressures.

We also represented in figure 12 (right) the relationship of the hysteresis width and pressure. The hysteresis loop decreases almost linearly as pressure increases in the range of 0.42 GPa - 0.69 GPa. This could indicate a decrease of the cooperativity of the ETCST. In other word, increasing pressure may reduce the synergistic effect of cooperative intermolecular elastic interactions that lead to large hysteresis. Actually, this trend is a normal ETCST behavior. Nevertheless, the originality of the present compound lies in the occurrence of a second regime, where pressure-induced diamagnetic pairs are back converted to paramagnetic ones above a pressure value (ca. 0.6 GPa). We hypothesize that this change might come from a crystal phase transition. The large thermal hysteresis opening of 3 under weak pressure is also somewhat surprising compared to that of 1, as 1 and 3 have similar core structures and intermolecular interactions mediated by direct contacts of vbik ligands. In order to confirm the pressure-induced phase transition and to relate the ETCST properties of 3 to its structure, XRD and Raman studies at variable pressure have been carried out.
5.1 Phase transition revealed by HP-XRD at ambient temperature

As discussed above, compound 3 shows a partial paramagnetic to diamagnetic conversion below 0.58 GPa at 200 K, and a sudden recovery of its paramagnetic state at 0.63 GPa, which might be due to a phase transition. In order to get additional experimental support on the occurrence of the assumed phase transition, we carried out the pressure-dependent XRD measurements at room temperature in collaboration with Maxime Deutsch from the Université de Lorraine.

The first XRD study at variable pressure was carried out using methanol and ethanol as a transfer medium. Since the crystals gradually decompose in these conditions, we then work with daphne oil which gave better results. Unfortunately, no clear evidence of a conversion from paramagnetic to diamagnetic states was observed. This is likely related to the temperature at which these experiments were carried out. Indeed, magnetic measurements showed that ETCST occurs at low temperature (below 270 K) under moderate pressure (0.58 GPa). At room temperature, 3 is essentially in paramagnetic state with P < 0.69 GPa.

The XRD experiments were conducted in the pressure range 0 - 1.77 GPa. The crystal structure could be resolved for low-pressure phase (P < 1.0 GPa). The selected crystal parameters under various pressures (pressure increase: P_up and pressure decrease: P_down) are shown in table 3 and table 4. The crystal structure of C11 was obtained by increasing pressure from ambient pressure, and that of C13 was done by directly applying pressure to 1.6 GPa then decreasing to ambient pressure. The space group of C11 and C13 belong to triclinic below 1.0 GPa and their unit cell parameters are similar. The phase of C11 is obtained by increasing pressure from ambient pressure, and that of C13 is obtained by directly applying pressure up to 1.60 GPa, then decreasing to ambient pressure.

Overall, the structural quality factor R1 and wR2 (%) are moderately high compared with those obtained at ambient pressure. Based on the R1 and wR2(%) value, only three crystal structures obtained are reliable: the structure at 200 K analysed at IPCM and those at 300 K at two pressures, 0.62 GPa (C11) and 0.76 GPa (C11).
Table 3. Unit cell parameters of compound 3 under various pressures ($P_{up}$)

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<th>Pressure (GPa)</th>
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<th>0.76</th>
<th>1.55</th>
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<td>C11</td>
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<td>b (Å)</td>
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<td>14.43(4)</td>
</tr>
<tr>
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<td>14.2884 (8)</td>
<td>18.31(3)</td>
<td>17.74(5)</td>
</tr>
<tr>
<td>α(°)</td>
<td>114.695(3)</td>
<td>114.189(7)</td>
<td>114.146(12)</td>
<td>93.40(6)</td>
<td>92.59(12)</td>
</tr>
<tr>
<td>β(°)</td>
<td>95.479(4)</td>
<td>97.054(16)</td>
<td>97.12(2)</td>
<td>89.78(7)</td>
<td>91.10(15)</td>
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<tr>
<td>γ(°)</td>
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<td>115.907(15)</td>
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<td>89.95(12)</td>
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<td>$R_{ex}$ (%)</td>
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<td>Sig</td>
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<td>7.95; 21.10</td>
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<td></td>
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Table 4. Unit cell parameters of compound 3 under various pressures (P_{down})

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<th>0.71</th>
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<td>Final (GPa)</td>
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<td>1.15</td>
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<td>0.7</td>
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<tr>
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<td>α (°)</td>
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<td>21.14</td>
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<td>23.67</td>
</tr>
<tr>
<td>Completeness</td>
<td>32.60%</td>
<td>22%</td>
<td>29.80%</td>
<td>28%</td>
<td>28.50%</td>
<td>31.20%</td>
<td>26.30%</td>
</tr>
<tr>
<td>Dmin(Å), I/Sig</td>
<td>0.89,2.5</td>
<td>0.84,1.5</td>
<td>0.83,3.9</td>
<td>0.83,3.7</td>
<td>0.83,4.3</td>
<td>0.83,3.0</td>
<td>0.84,4.4</td>
</tr>
<tr>
<td>R1, wR2, (%)</td>
<td>8.42, 25.96,</td>
<td>9.00, 26.43</td>
<td>7.86, 22.32</td>
<td>9.37, 29.25</td>
<td>8.58, 27.31,</td>
<td>8.58, 27.31,</td>
<td></td>
</tr>
<tr>
<td>Data/param.</td>
<td>6.52</td>
<td>6.29</td>
<td>6.96</td>
<td>7.64</td>
<td>6.90</td>
<td>6.90</td>
<td>6.90</td>
</tr>
</tbody>
</table>

The crystallographical results support the occurrence of a crystal phase transition above 1.15 GPa at 300 K, because a sudden change of crystal unit cell parameters in a/b/c and α/γ/β is clearly observed above 1.0 GPa. Especially for the unit cell parameters of c, α and γ, when increasing pressure from ambient pressure to 1.77 GPa, the value of c increases from 14.438 Å to 17.745 Å, and that of α and γ value decrease from 114.695 °, 116.910 ° to 92.59 ° and 89.95 ° separately.
Moreover, as shown in figure 13, all values return to the vicinity of their original positions (ambient pressure) in the process of decreasing pressure to ambient pressure, which means the XRD experiments are reproducible even the structure are not solved above 1.0 GPa. The occurrence of such crystal phase transition likely accounts for the magnetic behavior appearance in the second pressure regime (0.58 GPa - 0.69 GPa) of compound 3 (0.25 GPa difference based on P vs temperature dependence).

The figure 14 shows the variation of V/Z versus pressure, with V = unit cell volume and Z= number of asymmetric units per cell. The V/Z vs P curve shows a sudden change around 1.0 GPa, which points to the occurrence of a crystal phase transition as well.

![Figure 13. Unit cell parameters vibration under various pressure, solid line is for eye-guide](image)

![Figure 14. Molecular volume change of 3 under pressures](image)
Although the decrease of V/Z is important upon pressure, it is not possible to clearly assign it to an electronic state change. A para-di state change was not observed because there is no typical Co-N metal-ligand bond length change as shown in table 5. The average Co-N\textsubscript{CN} bond slightly decreases from 2.16 to 2.08 Å while the Co-N\textsubscript{vbik} ligand bond slightly decreases from 2.10 to 2.09 Å. As usual, the average Fe-C bridging bond decreases from 1.90 Å to 1.84 Å, a small decrease change also happens in the average Fe-N\textsubscript{Tp} ligand bond side. These four types of metal ligand bond length change are small. Besides, the value of $\Sigma$Co remains near 41 ° as pressure is below 1.0 GPa, which is a typical value for Co(II) ions, and that of $\Sigma$Fe is around 25 °.

| Table 5. Core structure parameters in the crystal cell at the three reliable pressures |
|---------------------------------|-----------------|-----------------|-----------------|
| **Pressure (GPa)**              | 0 (IPCM 200K)   | 0.62 (C11)      | 0.76(C11)       |
| $d[\text{Fe-}(\text{CN})\text{bridging}]$av (Å) | 1.918           | 1.944           | 1.832           |
| $d[\text{Fe-N(Tp)}]$av (Å)        | 1.975           | 1.968           | 1.908           |
| $d[\text{Co-}(\text{NC})\text{bridging}]$av (Å) | 2.112           | 2.101           | 2.094           |
| $d[\text{Co-N(vbik)}]$av (Å)      | 2.137           | 2.108           | 2.106           |
| (N-Co-N)av bite angle (*)         | 90.03           | 89.91           | 90.83           |
| $\Sigma^{12}_{1} \mid 90 - \alpha \mid$ for the Fe center (*) | 23.00           | 39              | 37              |
| $\Sigma^{12}_{1} \mid 90 - \alpha \mid$ for the Co center (*) | 38.06           | 45              | 43              |
| $[\text{Co-C-O(c=o)}]$av angle(*) | 174.64          | 162.85          | 166.96          |
| Dihedral $\angle 2$ (*)           | 8.83            | 11.16           | 12.43           |
| Dihedral $\angle 1$ (*)           | 11.69           | 13.58           | 14.40           |
| $[[\text{N-C-Fe}]]$av angle (*)   | 174.39          | 172.66          | 171.915         |
| $[[\text{C-N-Co}]]$av angle (*)   | 163.21          | 159.34          | 155.46          |

Like compound 1, the pressure modifies the core structure of the square 3 (table 5): the average metal-ligand distances tend to decrease slightly with increasing pressure, and the distortions of the coordination environments of both Fe(III) and Co(II) rise significantly upon pressure, especially for Fe(III); The average angle of $[\text{C-N-Co}]_{\text{bridging}}$ become smaller, as well as that of $[\text{N-C-Fe}]_{\text{bridging}}$ to a less
extent. On the contrary, the pressure does not significantly modify the crystal packing. As depicted above, at ambient pressure, the pseudo π-π interactions associated with the antiparallel pairs of C=O are stronger in 3 than that in compound 1 as the distance between C=O pairs is shorter than in compound 1 (compound 1: C17···O1/C16···O1 = 3.989/3.162 Å; compound 3: C15···O1/C16···O1 = 3.176/3.039 Å).

Unlike the four types of metal-ligand bond length, the contacts distance between adjacent molecules decreases obviously with increasing pressure. Between vbik1 pair, the contact distance of C16···O1 drops from 3.039 Å to 2.765 Å, and that of C15···O1 decreases from 3.176 Å (ambient pressure) to 2.926 Å (0.76 GPa) as shown in table 6. Between vbik2 pair, the contact of C25···O2 decreases from 3.144 Å to 2.951 Å. The value of ∆d% (the contact distance change difference ratio) at 0.76 GPa is 8.28%, which is slightly higher than that at 0.62 GPa (6.14%). Besides, a N···O contact in vbik2 pair appears as pressure increases to 0.62 GPa (dN···O = 3.095 Å at 0.62 GPa), then decrease to 3.029 Å at 0.76 GPa.

Even before the ETCST happens in 3, the contact distance of C16···O1 at 0.76 GPa is much shorter than those in 1 (dC17···O1 = 2.955 Å, ETCST occurring at 0.73 GPa), which means the pseudo π-π intermolecular interaction in 3 may be stronger for similar pressure application. Moreover, the value of ∆dC16···O1 (Δd, the contact distance change difference) between ambient pressure and 0.76 GPa is 0.274 Å, which is also slightly higher than the value of ∆dC17···O1 in 1 (compound 1: ∆dC17···O1 = 0.26 Å between ETCST pressure range). These stronger interactions in 3 that propagate along two perpendicular supra-molecular direction of square layer might contribute to the huge hysteresis loop observed at lower pressure. A higher connectivity of the PF6⁻ anion compared to BF4⁻ one may also explain the difference of the thermal hysteresis width between 1 and 3. The intermolecular interactions might explain also the geometric deformation of the square 3 by pressure.
The diagonal distances in both directions of Fe···Fe and Co···Co, decrease from 7.470 Å to 7.386 Å, and 6.926 Å to 6.831 Å respectively. As for the Fe···Co side distance, the value of d1 and d2 distance varies from 5.11, 5.07 Å to 5.05 and 5.0 Å, separately, as pressure increasing from ambient pressure to 0.76 GPa (as shown in table 7).

For compound 3, we should also crudely mention the disorder phenomenon under pressure. Based on the three reliable structures obtained, there is almost no disorder at ambient pressure, however, the disorder occurs associated with carbonyl group of vbik ligand at 0.62 GPa and 0.76 GPa as shown in figure 15( left). The oxygen of C=O group is found to be modeled over two opposite orientations occupations. The angle of ∠ O2-C18-O2 keeps steady at 116 ° when increasing pressure from 0.62 GPa to 0.76 GPa (because the crystal packing is almost the same with changing pressure), but decreases to 79 ° - 81 ° at opposite position under disorder model. This O2 disorder may be the reflection of the existence of two different Co(II) sites in the structure of 3 and could explain the partial para to dia conversion of 3 by pressure. The squares with strong C=O/O=C dipolar
interactions (lower C25⋯O2 distance) undergo easily pressure-induced para to dia conversion and that with weak C=O/O=C dipolar interactions (higher C25⋯O2 distance) remain paramagnetic, as the stronger intermolecular interactions propagate more efficiently the pressure effect. Actually, in several spin crossover systems, the changeover from well-defined coordination sphere to a disordered one (order – disorder transition) was associated to partial transition (eventually involving the counterions). Galina S. Matouzenko has described the compound of [Fe(Hpy-DAPP)](BF₄)₂ with a spin transition. In their studies, two different geometries of the [FeN₆] coordination core generated by the disorder in the ligand could be at the origin of the two-step spin-transition behavior.

Figure 15. The disorder of O₂ in 3 at 0.62 and 0.76 GPa (left); The H-bonds between the terminal CN groups and MeOH molecules (right).

The figure 15 (right) shows the H-bond between the terminal CN group and the MeOH solvent in the paramagnetic compound 3. The interatomic distance O(MeOH)⋯N(CN), dON, is 2.868 Å, similar with that of 1 (dON = 2.844 Å).

Unlike for 1, the pressure seems less efficient to shorten the distance dON in 3. The distance of O3-N2 is shortened from 2.868 Å to 2.835 Å when pressure varies from 0 to 0.75 GPa (table 8). One could also assume that the moderate shortening of the O3-N2 distance (strengthening the H-Bond) does not help the para-dia conversion in 3 and it may also explain the normal ETCST behavior of 3.

Very slight re-orientation of MeOH molecule is observed for pressure increase from 0 to 0.76 GPa. The angle ∠C₃₅-O₃-N₂ increases from 106° to 109° (Δ∠C₃₅-O₃-N₂ ≈ 3%) with increasing pressure to 0.76 GPa as shown in table 8.
In summary, the pressure application seems to trigger the disorder of the oxygen atom of the carbonyl group in one of the two vbik ligands. The pressure up to 1 GPa provokes the sudden change of crystal unit cell parameters (c, α/γ) indicating a crystal phase transition, which is coherent with the existence of the two pressure regimes for HP-magnetic measurements. Besides, the unobvious hydrogen bond change may help explain the normal magnetic behavior of 3 compared to that of 1.

### 5.2 Pressure-induced paramagnetic to diamagnetic ETCST in 3 probed by HP-μ Raman spectroscopy

The Raman spectroscopy under various pressures was used to further probe the pressure-induced conversion of compound 3 as shown in figure 16. The temperature was set at 200 K and the pressure was detected before and after each measurement (by using the ruby luminescence) to monitor the pressure stability.26–29

The Raman measurements were performed with stepwise pressure increase from 0.30 to 1.85 GPa (P$_{up}$), then, with releasing pressure from 1.85 to atmospheric pressure through three steps (P$_{down}$). At atmospheric pressure, the spectrum shows a high signal-to-noise ratio due to releasing helium gas in the pressure measuring cell. The quality of the spectra increases when pressure increases.

At 0.30 GPa, the Raman spectrum (detailed here after) is consistent with the IR spectrum described above and corresponding to a paramagnetic state of compound 3. The vibration of 2200 cm$^{-1}$ should belong to the bridging $\text{[Fe}^{III}_L\text{S(μ-CN)Co}^{II}_H\text{S]}$ units mode in agreement with the infrared spectrum. The overlapped peak at 1650 cm$^{-1}$ is due to the vibrations of four functional groups (carbonyl, vinyl and imidazole rings of vbik ligand, as well as the pyrazole rings of Tp ligand). The broad peak from 1250 cm$^{-1}$ - 1370 cm$^{-1}$ is due to diamond of the pressure cell. Two C-C vibration modes at 1222 cm$^{-1}$ and 1178 cm$^{-1}$ are from the Tp$^-\text{ligand}$.
of the \([\text{Fe}^{\text{III}}(\text{Tp})\text{CN}_3]^-\) unit. The peak at 976 cm\(^{-1}\) is ascribed to a vibration of the counter ion, PF\(_6^-.\) The peaks in the range of 2465 cm\(^{-1}\) - 2477 cm\(^{-1}\) should be associated with B-H stretching from Tp' ligand on the coordinated \([\text{Fe}^{\text{III}}(\text{Tp})\text{CN}_3]^-\) and \([\text{Fe}^\text{II}(\text{Tp})\text{CN}_3]^{2-}\) units. It is worth noticing that all the peaks are shifted to a higher wavenumber (cm\(^{-1}\)) value upon increasing pressure.

![Figure 16. Pressure - Raman spectroscopy of compound 3 at 200 K.](image)

From 0.3 to 0.80 GPa, the global intensity of the Raman peaks keeps decreasing, the residual intensity becoming actually very small at 0.80 GPa. This change could correspond to the partial conversion from the paramagnetic state to the diamagnetic one observed in the pressure region of 0 - 0.58 GPa in magnetometry measurements. Actually, we previously observed that the green diamagnetic phase of compound 1 absorbs the exciting laser light and yield very weak Raman spectra.

In contrast, the spectrum intensity increases suddenly as pressure further increases from 0.8 to 0.90 GPa. This could indicate a back conversion to the paramagnetic state. It would be coherent with the back conversion observed in magnetic measurements from 0.58 to 0.69 GPa. Besides, this paramagnetic state recovery at 0.9 GPa in Raman spectrum (200 K) is highly coherent with the phase transition phenomenon observed in HP-XRD experiment above 1.0 GPa (300 K).

The new peaks at 2137 cm\(^{-1}\) (either assigned to terminal \(\text{Fe}^{\text{III}}\text{LS}_{\text{CN}}\) unit or to \(\{\text{Fe}^\text{II}_{\text{LS}}(\mu-\text{CN})\text{Co}^{\text{III}}\text{LS}\}\) linkage) and 2097 cm\(^{-1}\) (associated to diamagnetic \(\{[\text{Fe}^\text{II}_{\text{LS}}(\mu-\text{CN})\text{Co}^{\text{III}}\text{LS}]\}\) units) become clearly
visible above 1.0 GPa as shown in figure 16. This would account for the partial conversion of the new crystal phase into a diamagnetic state.

By further increasing pressure to 1.80 GPa, no significant variation of the three cyanide stretching vibrations (2200, 2137 and 2097 cm\(^{-1}\)) is observed, which means the compound would remain in a mixed para/dia state even up to 1.85 GPa. Finally, when reducing pressure to 0.70 GPa, the peak intensity at 2200 cm\(^{-1}\) increases again obviously, and those at 2137 and 2097 cm\(^{-1}\) disappears, which indicates compound 3 returns reversibly to a full paramagnetic state.

It is observed also that the shape of the peak at 2200-2170 cm\(^{-1}\) are different in the two phases: sharp in low-pressure phase and large in the high-pressure phase as presented in figure 16. The reversibility is also observed in the shift of the cyanide stretching peak located around 2200 cm\(^{-1}\) (associated to the bridging cyanide). As shown in figure 17 left, it first moves from 2170 cm\(^{-1}\) to 2200 cm\(^{-1}\) with increasing pressure up to 1.85 GPa, then moves back to 2175 cm\(^{-1}\) as pressure decreases to 0.7 GPa, which means there is the elastic effect on the bridging cyanide bond.\[31\]

![Figure 17. Raman shifts of the CN stretching vibration (left); Variation of the paramagnetic molar fraction $\gamma_{\text{para}}$ observed from Raman spectra and magnetism in 3 under various hydrostatic pressures (right).](image)

We also attempted to extract the paramagnetic fraction, $\gamma_{\text{para}}$, from the Raman data in order to compare it with those extracted from the magnetic measurements. At first, we integrate the CN stretching peak in the range of 2160 cm\(^{-1}\) - 2200 cm\(^{-1}\), the integration of B-H peak in
the range 2461-2599 cm\(^{-1}\) is considered as the reference, and then calculate the ratio of the two areas: \(R(P) = \frac{A_{\text{CN bond integral area}}}{A_{\text{AB-H integral area}}}\). The \(\gamma_{\text{para}}\) value at any pressure \(P\), \(\gamma_{\text{para}}(P) = \frac{R(P)}{R(P=0)}\). Figure 17 (right) shows the \(\gamma_{\text{para}}\) versus pressure extracted from both physical measurements. Note that the pressure values calculated during the magnetic measurements (measuring \(T_c\) of Pb near 7K) were corrected according to the formula, \(p = p_{\text{SQUID}} + 0.38\times p_{\text{SQUID}} - 0.05\) GPa, since the pressure detected at low temperature evolves with temperature\(^{31-33}\). The two \(\gamma_{\text{para}}\)-\(P\) curves are similar and support a partial conversion from a paramagnetic to a diamagnetic state in the pressure range of 0 - 0.8 GPa and the occurrence of a phase transition observed in HP-XRD experiments near 1 GPa.

6 Conclusion

In this chapter, we have synthesized by controlling the crystallization temperature two similar compounds 3 and 4, \([\text{[Fe(Tp)(CN)\(_3\)]_2[Co(vbik)\(_2\)]_2}\text{(PF}_6\text{)}_2\text{]}\), in different electronic states (Fe\(^{\text{II}}\)-Co\(^{\text{III}}\) and Fe\(^{\text{III}}\)-Co\(^{\text{II}}\)). The paramagnetic state of 3 and the diamagnetic state of 4 can be straightforwardly probed at ambient temperature by FTIR spectroscopy thanks to characteristic cyanide stretching vibrations. Their magnetic properties were first probed at room pressure in the temperature range of 2 K - 330 K. We observed that compound 4 shows a thermally-induced ETCST phenomenon near room temperature, close to the temperature of the ETCST in solution. In contrast, the compound 3 is trapped in the paramagnetic state in the full range of temperature. In contrast with 1, the use of lower scan speeds does not allow revealing a kinetic blocking in the paramagnetic state. We thus assume that the compound 3 is better stabilized than the compound 1 in the paramagnetic state. At this stage, one can assume that the interactions in 3 compared to that in compound 1 put more constraints on the cobalt coordination sphere and lead to a higher distortion, \(\Sigma_{\text{Co}}\) value. The better stabilization of the Fe\(^{\text{III}}\)-Co\(^{\text{II}}\) paramagnetic state of 3 explains the need of higher pressure to partially convert the compound 3 into molecular switch.

Interestingly, we showed that the “blocked” paramagnetic crystal phase in 3 can be converted to a diamagnetic one by applying moderate pressure. In this case the conversion is partial: up to ca. 50% of the paramagnetic Fe-CN-Co pairs can be changed into diamagnetic ones, below approximately 270 K. The resulting para-dia mixed phase shows a thermally induced ETCST with a large hysteresis (as wide as 50 K at 0.42 GPa) which might be related to strong intermolecular interactions (or C=O group disorder). The ETCST is shifted toward higher temperature as the pressure increases but in
contrast with compound 1, the hysteresis width decreases as the pressure increases. The magnetic behavior in compound 3 is not monotonous as a new regime appears above a threshold pressure. The crystal structure study carried out at 300 K at variable pressure clearly showed the occurrence of a pressure-induced crystal phase transition that accounts for the existence of two distinct behavior under pressure. The crystal cell parameters suddenly change above 0.96 GPa. This phase transition is also confirmed by HP-Raman spectrum at 200 K according to the sudden increase peak at 2200 cm⁻¹ at 0.90 GPa (corresponding to the paramagnetic state recovery of magnetism at 0.63 GPa). Unfortunately, the experimental data in the lower symmetrical pressure-induced crystal phase are not good enough to solve the crystal structure.

With this new Fe₂Co₂ square, we have shown that it was possible to obtained following the same procedure as in chapter 2, other “blocked” paramagnetic crystal phases whose electronic state could be highly sensitive to pressure. The comparative study of 1 and 3 allows suggesting that: (i) the intermolecular interaction impacts the local distortion of the cobalt coordination sphere, and therefore the stability of the trapped paramagnetic state; (ii) the unobvious hydrogen bond change under pressure in compound 3 may help to explain the its normal ETCST behavior.

To better understand the ETCST properties under pressure, complementary and more precise experiments are going on, in collaboration with other colleagues. In particular, we will further investigate the pressure effect on this square family by changing other parameters such as the ligands coordinated on the cobalt ion, the counter ions and the crystallization conditions. Another member of the family will be described in the next chapter.

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Chapter 4

Pressure-induced conversion of paramagnetic

\([\text{[Fe(Tp\(^\ast\)](CN)\(_3\)]\(_2\)[Co}\text{Me\(_{\text{ebik}}\)]\(_2\)] \cdot (\text{BF}_4)\(_2\) \cdot 2\text{H}_2\text{O}\) (5) into a molecular switch
1 Introduction

For the design of FeCo switchable coordination clusters, the choice of blocking ligands on Fe and on Co sites is of paramount importance, as the nature of the ligand determines the redox potentials of Fe and Co sites and affects the intramolecular electron transfer. The research group of M. Nihei and H. Oshio has studied the ETCST transition of four Fe$_2$Co$_2$ complexes in a butyronitrile solution.\(^1\) They observed that the transition temperature, $T_{1/2}$, is closely related to the absolute value of the redox potential difference between the building blocks of Fe and Co, $\Delta E_{FeCo} = E_{1/2}(Fe) - E_{1/2}(Co)$. Note that $\Delta E_{FeCo}$ is negative at room temperature: the Co(III/II) redox potential is higher than the Fe(III/II) one and the electronic state of the precursors at room temperature are Co(II) and Fe(III). Nihei observed that $T_{1/2}$ decreases (i.e. the paramagnetic state Fe$^{III}$Co$^{II}$ is better stabilized) when $|\Delta E_{FeCo}|$ increases. In a recent review article,\(^2\) M. Nihei has drawn a general law for bistable FeCo coordination clusters featuring R$^\text{Tp}$ ligand on Fe and $\alpha$-diimine ligand on Co: if $|\Delta E_{FeCo}| \approx 0.8$ V, the cluster could be ETCST active. If $|\Delta E_{FeCo}|$ value is significantly lower than 0.8 V the clusters remain diamagnetic while if $|\Delta E_{FeCo}|$ is significantly higher than 0.8 V, the cluster remains paramagnetic. In a solid state, many other factors should be considered, such as crystal packing, intra- and inter-molecular interactions. Nevertheless $|\Delta E_{FeCo}|$ remains always the first criteria guiding the design of bistable FeCo clusters.

Our group has tried to focused since 2009 to the use R$^\text{bik}$ ligands on Co, which belongs to $\beta$-di-imine family. We observed for a large family of twenty squares that $|\Delta E_{FeCo}|$ values of 0.87-1.02 V (vs SCE, CH$_3$CN) correspond to bistable Fe$_2$Co$_2$ complexes, 0.57 - 0.58 V (vs SCE, CH$_3$CN) to diamagnetic ones and 1.10 V (vs SCE, CH$_3$CN) to paramagnetic ones in solid state. As for the Nihei’s compound, the $\Delta E_{FeCo}$ is negative and the Co(II) redox state is the stable one at room temperature for the Co(R$^\text{bik})_2$ precursor in solution. However, upon formation of the cyanide bridges, both Fe(III/II) and Co(III/II) redox potentials change: the Fe(III/II) increases (as some cyanide electron density is given toward the Co Lewis acid) and the Co(III/II) redox potential decreases (if NCN atom is a better donor than the solvent it replaces upon cluster formation). In the case of the compounds reported by Nihei, this change is not large enough to lead to an electron transfer in solution upon cluster formation. In contrast, in the R$^\text{bik}$ family, we observed the formation of diamagnetic pair at room temperature. According to our previous works,\(^3\)\(^-\)\(^7\) the redox potentials are - 0.81 and - 1.00 V (vs SCE, CH$_3$CN) respectively for the building blocks, \{Fe$^{III}$(Tp)(CN)$_3$\} and \{Fe$^{III}$(Tp$^*$)(CN)$_3$\}.\(^8\) The redox potentials for the building blocks \{Co$^{II}$(Mebik)$_2$\} and \{Co$^{II}$(vbik)$_2$\} have been measured in our group in 2011 and published by Mondal et al. in 2021: 0.10 and 0.38 V (vs SCE, in CH$_3$CN) respectively.\(^9\) Therefore, the
squares $\{[\text{Fe(Tp)}(\text{CN})_3]_2[\text{Co(vbik)}]_2\}_2$ (1) and $\{[\text{Fe(Tp}^*)(\text{CN})_3]_2[\text{Co(Mebik)}]_2\}_2$ (5) have very similar $|\Delta E_{\text{FeCo}}|$ values: 1.18 V for the first and 1.10 V for the second. As we have observed an ETCST in solution near room temperature in compound 1, we can expect a similar behavior here in compound 5. This means that we should be able to isolate 5 in a paramagnetic state by controlling the crystallization temperature and eventually observe a similar pressure-induced behavior as the one observed for 1. In that case, the study of the thermally activated and pressure-induced ETCST behaviors of $\{[\text{Fe(Tp)}(\text{CN})_3]_2[\text{Co(Mebik)}]_2\}_2$·$\text{PF}_6$·2$\text{CH}_3\text{OH}$ (3), compared with that of 1, will help revealing the combined effects of the core structure, intra and intermolecular interactions on the switchable behavior of Fe$_2$Co$_2$ complexes.

This chapter describes therefore the synthesis, characterizations and the study of pressure-induced ETCST behaviors of the square complex, $\{[\text{Fe(Tp}^*)(\text{CN})_3]_2[\text{Co(Mebik)}]_2\}_2$·$\text{BF}_4$·2$\text{H}_2\text{O}$ (5). The thermal ETCST transitions under various pressures have been studied by HP magnetic measurements. The pressure-induced ETCST transition at room temperature has been investigated by both HP-SC-XRD and HP $\mu$-Raman spectroscopy measurements.

2 Syntheses, spectroscopic and structural characterizations

2.1 Synthesis, FT-IR spectrum and TGA of $\{[\text{Fe(Tp}^*)(\text{CN})_3]_2[\text{Co(Mebik)}]_2\}_2$·$\text{BF}_4$·2$\text{H}_2\text{O}$ (5)

All reagents were obtained from commercial suppliers and were used without further purification. $(\text{Bu}_4\text{N})[\text{Fe}^{\text{III}}(\text{Tp}^*)(\text{CN})_3]$ was synthesized according to the procedure reported in the literature for the preparation of $(\text{PPh}_4)[\text{Fe}^{\text{III}}(\text{Tp}^*)(\text{CN})_3]$ but using $\text{NBu}_4\text{Br}$ instead of $\text{PPh}_4\text{Cl}$. The tetra-metallic complex $\{[\text{Fe}^{\text{III}}(\text{Tp}^*)(\text{CN})_3]_2[\text{Co}^{\text{II}}(\text{Mebik})]_2\}_2$·$\text{BF}_4$·2$\text{H}_2\text{O}$ (where the Tp* = hydrotris(3,5-dimethylpyrazol-1-yl) borate, Mebik = bis(N-methyl imidazole-2-yl) ketone) was obtained by reacting the metallo-ligand, $\text{NBu}_4[\text{Fe}^{\text{III}}(\text{Tp}^*)(\text{CN})_3]·\text{H}_2\text{O}$ and $\text{Co}^{\text{II}}(\text{Mebik})_2(\text{BF}_4)_2·\text{XH}_2\text{O}$. The solvent for each step is a mixture of acetonitrile and $\text{H}_2\text{O}$ (4:1). The yellow transparent solution of $\text{Co}^{\text{Mebik}}_2(\text{BF}_4)_2·\text{XH}_2\text{O}$ was prepared in situ by dropwise addition of 5 ml of Mebik ligand solution (38.0 mg, 0.2 mmol) into 5 ml solution of $\text{Co(BF}_4)_2·6\text{H}_2\text{O}$ (34.0 mg, 0.1 mmol) under stirring (note: if the adding process is reverse, the $[\text{Co(Mebik)}]_3(\text{BF}_4)_2$ will be formed as a yellow precipitate). Then the $\text{Co}^{\text{Mebik}}_2(\text{BF}_4)_2·\text{XH}_2\text{O}$ yellow solution was added drop-by-drop into the precursor solution of $\text{NBu}_4[\text{Fe}^{\text{III}}(\text{Tp}^*)(\text{CN})_3]·\text{H}_2\text{O}$ (71.9 mg, 0.1 mmol) dissolved in 10 ml of the mixture solvent. The compound 5 crystallizes as red plate-like crystals by slow evaporation of the solvent at
ambient temperature. Element analysis calculation (%): C, 44.78; H, 4.47; N, 23.99; Found: C, 44.39; H, 4.33; N, 24.51.

FT-IR spectrum was recorded at room temperature under ambient pressure in the range 400 - 4000 cm⁻¹ on a Bruker Tensor 27 ATR (attenuated total reflection) spectrometer.

The figure 1 shows the FTIR spectrum of compound 5. The typical cyanide stretching vibrations are observed at 2159, 2149 and 2132 cm⁻¹. The first two bands are assigned to [[Fe₃⁺(Tp*)][CN]₃][Co₂⁺(Mebik)₂] (BF₄)₂·2H₂O at ambient temperature.

The FTIR spectrum indicates that 5 is in a paramagnetic state [Fe₃⁺-CN-Co²⁺] at ambient temperature.
The thermogravimetric analysis of 5 has been performed under nitrogen flow up to 700 °C with heating rate of 10 °C/min as shown in figure 2. The result shows the weight loss of 5 versus the temperature. The compound undergoes a slight weight loss of about 3% from ambient temperature to 73 °C, associated to the removal of two crystallization water molecules. A plateau (of 97%) is observed between 73 and 215 °C. Then, a sudden weight drop of 39% (the decomposition of Mebik ligands) occurs in the temperature range of 215 °C to 304°C followed by a further slower weight reduction of 30% (the decomposition of Tp* ligands) from 304 to 394 °C. The important weight drops after 215 °C indicate the compound decomposition.

2.2 Structure and intermolecular interactions of 5 at ambient pressure

The XRD measurements on single crystal of 5 were carried out at 200 K according to the procedure described in our previous publications.\textsuperscript{10,12} The compound 5 crystallizes in the triclinic space group with the following unit cell parameters: a = 13.31 Å, b = 13.56 Å and c = 14.17 Å; α = 109.00 °, β = 102.80 ° and γ = 105.85 °; volume = 2197.06 Å\textsuperscript{3}. The figure 3 shows the molecular structure of the square complex in 5 at ambient pressure. The metal – ligand lengths in 5 have the typical values featuring paramagnetic Fe\textsubscript{2}Co\textsubscript{2} square complexes: the average Fe-CN\textsubscript{Bridging} length is 2.004 Å and the average Fe-CN\textsubscript{Tp*} length, 1.925 Å; the average Co-NC\textsubscript{Bridging} length is 2.107 Å and the average Co-N\textsubscript{bik} length, 2.139 Å; the distortion angles of Fe (ΣFe) and Co (ΣCo) sites are 24.83 ° and 38.82 ° respectively. The values of two CoNC angles (∠CoN1C1 = 176.10 ° and ∠CoN2C2 = 178.35 °, respectively) are near linearity (180 °). The two Mebik ligands on Co are not crystallographically

![Figure 2. TGA measurement of \([\text{Fe}^{III}(\text{Tp}^*)\text{(CN)}_3]_2[\text{Co}^{II}\text{(Mebik)}_2]_2 (\text{BF}_4)_2\cdot2\text{H}_2\text{O}\) under N\textsubscript{2} flow.](image-url)
identical: they are named $^{\text{Mebik1}}$ and $^{\text{Mebik2}}$ according to the labels of oxygen atom (O1 and O2) they bear.

Figure 3. Crystal structure of 5 at 200K under ambient pressure. Color code: Co = purple, Fe = green, N = blue, O = red, C = grey and B = beige. The H atom, counter-anion ($\text{BF}_4^-$) and H$_2$O have been omitted for clarity.

The average dihedral angle between the two imidazole rings is 16.47 ° and the average Co-C=O angle is 170.72 °. The last two angles feature the planarity of $^{\text{Mebik}}$ ligand, which influences its aromaticity and hence its $\pi$-acceptor capacity.$^{13}$ More planar is $^{\text{Mebik}}$ molecule, greater is the aromaticity of the ligand and stronger is the its $\pi$-acceptor ability.

Compared to the core structure of 1 obtained at 200 K,$^{12}$ the structure of 5 presents a greater distortion of Co environment and much smaller distortion of Fe-CN-Co moieties: the $\Sigma$Co value is 38.82 ° for 5 and 35.08 ° for 1 (lower than 3 : $\Sigma$Co = 38.06 °). This greater distortion is expected to lead to a better stabilization of the Co(II) redox state. The average CoNC angle is 177.2 ° for 5, which is slightly higher compared with 167.6 ° for 1. This core structure difference results are most likely from the different patterns of the intermolecular interactions in the two compounds. The Fe$_2$Co$_2$ squares in 1 are linked by the pseudo $\pi - \pi$ contacts of neighboring vbik ligands and one of two vbik pairs includes an antiparallel arrangement of the C=O group, as described in the chapter 2. In contrast, the Fe$_2$Co$_2$ squares in 5 experience only weak intermolecular interactions of CH-$\pi$ and CH-O types. The figure 4 shows the short contacts CH - $\pi$ between a methyl group of $^{\text{Mebik1}}$ and two pyrazole rings of Tp*. The distances CH - $\pi$ for the pair of short contacts are 2.511 Å and 2.565 Å.
respectively. The squares are connected to each other by two pairs CH - π contacts to form a square chain along the c direction. Besides, theses CH - π short contacts, the oxygen atom on each Mebik2 ligand forms CH-O short contact with one of methyl group of Tp* of the neighboring square, as showed in figure 5. These CH-O shorts contacts link the squares together in the direction forming an angle of β/2 = 51.40 ° with c direction, leading to the formation a 2D supramolecular square layer parallel to a/c plane. The square layers are separated by BF₄⁻ counter-anions. A C-H short contact can be observed between a pair of Tp* ligands in two neighboring layers, as showed in the figure 6.

Figure 4. The perspective view with four other neighboring squares through the CH – π short contacts between Mebik1 and Tp*, linking the squares of 5 into a chain alongside c direction (highlighted by light green color). Color code: Co = purple, Fe = green, N = blue, O = red, C = grey and B = beige. The counter-anion (BF₄⁻) and H₂O have been omitted for clarity.
Figure 5. The perspective view in b direction of 5 in interactions with the CH-O short contacts between a pair of Mebik2 and Tp* (green dotted lines). Color code: Co = purple, Fe = green, N = blue, O = red, C = grey and B = beige. The counter-anion (BF4-) and H2O have been omitted for clarity.

Compared with the square 1, the absence of strong intermolecular interactions in 5 seems to allow a higher interplanar dihedral angles between two imidazole rings (compound 5: 14.54 °, 18.39 °; compound 1: 9.71 °, 11.08 °). The methyl group on one side of the imidazole rings is fixed and other one is more flexible to form these two bigger dihedral angles between imidazole rings, which might lead to a higher distortion of Co environment (ΣCo) and a minimized twisting of the Co-NC-Fe linkages described by ∠CoN1C1, ∠CoN2C2.
3 Thermal ETCST under different pressures: results of High-Pressure (HP) magnetic measurements.

While square 1 exhibits a kinetically hindered ETCST around 140 K, which can be revealed at slow scan rate, 5 remains blocked in a paramagnetic state in the whole temperature range of 2 - 400 K under ambient pressure, whatever the temperature scan rate. It is worth noting that Mondal et al. published the ETCST study on a very similar Fe$_2$Co$_2$ square compound with exactly the same ligands on Fe and Co, but crystallized with a different solvent: \{[Fe(Tp*)(CN)$_3$]$_2$[Co(Mebik)$_2$]$_2$\}·(BF$_4$)$_2$·2DMF.$^{14}$ This compound has a supramolecular structure implying also weak but different intermolecular interactions (CH···F, CH···O, CH···N, CH···C), which undergoes a two-step ETCST transition at 178 K and 214 K without thermal hysteresis. This compound shows a smaller distortion of the Co coordination sphere at 240 K in the paramagnetic state, $\Sigma$Co = 31.86 °, as compared to compounds 1 and 5. The Co-cyanide bridge angles are comparable: $\angle$Co-NC = 169.6 °/178.2 ° at 240 K.
The influence of $\angle$CoNC and $\Sigma$Co on the ETCST behaviors of molecular and 3D Fe/Co PBAs are well known. Bleuzen et al. have pointed that a linear Co-NC-Fe linkage maximizes the ligand field around Co ion and stabilizes diamagnetic state in Fe/Co PBAs. Conspicuously, the bending of Co-NC angles diminishes the ligand field and favors the paramagnetic state [Co$^{ll}$-NC-Fe$^{III}$]. Regarding the distortion of Co environment represented by $\Sigma$Co, high values of $\Sigma$Co favors the paramagnetic state [Co$^{ll}$-NC-Fe$^{III}$], and decreases the transition temperature of ETCST. In extreme cases, too large $\Sigma$Co values would lead to compounds that remain blocked in the paramagnetic state. Our findings are somehow coherent with these data: the $\Sigma$ factor seems to have a stronger impact on the electronic state of the square than the bending of $\angle$CoNC angle. The compound 1 which shows an intermediate distortion of the Co coordination sphere, $\Sigma$Co = 35.08 ° (and more bent cyanide angles $\angle$Co-NC = 156.17 °/167.07 °) shows a transition at low T, below ca. 140 K (that is revealed only at low temperature scan rate). Compound 3 is more stable in the paramagnetic state with its $\Sigma$Co of 38.06 ° ($\angle$Co-NC = 159.31 °/167.21 °). The two compounds 1 and 3 have almost the same bent cyanide angles but relatively different distortion value of cobalt ions. Here, the compound 5 is also blocked in the paramagnetic state by its relatively high $\Sigma$Co of 38.8 ° (despite of its almost linear CoNC angles, $\angle$Co-NC = 176.1 °/178.35 °). The previously published solvatomorph that has a weaker distortion, $\Sigma$Co of ca. 31 °, shows (a two-step) transition at higher temperature (178 and 214 K), despite of small bending $\angle$Co-NC = 169.6 °/178.2 °. Therefore, by comparing these results, the $\Sigma$ factor might play a stronger effect on the electronic state of the square compared with the bending $\angle$CoNC angle.

The figure 7a shows the thermal variation of the paramagnetic molar fraction of 5, $\gamma_{HS}$, under four different pressures (0, 0.96, 1.05 and 1.16 GPa) in the temperature range of 2 - 250 K. The figure 7b shows the corresponding thermal variation of $\chi_M T$ product. $\gamma_{HS}$ is calculated by the ratio of $\chi_M T$ over the plateau value of $\chi_M T$, $(\chi_M T)_{max}$ after the thermal ETCST transition [$\gamma_{HS} = \chi_M T/(\chi_M T)_{max}$]. At ambient pressure (p = 0 GPa), the $\chi_M T$ value at 300 K is ca 7.55 cm$^3$ mol$^{-1}$ K, in agreement with the expected $\chi_M T$ value of paramagnetic square consisting of four magnetically independent ions: two Fe$^{III}_{LS}$ ions (S = 1/2, g ≈ 2.6) and two Co$^{II}_{HS}$ (S = 3/2, g ≈ 2.4).

The application of a pressure of 0.956 GPa, converts partially 5 from the paramagnetic state to a diamagnetic one. At 120 K, the value of $\gamma_{HS}$ is about 0.44, indicating that ca. 55 % of paramagnetic species have been converted into diamagnetic ones. Upon heating, the compressed 5 displays a thermal ETCST transition with a hysteresis of 6 K (T$_{1/2}$ ↑ = 173 K, (T$_{1/2}$)$_1$ ↓ = 167 K). When the pressure increases to 1.06 GPa, the para-dia conversion reaches
ca. 77 %. The compressed 5 exhibits a two-step ETCST transition with \((T_{1/2})_1 \uparrow = 161\) K and \((T_{1/2})_1 \downarrow = 153\) K, and \((T_{1/2})_2 \uparrow = 192\) K, \((T_{1/2})_2 \downarrow = 191\) K. The thermal hysteresis of the first transition remains 6 K and the second one shows a thermal hysteresis of 1 K. At 1.16 GPa, the para-dia conversion seems complete as the \(\chi_M T\) value is close to zero at 120 K. As expected, the two-step transition moves to higher temperature range: \((T_{1/2})_1 \uparrow = 203\) K and \((T_{1/2})_1 \downarrow = 198\) K, and \((T_{1/2})_2 \uparrow = 229\) K, \((T_{1/2})_2 \downarrow = 227\) K. The hysteresis width of the first step conversion decreases to 3 K, but that of the second step transition seems to increase to 5 K. Here it is quite difficult to accurately quantify the variation of the thermal hysteresis width versus pressure.

Figure 7. The thermal variation of the paramagnetic molar fraction of 5, \(\gamma_{\text{HS}}\), under four different pressures (a) and the corresponding thermal variation of \(\chi_M T\) (b)

4 Pressure-induced ETCST identification by X-ray diffraction at 300 K

In order to follow the structural modification of 5 during the pressure-induced ETCST, we performed single-crystal X-ray diffraction measurements under various pressures at ambient temperature (300 K). The table 1 lists the unit cell parameters for all the pressures. The space group of the crystal remains triclinic up to 1.85 GPa. The table 2 outlines selected parameters of the core structure of 5. The detailed analysis of the structural data is in the following sections.
Table 1. Unit cell parameters under different pressures

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>0</th>
<th>0.19</th>
<th>0.76</th>
<th>1.49</th>
<th>1.79</th>
<th>1.85</th>
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<td>Space group</td>
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<td>P 1(2)</td>
<td>P 1(2)</td>
<td>P 1(2)</td>
<td>P 1(2)</td>
<td>P 1(2)</td>
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<td>a (Å)</td>
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<td>13.2052(5)</td>
<td>13.1214(4)</td>
<td>12.8472(3)</td>
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<td>12.6818(3)</td>
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<tr>
<td>b (Å)</td>
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<td>13.3076(7)</td>
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<td>c (Å)</td>
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<td>102.423(5)</td>
<td>102.076(3)</td>
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<td>100.733(2)</td>
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<td>γ (°)</td>
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<td>106.081(4)</td>
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<td>107.064(2)</td>
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<td>( \rho_{\text{calc}} ) g/cm³</td>
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<td>1.469</td>
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<td>Reflections collected</td>
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<td>0.499</td>
<td>0.500</td>
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Note: Chemical formula: \([\text{Fe}^{\text{III}}(\text{Tp}^*)\text{(CN)}_3]_2[\text{Co}^{\text{II}}(\text{Mebik})_2]^2\) (BF₄)₂·2H₂O (C₇₄H₈₄B₂Co₂F₈Fe₂N₃₄O₆), Mw: 1948.85 g/mol, T = 300 K for all pressures except ambient pressure (200 K).
Table 2. Selected structure parameters of 5

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>0</th>
<th>0.19</th>
<th>0.76</th>
<th>1.49</th>
<th>1.79</th>
<th>1.85</th>
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<td>$d_{[\text{Fe-(CN)bridging}]_{\text{av}}}$ (Å)</td>
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<td>1.941</td>
<td>1.932</td>
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<td>1.944</td>
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<td>1.932</td>
<td>1.846</td>
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<td>1.911</td>
<td>1.910</td>
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<td>1.911</td>
<td>1.910</td>
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<td>$d_{[\text{Co-N(Mebik)}]_{\text{av}}}$ (Å)</td>
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Co···Co (Å)

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<tr>
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<td>2.769</td>
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Note: T = 300 K for all pressures except ambient pressure (200 K).

4.1 Changes of the core structure and interactions of 5 induced by pressure

The ETCST conversion of 5 can be detected by the changes of metal-ligand bond length (M-L), especially on the Co center. The figure 8 shows the variation versus pressure of four types of average metal-ligand length (M-L) (Co-$N_{bridge}$, Co-$N_{Meik}$, Fe-$C_{bridge}$ and Fe-$N_{Tp^*}$). At ambient pressure, the average length of Co-$N_{bridge}$ (2.107 Å), Co-$N_{Meik}$ (2.139 Å), Fe-$C_{bridge}$ (1.925 Å) and Fe-$N_{Tp^*}$ (2.004 Å) are characteristic of a paramagnetic Fe$^{III}_2$Co$^{II}_2$ square. When pressure is increased up to 1.79 GPa, all four types of M-L distances change significantly to reach values that are typical of the Fe$^{II}_2$Co$^{III}$ diamagnetic state: the length of Co-$N_{Meik}$ suddenly decreases from 2.139 Å to 1.932 Å, that of Co-$N_{bridge}$ diminishes from 2.107 Å to 1.880 Å. Meanwhile, the bond length of Fe-$C_{bridge}$ also lessens from 1.925 Å to 1.868 Å and the bond length of Fe-$N_{Tp^*}$ slightly increases from 2.004 Å to 2.025 Å. These average M-L distances are stable and show similar values above 1.49 GPa. Thus, as shown in figure 8, the para-to-dia ETCST transition takes place in the pressure range of 1.49 - 1.79 GPa for 5.

![Figure 8. M-L bond length versus pressure for 5 at room temperature. (The solid lines are for eye-guide)](image-url)
Besides M-L bond lengths, other structural parameters change more or less abruptly during ETCST transition. Figure 9 shows the variation of $\Sigma$Co and $\Sigma$Fe (9a), $\angle$CoN1C1 and $\angle$CoN2C2 (9b), the square side length, Fe···Co1 (through C1N1 linkage) and Fe···Co2 (through C2N2 linkage) (9c) and the two diagonal distances, Fe···Fe and Co···Co (9d). Regarding the distortion of the coordination environments of Co and Fe ions, the $\Sigma$Co and $\Sigma$Fe have the usual values for the Fe$_2$Co$_2$ squares containing Mebik ligands, 38.82 ° and 24.83 ° respectively at ambient pressure. Both $\Sigma$Co and $\Sigma$Fe increases notably in the pressure range 0.00 - 1.49 GPa, which shows that the pressure induces some distortion in the coordination spheres: from 38 ° to 47 ° for $\Sigma$Co and from 24.83 ° to 30.90 ° for $\Sigma$Fe. After the pressure-induced paramagnetic to diamagnetic ETCST, the $\Sigma$Co value decreases to 21 ° above 1.49 GPa, while $\Sigma$Fe keeps almost a constant value (30.87 °) from 1.49 to 1.85 GPa. Thus, the ETCST mainly impacts the cobalt coordination sphere.

No clear effect is observed on the Co-NC-Fe linkage as shown in figure 9(b): the CoN1C1 angle tends to decrease significatively for p > 0.79 GPa, before ETCST, while the CoN2C2 angle remains almost unchanged during the pressure variation up to 1.85 GPa.

Figure 9. Evolution of structural parameters upon pressure: $\Sigma$Co and $\Sigma$Fe (9a), $\angle$CoN1C1 and $\angle$CoN2C2 (9b), length of the square sides, Fe···Co1 and Fe···Co2 (9c) and the diagonal distances, Fe···Fe and Co···Co (9d), molecular deformation scheme(9e). The solid lines are for eye-guide.

The figure 10 shows the orientations of the two types of intermolecular interactions (CH- π and O-HC) versus that of the Co-NC-Fe linkages of 5. This might help us to understand why the pressure is
more efficient to twist $\angle \text{CoN1C1}$. The CH - $\pi$ short contacts involved in C atom on $^\text{Me}$bik ligand is almost along the line Co···Fe 1 ($\angle \text{C-CoFe} = 155.93^\circ$), and rather perpendicular to the linkage Co···Fe 2. Therefore, the pressure transmitted by CH- $\pi$ interaction bend more easily $\angle \text{CoNC1}$ than $\angle \text{CoNC2}$. As the orientation of interaction mediated by O-HC short contacts is out of the square’s plan ($\angle \text{OCFe} = 65.39^\circ$), it cannot twist neither $\angle \text{CoN1C1}$ nor $\angle \text{CoN2C2}$.

Figure 10. Intermolecular interactions: CH ··· $\pi$ (highlighted in light green) and O···HC (highlighted in light orange) types with respect to the linkage Co-NC-Fe 1 in 5. The C atom in CH···$\pi$ short contacts forms an angle of 155.93 ° with Co and Fe atoms, while the O atom in O···HC $\pi$ short contacts forms an angle of 65.39 ° with Co and Fe atoms. Color code: Co = purple, Fe = green, N = blue, O = red, C = grey and B = beige.

Concerning the square’s geometry, the two sides and two diagonal distances shrink during the paramagnetic to diamagnetic ETCST transition in the pressure range of 1.49 - 1.85 GPa. As expected, the side lengths of Fe···Co1 and Fe···Co2 decrease from average 5.1 Å to near 4.9 Å (typical values of para - and dia - magnetic states). Compared with compound 1, the changes in the diagonal distances are quite different. Only the Fe···Fe direction distance decreases in compound 1, while both the Fe···Fe and Co···Co distances descend in the pressure-induced ETCST in compound 5. The Fe···Fe diagonal distance decreases from 7.715 to 7.275 Å, and the Co···Co one drops from 6.743 Å to 6.570 Å in the ETCST pressure range. The percentage of the shrinkage from 1.49 to 1.85 GPa is 4.53% for the distance Fe···Co1, 4.14% for the distance Fe···Co2, 5.70% for Fe···Fe diagonal distance and 2.57% for Co···Co diagonal distance respectively. With the pressure increasing from 0 to 1.85
GPa, the average value of $\angle \text{Co-C}=\text{O}$ does not change significantly, while the average value of the dihedral angles of Mebik ligand rises steadily from $16.47^\circ$ to $20.26^\circ$. The vertex angles $\angle \text{FeCoFe}$ and $\angle \text{CoFeCo}$ remain almost constant in the whole pressure of 0 - 1.85 GPa.

As described in chapter 2, the compound 1 exists anisotropic deformation of molecular geometry in the square since only one diagonal direction distance change under pressure, here for compound 5, the diagonal distance decreases in both direction of Fe···Fe and Co···Co is more like an isotropic molecular deformation as shown in figure 9e, this should be related to their different intermolecular interactions between neighboring molecules.

4.2 Variation of the unit cell parameters of 5 versus pressure

Much the same as for previous compounds, the unit cell parameters of 5 ($a$, $b$, $c$) and the cell volume do not show any abrupt change during the ETCST transition. After an initial decrease upon pressure application, all these parameters decrease smoothly with increasing pressure, as shown in figure 11 (a and c). From ambient pressure to 1.85 GPa, the shrinkage of $a$, $b$, $c$ and volume are 4.73%, 6.05%, 6.56% and 15.3 % respectively. This is reminiscent of the previous report in pressure-induced abnormal ETCST conversion of 1: an obvious change is observed in Co-N distances but a smooth continuous decrease is observed in the cell parameters as already observed in SCO complexes as well.21 Regarding the angles, the variations of $\alpha$, $\beta$ and $\gamma$ (figure 11 b) are moderate: - 0.89%, - 2.35% and 1.44% respectively when the pressure increases from 0 to 1.85 GPa.

![Figure 11](image)

Figure 11. The modification of the unit cell parameters of 3 versus pressure : a, b and c (a); $\alpha$, $\beta$ and $\gamma$ (b); volume (c). The solid lines are for eye-guides.
4.3 Modification of the intermolecular interactions in 5 upon pressure

The pressure increases considerably the numbers of short contacts in 5. The table 3 summarizes the numbers of various short contacts against pressure and the figure 12 shows the change of contact quantity. It is commonly accepted that the most important intermolecular interactions in ETCST and SCO compounds are those mediated by the direct short contacts between neighboring ligands. Most of the contacts occur between the Mebik and Tp* ligands, especially the Mebik1 and Tp*. The obvious increase of the contact quantity takes place at 1.49 GPa from the Mebik and Tp* ligands, before the ETCST pressure range (1.49 - 1.79 GPa). It is also worth noticing that the conversion to lower-volume diamagnetic state does not lead to a decrease of the short contacts.

![Figure 12. Contact quantity change with increasing pressure.](image)

**Table 3. Pressure effect on the molecular contact quantity of the ligands and counterions**

<table>
<thead>
<tr>
<th>P(GPa)</th>
<th>Mebik1-Mebik1</th>
<th>Mebik1-Tp*</th>
<th>Mebik2-Tp*</th>
<th>Total Mebik-Tp*</th>
<th>Tp*-BF4⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>14</td>
<td>0</td>
<td>14</td>
<td>7</td>
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<tr>
<td>0.76</td>
<td>8</td>
<td>16</td>
<td>0</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>1.49</td>
<td>14</td>
<td>32</td>
<td>4</td>
<td>36</td>
<td>8</td>
</tr>
<tr>
<td>1.79</td>
<td>14</td>
<td>36</td>
<td>6</td>
<td>42</td>
<td>14</td>
</tr>
<tr>
<td>1.85</td>
<td>14</td>
<td>36</td>
<td>6</td>
<td>42</td>
<td>12</td>
</tr>
</tbody>
</table>
Unlike the square of $[[\text{Fe(Tp})(\text{CN})_3]_2[\text{Co(vbik)}]_2]_2\cdot(\text{BF}_4)_2$ or the $[[\text{Fe(Tp})(\text{CN})_3]_2[\text{Co(vbik)}]_2]_2\cdot(\text{PF}_6)_2$, the intermolecular interaction for compound 5 $[[\text{Fe(Tp}^*)](\text{CN})_3]_2[\text{Co(Mebik)}]_2]_2\cdot(\text{BF}_4)_2\cdot2\text{H}_2\text{O}$ results in the methyl group (CH$_3$) of the Mebik ligand and the two pyrazole rings of Tp* ligand, instead of the vinyl group (C=O) between vbik···vbik ligands for the $[[\text{Fe(Tp)}(\text{CN})_3]_2[\text{Co(vbik)}]_2]_2$ system.

Here below, the figure 13 illustrates the modification of the pair of CH···π short contacts between the methyl groups of Mebik1 ligand and the two pyrazole rings of Tp*, Py1 and Py2 (consist of two N atoms and three C atoms). Since the contact number between Mebik and Tp* ligands are too many to draw clear pictures, we analyzed the contact distance change between center of Tp* (Py1 and Py2 stand for the two centroids of pyrazole ring) and Mebik ligand in the pressure range of 0-1.49 GPa. At ambient pressure, the methyl group (on the Mebik ligand) is in interaction with four atoms of each pyrazole ring: C-N-N-C for centroid Py1 and C-C-C-N for centroid Py2. When the pressure is increased to 0.19 GPa, the methyl group is a little far away from Py1 (the direct contact disappears) and keeps contact with only a C atom of Py1. The contacting atoms in Py2 also change to (C-N-N-C) at 0.19 GPa. With further increase to 0.79 GPa, the initial CH···π pattern is again restored for Py1. From 1.49 GPa, all five atoms of Py2 are involved in the CH···π short contacts, while only 4 atoms of Py1 are implied in CH···π short contacts under all pressure except 0.19 GPa.

Moreover, compared with compound 1, the R1 and wR2 in compound 5 is almost the same. For example, the R1 and wR2 of 1 are separately 0.0997 and 0.1830 in 1 at 0.71 GPa, and that of 5 are separately 0.0667 and 0.2580 at 0.79 GPa. It means the XRD data in 5 under pressure application has the same reliability as that in compound 1.
The figure 14 shows the variation versus pressure of various contact distances for CH···π and CH···O interactions: Py1-H, Py1-C, Py2-H’, Py2-C, O\textsubscript{Mebik2}-H\textsubscript{Tp*} and O\textsubscript{Mebik2}-C\textsubscript{Tp*}. It is observed that the application of a weak pressure (0.19 GPa) brings some perturbations: Py1-H distance increases; Py2-C and O\textsubscript{Mebik2}-H\textsubscript{Tp*} distances diminish significantly. From 0.79 GPa, all these contact distances tend to decrease slightly with increasing pressure, but no one displays a sudden drop during pressure-induced ETCST transition, as does the distance of the antiparallel C=O pair in compound 1.

In summary, the different patterns of the intermolecular interactions in 1 and 5 yield different geometrical modifications of the squares during the pressure-induced ETCST transition. As mentioned above, both the diagonal distances Fe···Fe and Co···Co shrink for 5, whereas only the diagonal distance Fe···Fe becomes shorter in 1 (the diagonal Co···Co distance diminishes only slightly) and the Co site is obviously kept in place by the strong intermolecular interaction of vbik1 pair. For 5, the distortion of Co site shows a sudden decrease in the ETCST range, which is accompanied by a sudden drop of the cyanide bridge angle of CoC1N1 due to the weak intermolecular interaction along the CoC1N1 orientation. Therefore, unlike in the compound 1, the C/H···π interaction in compound 5 is not enough strong to strain the coordination metals so that both the Co metal and Fe metal ions become flexible under pressure application, which results in a similar decrease of both diagonal directions Fe···Fe and Co···Co in compound 5. This change can be considered as an isotropic molecular geometry deformation in contrast with the anisotropic molecular geometry deformation in compound 1.

![Figure 14. Distance variations against pressure of the two types of short contacts CH···π (Py1-H, Py1-C, Py2-H’, Py2-C) and CH-O (O-H, O-C). The solid lines are eye-guides.](image)
4.4 The influence of the H bond in the ETCST behaviors of 5.

The terminal CN group of the Fe subcomponents forms a H-bond with the solvent H$_2$O, which strength influences greatly the redox potential of Fe$^{III/II}$. The stronger the H bond is, the lower the redox potential of Fe$^{III/II}$ is, and the more stabilized the diamagnetic state is. Unfortunately, the precision of HP-SC-XRD is not sufficient to determine the position of H atom involved in the H bond. However, the distance N···O gives a rough estimate of the H-bond energy, if the orientation of the solvent versus Fe-CN remains unchanged with changing pressure in the compound. In 2017, Oshio et al. reported the study of the ETCST behaviors in a square compound, [{Fe(Tp*)CN$_3$}$_2$[Co(bpy*)$_2$]$_2$·PF$_6$·2CP·8BN (CP), with bpy* = 4,4'-diméthyl-2,2'-bipyridine and BN = Butyronitrile, co-crystallized with 4-cyanophenol (CP). The crystal cell of the compound contains two distinct squares, which terminal CN groups forms H-bonds with CP molecules. The CP molecule, which keeps the same orientation throughout the studied temperature range (50 K - 350 K), builds intermolecular interactions of $\pi-\pi$ type via short contacts with bpy* ligand, organizing the squares into 2D layers. The authors demonstrated that the electronic configuration of each square in the unit cell depends closely on the interatomic distance between NCN and OCP, d$_{NO}$, (dia: d$_{NO} \leq 2.655$ Å; para: d$_{NO} \geq 2.70$ Å). Here we use the same approach following the d$_{NO}$ variation to probe the hydrogen bond variation in compound 5.

The figure 15 shows the percentage of the variation versus pressure of the interatomic distance between NCN and O$_{H2O}$, $\Delta$d$_{NO}$ in 5, compared with that between NCN and O$_{MeOH}$ in 1. The variation of $\angle$CN···O (the average value is 170 °) did not take significant change with increase of pressure as shown in figure 15(c) in 5. Both of the two compounds 1 and 5 exhibit a pressure-induced ETCST at room temperature at 1.49 GPa for 5 and at 0.73 GPa for 1, as revealed by pressure-induced changes in Co-L bond lengths. A drastic decrease of d$_{NO}$ is observed around the ETCST transition for the two compounds, pointing to the H-bond reinforcement in the process. Furthermore, a change is also observed at low pressure: at 0.1 GPa, the absolute value change of $\Delta$d$_{NO}$ is more significant (more than 3%) in 1 than that in 5, which probably could explain the higher pressure-induced ETCST conversion efficiency in compound 1 (the complete para-dia conversion of 1 is observed at ca 150 K at a small pressure of 0.10 GPa). However, more accurate physical analyses are need to further confirm the relationship between H-bond and para/dia magnetic conversion.
5 Pressure-induced paramagnetic to diamagnetic ETCST transition in 5 probed by HP-μ Raman spectroscopy

The HP Raman spectra have been measured at room temperature under several pressures from 0.67 to 1.79 GPa, as shown in figure 16. When \( p \leq 1.11 \) GPa, the background noise is important in the spectra. In contrast, for \( p \geq 1.43 \) GPa, the signal-to-noise ratio is greatly improved. At 0.67 GPa, the three bands at 2165 cm\(^{-1}\), 2148 cm\(^{-1}\) and 2132 cm\(^{-1}\) correspond to the three FTIR peaks at 2159 cm\(^{-1}\) and 2149 cm\(^{-1}\) and 2132 cm\(^{-1}\) and have the same attributions. The first two bands are assigned to \([\text{FeIIILS-CN-CoIIHS}]\) moiety, and the last one to the terminal CN group linked to the Fe\(^{III}\) ion. The broad band at 2460 cm\(^{-1}\) is related to the stretching vibration of B-H on the \([\text{FeIII/II(Tp*)(CN)3}]\). The pressure application gives rise to a blueshift of the three cyanide bands, but their positions tend to be stabilized from 1.57 GPa. Interestingly, above \( p = 1.43 \) GPa, a band of weak intensity at 2114 cm\(^{-1}\) appears and its intensity increases with pressure. This band can be attributed to the diamagnetic \([\text{FeIILS-CN-CoIIILS}]\) moiety, and its appearance indicates the beginning of ETCST transition. This pressure range of ETCST (1.43 - 1.57 GPa) is in good agreement with that determined by HP-SC-XRD measurements (1.49 GPa), considering the experimental error in pressure determination (± 0.1 GPa). However, the Raman spectra indicate an incomplete para-dia conversion of 5 at 1.79 GPa, this is probably due to the pressure measurement difference (pressure is slightly overestimated for XRD measurements) and the different experimental set-up between HP-Raman and XRD. XRD experiments are carried out after HP-Raman (the pressure value is detected in HP-Raman experiments and will increase with time in a fixed temperature).
6. Conclusion

In this chapter, we described the thermally-induced ETCST of \([\text{Fe}^{III}(\text{Tp}^*)\text{(CN)}_3]\_2[\text{Co}^{II}(\text{Me}^\text{bik})_2]\_2\) (BF\(_4\))\(_2\cdot2\text{H}_2\text{O}\) (5) by HP magnetic measurements at variable temperature, and also analyzed the pressure-induced paramagnetic to diamagnetic conversion at room temperature by HP-SC-XRD and HP-Raman measurements.

Even though the compound 5 has a very similar |\(\Delta E_{\text{FeCo}}\)| value with the compound 1, both the Fe\(_2\)Co\(_2\) core structure and the intermolecular interaction pattern of the two square complexes are quite different at ambient pressure. The compound 5 is characterized by almost linear Co-NC-Fe moieties and a relative high distortion of the cobalt coordination sphere (\(\Sigma\text{Co} = 38.82^\circ\) for 5, and \(\Sigma\text{Co} 35.08^\circ\) for 1). The higher distortion, \(\Sigma\text{Co}\), is also coherent with a better stabilization of the paramagnetic state in the whole temperature range of 2 - 300 K in 5. Here, even at low scan rate of 0.01 K/min, it was not possible to reveal any ETCST at low temperature in 5. In contrast, a transition can be revealed at low temperature which is coherent with the lower \(\Sigma\text{Co}\) value in 1.

The pressure-induced paramagnetic to diamagnetic conversion of 5 is partial and becomes complete at higher pressure than in 1: \(p > 1.16\) GPa at 150 K and \(p > 1.79\) GPa for 300 K. Under pressure application, compound 5 displays two-step ETCST transitions with small hysteresis of 3 K - 6 K. Our limited X-ray data have not allowed determining if the partial transition was due to the occurrence of two crystallographically-independent square complexes. As usual, the value of \(\Sigma\text{Co}\) at paramagnetic states is typically much larger than that in diamagnetic states. The need for
higher pressures to realize the para-dia conversion in 5 in comparison to 1 is also coherent with the stronger distortion observed on the Co site. From the distortion on Co site, it can be concluded that, the better stabilization of the paramagnetic state: the higher distortion on the Co site is, the better stabilized the paramagnetic state is.

Moreover, intermolecular interactions are also expected to play a role on the p-induced phenomenon. The different intermolecular interactions in 5 results in an isotropic-like molecular geometry deformation with changing pressure compared with compound 1 (anisotropic geometry deformation for compound 1).

We also suspect that a change in the H-bond interaction involving the terminal cyanide may play a critical role on the transition.26 The analysis of the H-bond formed between the terminal CN group and the protic solvents in 1 and 5 suggests that the H-bond reinforcement can be associated with pressure-induced para-dia conversion. Pressure-induced ETCST makes the nitrogen getting more basic and attracts better the H-acid of water, those change under pressure is coherent with the efficiency of the applied-pressure in shortening the distance $\text{N}_\text{CN} \cdots \text{O}_\text{Solvent}$ (H-bond reinforcement). Nevertheless, for further analysis of relationship between hydrogen bonding and pressure conversion, more precise physical experiments (such as XRD study under pressure for compound 1D) are needed in the next step research.
Reference


(22) Secondary Metal Coordination Using a Tetranuclear Complex as Ligand Leading to Hexanuclear Complexes with Enhanced Thermal Barriers for Electron Transfer | CCS Chem.


Chapter 5

Thermal ETCST of \([\text{Fe(Tp)(CN)}_3\text{][Co(vbik)}_2\text{]}\text{[ClO}_4\text{]}_2 \cdot 2\text{CH}_2\text{Cl}_2 \text{ (6)}\) at ambient pressure and direct observation of its ETCST propagation by optical microscopy
1 Introduction

In chapters 2-4, we have reported that the ETCST equilibrium of Fe₂Co₂ squares observed in solution near room temperature could be either transferred or lost in the solid phase, depending on the crystal phase. For example, 1, \{[\text{Fe(Tp)(CN)}₃]_2[\text{Co(vbik)}]_2\}_2\cdot2\text{BF}_4\cdot2\text{MeOH}, is apparently paramagnetic whose kinetically hindered ETCST around 140 K is revealed by magnetic measurements; while 2, \{[\text{Fe(Tp)(CN)}₃]_2[\text{Co(vbik)}]_2\}_2\cdot(\text{BF}_4)_2\cdot\text{MeOH}\cdot10\text{H}_2\text{O}, crystallized from the same mother solution, shows a T-induced transition near \text{ca.} 335 \text{ K.} 3 \text{ and 4 have the similar magnetic properties with 1 and 2: the former is paramagnetic and the second presents an ETCST at \text{ca.} 325 \text{ K.} Interestingly, we observed that the application of a moderate pressure (> 0.1 GPa) on the compound 1 could force the sample to switch to the diamagnetic state (which has a lower volume due to shorter Co-N bonds) and the pressure greater than 0.32 GPa on compound 3, \{[\text{Fe(Tp)}(\text{CN})₃]_2[\text{Co(vbik)}]_2\}_2\cdot2\text{PF}_6\cdot2\text{MeOH} \text{ could convert the sample to partially switch with more complicated magnetic behavior.}

The blocking ligands on Fe and Co sites being the same for 1, 2, 3, and 4, we have observed that the different counter-anions and co-crystallized solvents can induce subtle variations of the core structures and of supramolecular structures. The solid-state interactions can alter drastically the magnetic properties of these Fe₂Co₂ squares. In continuation to these works, we have prepared another Fe₂Co₂ square bearing Tp ligand on Fe site and vbik ligands on Co site but with ClO₄⁻ as counter-anion, \{[\text{Fe(Tp)}(\text{CN})₃]_2[\text{Co(vbik)}]_2\}_2\cdot2\text{ClO}_4\cdot2\text{CH}_2\text{Cl}_2 \text{ (6).} On the contrary to all the squares described in previous chapters, 6 can be isolated only at a paramagnetic state at room temperature. The complex shows a reversible thermally-induced ETCST with a hysteresis loop of 18 K, revealed by magnetic measurements. In order to rationalize this distinct ETCST behavior, we have carried out the XRD measurements on a single crystal of 6 at 240 and 270K respectively to obtain the structures at both diamagnetic and paramagnetic states. We have carefully analyzed the high temperature (HT) and low temperature (LT) structural data of 6 and compared them with that of other squares to draw the structure-properties correlation for this Fe₂Co₂ square family. Furthermore, we have performed the optical microscopy measurements on the single crystal of 6 to observe directly the nucleation and the propagation of the thermal ETCST.
2 Syntheses, structural and spectroscopic characterizations

2.1 Preparation of \([\text{[Fe(Tp)(CN)₃]₂[Co(vbik)₂]₂}(\text{ClO}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2 \ (6)}\)

A 5.0 mL aqueous solution of Co(\text{ClO}_4)_2·6\text{H}_2\text{O} (9.14 mg, 0.025 mmol) was placed at the bottom of a test tube, and a mixture of methanol and dichloromethane (1:1, v/v, 5 mL in total) was gently layered on the top of the solution, then a 5.0 mL dichloromethane solution of \text{Bu}_4\text{N}[\text{Fe}^{III}(\text{Tp})(\text{CN})_3] (14.7 mg 0.025 mmol) and vbik (10.7 mg, 0.05 mmol) was carefully added as the third layer. After a few weeks, red square crystals were collected. Yield: 38\%. based on Co (\text{ClO}_4)_2·6\text{H}_2\text{O}. Anal. calc (%) for \text{C}_6\text{H}_6\text{B}_2\text{Co}_2\text{Fe}_2\text{N}_{34}\text{O}_4·2\text{ClO}_4·2(\text{CH}_2\text{Cl}_2); \text{C}: 41.27; \text{H}: 3.17; \text{N}: 23.37; Found: \text{C}: 40.98; \text{H}: 3.26; \text{N}: 22.89. IR (KBr, cm⁻¹): several characteristic peaks are observed at 2508 cm⁻¹ (ν_B⁻H), 2163 cm⁻¹ (ν_C-N), 2117 cm⁻¹ (ν_C-N), 1647 cm⁻¹ (ν_C-O), 1420 cm⁻¹ (ν_C-O), 1106 cm⁻¹ (ν_ClO_4).

Since the heavy metal perchlorate is very sensitive to temperature, we heat the compound 6 to 200 °C under N₂. From the weight loss in figure 1 (left), we can see the compound, is stable below 40 °C, and starts to lose mass with increasing temperature and almost reaches the plateau when the temperature is up to 200 °C. In the increasing temperature process, approximately 10\% of the mass is lost, which can be associated with the methylene chloride molecules escaping from the crystal cell (8.34\% of the solvent molecule mass based on the XRD structure). A higher amount of solvent content in TGA measurements compared with XRD is due to the fast sample loading together with a little solvent from the mother liquid. As shown in figure 1(right), the FT-IR data provide additional confirmation of the electronic states of compound 6 at room temperature. The observed cyanide stretching vibrations at 2163 cm⁻¹ is typical of Fe^{III}-CN-Co^{II} linkage. Besides, the peak at 2117 cm⁻¹ indicates some proportion of Fe^{II}-CN-Co^{III} linkage, which is due to the thermochromism and solvatochromism process near room temperature (more explanation is shown below).[6,7] The peak at 2508 cm⁻¹ is from the B-H vibration of the Tp⁻ ligand coordinated on the iron metals. The 1647 cm⁻¹ and 1420 cm⁻¹ peaks are from the C=O groups of vbik ligand, and the vibration peak at 1106 cm⁻¹ is due to the counterion ClO_4⁻. The FTIR spectrum shows the common paramagnetic states of \([\text{[Fe}^{III}(\text{Tp})(\text{CN})_3]_2[\text{Co}^{II}(\text{vbik})_2]_2](\text{ClO}_4)_2 2\text{CH}_2\text{Cl}_2 \ (6)}\) at ambient temperature.
2.2 Visual observation of thermochromism and solvatochromism of 6.

Compound 6 was crystallized as red plate-like at ambient temperature (300 K). Interestingly, the crystals show apparent thermochromism and solvatochromism: their color changes from red to green just after being removed from the mother solution and turn back to red again after a few minutes in the air (see pictures in figure 2).[3] If adding a little solvent dichloromethane to the crystal at stage D (figure 3) the color changing process will happen again, it is reversible and producible. We assume that this transitory color change could be first due to the temperature decrease induced by the evaporation of volatile solvent molecules that converts the red FeIII2CoII2 state into a green FeII2CoIII2 at a lower temperature. Then the change from green to red could be associated with a partial solvent loss or the return to room temperature. As described above, the thermochromism and solvatochromism phenomenon might lead to some green crystal phase (related to 2117 cm⁻¹ FTIR wavenumber) during some physical measurements.

Fresh crystals of 6 that are dipped in an N₂ bath at 240 K turn to green, in contrast with those of 1 and 3 that remain red at temperatures as low as 200 K. These empirical observations point to an occurrence of ETCST and prompt us to carry out variable temperature magnetic measurements.
2.3 Thermal ETCST by magnetic measurements

Magnetic susceptibility measurements were performed on fresh crystals of compound 6 in the temperature range of 230 K – 280 K as shown in figure 3(a). The fresh compound 6 shows a moderately large hysteresis of 18 K with transition temperature upon heating and cooling, $T_{1/2}^{\uparrow} = 273$ K and $T_{1/2}^{\downarrow} = 255$ K. The $\chi_M T$ values measured below 252 K, ca. 0.1 cm$^3$ mol$^{-1}$K, and above 278 K, ca. 7.547 cm$^3$ mol$^{-1}$ K ($\chi_M$ is the molar magnetic susceptibility per $\{Fe_2Co_2\}$ formula unit), match with the expected values of the diamagnetic Fe$^{II\_LS}$Co$^{II\_LS}$ and the paramagnetic Fe$^{III\_LS}$Co$^{II\_HS}$ states, respectively. In particular, the $\chi_M T$ value near room temperature accounts for the presence of magnetically independent two Fe$^{II\_LS}$ ions ($S = 1/2, g \approx 2.6$) and two Co$^{II\_HS}$ (S = 3/2, g = 2.4) ions.

The $\chi_M T$ versus $T$ curve of compound 6 dried in the TGA under N$_2$ to 200 °C is also shown in figure 3(a). Compared with solvated 6, the transition temperatures shift downward ($T_{1/2}^{\uparrow} = 258$ K and $T_{1/2}^{\downarrow} = 252$ K) with a narrower hysteresis width of 6 K. These changes due to the loss of solvent molecules was already observed in related square-like or chain-like complexes, and it was recently explored to demonstrate the chemo-sensing potentialities of such switchable complexes.$^7$

The photo-excitation kinetic of 6 was followed by photomagnetic measurements as showed by figure 3(b). The experiments have been carried out at 20 K to minimize the thermal effect due to laser light irradiation and the end of the optical fiber rod is located 5 cm above the sample. The $\chi_M T$ value reaches the plateau ca. 4.9 mol$^{-1}$ cm$^3$ k with 808 nm (red light, 5 mW/cm$^2$) and ca. 1.0 mol$^{-1}$
cm³ k with 532 nm (green light, 5 mW/cm²) after irradiated 40 mins and 160 mins respectively. It indicates that a paramagnetic metastable state can be populated by light irradiation, and that the green light (532 nm) is much less efficient than the red light (808 nm). After switching off the red light, the χₘT value was measured to ca. 5.5 mol⁻¹ cm³ K, and no on-off switching phenomenon was observed when the sample at metastable state was irradiated again at 532nm. When heated slowly (0.4 K/min), the χₘT shows a sharp decrease from 80 (χₘT: ca. 5.67 mol⁻¹ cm³ K) to 100 K (χₘT: ca. 0.01 mol⁻¹ cm³ K). The relaxation temperature determined as the inflection point is ca. 90 K as shown in the figure 3(c).

Figure 3. Temperature dependence χₘT of compound 6 before (red) and after (black) TGA under N₂ (a); time dependence χₘT of the metastable photoinduced state under 808 (red), 532 (green) nm laser light irradiation(b); temperature dependence χₘT of 6 during thermal relaxation process (c).

2.3 Determination of the structures of 6 at diamagnetic (240 K) and paramagnetic (270 K) state by XRD measurements

X-ray diffraction experiments have been performed at diamagnetic state (240K) and paramagnetic state (270 K) for 6. The core structural features of the compound are given in table 1. 6 crystallizes in the monoclinic space group P2₁/n at 240 K and remains in the same space group at 270 K. Like compounds 1 - 5, the metal-ligand distances in compound 6 are very useful for distinguishing its electronic state. At 240 K, the average Co-ligand length are typical of an octahedral Co (III) LS (t²g⁶) with d[Co-(NC)bridging]av = 1.882 and d[Co-N(vbik)]av = 1.940 Å; At 270 K the two Co-ligand bond lengths increase to 2.100 and 2.128 Å, featuring a Co(II) HS (t²g⁵e²g). This significant lengthening in the Co-ligand distances is a typical signature of the temperature-induced ETCST phenomenon due to the change in the population of the antibonding e₈ orbitals from cobalt metals. Besides the obvious change of Co-N length, there are also slight variation on Fe-ligands distance: the Fe-CNbridging average distance is 1.87 Å at 240 K, and goes up to 1.92 Å with increasing temperature to 270 K. In

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a word, the XRD data at 240 K and 270 K are in agreement with the results of magnetic measurements from 230 K to 270 K. The significant change of Co-ligand local coordination from 240 to 270 K confirm the ETCST observed previously.

Regarding the geometry modification of the core structure from diamagnetic to paramagnetic state, the average (N-C-Fe) bridging angle changes hardly and remains almost straight (176.9 °/177.5 °), as well as the average bite angle of N-Co-N. While the average (C-N-Co) bridging angle decreases from 170.9 ° to 167.5 ° and that of C-Fe-C, from 88.5 ° to 85.2 °. The conformation of two vbik ligands evolves also: the dihedral angles of vbik1 (13.79 °) and of vbik2 (21.52 °) at 240 K decrease to 10.78 ° and 17.56 ° respectively at 270 K, while the average Co-C-O(c=o) angle remains unchanged.\[4–11\]

| Table 1. Core structure features of compound 6 at 240 and 270 K |
|-----------------|-----------------|-----------------|
|                   | 6 (240K)        | 6 (270K)        |
| \(d[Fe-(CN)_{\text{bridging}}]\)av (Å) | 1.875(8)        | 1.916(0)        |
| \(d[Fe-(C1N1)]\) (Å) | 1.866           | 1.913           |
| \(d[Fe-(C2N2)]\) (Å) | 1.884           | 1.918           |
| \(d[Fe-N(Tp)]\)av (Å) | 1.999(2)        | 1.973(1)        |
| \(d[Co-(NC)_{\text{bridging}}]\)av (Å) | 1.882(6)        | 2.100(4)        |
| \(d[Co-(N1C1)]\) (Å) | 1.885           | 2.099           |
| \(d[Co-(N2C2)]\) (Å) | 1.879           | 2.100           |
| \(d[Co-N(vbik)]\)av (Å) | 1.940(5)        | 2.128(8)        |
| \(\sum_{1}^{12} | 90 - \alpha | for the Fe center | 21.13 ° | 24.43 ° |
| \(\sum_{1}^{12} | 90 - \alpha | for the Co center | 18.30 ° | 30.44 ° |
| \(\text{av } \angle \text{Co-C-O}(\degree)\) | 172.34 | 171.9 |
| \(\angle \text{Co-C}=O1(\degree)\) | 169.86 | 170.56 |
| \(\angle \text{Co-C}=O2(\degree)\) (to reverse) | 174.83 | 173.24 |
| Dihedral \(\angle 2(\degree)\) | 13.79 | 10.78 |
| Dihedral \(\angle 1(\degree)\) | 21.52 | 17.56 |
The table 2 presents the unit cell parameters of 6 at the two temperatures and the percentage of their thermal variations. From diamagnetic state to paramagnetic one, the unit cell parameters b and c of 6 increase by 2.49 % and 3.02 % respectively and the unit cell parameter of a remains almost unchanged, as well as α and γ. The β angle diminishes very slightly. The diagonal distance of Fe···Co increases from 4.888 Å to 5.115 Å (4.64% increase), the variation of the unit cell volume is about 230.22 Å³ (5.45% expansion).

### Table 2. The unit cell parameters of 6 at 240 and 270 K

<table>
<thead>
<tr>
<th>Temperature</th>
<th>6 (240K)</th>
<th>6 (270K)</th>
<th>Δ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol Wt.</td>
<td>2037.37</td>
<td>2037.37</td>
<td>-</td>
</tr>
<tr>
<td>space group</td>
<td>P 2₁/n</td>
<td>P 2₁/n</td>
<td>-</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.2868</td>
<td>10.273</td>
<td>-0.13</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.7389</td>
<td>15.106</td>
<td>2.49</td>
</tr>
<tr>
<td>c (Å)</td>
<td>27.8740</td>
<td>28.716</td>
<td>3.02</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.574</td>
<td>90.329</td>
<td>-0.27</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>4225.94</td>
<td>4456.16</td>
<td>5.45</td>
</tr>
<tr>
<td>Z</td>
<td>Z: 2</td>
<td>Z: 2</td>
<td>-</td>
</tr>
<tr>
<td>R1 [l≥2σ(l)]</td>
<td>0.0526</td>
<td>0.0648</td>
<td>-</td>
</tr>
</tbody>
</table>
2.4 Intermolecular interaction analysis of compound 6

Similar to compound 1 and 3, the squares of 6 are also organized into 2D layer parallel to ab plane by two long-rang intermolecular interactions running in two orthogonal directions. The figure 4 shows its perspective view from c direction. At 240 K the weak H-bonds were formed between the terminal CN group and the CH of two imidazole rings alongside a direction: N3-H14C14(vbik1) and N3-H29C29(vbik2). The short contacts H4(vbik2)-C34(vbik2) and C7(Tp)-C21(vbik1) contribute also to link the squares into 1D in a direction. The π - π stackings of the adjacent vbik2 associate the squares into another 1D chain parallel to b direction. They involve 10 C-C shorts contacts inside each vbik2 pair (double C26-C31, double C27-C31, double C27-C32, double C28-C32) but without the antiparallel arrangement of carbonyl, as showed in figure 5.

Figure 4. Perspective view of crystal packing of 6 in c direction. The squares are organized into a 2D layer parallel to ab plane.
The figure 6 illustrates the weak H-bonds and C···C, C···H short contacts in a direction at 240 and 270 K, and the table 3 specifies the H-N distances in the H-bonds. At diamagnetic state the inter-atomic distances for N3-H14, N3-H29 are 2.703 and 2.771 Å respectively. These two H-bonds vanish and a new H-bond appears between N3 and H11 of Tp ligand at 270 K with a N3-H11 distance of 2.721 Å. The global strength of H-bonds is stronger at 240 K in comparison to that at 270 K. It also keeps consistency with the analysis in previous chapters: a stronger H-bond interaction favors diamagnetic state. Moreover, a contact of C27···C7 increases up from 3.374 Å at 240 K to 3.397 Å at 270 K, that occurs in pyrazole rings of Tp ligand and imidazole ring of vbik1.

Figure 5. View of pseudo π-π stacking between vbik2···vbik2 in b direction
Figure 6. Perspective view of H-bonds at 240 K (left) and 270 K (right) in a direction.
Table 3. The H-bonds distances in 6 at 240 K and 270 K

<table>
<thead>
<tr>
<th>Temperature</th>
<th>240 K</th>
<th>270 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{C34-H4}$ (Å)</td>
<td>2.779</td>
<td>2.815</td>
</tr>
<tr>
<td>$d_{N3-H29}$ (Å)</td>
<td>2.711</td>
<td>-</td>
</tr>
<tr>
<td>$d_{N3-H14}$ (Å)</td>
<td>2.703</td>
<td>-</td>
</tr>
<tr>
<td>$d_{N3-H11}$ (Å)</td>
<td>-</td>
<td>2.721</td>
</tr>
<tr>
<td>$d_{C7-C21}$ (Å)</td>
<td>3.374</td>
<td>3.397</td>
</tr>
</tbody>
</table>

Table 4. Contact distances of vbik2 pair at 240 K and 270 K

<table>
<thead>
<tr>
<th>Temperature</th>
<th>240 K</th>
<th>270 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{C28-C32}$ (Å)</td>
<td>3.358</td>
<td>3.383</td>
</tr>
<tr>
<td>$d_{C27-C32}$ (Å)</td>
<td>3.348</td>
<td>3.357</td>
</tr>
<tr>
<td>$d_{C27-C31}$ (Å)</td>
<td>3.296</td>
<td>3.320</td>
</tr>
<tr>
<td>$d_{C26-C31}$ (Å)</td>
<td>3.337</td>
<td>3.327</td>
</tr>
</tbody>
</table>

The table 4 lists the distances of C-C short contacts in the $\pi - \pi$ stacking of vbik2 pair at 240 and 270 K. The contact distances of C28-C32, C27-C32, and C27-C31 increase from 3.358, 3.348, and 3.296 Å at 240 K to 3.383, 3.357, and 3.320 Å respectively at 270 K. The distance of C26-C31 slightly decreases from 3.337 Å to 3.327 Å.

The figure 7 shows the connectivity of the counter-anion ClO$_4^-$ in 6 at 240 and 270 K. In both diamagnetic and paramagnetic state, the ClO$_4^-$ anions connect the squares alongside a direction, as the weak H-bonds do. This reinforces considerably the cohesion of the squares in this direction, which explains the thermal stability of a parameter. It’s curious that the enhancement of the intermolecular interactions via indirect contacts between ligands does not seem to distort the core structure of the square. The counter-anions ClO$_4^-$ link also two adjacent square layers. The number of the short contacts of ClO$_4^-$ is less important at 270 K compared to that at 240 K.
Figure 7. The connectivity of the counter-anion ClO$_4^-$ in 6 at 240 (above) and 270 K (below). The hydrogen atoms have been omitted for clarity.
2.5 Structure-property relationship of Fe$_2$Co$_2$ squares having general formula \{[Fe(Tp)CN$_3$]$_2$ [Co(vbik)$_2$]$_2$·(A)$_2$·S\}

The Fe$_2$Co$_2$ squares having general formula \{[Fe(Tp)CN$_3$]$_2$ [Co(vbik)$_2$]$_2$·(A)$_2$·S\} display very diversified magnetic behaviors. The establishment of their structure-property relationship is of pivotal importance for further study in molecular switches. The table 5 summarizes the core structure parameters and the ETCST properties for these Fe$_2$Co$_2$ square compounds. Among the three bistable squares in the table 5, only 6 has both structures at diamagnetic state (6dia) and paramagnetic state (6para). The HT structures are not available for 2 and 4 due to the loss of solvent during the thermal ETCST.

At diamagnetic states, compounds 2, 4, and 6dia, have comparable distortion parameters. Their $\Sigma$Fe values are in the range of 19.98 ° - 21.13 °, and the $\Sigma$Co value of 4 (18.44 °), is close to that of 6dia (18.30 °), and slightly higher than that of 2 (16.21 °). However, the $T_{1/2}$ of 2 (315 K) is close to the $T_{1/2}$ of 4 (325 K), and much higher than that of 6dia (240-270 K). The parameters $\Sigma$Fe and $\Sigma$Co appear not related to ETCST transition temperature. Such analysis results are consistent with the studies in CoFe PBAs by A. Bleuzen: the crystal field strength of Co(III) LS is not influenced by long-range interactions in PBAs.[12]

Regarding the paramagnetic squares, as described in previous chapters, both 1 and 3 are paramagnetic with a temperature scanning rate of 2 K/min for magnetic measurements. However, the compound 1 exhibits a kinetically trapped ETCST around 140 K when the temperature scanning rate is slowed down to 0.1 K/min, and 3 still keeps its paramagnetic state in the same conditions. The average Co-N≡C angle of 6dia (167.46 °) is higher than that of 1 and 3, (163 °). It seems that bending of Co-N≡C angle stabilizes the paramagnetic states. Actually, A. Bleuzen et al has also investigated the relationship between cyanide bridge angles in PBAs. They find that the bending of Co-N≡C angle decreases the crystal field of cyanide ligand. But the two structural parameters, $\angle$Co-N≡C and $\Sigma$Co, seem to be correlated, and the magnetic properties of the squares appear highly sensitive to the variation of $\Sigma$Co and much less to that of $\angle$Co-N≡C.

The distortion of 3 ($\Sigma$Co = 38 °) is higher than that of 1 ($\Sigma$Co = 35 °) and the compound 6para shows the lowest value of Co (30.44 °). The $\Sigma$Co value can be related to the strength of the intermolecular interactions in the complexes. All of the three compounds 1, 3 and 6para show pseudo $\pi$-$\pi$ intermolecular interactions at ambient pressure. One of the two $\pi$-$\pi$ stackings in both 1 and 3 bears an antiparallel arrangement of carbonyl which enhance considerably the stacking energy. The carbonyl pairs have nearer distance in 3 than that in 1: the short contact distance, d(C16-O1) = 3.038...
Å in the former and d(C16-O1) = 3.106 Å in the later. Furthermore, the π-π stacking in 3 includes more C-C short contacts than in 1. On the contrary to 1 and 3, the only π-π stacking in 6para has no antiparallel C=O pairs contacts and the stacking energy must be the weakest among the three compounds. Their strength of the intermolecular interactions mediated by the direct contacts between adjacent ligands decreases in the following order: 3 > 1 > 6para. The stronger intermolecular interactions lead to more bending ∠Co-N≡C, and/or increase of ∑Co, which better stabilizes the paramagnetic states.[13,14]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>∠Co-N≡C (°)</th>
<th>∑Fe (°)</th>
<th>∑Co (°)</th>
<th>magnetic state: T₁/₂(K)</th>
<th>Hysteresis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>173.06</td>
<td>19.98</td>
<td>16.21</td>
<td>325</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>172.20</td>
<td>25.63</td>
<td>18.44</td>
<td>315</td>
<td>0</td>
</tr>
<tr>
<td>6dia</td>
<td>170.89</td>
<td>21.13</td>
<td>18.30</td>
<td>255-273</td>
<td>18</td>
</tr>
<tr>
<td>6para</td>
<td>167.46</td>
<td>24.43</td>
<td>30.44</td>
<td>255-273</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>163.65</td>
<td>25.59</td>
<td>35.08</td>
<td>Kinetically trapped</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>163.21</td>
<td>23.0</td>
<td>38.06</td>
<td>Partial ETCST: 140K</td>
<td>0</td>
</tr>
</tbody>
</table>

1: A = BF₄⁻, S = 2CH₃OH; 2: A = BF₄⁻, S = 2CH₃OH·10H₂O; 3: A = PF₆⁻, S = 2CH₃OH; 4: A = PF₆⁻, S = 17CH₃OH·11H₂O; 6: A = ClO₄⁻, S = 2CH₂Cl₂

### 3 Thermal ETCST of 6 on single crystal – nucleation and propagation of the transition observed by optical microscopy

To observe directly the nucleation and the propagation of the thermal ETCST of 6, we have carried out the optical microscopy measurements on a single crystal with variable temperature. The thermal cycle (cooling-heating), firstly started by cooling from 280 K to 240 K with a speed of 0.5 K/min, then continued to decrease the temperature from 240 K to 230 K with the same temperature scanning rate, as the ETCST was not complete at 240 K according to the crystal’s color change.

Then the crystal was heated from 230 K to 280 K with a speed of 1 K/min due to the lack of space on the hard disk, the recording of the images being highly memory consuming. We have previously examined the effect of the temperature scan rate on the transition temperature points (1-2 K decrement of the transition temperature when increasing the temperature speed of 0.5 to 1 K
The figure 8 shows the images of the crystal at paramagnetic and diamagnetic states at 280 K and 230 K respectively, which also shows a responsibility of the magnetic properties and XRD measurements. The transparent red crystal at paramagnetic state becomes darker green at diamagnetic state. The following paragraphs analyze the snapshots of the single crystal and the evolution of its optical density during the thermal cycle extracted from the images taken, as well as the variation of the crystal’s size derived from a fine analysis.

**Figure 8.** The crystal images of 6 at paramagnetic state (left) and diamagnetic state (right)

### 3.1 Snapshots of the ETCST transition of 6

As shown in figure 9, the single crystal is robust and undergoes a thermal cycle without any damage. The transition starts with the appearance of a macroscopic domain. On cooling, the diamagnetic domain appears first around the center like a filament, whose propagation follows a two steps process: a quick extension of the filament along \( x \)-direction at first and then a slow widening along the \( y \)-direction. On heating, the process is quite similar. The transition starts from the two vertical borders forming again filaments of the paramagnetic phase grows along \( x \)-direction towards the center, followed by a slow enlargement of the phase.

**Figure 9.** Snapshots images on cooling from 280 to 230 K (left); and heating from 230 to 280 K (right)
We have checked on one crystal that X and Y axes correspond respectively to a and b directions. As the form and the size of the crystals are quite homogeneous, it’s very probable that x = a and y = b is true for all of them. The thermal variations of X and Y measured by optical microscopy (see the table) confirm this hypothesis. From 230 to 280 K, the thermal variation of X is near 0 like the unit cell parameter a, and that of Y is 2.4 %, comparable to that of the parameter b (2.5%). The propagation of the ETCST transition is at first alongside a direction, the “hardest” direction, and then the b direction which is parallel to the long-range $\pi - \pi$ stackings of vbik2.

**Table 6. Crystal’s size change in x and y direction**

<table>
<thead>
<tr>
<th>Magnetic state</th>
<th>paramagnetic</th>
<th>diamagnetic</th>
<th>$\Delta$ (para-dia)</th>
<th>$\Delta$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>y (b)</td>
<td>63.6 ± 0.2 $\mu$m</td>
<td>62.1 ± 0.2 $\mu$m</td>
<td>1.5 ± 0.4 $\mu$m</td>
<td>2.4 ± 0.6 %</td>
</tr>
<tr>
<td>x (a)</td>
<td>86.6 ± 0.2 $\mu$m</td>
<td>86.4 ± 0.2 $\mu$m</td>
<td>0.2 ± 0.4 $\mu$m</td>
<td>0%</td>
</tr>
</tbody>
</table>

**3.2 Optical density (OD) variation in heating and cooling process**

The Figure 10 shows the evolution of the optical density (OD) as a function of temperature for the three colors (Red, Green, and Blue) in cooling and heating process. A clear hysteresis loop is obtained for the three pixels, which is shifted to low-temperature region compared to that revealed by magnetic measurements. This kind of “discrepancy” is quite common because we are measuring here on only one single crystal, while in magnetism we get an average response. A small change (cusp) especially on the blue color was observed after the transition in cooling and before heating. This phenomenon also appears in the green and red colors but in a weaker fashion. The figure 10 presents three images of the crystal during the heating process, at 230 K (diamagnetic state), 252 K (in the “cusp” before the transition) and 260 K (paramagnetic state) respectively. Curiously, the image at 252 K is darker than that at 230 K. At this stage, we do not know the physical meaning of theses “cusps”, but study is in progress to clarify the phenomenon.
Overall, these results demonstrate the existence of crystallographic precursor phenomena that take place before the emergence of the cooperative change related to ETCST. It is hard at this stage to separate the electronic aspects from the structural ones. Additional more optical measurements have to be carried out. The ETCST transition on a single crystal of $6$ is more complicated than that revealed by magnetic measurement.

4 Conclusion

In this chapter, a new square compound $6$ of $\text{[Fe(Tp)(CN)₃]₂[Co(vbik)₂]₂(ClO}_4)₂·2\text{CH}_2\text{Cl}_2$ was synthesized and shows an ETCST transition with a thermal hysteresis of 18 K in solid state. The structural data at both diamagnetic and paramagnetic state have been determined and carefully analyzed. The core structure of $6$ is characterized by a relatively modest distortion of the coordination environment of Co(II) compared with the paramagnetic squares of the same family ($1$ and $3$). The squares form a 2D layer in bc plane via two long-rang intermolecular interactions: the $\pi – \pi$ stacking of vbik2 ligands parallels to b direction and the supramolecular interactions mediated by weak H-bonds, H-C and C-C contacts running along a direction. The connectivity of the counter-anion ClO₄⁻ consolidates considerably the cohesion of the squares in a direction, and explains the quasi-absence of the thermal variation of the parameter a. The optical microscopy measurements
on single crystal reveal that the propagation of the ETCST transition follows the similar two steps process in both cooling and heating: the preferential propagation direction is along with $a$ axis (very quick) and the secondary propagation direction, $b$ axis (slow).

By comparing the structural features of 6 at paramagnetic state with that of paramagnetic complexes 1 and 3, we observed that the stability of paramagnetic state seems depend preponderantly on the value of $\Sigma\text{Co (II)}$: greater is the $\Sigma\text{Co (II)}$ value, more stable is the paramagnetic state. The $\Sigma\text{Co(II)}$ value appears related to the strength of the intermolecular interactions mediated by the direct short contacts between ligands: stronger are the intermolecular interactions, greater is the $\Sigma\text{Co(II)}$ value. Therefore unlike for the mononuclear Fe(II) SCO compounds, strong supramolecular interactions can deform more the core structure of the Fe$_2$Co$_2$ square compounds and trap them in paramagnetic state, instead of giving large thermal hysteresis.
Reference


General conclusions
In this work, we synthesized different Fe$_2$Co$_2$ square complexes in one or two crystal phases. All complexes show the same cyanide bridged Fe$_2$Co$_2$ core but they may feature different counter ions and different blocking ligands. For all compounds, we have studied their magnetic properties by SQUID magnetometry and explored the possible occurrence of pressure-induced ETCST and structural phase transition by HP-XRD experiments. Raman spectra under various pressures were also measured to support the findings obtained by XRD analysis and magnetometry.

In chapter 2, we described the conversion by pressure of a first pseudo-paramagnetic Fe$_2$Co$_2$ square, of formula \([\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}(\text{vbik})_2]_2\text{(BF}_4)_2\cdot2\text{MeOH}\) (1), into a bistable complex (vbik = bis(1-vinylimidazol-2-yl)ketone, Tp = hydrotris(pyrazol-1-yl)borate). The square compound 1 is in fact an ETCST compound that is kinetically trapped in the paramagnetic state by solid state interactions at ambient pressure. Upon pressure application, 1 recovers its magnetic bi-stability and shows ETCST transition in the solid state. Remarkably, the pressure-induced conversion of the Fe$^{III}$Co$^{II}$ paramagnetic state into a Fe$^{II}$Co$^{III}$ diamagnetic state is reversible and complete even at a small pressure of 0.11 GPa. More importantly, 1 displays an unprecedented abnormal behavior for charge transfer switchable complexes: a hysteresis increasing upon increasing pressure. A theoretical Ising model directly inspired by works on SCO complexes is used to rationalize this phenomenon and suggests that an enhancement of ferro-elastic interactions induced by pressure occurs in 1.

An in-depth investigation of the XRD structure data of 1 under various pressures was carried out by using synchrotron radiation. Our goal was to determine the ETCST transition pressure at ambient temperature. This study also aimed at providing us with detailed data to establish structure – properties relationship and eventually propose a hypothesis for the occurrence of this abnormal magnetic behavior. The crystal packing is not affected a lot by the applied pressure, and no crystal phase transition is observed. The square complexes are linked in a 2D supra-molecular framework through intermolecular interactions involving the peripheral vbik ligands. We observed two types of π-π -like intermolecular interactions between the vbik ligands, and an antiparallel arrangement of the carbonyl groups in one of these two π-π stackings. The polar interactions of the carbonyl pair enhance greatly the energy of the π-π stacking, which could explain the cooperative behavior (hysteresis opening). It was also shown that the terminal cyanide of the square complex is involved in an H-bond with a methanol solvent molecule. This H-bond is notably shortened upon pressure application. This could trigger the paramagnetic to diamagnetic transition since it is known that a
strong H-bond interaction stabilizes the Fe$^{II}$/Co$^{III}$ diamagnetic state. Actually, we prepared the same compound containing CD$_3$OD solvent by replacing MeOH(1D). 1D shows the same XRD crystal structure than 1 at room pressure, but displays normal thermal ETCST behaviors under pressure. 1D is less-pressure-sensitive and its thermal hysteresis diminishes with increasing pressure. This indicates that H-bond impacts not only the para-dia conversion efficiency but also the elastic properties of compound 1.

To further evaluate the impact of the structural changes on the switchable properties, the BF$_4^-$ counter ion in 1 has been replaced by a PF$_6^-$ counterion in chapter 3. We thus kept the same core complex, which allows maintaining the transition temperature in solution close to room temperature. By controlling the crystallization temperature, we were thus able to isolate again two different crystal phases: a red phase of $\{[\text{Fe(Tp)}][\text{CN}]_3]_2[\text{Co(vbik)}]_2\}_2$(PF$_6$)$_2$·2MeOH (3) and a green-phase of $\{[\text{Fe(Tp)}][\text{CN}]_3]_2[\text{Co(vbik)}]_2\}_2$(PF$_6$)$_2$·MeOH·15H$_2$O (4) (solvent molecules are estimated by XRD). The change of the counterion aims at varying the intermolecular interactions, and a comparative study may help understanding the impact of supramolecular interaction on the pressure behavior of these compounds.

3 has a similar 2D supramolecular structure as 1, but the energy of its π-π stacking including the antiparallel arrangement of carbonyl pair is higher, as the carbonyl pair has shorter distance in 3 than in 1. The stronger intermolecular interactions in 3 put more constraints on the cobalt coordination sphere and lead to a higher value of the distortion parameter, $\Sigma$Co. Therefore, 3 is better stabilized in its paramagnetic state in solid state. Furthermore, it is shown that under pressure application 3 shows a partial ETCST below room temperature. Half of the paramagnetic pair can be converted into diamagnetic ones. The HP-XRD measurements on single crystal at room temperature allowed revealing the occurrence of a pressure-induced phase transition in 3. Unfortunately, the exact crystal structure of the high-pressure phase could not be obtained above 1.0 GPa. In summary, this study clearly reveals that the intermolecular interactions strongly impact the magnetic behavior of these switchable systems under pressure.

In the fourth chapter, we continue our efforts to study the pressure-induced electron transfer by changing not only the counterion but also the blocking ligands on Fe and Co sites. The redox potential difference between the ligands Tp$^*$ [hydrotris(3,5 - diméthylpyrazoyl)borate] and Mebik [bis(1-methyl imidazole-2-yl)ketone] is the same than that between Tp and vbik, so we can relate the ETCST properties of the new compounds uniquely to its structural parameters. We
described here the synthesis, characterizations, and the study of the ETCST behavior of the square complex, of formula \([\text{Fe(Tp}^\ast\text{)(CN)}_3]_2\text{[Co(Mebik)}_2\text{]}_2\cdot(\text{BF}_4)_2\cdot2\text{H}_2\text{O}\) (5). 5 does not presents ETCST transition in its mother solution at room temperature, and we have obtained only the paramagnetic phase of the complex. The magnetic measurements showed that 5 is paramagnetic in the temperature range of 2 - 400 K, like 3. This is coherent with the high SCo value. As expected, the XRD structural analyses showed a completely different crystal packing in 5. The intermolecular interactions are mediated by the weak H-bonds and other in-directional interatomic contacts and the \(\pi-\pi\) interactions are absent. We have studied pressure-induced thermal ETCST behaviors of 5, and compared it with that of 1, looking for combined effects of the core structure, intra and intermolecular interactions on the switchable behavior of \(\text{Fe}_2\text{Co}_2\) complexes. The threshold pressure which is required to promote the paramagnetic to diamagnetic transition is much higher in 5 than in 1 and 3, which is coherent with a higher distortion on the cobalt coordination sphere again. Having a normal ETCST, 5 shows a two-step transition with small hysteresis under - pressure. Comparing the results obtained for the compounds 1 and 5, we observe that the H-bond between the terminal CN and the protic solvent is significantly reinforced when the ETCST transition occurs. This confirms the important role played by the H-bond in both paramagnetic to diamagnetic transition and in the thermal ETCST transition.

In chapter 5, a new square compound 6 of \([\text{Fe(Tp)(CN)}_3]_2\text{[Co(vbik)}_2\text{]}_2\cdot(\text{ClO}_4)_2\cdot2\text{CH}_2\text{Cl}_2\) was synthesized and shows an ETCST transition with a 18 K thermal hysteresis in solid state. The core structure of 6 is characterized by a relatively modest distortion of the coordination environment of \(\text{Co(II)}\) compared with the paramagnetic squares of the same family (1 and 3). This results from its weaker intermolecular interactions mediated by direct ligand short contacts. By comparing the structural features of 6 (270 K) at paramagnetic state with that of paramagnetic complexes 1 and 3, we have tentatively established a relation-property relationship for the family of squares bearing Tp and vbik ligands. 6 has a very interesting peculiarity: the counter-anions, ClO4–, connect the Fe2Co2 squares into 1D chain along a direction so efficiently that the unit cell parameter, a, shows almost no variation during the thermal ETCST transition. The thermal hysteresis of 6 is probably due to the great cohesion of the squares in a direction than to its weak molecular interactions. The direct observation of the ETCST transition by optical microscopy reveals that the preferential direction of the ETCST propagation is parallel to a direction.

Overall, the above-mentioned results showed that pressure can be an efficient tool to switch
magnetic properties of cyanide-bridged $[\text{Fe}_2\text{Co}_2]$ charge transfer molecular complexes. To date, these studies remain very limited in comparison to those involving the temperature or the light stimuli, because the magnetic and structural studies at high pressure are significantly more challenging than those carried out at ambient pressure. In this PhD, which is the first one dealing with pressure-induced ETCST in our group, we have benefited from the collaboration of different crystallographers. We hope the original switchable properties that have been obtained will motivate other colleagues to explore the potentialities of the FeCo molecular system as pressure-sensitive molecular switches.
Experiment section

Synthesis of organic ligands and inorganic complexes:

all the chemical products in these reactions below are commercial and have no further purification.

Bis(1-methylimidazol-2-yl)ketone (Mebik):[^1,^2]

Under an argon atmosphere, a solution of 1-methylimidazole (12.5 mL, 157 mmol) in dry THF (150 mL) was cooled to -78 °C in a 500 mL three-necked round-bottom flask, and the solution was stirred at this temperature for 30 min. A 1.6 M solution of n-butyllithium in hexanes (100.0 mL, 0.16 mol) was added via syringe slowly. Then the resulted yellow solution was stirred at -78°C for 90 min, diethyl carbonate (9 mL, 75 mmol) was added very slowly with a syringe as well, the solution color changed from pale yellow to light pink and thickened. The reaction mixture was allowed to reach 0°C over the period of 4 h, then the ticked mixture was quenched by a 15 mL cold water leading to a white precipitate, then leave the reaction up to ambient temperature overnight. The white precipitate was filtered and identified as lithium carbonate (ATR-IR: $\nu = 1395$ cm$^{-1}$ ($\nu$C=O)). The THF filtrate was removed in vacuo to give an orange oil, then extracted with CH$_2$Cl$_2$ (6×50 mL). The CH$_2$Cl$_2$ layers were pooled and dried over MgSO$_4$, filtered and evaporated to lead to a yellow solid. The pure product was obtained as colorless crystals after recrystallization from CH$_2$Cl$_2$ (80 mL); yield: 7.8 g (55%). ATR-IR: $\nu = 1629$ (C=O) cm$^{-1}$.

$^1$H NMR: (300 MHz, CDCl$_3$): $\delta$ (ppm) = 7.43 (s, 1H, Himid), 7.21 (s, 1H, Himid), 4.05 (s, 3H, NCH$_3$).

$^{13}$C NMR: (75 MHz, CDCl$_3$): $\delta$ (ppm) = 173.90(C=O), 142.78 (C=N), 128.83 (C$_{imid}$), 127.25 (C$_{imid}$), 34.64 (NCH$_3$).
Bis(1-vinylimidazol-2-yl) ketone (vbik):[3]

Under an argon atmosphere, a solution of 1-vinylimidazole (5.30 mL, 58.2 mmol) in diethyl ether (60 mL) is cooled to -60 °C. After addition of n-butyl lithium (40 mL, 1.6 M in hexane, 64 mmol), the solution is stirred for 2 h at -60 °C. Subsequently the mixture is cooled to -90 °C, and diethyl carbonate (3.53 mL, 0.0291 mmol) is added dropwise. The mixture is warmed to room temperature overnight (slowly). In the meantime, it forms a thick slurry, which is dissolved in 6 M HCl (40 mL). The phases are separated, and the organic phase is extracted with diluted HCl (3 x 20 mL). Afterwards the combined aqueous phases are neutralized with Na₂CO₃ (until pH = 5-6) and extracted with dichloromethane (4 x 40 mL). The combined organic phases are dried over MgSO₄, and the solvent is removed in vacuo to yield a yellow solid. Light yellow or white crystals can be precipitated from acetone solvent. If the residue is obtained as a dark brown oil mixture, the crude product can be obtained as a yellow solid by precipitation with acetone and subsequent evaporation of the solvent. Slow evaporation of the acetone solution usually leads to a second crop of product (or even crystals). Yield: 1.55 g (6.90 mmol, 24%). m.p.: 137 - 139 °C.

¹H NMR: (300 MHz, CDCl₃): δ (ppm) = 5.09 (dd, J₄,J₅ = 8.8 Hz, J₅,J₆ = 1.6 Hz, 2H, CH vinyl,trans), 5.40 (dd, J₄,J₅ = 15.7 Hz, J₅,J₆ = 1.6 Hz, 2H, CH vinyl,cis), 7.38 (d, Jₑ,J₂ = 0.6 Hz, 2H, CH imidazole), 7.50 (d, J₃,J₄ = 0.9 Hz, 2H, CH imidazole), 7.71 (dd, J₅,J₆ = 8.7 Hz, J₆,J₇ = 15.6 Hz, 2H, CH vinyl).

¹³C NMR: (75 MHz, CDCl₃): δ (ppm) = 142.03 (NCN), 131.39 (CH imidazole), 130.89 (CH vinyl), 121.24 (CH imidazole), 105.42 (CH₂ vinyl).

Note: Be care with the use of n-butyl lithium, the whole process is always under argon protection.
Potassium hydrotris(1-pyrazolyl) borate (KT$p$:)[4]

Potassium borohydride (4.92 g, 90 mmol) was mixed to a slight excess of pyrazole (21.50 g, 32 mmol) in a 50 mL round bottom flask. The solid mass was heated first at 90 °C in an oil bath about an hour. The flask was covered with an aluminium foil. Then the reaction mixture was heated to 120 °C and kept at that temperature until hydrogen evolution was ceased. Finally, the temperature was gradually raised to 185 °C over 2 hours and left overnight for heating. The melt was cooled to 120 °C and was poured into hot toluene (100 mL) giving a white precipitate. The white solid was filtered then washed successively with hot toluene (60 mL) and hexane (60 mL), then air dried; yield = 22.6 g (89 %).

ATR-IR: ν (cm$^{-1}$) = 2501 (B-H), 1501, 1399, 1310, 1213, 1107, 1046.

$^1$H NMR (300 MHz, CD$_3$OD): δ (ppm) = 7.61 (d, 1H, $^3$J$_{H-H}$ = 1.0 Hz NCH), 7.17 (d, 1H, $^3$J$_{H-H}$ = 1.0 Hz NCH), 6.17 (s, 1H, CCH).
Potassium hydrotris(3,5-dimethylpyrazol-1-yl) borate (KTP*):[1–3,5,6]

Potassium borohydride (3.24 g, 60 mmol) was mixed to a slight excess of 3,5-dimethylpyrazole (24.44 g, 25 mmol) in a 50 mL round bottom flask. The solid mass was heated first at 90 °C in an oil bath about an hour. The flask was covered with an aluminium foil. Then the reaction mixture was heated to 120 °C and kept at that temperature until hydrogen evolution was ceased. Then the temperature was gradually raised to 185 °C over 2 hour and keep stirring for 30 min. Finally, the temperature was stepwise increased to 235 °C, stop heating until there is no hydrogen bubbles (about 15 - 20 min). The melt was cooled to 160 °C and was poured into hot toluene (150 mL) giving a white precipitate. The white needle-like crystals are directly obtained by washing with toluene (50 mL), too much toluene should be avoided to decrease the yield, air dried; yield = 16.05 g (80 %). Mw = 336 g/mol.

ATR-IR: ν (cm\(^{-1}\)) = 2520 (B-H).

\(^1\)H NMR (300 MHz, CD\(_3\)OD): δ (ppm) = 5.68 (d, 1H, CCH), 2.15 (d, 3H, NCH\(_3\)), 1.8 (m, 3H, NCH\(_3\)).

\(^{13}\)C NMR: (75 MHz, CDCl\(_3\)): δ(ppm) =146.75(NCH), 144.35(NCH), 104.40(CH\(_{\text{imidazole}}\)), 10.57(CH\(_{\text{imidazole}}\)), 11.93 (CH\(_{\text{imidazole}}\)).

Fe\(^{II}\)(Tp)\(_2\): FeSO\(_4\)·7H\(_2\)O (11 g, 40 mmol) and KTP (20 g, 80 mmol) were separately dissolved in water (100 mL and 20 mL, respectively). The iron sulfate solution was added to the KTP solution and a
pinch of ascorbic acid (0.5g, 40ml H₂O) was added to it. A purple solid was precipitate and the reaction mixture was stirred for 30 min. After filtration, the purple solid was washed with absolute ethanol and air-dried. (yield: 17g, 90%)

**NBu₄Fe³⁺(Tp)(CN)₃:**

K₂Fe(Tp)(CN)₃ was prepared as follow: Fe²⁺(Tp)₂ (17 g, 34 mmol) and ground KCN (6.7 g, 103 mmol) were mixed in isopropanol (240 mL), here the resulting suspension was heated to reflux at 90 °C for 12 hour under continuous stirring. The colour of the reaction mixture changed from purple to yellowish brown. After cooling the reaction mixture down to room temperature, a yellowish brown precipitate containing K₂Fe(Tp)(CN)₃ was obtained, filtered and air dried.

A solution of K₂Fe(Tp)(CN)₃ (15 g, 34.6 mmol) which was dissolved in warm water (400 mL) was placed into a large erlenmeyer flask (1 L) covered with aluminum foil under continuous stirring. Then a solid tetrabutylammonium bromide (11.15 g, 34.60 mmol) was added into the stirring solution. Hydrogen peroxide (30 % in water) was added stepwise in 1 mL amounts until reaching a total amount of 20 mL (2 mL/time). The starting brown solution gradually turned orange-red, then the orange-red silky precipitate which was filtered and air-dried. The pure products of are recrystallized from methanol. All the chemicals containing cyanide will be neutralized with sodium hypochlorite during reaction and chemical waste treatments for security.

Overheating and more hydrogen peroxide can cause decomposition of the product, so it must be avoided during the oxidation step, and following the reaction by ATR spectrum.

ATR-IR: ν (cm⁻¹) = 2500 (B-H), 2116 (Fe³⁺).

\[ ^{1}H-NMR \text{ (300 MHz, CD3CN)}: \delta \text{ (ppm)} = 39.8 \text{ (1H; B-H), -1.5 (3H; 3- or 5 -H)}, -5.6 \text{ (3H; 3- or 5 -H), -51.5 (3H; 4-H).} \]

**KFe³⁺(Tp*)(CN)₃:**

All the operation for this complex should be done under Ar. FeCl₂·4H₂O (1.12 g, 5 mmol) was firstly dissolved in 10 ml degassed methanol with ascorbic acid (0.4 g), the was mixed with solution of KTp*(3.38 g, 10 mmol) which was dissolved in 5 mL degassed methanol solvent under argon atmosphere as well. The suspension color turned to green immediately, then changed into light violet color. After stirring one hour, the light violet suspension was transferred into a degassed methanolic solution containing ground KCN (1.4 g, 20.4 mmol), the suspension color was yellowish, keep it stirring for another one hour under argon. Finally, the reaction was opened to air, and kept
stirring overnight. The solid was collected by evaporated methanol solvent completely, then dissolved in acetonitrile solvent. The red filtrate was kept for one day in the air for complete oxidation. Then the red crystals can be obtained by slowly evaporating acetonitrile, the yield of KFeIII(Tp*)(CN)3 is 630 mg (33%, Mw = 416 mg/mol). All the chemicals containing cyanide will be neutralized with sodium hypochlorite during reaction and chemical waste treatments for security. The NBu4FeIII(Tp*)(CN)3 can be easily precipitated out by mixing KFeIII(Tp*)(CN)3 with NBu4Br (much more than a 1:1 molar ratio with KFeIII(Tp*)(CN)3) in water at ambient temperature.

ATR-IR: 2534 cm⁻¹ (B-H), 2126 cm⁻¹ (FeIII).

**Physical measurements:**

**FT-IR spectra:**
The spectra were collected in the 400 - 4000 cm⁻¹ range. Measurements were carried out on a Vertex 70 Bruker instrument using the attenuated total reflection (ATR) technique on solid samples (with a 4 cm⁻¹ resolution). The intensity of the absorption band is indicated as vw (very weak), w(weak), m (medium), s (strong), vs (very strong), and br (broad).

**TGA analysis:**
TGA measurements were performed on a Perkin Elmer STA-Q600 simultaneous thermal analyzer.

**Elemental analyses (C, H, N):**
The EA experiments were carried out by combustion analysis using a vario MICRO cube apparatus from Elementar.

**UV-vis spectroscopic measurement:**
UV-visible spectra were recorded on a JASCO V-670 equipped with an ETC - 717 Peltier module. The spectra were recorded in pure acetonitrile solutions at room temperature. Samples were placed in 1 cm path length quartz cuvette and generally data were collected in the range 300 - 1200 nm.

**Crystal Structure Data Collection and Refinement at ambient pressure:**
A single crystal of each compound was selected, mounted onto a Hamilton cryoloop using paratone oil and placed in the cold flow produced with an Oxford Cryocooling device. Due to rapid solvent
loss, even in oil, all the crystals were fully recovered with glue and exposure time for frames was minimized for data collection at high temperature. Intensity data were collected with a Bruker Kappa-APEXII with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection was performed with APEX2 suite, Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program. SADABS was used for multi-scan absorption corrections. In the WinGX suite of programs, the structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares methods using SHEXL-97. Almost non-hydrogen atoms refined anisotropically; only atoms of solvent molecules or disordered parts were refined isotropically. Hydrogen atoms were placed at calculated positions and refined with a “riding model”.

**X-ray diffraction on single crystal under pressure:**

The high pressure X-ray diffraction experiments were performed at 293K using a home-made membrane diamond anvil cell (DAC) with a culet of 600 μm in diameter. A 300 μm-diameter hole was drilled in a stainless-steel gasket with a thickness of 200 μm pre-indentened to 80 μm. A single crystal of around 100 μm diameter was loaded in the gasket hole together with a ruby ball as pressure sensor (R1 ruby fluorescence method). Daphnee 7474 oil was used as a hydrostatic pressure transmitting medium. Before and after each measurement, the pressure was determined by recording the ruby fluorescence spectra using a spectrometer with a 532 nm excitation laser. The calculated error for the pressure values is 0.1 GPa and the sensitivity was 0.05GPa. The DAC was mounted on a Rigaku MM007HF diffractometer equipped with a Mo rotating anode (λ = 0.71073 Å). Varimax focusing optics, a Raxis4++ image plate detector and a Newport phi rotation stage as goniometer. The data coverage was obviously limited due to the DAC opening cone shadow. The first was obtained using a phi scan (0.5° step width with total angular amplitude of 80°) on the DAC placed perpendicularly to the X-ray beam. Then, the DAC was maintained face to the beam but rotated 15° in the plane perpendicular to the beam and a second phi scan was measured, and so on to get finally four data sets. Following an equivalent procedure as described by A. Rothkirch et al., the collected images were converted to the esperanto format with an in-house program (not published) and the four data sets were independently processed with CrysAlisPro software. This last program offers a very efficient procedure to correct the background and also provides a useful way to truncate the non-interesting part of the diffraction image by applying a mask according to the opening angle of the DAC (33° in this case). The crystal structure can be solved from each independent and very incomplete data set. The corresponding refinements were unstable or
needed too many restraints (interatomic distances and constraints on heterocycles geometry). That’s why the data sets were finally merged and scaled with XPREP (Bruker 2004. XPREP. Bruker AXS Inc. Madison. Wisconsin. USA) to give rise to a combined set of reflections with 25% completeness (1786 reflections merged, Rint = 0.0951 and Rsigma = 0.0295). Then, the structure was solved using SHELXT implemented in Olex2 program. The refinement was then carried out with SHELXL by full-matrix least squares minimization and difference Fourier methods. Due to the low completeness, only Co, Fe, and F atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms with isotropic thermal parameters. Neither constraint nor restraint was used to refine the model using the merged data.

The other high-pressure experiments were performed at SOLEIL synchrotron on another single crystal of the sample, using the 6-circle diffractometer of CRISTAL beamline at 0.4167 Å. We used another home-made membrane diamond anvil cell (DAC)\(^7\) with a wide opening angle (50 °) and a culet of 800 μm in diameter. For each pressure, we carried out only a single phi scan (1° step width with total angular amplitude of 80 °) and these single scans at high energy were sufficient to solve and refine the structures using the same program and procedure as for the laboratory experiments.

**Raman spectroscopy of the single-crystal under pressure:**

The sample was loaded in a Chervin-type membrane diamond anvil cell (DAC) with diamond culets of 600 μm in diameter and helium gas as the pressure transmitting medium. The sample chamber consisted of a rhenium gasket that was pre-indentented to 60 μm, and then drilled by a fs Nd: YAG pulsed laser to make a 300 μm hole. Three single crystals were loaded in the DAC cell together with a ruby as pressure sensor. The pressure was determined by the fluorescence spectrum shift of a ruby sphere loaded in the DAC, using the calibration of Mao et al.\(^8\) The Raman spectra under pressure were performed using a Jobin-Yvon/Horiba HR-460 spectrometer equipped with a monochromator with 1500 grooves/mm and an Andor CCD. An Argon laser operating at 514.5 nm was focused on the sample with an optical lens and the backscattered Raman spectra were collected with a laser power of ~50 μW and a collection time of 600 s.
Magnetic and photomagnetic measurements at ambient pressure:

All the magnetic measurements were carried out using the Quantum Design SQUID magnetometer (MPMS 5S and MPMS XL-7). Variable-temperature magnetic measurements were carried out in 2.0400 K temperature range applying external magnetic field of 10000 Oe. In order to prevent the loss of uncoordinated solvent, a fresh sample was introduced at 200 K under helium flow and frozen before purging under vacuum. The measurements were carried out from 200 K to 2.0 K first and then from 2.0 K to higher temperatures with a sweep rate 2 K/min. Photomagnetic measurements were carried out by using a sample holder equipped with an optical fiber. In a typical experiment 1 mg of finely ground crystals were deposited on an adhesive tape.

A halogen lamp has been used as irradiation source for the preliminary photomagnetic measurements. For this experiment the temperature was set to 20 K. All the photomagnetic measurements have been carried out by using laser sources in the visible range at 405, 532, 635, and 808 nm. The end of the optical fiber being located at 55mm above the sample. In these experimental conditions, the estimated light powers were 5, 10, 12, and 6 mW/cm², respectively. The temperature was also set to 20 K in order to minimize the heating of the sample due to the laser irradiation. The experimental data were corrected for the diamagnetic contribution of the constituent atoms as well as by the residual diamagnetic signal from the holder.

Magnetic measurements at various pressure:

Variable-temperature magnetization of fresh crystals under various hydrostatic pressures was measured on a Quantum Design MPMS-XL7 SQUID magnetometer at a magnetic field of 1 T. In a typical experiment. 5-7 mg of sample are placed in a HMD high-pressure cell made of hardened beryllium bronze, together with Daphne 7373® oil as pressure transmitting medium and a small piece of pure lead wire as pressure sensor. The cylindrical sample holder inserted in the pressure cell is a Teflon® tube with an external diameter of 2.6 mm and a length of 5 mm, which was sealed by two Teflon® caps. The relationship of the applied pressure, Δp, and the transition temperature shift of the lead’s super-critical temperature, ΔT, is expressed by:

\[ Δp = ΔT / 0.379 \text{ GPa} \]
Under reduced Helium atmosphere, inside the magnetometer, the transition temperature of lead is measured at 7.20 K. The experimental error of the pressure measurement is estimated to be 0.02 GPa.

In order to estimate the background signal of the whole sample holder (the pressure cell with capped Teflon® tube containing three drops of Daphne 7373 oil), the magnetization of a given amount of 1 has been measured in the temperature range of 2 - 400 K in the pressure cell (at room pressure) and in standard conditions (wrapped in a piece of PVC film). The subtraction of the two magnetization curves gave the magnetic contribution of the sample holder versus temperature. (Remarque : le signal de fond de la cellule devrait être très faible, le signal de ce qui est autour de l’échantillon (Teflon + Huile) est important.) The high-spin fraction, $\gamma_{HS}$, was calculated by equation below:

$$\gamma_{HS} = \frac{\chi_T}{\chi_{T\ max}}$$

where $\chi_T$ is the product of the molar susceptibility of 1 and temperature, and $\chi_{T\ max}$, the plateau value of $\chi_T$ reached in the high-spin state. The $T_{1/2}$ of the ETCST transition was determined by the maximal value of the derivative of $\chi_T$ versus $T$.

The process of sample preparing in high-pressure cell is complicated compared with other magnetism measurements (such as light or thermal-induced ETCST measurements in the magnetism device), and the sample preparing process for pressure measurements has been specifically depicted as follows.

**High-pressure cell user illustration for preparing sample:**[9]

The high-pressure cell is easy to use Beryllium Copper (BeCu) cylindrical cell for pressuring samples for use in the Quantum Design MPMS, PPMS VSM, and VersaLab VSM systems.

Following is some of the features of the high-pressure cell: Maximum applied pressures up to 1.1 GPa; Up to 2.6mm diameter high-pressure region (2.2 mm actual sample space diameter); Novel pressurization system that requires no external press; No copper rings to secure the pressure – ensures easy sample removal and low running costs; Compatible with DC, RSO, and VSM sample transports.

The pressure cell features an all BeCu design in and near the sample region, including the pistons and other parts for sealing the sample in the high-pressure region. The use of non-BeCu parts is minimized throughout the pressure cell assembly. This ensures a more uniform magnetic background, making the high-pressure cell suitable for studying the magnetization of small samples. The high-pressure cell comes
with both 2.1 and 2.6 mm ID cylinder housings to allow for various sample sizes and configurations. Also included with the standard kit are sufficient consumables to perform about 60 experiments.

An important feature of the cell is an integrated bearing that is built into the pressurization nuts. This prevents the pressurization piston and other parts from rotating during the pressurization process, allowing for easier pressurization and for slightly higher applied pressures compared to traditional BeCu pressure cells. A second important feature is the use of a teflon sample tube and teflon caps to form the high-pressure cell seal. It insures that the sample removes relatively easily with the included sample removal rod with little risk of damage to any of the pressure cell components.

As shown in figure 1, teflon sample tube preparation and sample insertion follow several steps below:

1) After selecting the teflon tube (either 2.1 or 2.6 mm OD), use the included teflon tube cutting fixture to cut a desired length of tube for inserting the sample. The cell kit includes all necessary parts to accommodate either size teflon tube. The diameter of teflon tube depends primarily on the volume of sample to be measured. A 4.5 to 5.0 mm length of teflon tube is recommended. Slightly longer teflon tubes, up to 7 mm, can be used if desired. However, the maximum pressure might decrease slightly.

2) Seal one end of the teflon sample tube with a teflon cap, slide the teflon sample tube/teflon cap combination into the center cylinder leading with the open another end of the teflon sample tube. Push in with the appropriate diameter sample push rod until the sealed end of the teflon sample tube is about even with the bevel of the center cylinder.

3) Insert the sample, manometer, and pressure transmitting media into the open end of the teflon sample tube. If using the included Sn or Pb wire for the manometer, about 1mm length is sufficient. Leave enough space at the top of the teflon sample tube to allow the second teflon cap to be
inserted. The pressure cell kit includes Daphne 7373 oil as a pressure transmitting media. The included syringe can be used to help apply the transmitting media to the teflon sample tube.

4) Seal the second end of the teflon sample tube with a teflon cap, using for example a Kimwipe, remove any excess oil or any other foreign particles from the threads of the center cylinder and around the teflon caps.

5) Using the appropriate diameter sample push rod, carefully push the teflon sample tube so it is roughly centered within the center cylinder, then clean any excess grease or oil around the center cylinder, then insert the two pistons into the center cylinder. After this, using a toothpick or small wire, apply a thin coat of teflon powder to the threads of the center cylinder.

6) With the center cylinder held horizontally, place a piston backup on each piston. Thread the side cylinders finger tight to the center cylinder. There should be no gap between the side and center cylinders. Coat the threads of the two cylinder pressurization nuts with teflon powder.

7) Thread the cylinder pressurization nuts to the side cylinders finger tight, thread the cylinder pressurization nuts to the side cylinders finger tight. Loosen one of the pressurization nuts about two turns and tighten the opposite pressurization nut. The nut should tighten smoothly, indicating the pistons and teflon sample tube are moving smoothly.

8) Next, loosen the tightened pressurization nut about 3 turns and tighten the opposite pressurization nut. Again, the pressurization nut should tighten smoothly. Work the pistons and teflon sample tube back and forth in this manner about 3 times. When finished, finger-tighten both pressurization nuts so the sample is centered within the center cylinder. This is indicated by noting the gap between the pressurization nut and side cylinder being roughly equal on both sides as shown in figure 2.

Figure 2. Final assembly before pressurizing
Pressurizing the sample in the cell before measuring:

Prior to pressuring the sample, it is normally recommended to measure the manometer to determine a zero-pressure manometer transition reference. Perform the following steps to pressurize the sample.

1) Measure the pressure cell length. This will be used as a reference so the amount of compression can later be determined (figure 3 for the recommended dimension to measure).

2) Insert the pressure cell to the cell clamp. Cinch the pressure cell in place with the two hex screws. Note the third hex screw is used to slightly pry the cell clamp apart in case the cell does not easily slide into the cell clamp (figure 3).

3) Attach the custom spanners to the pressurization nuts (figure 4).

4) Use a vice or large adjustable wrench to hold the cell clamp stable and tighten one of the pressurization nuts 90 degrees, then the opposite pressurization nut by 90 degrees. Continue tightening the pressurization nuts, alternating between the two pressurization nuts in 90-degree steps until the total cell compression is about 1 mm. For compression greater than about 1 mm, rotate the pressurization nuts in smaller steps, 30 to 45 degrees being recommended. Note the maximum sample compression is about 2.0 mm. 90 degree of pressurization nut rotation represents about 0.1 mm of compression.

Figure 3. Measuring compression and inserting pressure cell to clamp

Figure 4. Setting the pressurization spanners
Removing the sample:

1) Insert the cell into the cell clamp and tighten the two hex bolts to cinch the cell in the cell clamp.

2) Attach the pressurization spanners to the pressurization nuts.

3) Slowly unscrew the pressurization nuts and remove them from the cell.

4) Unthread the side cylinders, if they can’t be loosened by hand, use the pressurization spanners to grip the side cylinders.

5) Remove the piston backups and pistons.

Reference:


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