



HAL
open science

Using polymorphism to master the spin crossover mechanism in $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$

Élodie Tailleur, Mathieu Marchivie, Philippe Négrier, Dominique Denux, Stéphane Massip, Denise Mondieig, Guillaume Chastanet, Philippe Guionneau

► **To cite this version:**

Élodie Tailleur, Mathieu Marchivie, Philippe Négrier, Dominique Denux, Stéphane Massip, et al.. Using polymorphism to master the spin crossover mechanism in $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$. CrystEngComm, 2019, 21 (41), pp.6246-6251. 10.1039/C9CE01137D . hal-02318101

HAL Id: hal-02318101

<https://hal.science/hal-02318101>

Submitted on 8 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Polymorphism to master the spin crossover mechanism in $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Elodie TAILLEUR^a, Mathieu MARCHIVIE^a, Philippe NEGRIER^b, Dominique DENUX^a, Stéphane MASSIP^c, Denise MONDIEIG^b, Guillaume CHASTANET^a, Philippe GUIONNEAU^{*a}

In the crystalline state, a given molecule can lead to very different physical properties depending on the molecular packing within the sample. Despite the spin crossover is by essence a molecular scale phenomenon, polymorphism lead to a large diversity of the spin-switch features. The comparison of the structural and physical properties of spin crossover polymorphs can therefore give crucial information about the phenomenon itself. As revealed by this study, the investigated molecular iron(II) complex can be crystallized into two polymorphs, one showing a first order spin crossover with a large hysteresis centered at room temperature and the other one showing a fully reversible gradual spin crossover at lower temperature. The distinction between the two polymorphs is subtle and lies in the molecular stacking with regard to the interatomic contacts of the H...H type, which underlines the extreme sensitivity of this physical phenomenon to the crystalline stacking. Interestingly, the purposeful crystallization of these polymorphs opens up perspectives since it allows to choose dissimilar spin crossover mechanisms starting from the same molecule.

Introduction

In the investigation of the Spin crossover (SCO) phenomenon, polymorphism represents an exciting opportunity to understand the complex relationships between the structural properties and the switching features in the solid-state.¹⁻³ Note that despite solvatomorphism is also an interesting route⁴, polymorphism seems more suitable for orienting towards a choice of the SCO properties of a given compound, since for the first one, the possibility of a solvent departure greatly complicates the process. Hereafter, we are thus discussing about solvent-free polymorphism. The SCO originates on the metallic site, here iron(II). However, the SCO features are affected by all the physical scales of the solid, from the atom up to the crystal.⁵ The structure-property relationships in SCO materials start to be well documented and the main learning of the literature on this subject is the complexity of corresponding close and subtle links. In this context, having different crystal packing for identical molecular complexes, *i. e.* polymorphs, makes it possible, for example, to track the structural origin of some physical behavior, such as magnetic properties, by meticulously comparing polymorphs' features.^{1-3, 6-9} This paper

provides a cornerstone to this building by probing two well-crystallized polymorphs with radically different magnetic properties - one with hysteresis at room temperature and the other one with a continuous conversion occurring at low temperature - using the crystal structures determined both at high temperature when the iron is High-Spin (HS) and at low temperature when the iron is Low-Spin (LS).

Crystals of the molecular complex $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ [with PM PeA = N-(2'-pyridylmethylene)-4-(phenylethynyl) aniline] have been reported as being among the very rare - almost the unique so far - to undergo a thermal-induced SCO centered at room temperature (286 K) with a large hysteresis width (41 K).¹⁰ In that case, the SCO is accompanied by a peculiar structural transition from $mP2_1/c$ (HS) to $oPccn$ (LS) that was also recently observed with high-pressure acting as a stimulus.¹¹ The already reported polymorph will be hereafter named polymorph-I since another polymorph, therefore named polymorph-II, has been crystallized and constitutes the main purpose of this paper. The objective, here, is to highlight the structural origin of the SCO features differences shown by the two polymorphs. First, the structural, magnetic and thermodynamics properties of polymorph-II are reported then the comparison of selected features of the two known polymorphs allows some progresses on the knowledge of structure-property relationships in SCO crystals.

Results and Discussions

^a CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

^b Univ. Bordeaux, LOMA, UMR 5798, 33400 Talence, France

^c CNRS, IECB, UMS 3033, 33600 Pessac, France; Univ. Bordeaux, IECB, UMS 3033/US 001, Pessac, France

Electronic Supplementary Information (ESI) available: X-ray patterns for different batches, temperature dependence of all unit-cell parameters, elementary analyses, full data collection strategies for single-crystal X-ray data. Cif files are deposited at the CSD with numbers 1937630 (293 K) and 1937632 (100 K). See DOI: 10.1039/x0xx00000x

Getting powders and single-Crystals of Polymorph-II

In order to study more deeply the peculiar properties of polymorph-I, notably under pressure, numerous syntheses were performed and many batches of powder and single-crystal were obtained. Almost all of the single crystal batches obtained are composed of the targeted polymorph-I. Powder diffractograms of single crystal batches confirmed the absence of other polymorphs. On the other hand, at least one batch obtained was made up of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ crystals with a different crystal unit-cell (see below for structural data), therefore polymorph-II. From a morphological point of view, there is no way to distinguish by optical microscopy the crystals of polymorph-II from those of polymorph-I, both of which appearing as black needles. Examples of SCO polymorphs with very different crystal morphologies allowing their differentiation using a microscope are not usual but already reported in the literature¹². X-ray diffraction is therefore the best mean to sort the batches in the present case. The synthesis protocol used to get polymorph-II single-crystals was exactly the same as the one used to get polymorph-I and already reported. If there was a difference, it was accidental, unidentified and obtaining single-crystals of polymorph-II was non-reproductive. On the other hand, it was possible to deliberately obtain powder batches of polymorph-II. The powder synthesis is very similar to that of polymorph-I.¹⁰ The difference in the synthesis protocol lies in the addition of the $\text{Fe}(\text{NCSe})_2$ solution, drop by drop, to the ligand solution, instead of the reverse operation (addition of the ligand solution to the $\text{Fe}(\text{NCSe})_2$ solution). Very-well crystallized powders are obtained by this mean, allowing good-quality Rietveld refinements that, together with elementary analysis, confirmed that these powders are exclusively composed by polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ (see supplementary material). These pure powders were therefore used for the physical measurements. It is worth noting that among the different attempts to get polymorph-II, it was also obtained powder batches containing a mixture of the two polymorphs, X-ray diffraction allowing easily to identify their presence due to specific Bragg peaks (see supplementary material).

To sum-up, though single-crystals of polymorph-II were obtained accidentally, pure batches of polymorph-II powders can be rationally and reproducibly obtained. Some trials lead to a mixture of polymorphs which confirms that in some circumstances, these polymorphs can be concomitants. All attempts to transform one polymorph into another by heat treatments in the range [80 - 500 K] were not successful. It is also worth to mention that the application of pressure does not allow to transform one polymorph into another. Indeed, the previously reported detailed high-pressure study of polymorph-I as a function of temperature has shown no trace of polymorph-II¹¹ (the studied range was [0- 10 kbar] at [293-353 K]) and, second, the application of pressure on the powder of polymorph-II does not lead to a transformation towards polymorph-I, at least up to 12 kbar.

Magnetism and Heat Capacity of Polymorph-II

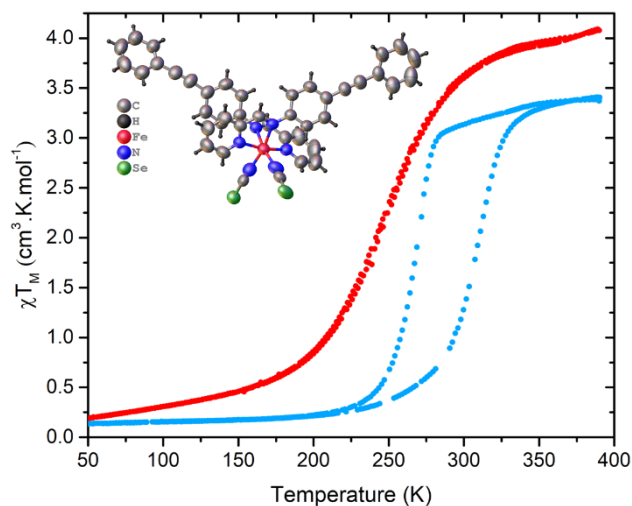


Figure 1: χ_{MT} as a function of temperature determined on polymorph-II (red) and polymorph-I (light blue) of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ with in insert, the scheme of the molecular complex..

Since powders and single-crystals of polymorph-II were systematically checked to be strictly isostructural and since powders containing only polymorph-II can be easily obtained (see above), magnetic measurements were performed on powder batches. The magnetic properties were studied using a SQUID magnetometer between 50 K and 390 K, under a magnetic field of 5 000 Oe, on a 43.1 mg powder sample placed in a polypropylene bag. The measurement was made in temperature scanning mode with a constant maintained rate at cooling and heating. One full spin crossover cycle was measured at 5 K.min⁻¹. After subtracting the diamagnetic contributions from the polypropylene bag and the compound, the product of molar magnetic susceptibility with temperature, χ_{MT} , was plotted as a function of temperature (Figure 1). At 390K, the χ_{MT} product around 4.0 cm³ K mol⁻¹ is slightly higher than the expected value for a iron(II) cation in the HS state. It remains constant on cooling to ca. 300K where it starts to decrease down to 150 K. Upon further cooling, a constant and weak decrease of the χ_{MT} product is observed. Together with the slightly high value at 390 K, this could be an indication of the presence of Temperature-Independent Paramagnetism even though a small magnetic impurity cannot be totally excluded.¹³ The polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ thus shows an almost complete and reversible gradual spin conversion with $T_{1/2}=245\text{K}$. This behavior fully contrasts with the large hysteresis shown by polymorph-I around room temperature but recalls the SCO feature of a few other compounds of the same $[\text{Fe}(\text{PM-L})_2(\text{NCX})_2]$ family such as $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$ ⁷ or $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ ¹⁴ for example.

Differential scanning calorimetry measurements were carried out with 34.853 mg of polymorph-II powder in the range [125 K - 350 K]. Ten successive full thermal cycles were performed using a temperature scanning rate of 10 K.min⁻¹ (Figure 2). The

very large and extended calorific capacity dependence with temperature is typical of a second-order transition associated with a gradual spin transition, revealing here the full coherence of magnetic and thermodynamic measurements. The SCO temperature, estimated by taking the top of the signal, is very close to the $T_{1/2}$ temperature determined by the magnetic measurements (around 245 K). First and tenth cycles overlap fine which characterizes a perfect reproducibility of the SCO.

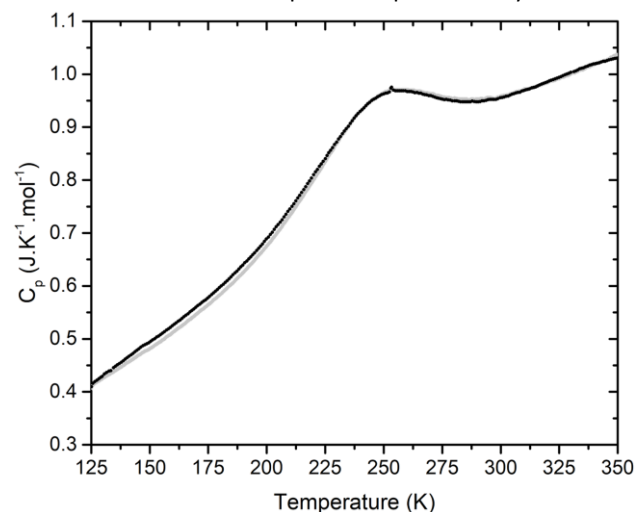


Figure 2 : Calorific capacity as a function of temperature for polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ showing the first (black) and the tenth (light grey) warming.

Table 1 : Experimental and crystallographic data from single-crystal X-ray diffraction investigation of the polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$.[‡]

T(K)	293	100
Chemical formula	$\text{FeN}_6\text{C}_{42}\text{H}_{28}\text{Se}_2$	
Molar mass ($\text{g}\cdot\text{mol}^{-1}$)	830.47	
Space group	$\text{mP}2_1/\text{c}$	
Z-formula	4	
Unit-cell (\AA , °)	$a = 16.9943$ (7)	$a = 16.8161$ (4)
	$b = 14.9296$ (5)	$b = 14.6779$ (2)
	$c = 17.2155$ (6)	$c = 17.1039$ (3)
	$\beta = 117.370$ (5)	$\beta = 117.901$ (3)
Unit-cell volume (\AA^3)	3878.9 (3)	3730.93 (14)
Calc. ρ ($\text{g}\cdot\text{cm}^{-3}$)	1.422	1.478
μ (mm^{-1})	5.551	5.771
Collected Refl.	28 515	27 081
Completeness at 0.81 \AA resolution (%)	98	98
Indep. Refl.	7 579	7 269
R_{int}	0.041	0.025
Refined parameters	460	460
R_{obs}	0.0561	0.0491
$wR_{2\text{obs}}$	0.165	0.142
S	1.056	1.019

Single-Crystal investigations of Polymorph-II in the High-Spin and Low -Spin states

A good-diffracting tiny single-crystal of approximate dimensions $50 \times 10 \times 10 \mu\text{m}^3$ was mounted on a loop and positioned on a microfocus Rigaku FRX equipped with a rotating anode as X-ray source ($\text{CuK}\alpha$, $\lambda = 1.54184 \text{\AA}$) and a 200K Dectris Pilatus detector. Full data collections were performed at 293 K (HS) and 100 K (LS) (strategy details in supplementary material) and lead to high-quality crystal structures (Table 1). At 293 K, Polymorph-II crystallizes in $\text{mP}2_1/\text{c}$ space group in HS with unit-cell parameters a and β notably different from those of polymorph-I though the resulting unit-cell volume appears similar in both polymorphs, which may be related to the possible occurrence of both polymorphs at room temperature. At low temperature, in LS, the space group is unchanged for polymorph-II that exhibits a significant decrease of the unit-cell volume as usually observed in conjunction with the SCO (about $0.8 \text{\AA}^3/\text{K}$ here). Note that a quasi-isotropic evolution of the unit cell due to both thermal contraction and SCO is observed upon cooling in contrast with the polymorph-I and other SCO compounds of this family even with those undergoing a gradual conversion (see below and supplementary material for details).¹⁴

Molecular geometry in $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ polymorphs

It is now well recognized that the geometric properties of the coordination sphere not only reflect the spin state - and thus allow visualizing the SCO - but also influence the transition characteristics.^{15,16} For example, from one compound to another, if the volume of the coordination sphere always varies by the same order of magnitude (from $13.0(2) \text{\AA}^3$ to $9.9(2) \text{\AA}^3$) from HS to LS in FeN_6 , the bond lengths may be very different depending on the concerned ligand while the average variation is always similar ($\sim 0.2 \text{\AA}$). On the other hand, the distortion of the coordination sphere at the SCO appears very different from one compound to another and probably plays a major role in certain characteristics still to faithfully identify.¹⁷ In this context, the comparison of the geometry of polymorphs' coordination spheres therefore remains an important point, as done in Table 2 for the two polymorphs. The bond lengths and the polyhedron volume reflect the spin state which allows to confirm the occurrence of the SCO. These values for polymorph-II at 293 K show that, while mainly HS the crystal contains a significant LS part (estimated at roughly 30% from the polyhedron volume) and values exhibited at 100 K clearly indicate a 100 % LS, the whole being consistent with magnetic measurements. Keeping in mind such results, the geometry of the coordination sphere appears rather similar in both polymorphs for a given spin state. The structural difference between both polymorphs is then visible at the upper physical scales, starting by the entire molecular scale, often addressed using the average deviation parameter (RMSD).⁵ In polymorph-II, the superposition of the molecular complexes in HS and LS shows a RMSD of 0.13\AA . The latter is slightly underestimated due to the LS residue but this value is much lower than the 0.46\AA determined for polymorph-I, which indicates a much smaller molecular rearrangement between the HS and LS states for polymorph-II than for polymorph-I. This confirms the spectacular nature of the molecular-scale reorganization in polymorph I. The present study highlights that, within the $[\text{Fe}(\text{PM-L})_2(\text{NCX})_2]$ family, the

molecular structural differences between HS and LS quantified by the RMSD follows the nature of the SCO since abrupt transition (L/X = PeA/S¹⁸, PeA/Se¹⁰, BiA/S-I⁷) correspond to RMSD greater than 0.4 Å and gradual transitions (L/X = BiA/S-II⁷, AsA/S¹⁴, PeA/Se) correspond to RMSD lower than 0.2 Å. Here, the main difference between the molecular complexes within the two polymorphs comes from the NCSe branches in the HS state, showing a larger distortion in polymorph I (Figure 3). This has certainly repercussions at the crystal-packing scale, which is examined hereafter.

Table 2 : Coordination sphere geometric parameters for the two polymorphs of [Fe(PM-PeA)₂(NCSe)₂] from single-crystal X-ray diffraction. Selected parameters are the Fe-N bond lengths (Å) with the distinction of the ligand parts (NCSe, Py or PM) and the overall average value, the polyhedron volume (Å³) as well as the angle distortion Σ (°), the trigonal distortion Θ (°) and the length distortion ζ (Å) known to be appropriate in this description.^{5, 15}

	Polymorph-I		Polymorph-II	
	HS	LS	HS/LS	LS
T(K)	293	230	293	100
Spin state	HS	LS	HS/LS	LS
d(Fe-NCSe)	2.063(5)	1.947(7)	2.042(3)	1.942(3)
d(Fe-N-Py)	2.164 (4)	1.976(6)	2.085(4)	1.968(3)
d(Fe-N-PM)	2.231(4)	1.977(5)	2.137(5)	1.980(3)
<dFe-N>	2.152(5)	1.967(6)	2.088(5)	1.963(3)
Vp	12.88(2)	9.99(2)	11.86(2)	9.96(2)
Σ	80(2)	60(4)	68(4)	53(2)
Θ	213(4)	168(8)	187(8)	151(4)
ζ	0.360(5)	0.078(7)	0.184(4)	0.086(3)

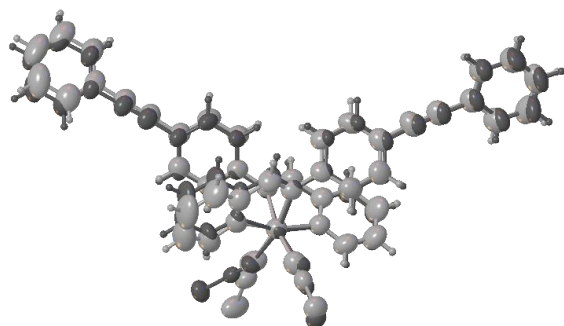


Figure 3. Superposition of the molecular complexes of polymorph -I (dark grey) and polymorph-II (light grey) for [Fe(PM-PeA)₂(NCSe)₂] at room-temperature showing the main difference in the NCSe ligands.

Crystal Packing in [Fe(PM-PeA)₂(NCSe)₂] polymorphs

The fingerprints¹⁹ of the intermolecular interactions in the polymorph-II of [Fe(PM-PEA)₂(NCSe)₂] show that though not completely different the crystal packing is slightly modified at the SCO (Figure 4). Most of the crystal cohesion is built from Se...H (17% of the whole contacts) and H...H contacts (37%) with unchanged proportions from HS to LS. The intermolecular contacts are notably shorter in LS than in HS. Interestingly, the fingerprints of the intermolecular interactions in polymorph-I appear quite similar with exactly the same crucial Se...H and H...H role and proportion, again almost unchanged from HS to

LS. The individual atoms involved in the contacts are not the same within polymorphs, however, highlighting the differences in the crystal-packings (The labelling of the atoms is given in supplementary material). The main difference between polymorphs concern the length of the shortest contact, *i.e.* the low-left tip of the fingerprints (Figure 4), that corresponds to an H...H contact. From HS to LS, the latter decreases from 2.421 Å to 2.311 Å in polymorph-II while it increases from 2.354 Å to 2.483 Å in polymorph-I. This unusual elongation of the H...H contact from HS to LS is probably to be related to the unusual structural behavior of polymorph-I, as already suspected and now emphasized here by the comparison with polymorph-II, though it is difficult to detail it more. Understanding H...H contacts in crystalline cohesion is indeed a current and growing research field.^{20, 21} The present result suggests to integrate SCO compounds into this field of investigation, both parties would probably benefit greatly from this knowledge crossing.

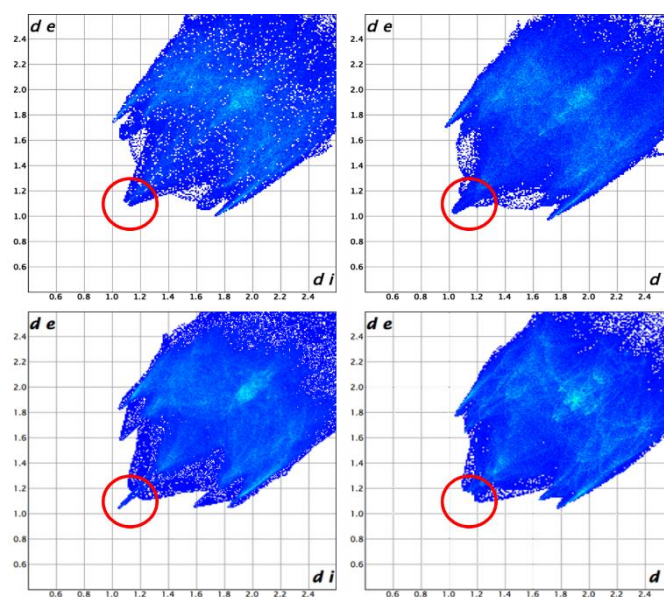


Figure 4. Fingerprints of the intermolecular interactions in [Fe(PM-PEA)₂(NCSe)₂] polymorph-II (high) and polymorph-I (low) in HS (left) and LS (right). The red circles highlight the relevant H...H intermolecular interaction in both polymorphs.

Unit-cell of Polymorph-II as a function of temperature

The temperature dependence of the unit-cell parameters was investigated using the same single-crystal as for full crystal structure determination from nineteen data collection performed by cooling from 293 to 115 K (Figure 5). In perfect agreement with the magnetic curve, the unit-cell parameters smoothly decrease which contrasts with the discontinuous behavior of the polymorph-I unit-cell at the SCO¹¹. The volume decreases by 4.4% from 293 K to 115 K, which includes both SCO and pure thermal effects. In a very similar compound of this molecular complex family that is also showing a continuous SCO, namely [Fe(PM-AzA)₂(NCSe)₂], the same observed volume variation (4.5%) was attributed to about 3% to pure thermal effects and thus 1.5% to the SCO itself.¹⁴ This deconvolution was obtained from a meticulous comparison between iron and zinc

isomorphs. In the present case this study was not possible since the zinc isomorph of polymorph-II was not successfully crystallized but the ratio of the thermal/SCO contribution is probably of the same order of magnitude for polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ than in the previous study of $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ since the unit-cell features, the SCO mechanism and the molecular complexes are very close in both cases. Additionally, the zinc and sulfurocyanide isostructural analogue $[\text{Zn}(\text{PM-PeA})_2(\text{NCS})_2]$ ²², which does not undergo a SCO, can be used to evaluate the pure thermal decrease of volume at 2.4% leading to a contraction due to the SCO for polymorph-II of 2% approximatively.

The thermal contraction affects the unit-cell parameters concomitantly to the occurrence of the SCO while, on the contrary, the β angle seems only affected by the SCO since this angle does not change outside the SCO temperature range (Figure 5). Consequently, it can be efficiently used to witness the SCO. The sudden increase of this angle corresponds to the SCO and gives $T_{1/2}$ at about 253 K. This value is in relatively good agreement with the $T_{1/2}$ obtained from magnetic and thermodynamic measurements (245 K) especially when taking in mind that the latter are performed on powders and not on single-crystals, which is known to potentially generate transition-temperature shifts.

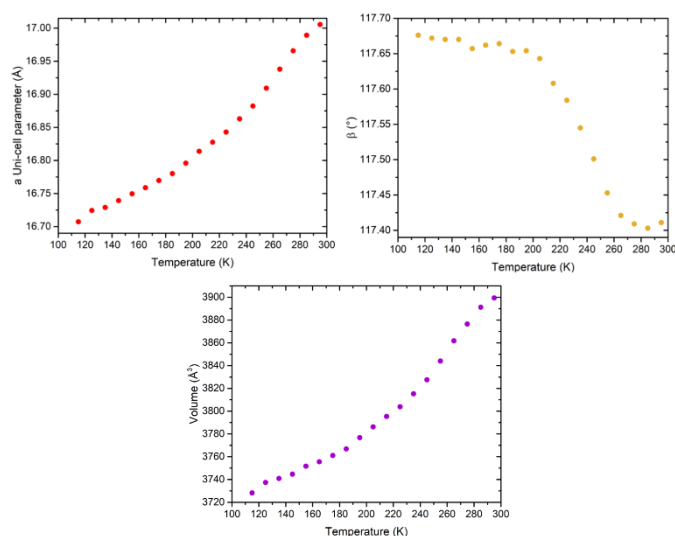


Figure 5. Unit-cell temperature dependence for the polymorph-II of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ showing the a parameter (top left), the β angle (top right) and the unit-cell volume (down).

Conclusions

Following the previous reports on polymorph-I of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$,^{10,11} one of the rare SCO compounds exhibiting a large hysteresis centered on room temperature, a second polymorph has been obtained here. This new polymorph undergoes a continuous SCO at low temperature, as attested by magnetism, calorimetry and X-ray diffraction and can be obtained in form of single-crystals or powders; the latter being reproducibly synthesized in a controlled way allowing to master the SCO mechanism for this compound. The drastic change

between the SCO features for the two polymorphs - from hysteretic to continuous - is reflected by the structural properties that are appropriately impacted from the coordination-sphere geometry to the unit-cell. Conversely, the structural difference that could be closely related to the distinct SCO mechanisms for the two polymorphs is probably due to differences in the H...H network within the crystal packing, as already observed in other SCO polymorphs.⁹ Here, the contrast between the subtlety of the structural differences between polymorphs of $[\text{Fe}(\text{PM-PeA})_2(\text{NCSe})_2]$ and its strong consequences on the spin transition features illustrates the high sensitivity of the SCO phenomenon in the solid-state.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

The authors gratefully acknowledge the Agence Nationale de la Recherche for the financial support under the grant ANR FemtoMat 13-BS046002 and the Region Nouvelle Aquitaine. The University of Bordeaux has provided the PhD grant for ET. This work has benefited from the facilities and expertises of the Biophysical and Structural Chemistry platform (BPCS) at IECB, CNRS UMS3033, Inserm US001, Bordeaux University. <http://www.iecb.u-bordeaux.fr/index.php/fr/plateformestecnologiques>.

Notes and references

‡ The unit-cell of polymorph I is $\text{mP}2_1/\text{c}$ at 300 K in HS with $a = 15.7175$ (13) Å, $b = 14.6860$ (13) Å, $c = 16.9957$ (13) Å, $\beta = 93.399$ (3) and $V = 3916.2$ (6) Å³ and oPccn at 230 K in LS with $a = 14.444$ (5) Å, $b = 14.705$ (4) Å, $c = 17.595$ (4) Å and $V = 3737.2$ (17) Å³.

- J. Tao, R.-J. Wei, R.-B. Huang and L.-S. Zheng, *Chem. Soc. Rev.*, 2012, **41**, 703–737.
- T.M. Ross, B. Moubaraki, S.M. Neville, S.R. Batten and K.S. Murray, *Dalton Trans.*, 2012, **41**, 1512.
- C. Bartual-Murgui, L. Piñero-López, F.J. Valverde-Muñoz, M. Carmen Muñoz, M. Seredyuk and J.A. Real, *Inorg. Chem.*, 2017, **56**, 13535–13546.
- S. Rat, K. Ridier, L. Vendier, G. Molnár, L. Salmon and A. Bousseksou, *CrystEngComm*, 2017, **19**, 3271.
- E. Collet and P. Guionneau, *C. R. Chimie*, 2018, **21**, 1133–1151.
- B. Gallois, J. A. Real, C. Hauw and J. Zarembowitch, *Inorg. Chem.*, 1990, **29**, 1152–1158.
- M. Marchivie, P. Guionneau, J.-F. Létard and D. Chasseau, *Acta Cryst.*, 2003, **B59**, 479–486.
- B. Moubaraki, B.A. Leita, G.J. Halder, S.R. Battern, P. Jensen, J. P. Smith, J.D. Cashion, C.J. Kepert, J.-F. Létard and K. S. Murray, *Dalton Trans.*, 2007, 4413–4426.
- H. Hagiwara and S. Okada, *Chem. Commun.*, 2016, **52**, 815–818.
- E. Tailleux, M. Marchivie, N. Daro, G. Chastanet and P. Guionneau, *Chem. Commun.*, 2017, **53**, 4763–4766.
- E. Tailleux, M. Marchivie, J.-P. Itié, P. Rosa, N. Daro and P. Guionneau, *Chem. Eur. J.*, 2018, **24**, 14495–14499.

- 12 H. Hang, B. Fei, X.Q. Chen, M.L. Tong, V. Ksenofontov, I.A. Gural'skiy and X. Bao, *J. Mater. Chem. C*, 2018, **6**, 3352–3361.
- 13 O. Kahn. *Molecular Magnetism. VCH: New York, NY*, 1993. xvi + 380 pp. ISBN 3-527-89566-3
- 14 S. Lakhouloufi, M.H. Lemée-Cailleau, G. Chastanet, P. Rosa, N. Daro, P. Guionneau, *Phys. Chem. Chem. Phys.*, 2016, **18**, 28307-28315.
- 15 P. Guionneau, *Dalton Trans.*, 2014, **43**, 382-393.
- 16 M.A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119–4142.
- 17 G. Chastanet, C. Desplanches, C. Baldé, P. Rosa, M. Marchivie and P. Guionneau, *Chem2*, 2018, 2-2. doi: 10.28954/2018.csq.07.001.
- 18 P. Guionneau, J.-F. Létard, D.S. Yuffit, D. Chasseau, J.A.K. Howard, A.E. Goeta and O. Kahn, *J. Mater. Chem.*, 1999, **4**, 985-994.
- 19 Spackman, J.J. McKinnon, *CrystEngComm*, 2002, **4**, 378-392.
- 20 P.A. Wood, J.J. Mc Kinnon, S. Parsons, E. Pidcock and M. A. Spackman, *CrystEngComm*, 2008, **10**, 368–376.
- 21 N.K.V. Monteiro and C.L. Firme, *J. Phys. Chem. A*, 2014, **118**, 1730–1740.
- 22 F. Le Gac, P. Guionneau, J.-F. Létard and P. Rosa, *Inorg. Chim. Acta*, 2008, 361, 3519–3524.