

Supplementary Materials: Solvent-Induced Hysteresis Loop in Anionic Spin Crossover (SCO) Isomorph Complexes

Emmelyne Cuza ¹, Samia Benmansour ², Nathalie Cosquer ¹, Françoise Conan ¹, Carlos J. Gómez-García ^{2,*}, Smail Triki ^{1,*}

¹ Univ Brest, CNRS, CEMCA, 6 Avenue Le Gorgeu, C.S. 93837, 29238 Brest CEDEX 3, France; Emmelyne.Cuza@univ-brest.fr (E.C.); nathalie.cosquer@univ-brest.fr (N.C.); Francoise.Conan@univ-brest.fr (F.C.)

² Instituto de Ciencia Molecular (ICMol), Departamento de Química Inorgánica, Universidad de Valencia, C/Catedrático José Beltrán 2, 46980 Paterna, Spain; sam.ben@uv.es

* Correspondence: carlos.gomez@uv.es (C.J.G.-G.); smail.triki@univ-brest.fr (S.T.); Tel.: +34-963-544-423 (C.J.G.-G.); +33-298-016-146 (S.T.)

1- Characterization of the Materials

Infrared spectra of complex **3** have been performed at room temperature, in the 4000–400 cm⁻¹ range, using a platinum ATR Vertex 70 BRUKER spectrometer. Temperature dependence of the IR spectra was performed in the 2130–1975 cm⁻¹ range, using a Vertex 70 BRUKER spectrometer with variable temperature cell holder (VT Cell Holder typer P/N GS21525). The IR data have been qualitatively analyzed in the form of absorbance (ABS) *vs.* wavenumber (in cm⁻¹). For the quantitative analysis and comparison with the thermomagnetic measurements, the intensities of the *HS* vibration bands were represented as ABS *vs.* *T*, while the intensities of the *LS* vibration bands were represented as (1-ABS) *vs.* *T*. All NMR spectra (¹H and ¹³C) were performed using BRUKER DRX 300 MHz, Advance 400 MHz and Advance III HD 500 MHz equipment. All chemical shifts are defined in ppm and determined by using the rightful deuterated solvent as a reference. TGA measurements were performed on ATG-LabsysTM, Setaram. The sample was preliminary put under vacuum and then heated at 5°C.min⁻¹ under nitrogen atmosphere.

2- Crystallographic characterisation

a – Single crystal characterisations

Table S1. Crystal data of [Fe(py₃C-OEt)₂][Fe(py₃C-OEt)(NCE)₃]₂·2CH₃CN (E = S (**1**), BH₃ (**2**), Se (**3**)).

	1	2	3
Temperature / K	293	100	100
Colour	Orange	Red	Red
Formula	C ₈₂ H ₇₄ Fe ₃ N ₂₀ O ₄ S ₆	C ₈₂ H ₉₂ Fe ₃ N ₂₀ O ₄ B ₆	C ₈₂ H ₇₄ Fe ₃ N ₂₀ O ₄ Se ₆
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	11.6683(5)	11.432(5)	11.6827(8)
<i>b</i> / Å	11.9026(7)	11.829(5)	12.0204(10)
<i>c</i> / Å	17.1711(9)	16.857(5)	16.9162(11)
α / °	78.192(5)	78.072(5)	78.389(6)
β / °	88.279(4)	88.037(5)	87.805(6)
γ / °	66.544(5)	65.879(5)	65.767(7)
<i>V</i> / Å ³	2137.9(2)	2032.4(14)	2119.3(3)

b – X-ray powder diffraction.

X-ray powder diffraction (XRPD) data for **3** were collected on a polycrystalline sample filled into a 0.7 mm glass capillar (within a saturated CH₃CN atmosphere) that was mounted and aligned on an Empyrean PANalytical powder diffractometer, at 45 kV, 40

mA using Cu K α radiation ($\lambda = 1.54177 \text{ \AA}$). A total of four scans were collected and merged at room temperature in the 2θ range of $5\text{--}40^\circ$.

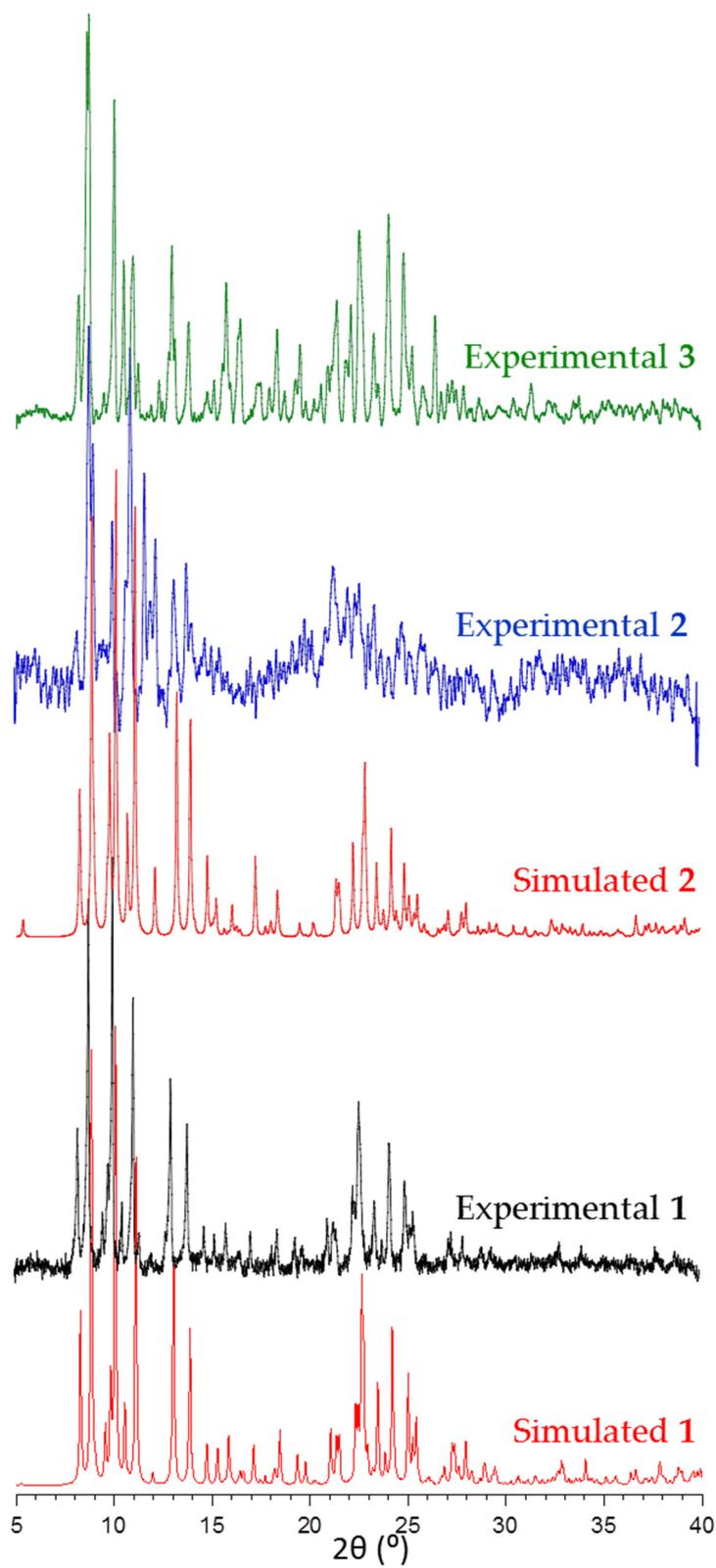


Figure S1. Experimental and simulated XRPD patterns for compounds 1 and 2, and experimental one for complex 3.

3-. Magnetic characterisation

Magnetic susceptibility measurements were carried out in the temperature range 2–400 K with an applied magnetic field of 0.1 T, on a polycrystalline sample of **3** (with a mass of 5.896 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer (San Diego, CA, USA). The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables [1]. The photomagnetic studies were performed by cooling the samples down to 10 K at a rate of 1 K min⁻¹ and then irradiating them with a green Diode Pumped Solid State Laser DPSS-532-20 from Chylas ($\lambda = 532$ nm, power = 20 mW) coupled *via* an optical fibre to the cavity of the SQUID magnetometer. When saturation of the magnetization was reached (after *ca.* 4 hours), the laser was switched off and the sample was heated up to 300 K at a rate of 0.4 K min⁻¹. The sample for the LIESST studies consisted of a thin layer of microcrystalline powder of compound **3**.

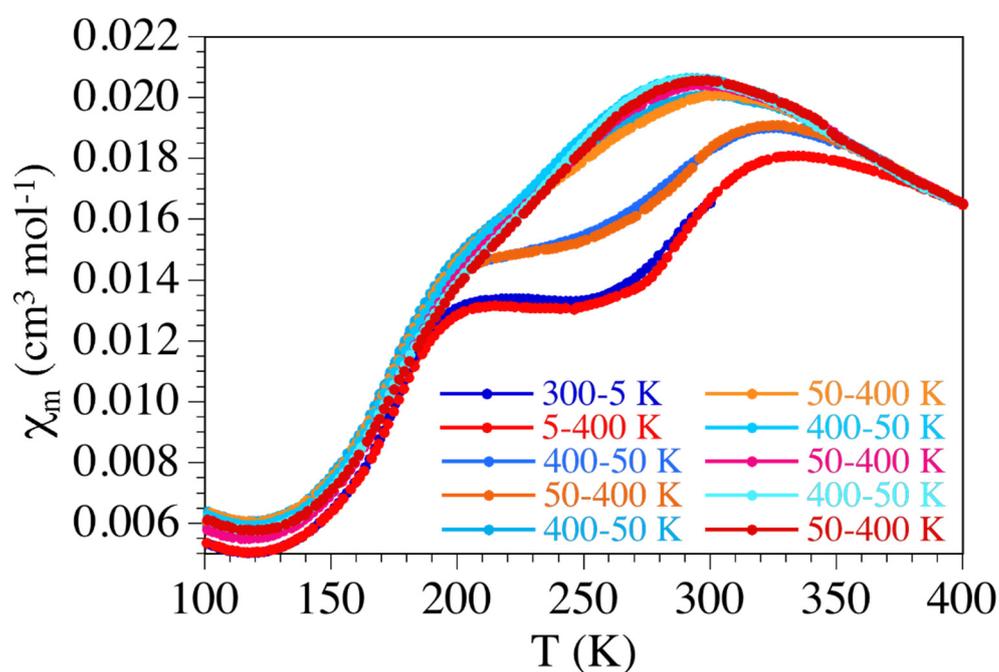


Figure S2. Thermal variation of χ_m of a freshly prepared sample of compound **3** for different consecutive heating and cooling scans.

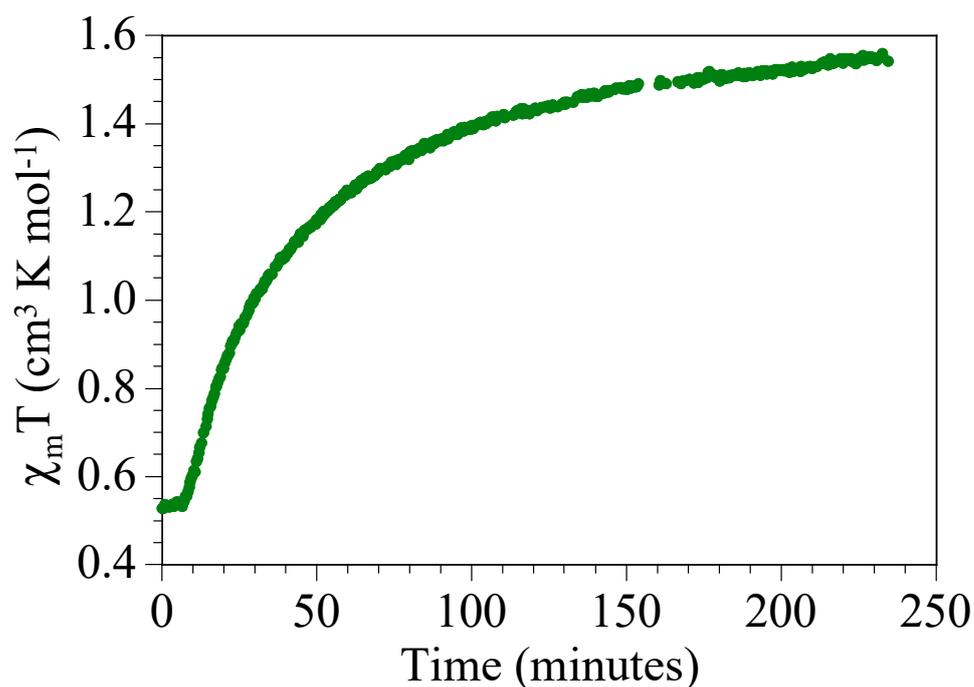


Figure S3. Time dependence of $\chi_m T$ at 10 K for compound 3 under laser irradiation with green light ($\lambda = 532 \text{ nm}$, switched on at time *ca.* 10 min).

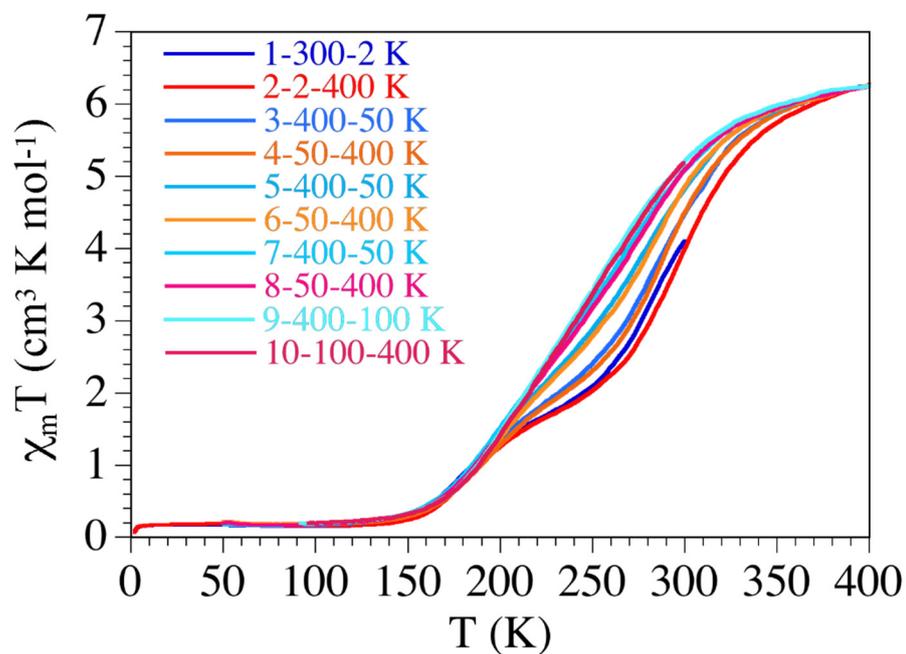


Figure S4. Different heating and cooling scans of the $\chi_m T$ product performed on the de-solvated compound 3 after re-solvation with two drops of CH_3CN .

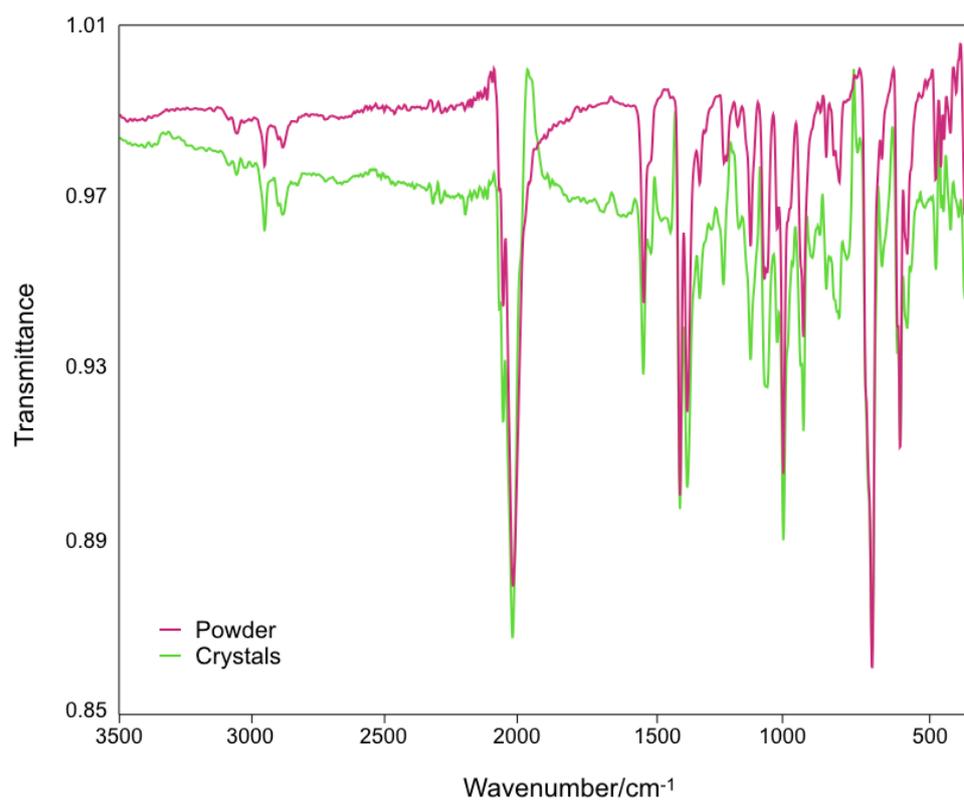


Figure S5. IR spectra of single crystals and polycrystalline powder of complex 3.

References.

1. Bain, G. A.; Berry, J. F. Diamagnetic corrections and Pascal's constants. *J. Chem. Educ.* **2008**, *85*, 532-536.