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**Tuning spin crossover behavior in the $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$
trimer: dilution and contraction effects
($\text{L} = 4\text{-(1,2,4-triazol-4-yl) ethanedisulfonate}$)**

Supervised by José Ramón Galán-Mascarós

MASTER'S DEGREE FINAL PROJECT

MASTER'S DEGREE IN NANOSCIENCE, MATERIALS AND PROCESSES



UNIVERSITAT ROVIRA I VIRGILI



Tarragona

2017

Tuning spin crossover behavior in the $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ trimer: dilution and contraction effects (L = 4-(1,2,4-triazol-4-yl) ethanedisulfonate)

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Master Program in Nanoscience, Materials and Processes, 2016-2017

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Abstract: In spin crossover (SCO) systems, external stimuli (temperature, pressure, light irradiation, etc.) may trigger a transition from the low spin ground state (LS) to the high spin excited state (HS), which is metastable. The characteristics of this switchability (shape, energy difference between states, cooperativity, external stimuli response...) are determined by the crystal structure in the solid state and, therefore, may be tuned by chemistry design. The $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6] \cdot n\text{H}_2\text{O}$ (L=4-(1,2,4-triazol-4-yl) ethanedisulfonate) has shown extraordinary SCO features, at very high temperatures and bistability in a long temperature range, with a hysteresis over 90 K. In this work, we have studied the effect on the SCO phenomena provoked by modifications on the crystal structure of the material: on one end, by dilution in a non-SCO isostructural crystal; on the other end, through methatesis with another contraction. Our results indicate that the memory effect may be tuned by contraction substitution and, remarkably, that SCO hysteresis still remains in ultradiluted samples, suggesting the appearance of single molecule memory effect.

Introduction

In the last decades, “molecular materials” have become relevant in the miniaturization of components for devices, such as modulators, transistors, wires, switches, etc [1, 2]. Nowadays, there is an effort to synthesize new coordination complexes with promising applications in this field. Among them, spin crossover (SCO) compounds are excellent candidates due to the possibility to obtain bistability near room temperature, becoming technologically relevant. They could have potential application in molecular electronics, display devices, photomagnetism, data storage, non-linear optics, etc [3, 4].

SCO systems are coordination complexes with a $d^4\text{--}d^7$ electronic configuration in the metal atom. Ligands produce a static electric field and remove the degeneration of d (and f orbitals) in the free ion, where two electronic ground states are possible, low spin (LS) and high spin (HS). The ground state is determined by the crystal field imposed by the ligands [5]. When this energy is comparable to the pairing energy for the electrons (P), LS and HS are very close in energy. This allows the appearance of a spin transition, where population of the excited state (HS) can be triggered by external stimuli [6] such as pressure, temperature, light or magnetic field.

The most common configuration in SCO compounds is octahedral [7], where six ligands are distributed around the metal ion. The ligand field splits the d orbitals into two different energy sets: three orbitals of lower energy with t_{2g} symmetry and two orbitals of higher energy with e_g symmetry. The energy difference between both set of orbitals is the crystal field splitting energy (Δ ; Δ_o in octahedral configuration) and depends on the strength of the ligand field. The spectrochemical series orders ligand strength depending on the size, charge, oxidation number, group and identity of the ligand [8]. If Δ is greater than pairing energy, then the spin configuration will be LS. Otherwise, if $\Delta \ll P$, the spin configuration will be HS [9]. As an example, [Figure 1](#) shows the two different spin states of Fe (II) (d^6) in an octahedral configuration.

The SCO transition can occur gradually, abruptly, in different steps, be incomplete and, if the material presents cooperativity, it can show hysteresis [10]. For transitions that display hysteresis, two transition temperatures ($T_{1/2}(\uparrow)$ and $T_{1/2}(\downarrow)$) define the width of the loop.

Iron (II) and iron (III) complexes have been the most studied, but SCO phenomena can be also observed in compounds with chromium (II), chromium (III), manganese (II), manganese (III),

cobalt (II) and cobalt (III) [11-15]. In Fe (II) compounds, the SCO transition from the diamagnetic state ($\Delta S = 0$) to the paramagnetic state ($\Delta S = 2$) is accompanied by a change in color (from pink to white), an increment of 15% of the metal-ligand distances and changes in the spectroscopic properties [16].

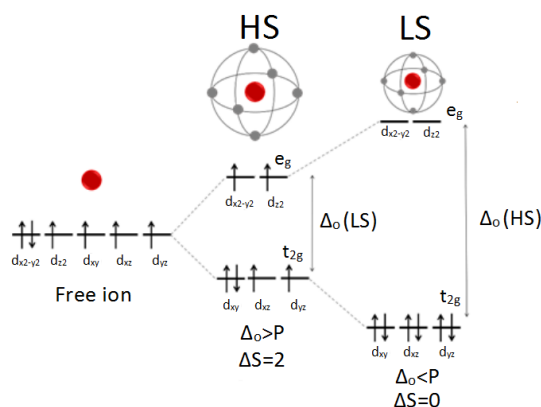


Figure 1: Low Spin (LS) and High Spin (HS) states for a Fe(II) ion in octahedral configuration.

Another phenomenon that occurs in this kind of complexes is the Temperature-induced excited spin state trapping (TIESST). This process refers to the trapping of the excited state (HS) at low temperatures, via rapid cooling, achieving a metastable state. L  tard et al observed TIESST for the first time in 1997. The characteristic T_{TIESST} is the main parameter of this thermal trapping [17].

In this report we present our studies on the influence of the solid state environment in a very interesting SCO system, the SCO trimer $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ ($\text{L} = 4\text{-(1,2,4-triazol-4-yl)ethanedisulfonate}$). Indeed, this trimer presents a HS–LS–HS ground state, undergoing a gradual SCO transition to HS–HS–HS above room temperature, which is almost complete at 400 K [18], it exhibits a very wide hysteresis (85 K), although heavily dependent on temperature scan rate. In addition, this compound shows TIESST, with the highest T_{TIESST} reported until the moment (250 K). During this work, we studied the cation influence in the solid state, by substituting $(\text{Me}_2\text{NH}_2)^+$ by Cs^+ monocations.

We also carried out dilution studies, by doping the $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ salt with the isostructural and non-SCO anion $[\text{Zn}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$.

Experimental Techniques

Nuclear Magnetic Resonance (NMR) measurements were performed using a 500 MHz spectrometer at the NMR Unit in the Institute of Chemical Research of Catalonia (ICIQ).

Powder X-Ray Diffraction (PXRD) data were collected on a Bruker D8 Advance Powder Diffractometer at ICIQ. This equipment has a $\text{K}\alpha_1$ germanium monochromator for Cu radiation ($\lambda = 1.5406 \text{ \AA}$), fixed divergence slits and a diffracted beam radial Soller slit. Single crystal X-ray diffraction was performed in the same unit using a Bruker Apex II DUO Single Crystal Diffractometer which combines molybdenum and copper X-ray μ -sources and is equipped with an APEX II 4K CCD area detector.

X-ray absorption near edge structure (XANES) and X-ray emission spectroscopy (XES) were done at the beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble.

Magnetic susceptibility measurements between 2–400 K were carried out in a Quantum Design MPMS-XL SQUID magnetometer under a 1000 Oe field. Each sample was secured inside a gel capsule with glass wool, and the capsule was pinched (0.5 mm diameter hole) on the top to allow convenient purging of the interior of the capsule.

Differential scanning calorimetry (DSC) measurements were performed in the Chromatography, Thermal Analysis and Electrochemistry Unit at ICIQ by using a Differential Scanning calorimeter (model DSC822e) from Mettler Toledo.

UV/VIS/NIR spectra were recorded in 1 cm quartz cells by using an Agilent 8453 diode array spectrophotometer ($\lambda = 190\text{--}1100 \text{ nm}$ range) and a cryostat from Unisoku Scientific Instruments was used for temperature control.

Experimental section

The ligand Dimethyl ammonium 4-(1,2,4-triazol-4-yl)-ethanedisulfonate(L) and $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ (**1**) were prepared according to the literature procedures [19-21] and the syntheses are explained in the supplementary information.

$\text{Cs}_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ (**2**). 180 mg (1 eq.) of **1** were diluted in 5 mL of distilled water with ascorbic acid to avoid the iron oxidation from Fe (II) to Fe (III) and 275.6 mg (20 eq.) of CsCl_2 were diluted in 5 mL of distilled water, also with ascorbic acid. Both solutions were mixed for 10 minutes under stirring. **2** Crystals were obtained after two days by vapor diffusion crystallization method, using ethanol as the precipitant.

$(\text{Me}_2\text{NH}_2)_6[\text{Zn}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ (**3**). A stock solution was prepared dissolving 0.23 g of ZnCl_2 and 0.60 g of L in 10 mL of distilled water. After mixing it during 10 minutes, 15 mL of Ethanol were added to precipitate the compound. The precipitate obtained was separated from the suspension by centrifugation and it was washed two times with ethanol and one time with diethyl ether. The solid obtained was dried at room temperature for one day.

Compound **1** was diluted in **3** in different weight percentages: 50, 10, 5 and 1 % (w/w), and the powders obtained were named dilution **A**, **B**, **C** and **D**, respectively.

Dilution A. 30,5 mg of **1** and 29,7 mg of **3** were diluted separately in 2 mL of distilled water with ascorbic acid and an excess of L. Then, the solutions were mixed during 10 mL and 15 mL of ethanol were added to precipitate the salt. **Dilution B**, **C** and **D** were prepared like dilution **A** but different amounts of **1** and **3** were weighed ([Table 1](#)).

Dilution (w/w)	1 weight (mg)	3 weight (mg)
B (10 %)	6,6	53,1
C (5 %)	3,3	56,8
D (1 %)	0,8	59,3

Table 1: weights of **1** and **3** for dilutions **B**, **C** and **D**.

Characterization

PXRD of all pure synthesized compounds are shown in ([Figure 2](#)). Most intense peaks in **1** and **3** follow the same diffraction pattern and are observed at same degrees (2θ): 6,3; 7,3; 7,8; 8,4; 10,9; 11,2; 12,6; 13,0; 13,7; 14,9; 15,2; 17,0; 17,8; 18,5; 20,0; 21,5; 22,1 and 23,0°.

The difference in intensity between **3** and **1** is due to the lack of crystallinity of the powder. Therefore, these two samples are isostructural. As can be seen in [Figure 2](#), the diffraction pattern for **2** does not match the obtained for **1**

and **3**. This is a clear indicator of a different packing and structure caused by the cation exchange.

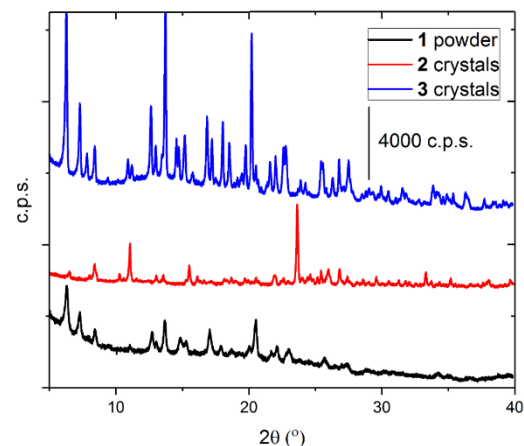


Figure 2: PXRD of **1** powder (black) and **2** and **3** crystals (red and blue, respectively).

The two spin states for compound **1** were characterized by XANES ([Figure 3](#), up) and XES ([Figure 3](#), down). A pellet of **1** mixed with cellulose (30 % w/w) was used to perform the experiments. 5 Tons of pressure were employed in a 13 mm diameter holder. The experiments were carried on under vacuum atmosphere (10^{-6} bar). XANES and XES spectra were recorded at two temperatures, 298 K (black line), when the sample is in the HS–LS–HS state, and at 398 K (red line), when the sample is in HS–HS–HS state.

Comparing the XANES spectra at 298 K and 398 K, a clear difference appears in the pre-peak zone ([Figure 3](#), up–inset), a shoulder appears at 7,122 keV and an energy shift of the most intense peak from 7,128 keV (HS–LS–HS) to 7,127 keV (HS–HS–HS). XES spectra of **1** also shows differences between both spin states. The peak at 7,045 keV is more intense in the HS–HS–HS state than in the HS–LS–HS configuration.

The magnetic susceptibility (χ) for **1** was determined over the 200–400 K temperature range. The χT versus T plot (where T is the temperature) is displayed in [Figure 5](#), left. In the low temperature region, the χT value is consistent with a HS–LS–HS configuration with a value of $5,9 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and it increases at 400 K to $8,4 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which belongs to the excited configuration (HS–HS–HS) and The hysteresis loop was of 90 ($T_{1/2}(\uparrow) = 400 \text{ K}$, $T_{1/2}(\downarrow) = 310 \text{ K}$). These values were the same as the reported

[19]. The only variation observed was a decrease of 10 K in the T_{TIESST} of the compound synthesized (Figure 5, right).

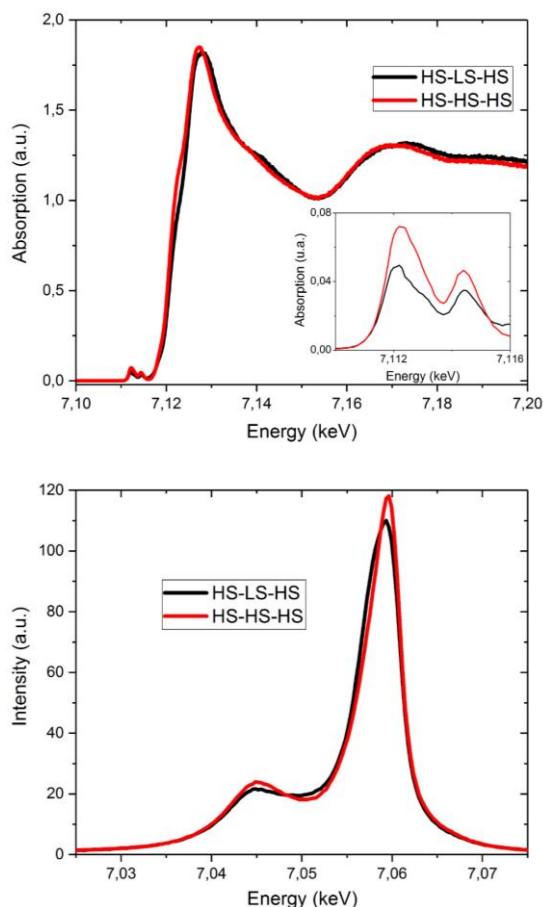


Figure 3: XANES (up) and XES (down) spectra for **1**.

Results and discussion

The structure of the $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3\mu\text{-L}_6(\text{H}_2\text{O})_6]$ (**1**) salt contains anions formed by linear trinuclear arrays of face-sharing octahedral iron centers (Fe1-Fe2-Fe1). The outer irons (Fe1) are coordinated by three triazoles and three water molecules. Their ground state should be HS, due to the weak field H_2O ligands. The central iron (Fe2) is hexacoordinated to intermediate-field triazoles, prone to promote SCO. The anionic charges in these trimers are compensated by dimethylammonium cations. The corresponding Cs^+ salt could be obtained by methathesis.

The crystal structure of $\text{Cs}_6[\text{Fe}_3\mu\text{-L}_6(\text{H}_2\text{O})_6]\cdot 13\text{H}_2\text{O}$ (**2**) contains the same anion as the Me_2NH_2^+ salt (Figure 4), but with a different crystal packing: monoclinic C2/c vs triclinic P-1 . The number of hydration water molecules increases, 13 for **2** vs 5 for **1**. We also observed that the crystal structure obtained for **2** indicate

HS-LS-HS configuration, suggested by the Fe–N distances in the central Fe2 position (Table 2).

Bond	1 (Å) [19]	2 (Å)
Fe2–N4	1,99	1,97
Fe2–N2	1,98	1,96
Fe2–N7	2,01	1,97
Fe1–N5	2,16	2,18
Fe1–N1	2,15	2,19
Fe1–N8	2,17	2,20
Fe1–O1	2,13	2,08
Fe1–O2	2,12	2,17
Fe1–O3	2,09	2,10

Table 2: Fe–N and Fe–O distances in **1** and **2** crystals

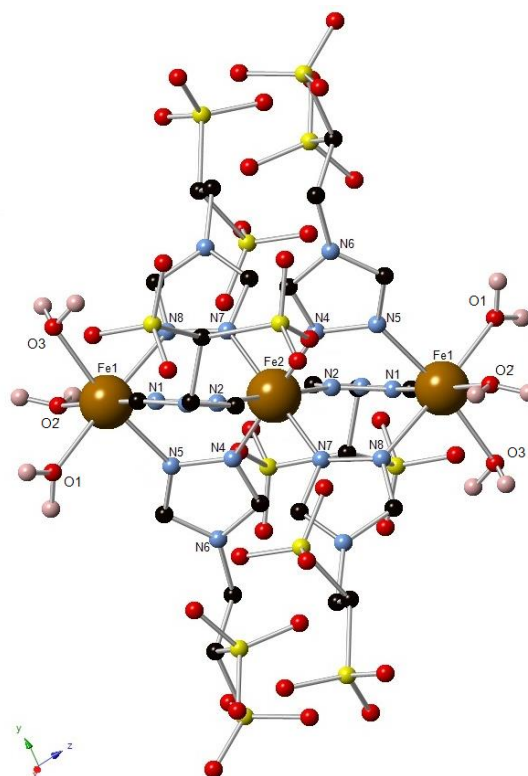


Figure 4: molecular structure of $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ trimer. Color code: Fe: brown; nitrogen: Blue; oxygen: red; sulfur: yellow; carbon: black; hydrogen: pink.

Figure 6 shows the thermal dependence of the product of magnetic susceptibility and temperature product (χT) for **2**. **2** exhibits a quite abrupt SCO transition $T_{1/2}(\uparrow) = 355$ K and $T_{1/2}(\downarrow) = 305$ K. The width of the thermal hysteresis depends on scan rate, with 61 K at 2 K/min and 45 K at 0.3 K/min. When compared with **1**, transition temperatures have decrease, and hysteresis is narrower. χT values are similar, as expected. Although the cycle is more abrupt, it is still possible to trap **2** in the metastable state by fast cooling. The characteristic T_{TIESST} is 240 K

(Figure 6, right-inset), very close to the obtained for the dymetilammonium salt.

Compound	1 [19]	2
a (Å)	14,228	34,427
b (Å)	15,158	11,411
c (Å)	21,326	26,132
α (°)	80,378	90,000
β (°)	84,280	128,229
γ (°)	83,773	90,000
Z	2	4
V (Å ³)	4492,5	8064,0
Mw(g/mol)	2173,66	2838,69

Table 3: lattice and other parameters of **1** and **2**.

The thermal hysteresis cannot be related to a simple hydration/dehydration process, as confirmed by multiple consecutive cycles obtained in the absence of water. Hydration molecules should be lost in the first heating branch, as confirmed by DSC data (Figure S 4), and then no additional features are observed, although the transition cycle is perfectly reproducible.

The abrupt transition in **2** suggests an increase in cooperativity. This may be rationalized with structural correlations. For instance, related to the distances between SCO centers. Table 4, Figure S 5 and Figure S 6, show the distances among a SCO center and the eight closest SCO centers from other trimers. If we compare the average distances ($\bar{X}$ = 13,95 Å for **1** and 13,41 Å for **2**), it can be determined that the SCO centers

are closer in **2**, what explains the increase in cooperativity.

Furthermore, **1** shows a tetragonal packing with AA stacking. Meanwhile, **2** present an hexagonal close packed (HCP) with a stacking ABAB. As a consequence, the volume per unit formula is 2246,25 Å³ in the case of **1** and 2016,00 Å³ for **2**. This also means that molecules are closer in **2** and, therefore, the cooperativity increases among the metallic central atoms.

The number of water molecules plays an important role in the increase of cooperativity. In **2**, the six cesiums show an electro-affinity to oxigens from water molecules and from the sulfate groups from [Fe₃μ-L₆(H₂O)₆]⁶⁻, having each cesium 6 oxigens at a distance around 3 Å. This network stabilize the packing, reduce the distance between SCO centers and create a pathway that will favor the cooperativity.

1		2	
nº Fe	d (Å)	nº Fe	d (Å)
1	11,29		
1	11,34		
		2	11,41
		2	13,74
2	14,23		
		4	14,26Å
1	14,82		
2	15,16		
1	15,38		
$\bar{X}$	13,95	$\bar{X}$	13,41

Table 4: distances among a Fe2 and its eight closest Fe2 neighbours.

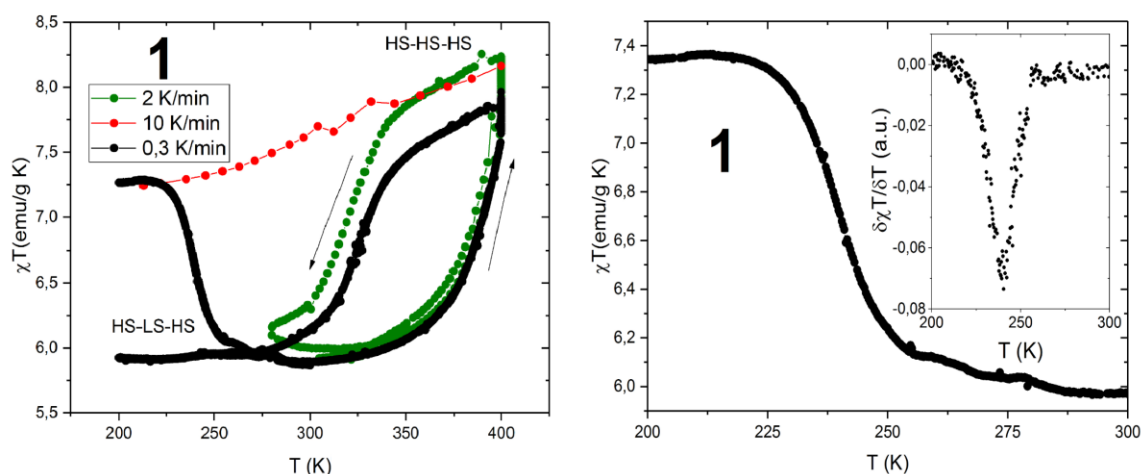


Figure 5: χT vs T plot for **1** in the 175–425 K range at different scan rates (left). χT vs T plot for **1** (right) and $\delta\chi T/\delta T$ vs T plot (inset) in the 200–300 K range at 0,3 K/min.

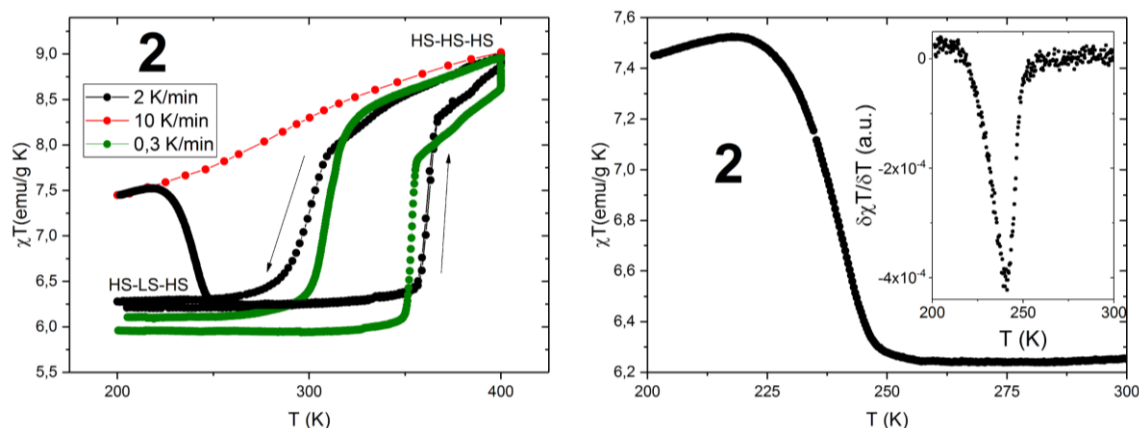


Figure 6: χT vs T plot for **2** in the 175–425 K range at different scan rates (left). χT vs T plot for **2** (right) and $\delta\chi T/\delta T$ vs T plots (inset) in the 200–300 K range at 0,3 K/min.

We also studied the magnetic dilution effect in the series of solid solutions $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3\mu\text{-L}_6(\text{H}_2\text{O})_6]_x[\text{Zn}_3\mu\text{-L}_6(\text{H}_2\text{O})_6]_{(1-x)}$ at several concentrations (Table 1): Dilution A (50%), Dilution B (10%), Dilution C (5%) and Dilution D (0,1%). By decreasing the SCO-active trimer in the structure, cooperativity should also decreased, since only part of the trimers in the solid would contribute to the structural transition associated with the spin transition. Magnetic susceptibility (χ) data of all the dilutions are shown in Figure 7, as the HS fraction (γ_{HS}):

$$\gamma_{\text{HS}} = \frac{\chi T - \chi T_{\text{HS}}}{\chi T_{\text{HS}} - \chi T_{\text{LS}}}$$

Where χT_{HS} is the maximum value of χT when the sample is in HS and χT_{LS} is the minimum χT value when the sample is in the LS configuration.

The hysteresis is clearly retained in all samples, even at concentrations down to 0,1 %. $T_{1/2}$ ($\uparrow$) for dilutions A, B and C is maintained around 380 K. However, it decreases to 340 K for dilution D. This indicates, as expected, a loss of cooperativity, which is typically associated with lower $T_{1/2}$ ($\uparrow$). Additionally, the LS–HS transition is more gradual in D, another clear sign of loss of cooperativity. Surprisingly, in all these diluted samples, very slow temperature scan rates trap the metastable TIESST state in the cooling sample, even at 2 K/min. For the sake of time, we only determined $T_{1/2}$ ($\downarrow$) for dilution B ($T_{1/2}(\downarrow) = 297$ K), because a 0.3 K/min rate from 400 K to 200 K was needed (≈ 11 hours). This hysteresis ($\Delta T = 83$ K) is comparable to the obtained in **1**. Table 5 presents the T_{TIESST} for all dilutions. Diluting the sample at 50 %, increases

the T_{TIESST} by 6 K. Below 10 %, T_{TIESST} remains constant at 255 K. Relaxation studies will be fundamental to completely understand this trend.

Sample	T_{TIESST} (K)
1	240
Dilution A	246
Dilution B	255
Dilution C	256
Dilution D	254

Table 5: TIESST temperatures for **1** and dilutions A, B, C and D.

Thermal hysteresis was observed at as low as 0,1%, where cooperativity is residual and marginal. This is in contrast to all other and previous SCO examples. Upon magnetic dilution, hysteresis decreases and it is typically lost at dilutions as high as 80% of Fe (II) [22]. On a first approximation, our results suggest that cooperativity is not at the origin of the hysteretic behaviour. However, hysteresis at the molecular level for a SCO system is theoretically impossible. What's the origin of this phenomenon?

A plausible explanation may be found looking at the molecular structure of our trimer. Each Fe2 center is linked to six triazol derivatives bearing two SO_3^- groups each. Upon spin transition, the Fe–N distances change, and this will affect the distance between ligands. Fe2–N distance in HS state cannot be determined due to the amorphization of the sample at 400 K (Figure 5). Comparing the Fe–N distances (Table 2) for Fe1 (HS at 300 K) and Fe2 (LS at 300 K), it can be estimated a difference of 0,17 Å in the Fe–N distances between its LS and HS state.

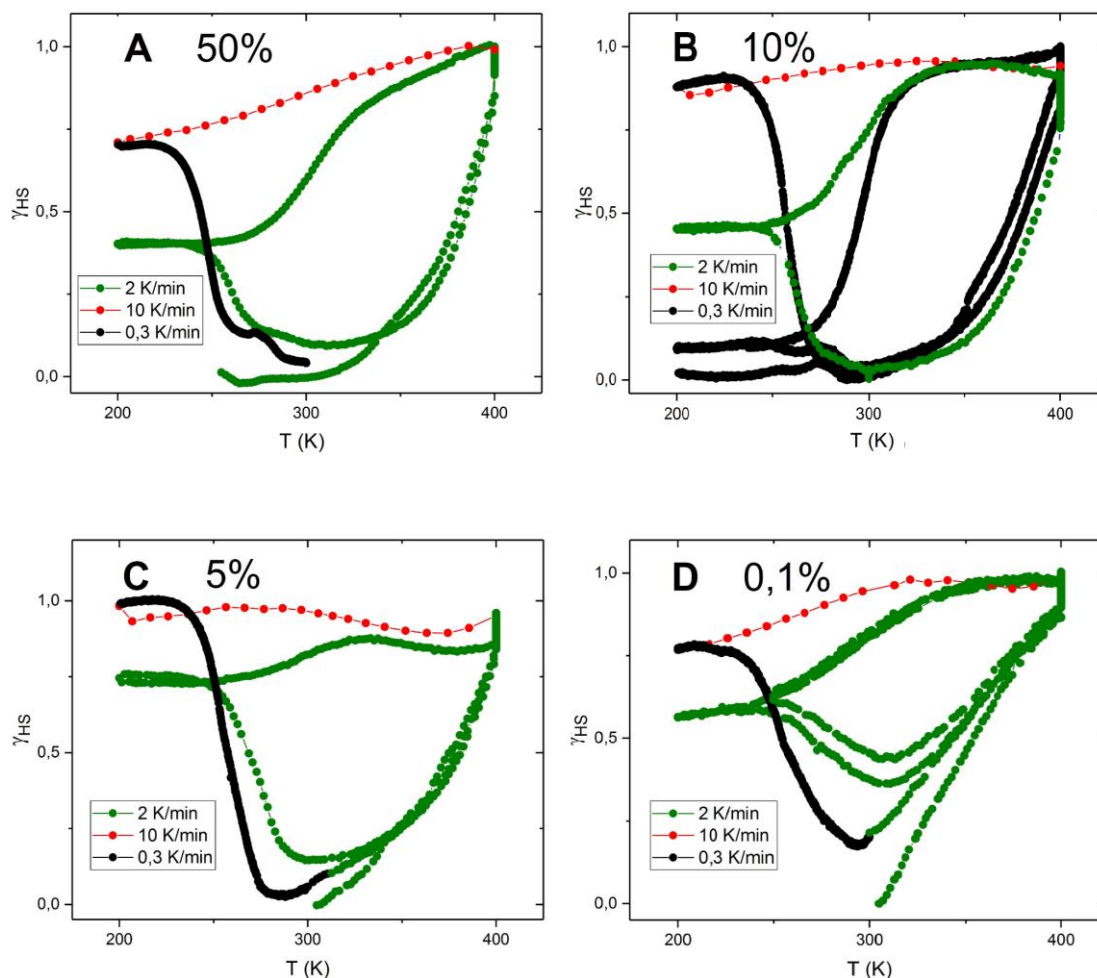


Figure 7: χ_T vs T plots for Dilutions **A** (left-up), **B** (right-up), **C** (left-down) and **D** (right-down) and **2** (left-down) in the 175–425 K range at different scan rates.

Thus, SO_3^- groups will also separate, what is electrostatically favorable. Meanwhile, a HS–LS transition implies a reduction in Fe–N distances, hence approaching the peripheral negative charges. This may give rise to the appearance of an energy barrier, corresponding to the electrostatic repulsion that needs to be overcome. This barrier will difficult Fe2 to go back to its ground state during the cooling branch. This molecular origin of the hysteresis, may also explain why reduction in the cooperativity makes easier to trap the metastable HS state when cooling down the sample, since no associated structural transition would favour the transition to LS (Figure S 7).

To further prove the existence of hysteresis at the single molecule level for a SCO complex, we tried to gather information directly from solution. SQUID magnetometer does not allow us to measure liquid samples due to the lack of sensibility. As alternative, we measured the UV-

vis spectra as a function of temperature. 110 mg of **1** were dissolved in 3 mL of a water/ethylene glycol solution (40 % vol% of ethylene glycol), to avoid freezing at 253 K.

Comparing the spectrum obtained at 253 K and 303 K, the signature peak of the LS state at 545 nm disappears (Figure 8, left). We monitored the dynamics of this peak in the 253 K–303 K range, in the cooling and heating branches (Figure 8, right). Both branches are not identical, and a thermal hysteresis opens between 250 and 290 K.

In solution, the appearance of a hysteresis cycle, can only be associated with a single molecule phenomena. Being a single molecule process, obviously, we still observe a clear effect of the molecular surroundings. When the molecule is in the solid state, the proposed activation energy needed for the single molecule to expand, is also participating for the volume

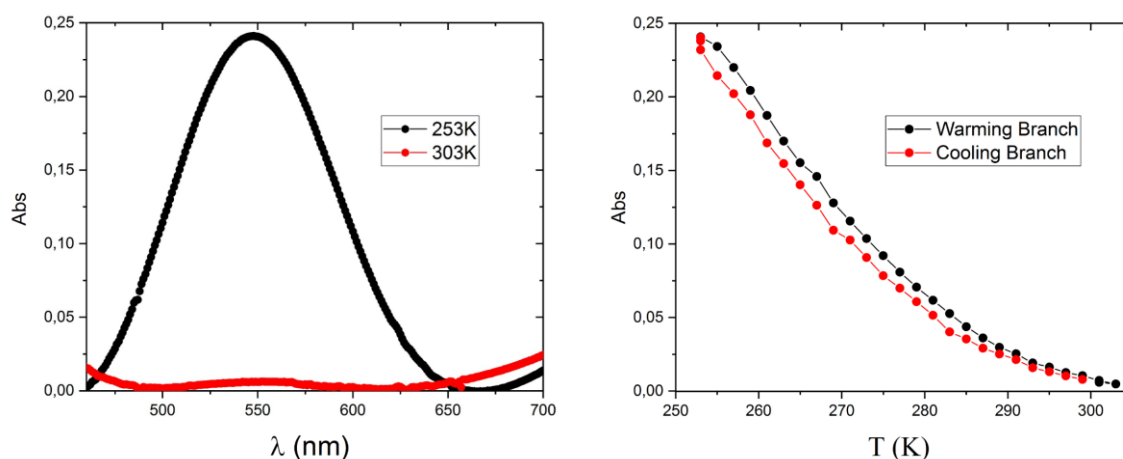


Figure 8: Abs vs λ at 277 K (LS) and 307 K (HS) (left) and Abs vs λ plot in the 250-305 nm range when it is warmed up from 277 K to 307 K and cooled down from 307 K to 277 K (right).

change needed in the solid. This component is much weaker in solution, where thermal energy near room temperature allows for an easy movement of the solvent molecules around the polyanion. Indeed, polar solvents, as in this case, may lower the activation energy, screening and tuning down the electrostatic repulsion. For this reason, the thermal hysteresis in solution occurs at lower temperatures, and with a very narrow hysteretic cycle.

Conclusions

A new SCO compound ($\text{Cs}_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$) has been synthesized by metathesis from the $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ salt. The cation exchange modifies the crystalline structure and hence the magnetic properties. A closer packing and a different supramolecular network increases cooperativity, causes a more abrupt spin transition. Cation substitution does not affect T_{TIESST} temperature.

Furthermore, $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]_x[\text{Zn}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]_{(1-x)}$ solid solutions have been analysed, delivering mixed materials that maintain thermal hysteresis in their SCO behaviour down to ultradiluted samples ($\approx 0.1\%$). Additionally, these diluted samples increase the TIESST capabilities, making very easy to trap the excited state by slow cooling (≈ 2 K/min).

These observations suggest a molecular origin for the SCO behavior of these materials, what is in contrast with theoretical work. In SCO materials, hysteresis is only allowed when the

spin transition is associated with a crystallographic phase transition. But a crystallographic phase transition is not occurring in these solid solutions.

An additional experimental evidence was found in solution UV-Vis spectra. Optical data indicates appearance of hysteresis between the cooling and heating branches, finally confirming the existence of a molecular origin for this memory effect.

Therefore, it can be concluded that cooperativity is not the only cause of hysteresis. It also has been postulated that the reason why hysteresis occurs at low concentrations are the electrostatic forces among SO_3^- groups present in the triazol derivatives ligands.

This is the first compound in which hysteresis of purely molecular origin has been found, opening the possibility to use single molecules at room temperature for functional and real devices.

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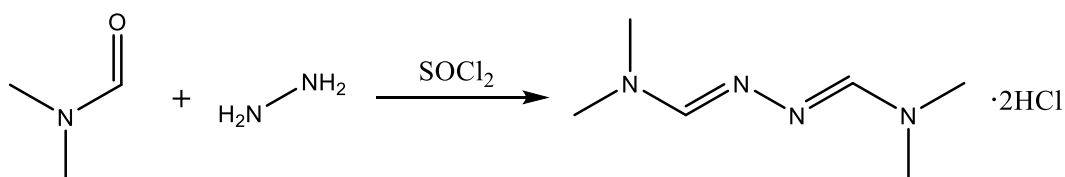
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SUPPLEMENTARY INFORMATION

Synthesis of $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ (1)

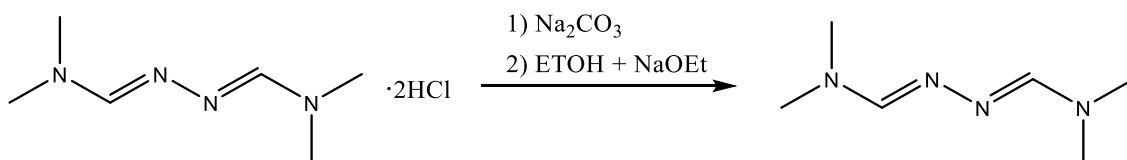
Reagents were obtained from commercial sources and not purification was required. Yields were determined by taking into account the stoichiometric reaction. $(\text{Me}_2\text{NH}_2)_2\text{L}$ was synthesized from N,N-dimethylformamide azine and 2-aminoethane-1,1-disulfonic acid.

N,N- dimethylformamide azine dihydrochloride: 30 mL of thionyl chloride (SOCl_2) were added dropwise in a 500 mL round bottom flask which contained 150 mL of dimethylformamide (DMF), the round bottom flask was resting in an ice bath. The solution was under stirring during 24 hours. Then, under an ice bath, a dissolution of 5 mL of hydrazine monohydrated with 20 mL of DMF was dropwise added and a white solid started to appear. The mixture was stirred at room temperature for 2 days. The dissolution was filtered and washed with DMF, ethanol and diethyl ether, obtaining a white solid ([Scheme 1](#)).



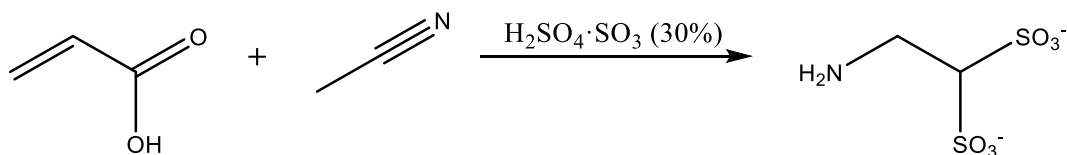
Scheme 1: reaction to obtain **N,N- dimethylformamide azine dihydrochloride**.

N,N- dimethylformamide azine was obtained after N,N-dimethylformamide azine dihydrochlorine neutralization ([Scheme 2](#)). N,N- dimethylformamide azine dihydrochloride (1 eq.; 40 g) was diluted in water (150 ml). A dilution of Sodium carbonate (1 eq.; 19.7 g) in 150 mL of water was added. This mixture was continuously extracted with diethyl ether for 2 days. Pink-Orange solid appeared after evaporating the Diethyl ether under pressure and temperature. ([Figure S 1](#) shows the NMR spectrum obtained)



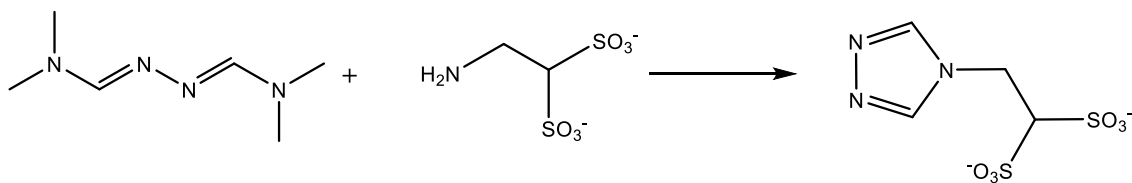
Scheme 2: reaction to obtain **N,N- dimethylformamide azine**.

2-aminoethane-1,1-disulfonic acid: Acrylic acid (6,8 ml) and acetonitrile (16 ml) were mixed in a 500 mL round bottom flask. The mixture was cooled with an ice-salt bath. 33 mL of fuming sulphuric acid (30% SO_3) were added dropwise from a pressure-equalizing dropping funnel over 60 minutes. Afterward, the mixture was heated to reflux at 100°C for 40 minutes and left it overnight at room temperature. 85 mL of water were dropwise added and the mixture was heated at 100°C for 24 hours, taking place the hydrolysis of N-acetyl group. The solution was introduced in the fridge for 1 day at 4°C and a white precipitate appeared and it was filtered and washed with EtOH and diethyl ether. [Figure S 2](#) shows the NMR spectrum of the product obtained.



Scheme 3: reaction to obtain **2-aminoethane-1,1-disulfonic acid**.

Dimethyl-ammonium 4-(1,2,4-triazol-4-yl)ethanedisulfonate ((Me₂NH₂)₂L): 3 g of N,N-dimethylformamide azine and 1.44 g of 2-aminoethane-1,1-disulfonic acid were dissolved in water (15 ml). The pH of the mixture was adjusted at around 6.5 by adding HCl. The solution was heated at 92°C with reflux during 19 hours. The solvent was removed by rotary evaporator and 15 mL of EtOH were added in order to induce the precipitation. [Figure S 3](#) shows the NMR spectrum.



Scheme 4: reaction to obtain Dimethyl-ammonium 4-(1,2,4-triazol-4-yl)ethanedisulfonate.

((Me₂NH₂)₆[Fe₃(μ-L)₆(H₂O)₆] (1): ((Me₂NH₂)₂L (2.5 eq ; 0,305 g) and of Fe(ClO₄)₂ (1 eq.; 0,089 g) were mixed in 5 mL of water with ascorbic acid to avoid the Fe(II) oxidation. After 15 minutes stirring the solution, 15 mL of EtOH were added and, immediately, a pink precipitate appeared. The pink powder was isolated by centrifugation and it was washed with EtOH and diethyl ether.

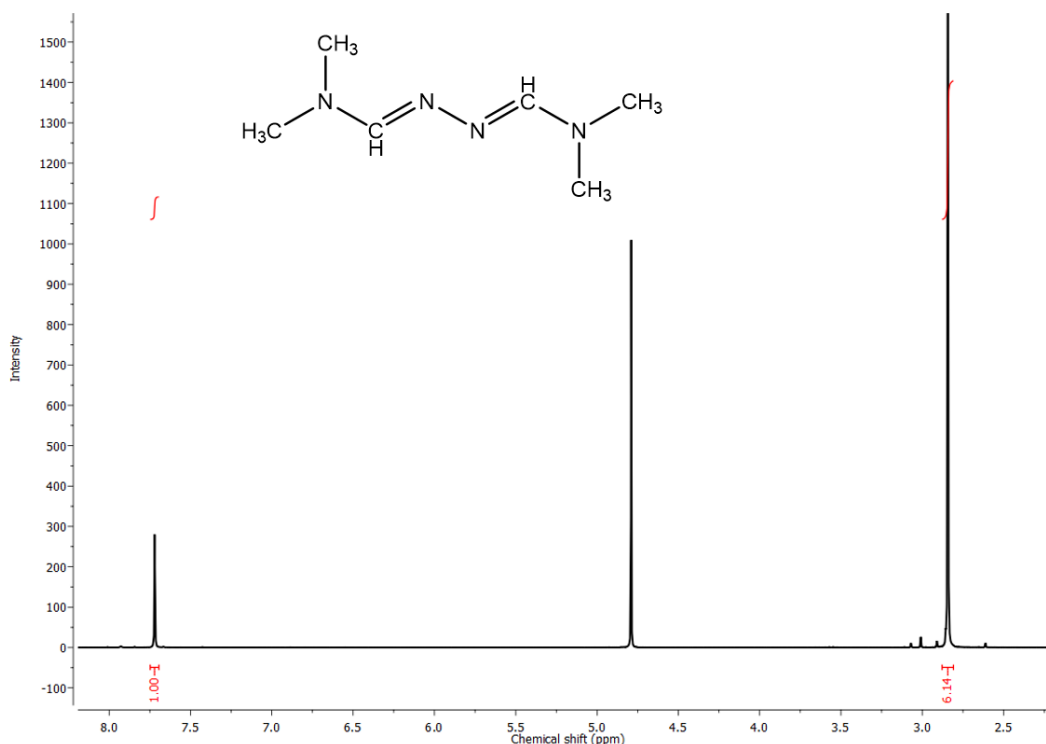
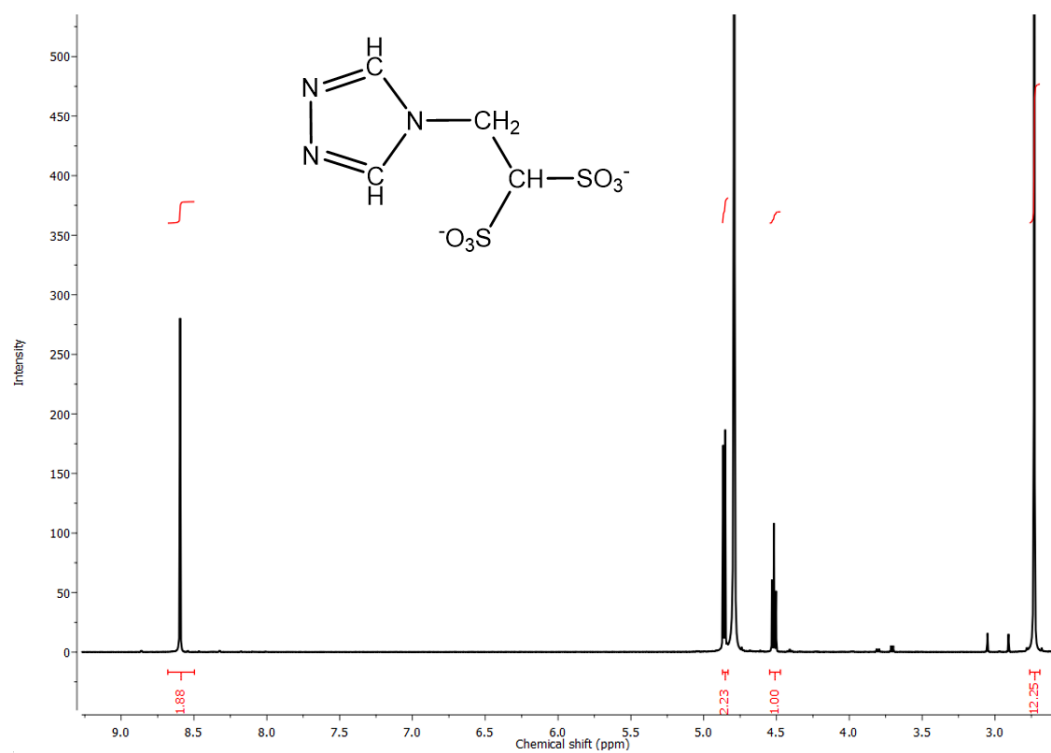
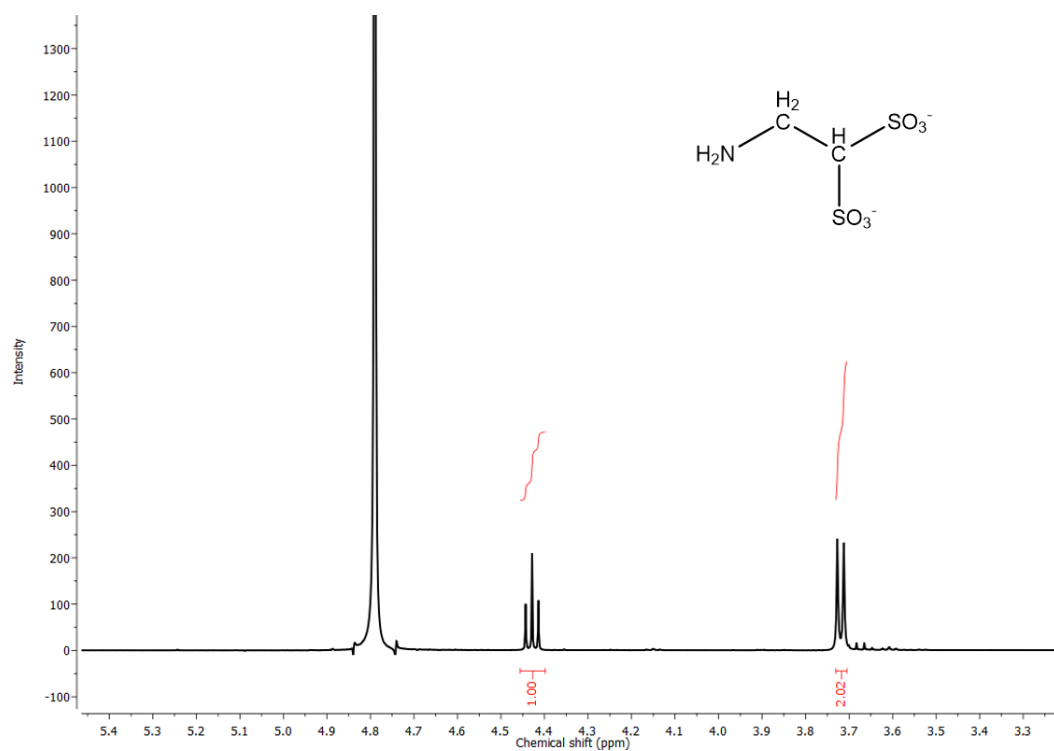


Figure S 1: N,N- dimethylformamide azine acid 1H NMR (500mHz, D2O) spectra: δ(ppm) = 2,82 (s, 6H), 7,73 (s, 1H).



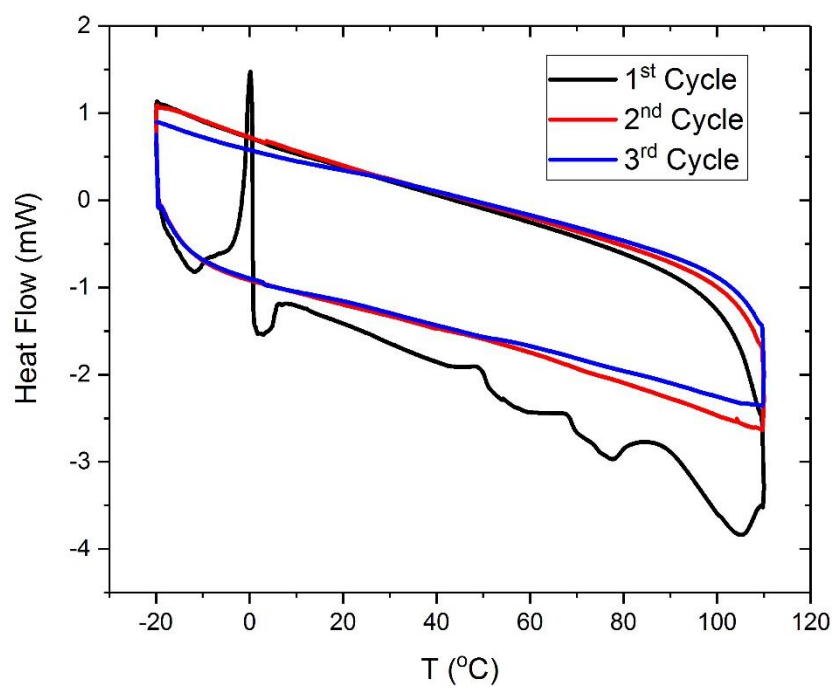


Figure S 4: three first DSC cycles scans for **2** in the -20-110°C range.

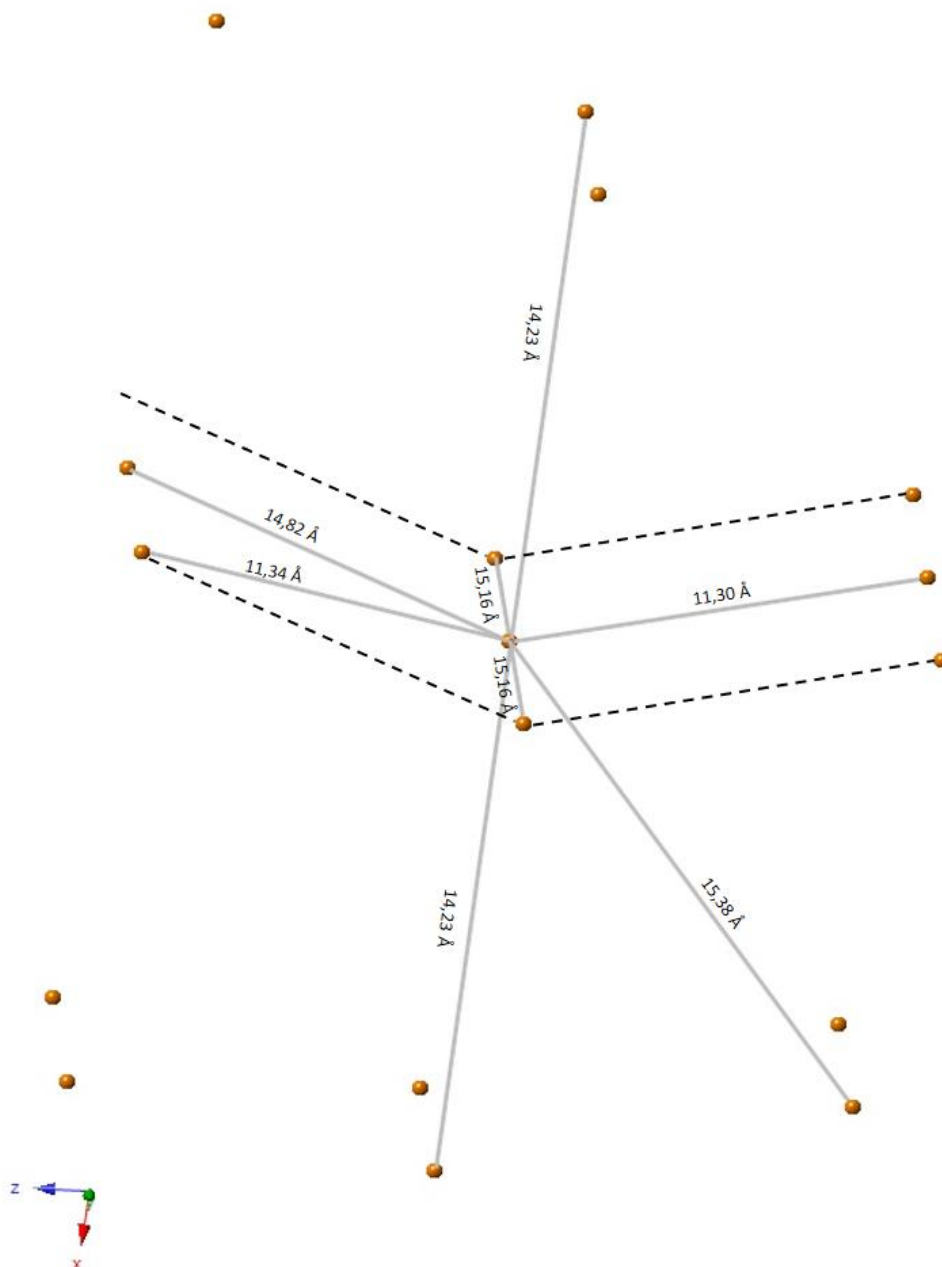


Figure S 5: All the SCO centers around a SCO center at lower distances than 19 Å for **1**. Only distances lower than 15.39 Å are remarked. In the image, it can be also observed the zig-zag packing and the AA stacking of the SCO centers.

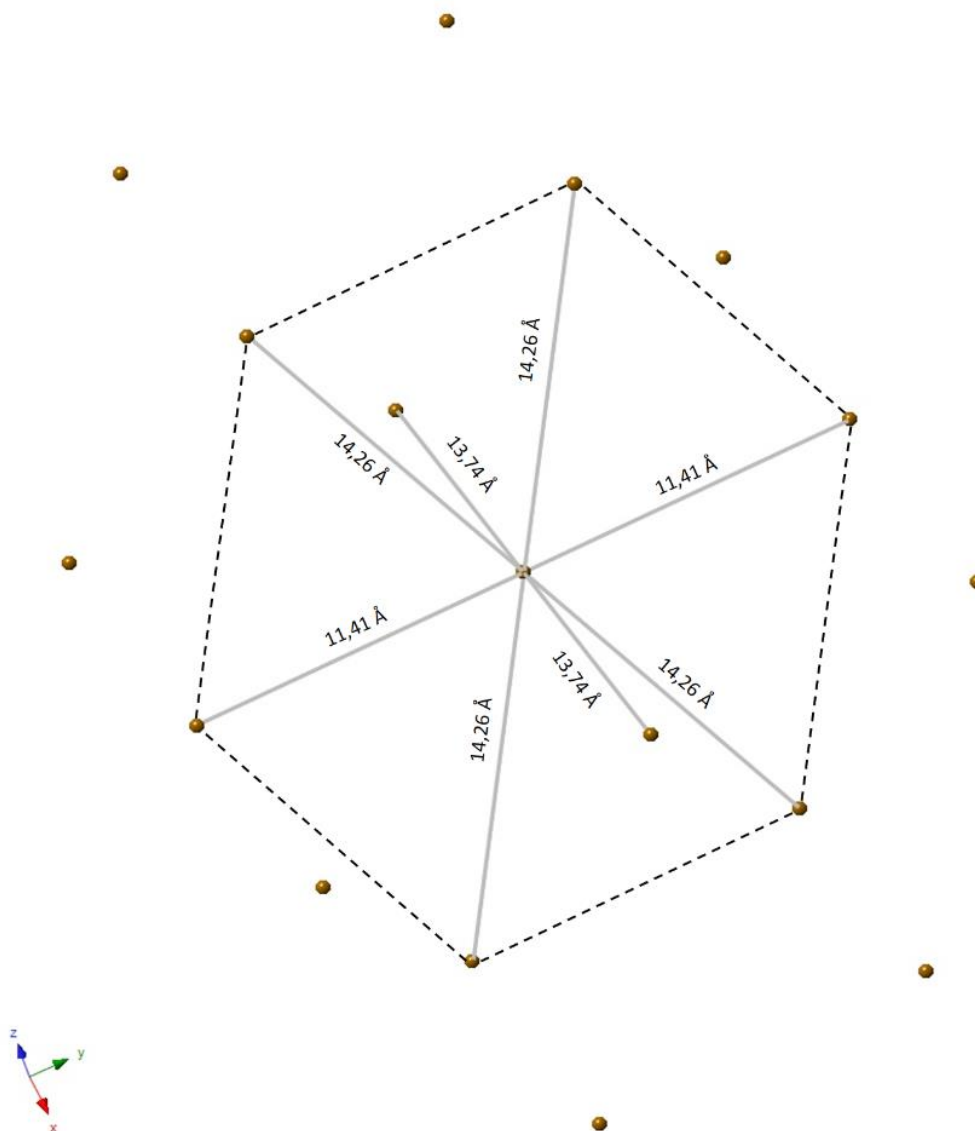


Figure S 6: All the SCO centers around a SCO center with lower distances than 19 Å for **2**. Only distances lower than 14,27 Å are remarked In the image, it can be also observed the HCP packing and the ABAB stacking of the SCO centers.

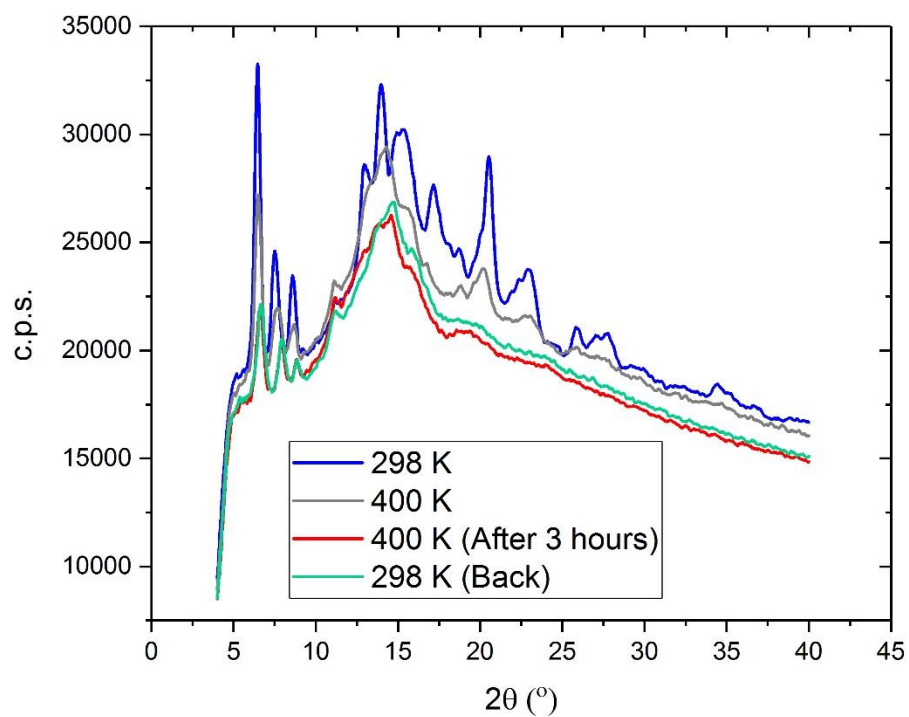


Figure S 7: PXRD of **1** at 298 K, 400 K, after 3 hours at 400 K and again at 298 K.