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Temperature dependence of desolvation effects in hydrogen-bonded spin crossover complexes[†]

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The synthesis, crystal structure and (photo)magnetic properties of the anhydrous spin crossover salt of formula [Fe(bpp)_2](C₆H₈O₄) (**1**) (bpp = 2,6-bis(pyrazol-3-yl)pyridine; C₆H₈O₄ = adipate dianion), obtained by desolvation at 400 K of the original tetrahydrate in a single-crystal-to-single-crystal (SC–SC) transformation, are reported. This work offers a comparison between this compound and the previously reported hydrated material ([Fe(bpp)_2](C₆H₈O₄)·4H₂O, **1**·4H₂O), highlighting the significance of the thermal conditions used in the dehydration-rehydration processes. In both compounds, a hydrogenbonded network between iron(II) complexes and adipate anions is observed. The original tetrahydrate (**1**·4H₂O) is low-spin and desolvation at 450 K triggers a low-spin (LS) to high-spin (HS) transition to an amorphous phase that remains stable over the whole temperature range of study. Surprisingly, the dehydrated compound at 400 K (**1**) keeps the crystallinity, undergoes a partial spin crossover ($T_{1/2} = 180$ K) and a quantitative LS to HS photomagnetic conversion at low temperatures, with a *T*(LIESST) value of 61 K.

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Introduction

Among the wide variety of responsive switchable materials, spin crossover (SCO) compounds represent one remarkable class and they have been extensively studied in recent years.¹ The vast majority of SCO centres are pseudo-octahedral iron(π) complexes that exhibit labile electronic configurations switchable between the ¹A₁ low-spin (LS; S = 0) and ⁵T₂ high-spin (HS; S = 2) states as a response to external physical stimuli (light irradiation, temperature, pressure, and magnetic or electric fields).^{2–4} In addition to these external disturbances, solvent molecules also influence strongly SCO properties.⁵ The variation in the spin is accompanied by changes in many physical properties such as magnetic susceptibility, dielectric constant, colour, vibrational properties and, furthermore, in metal–ligand bond lengths and structure. These features make

SCO materials promising candidates for a wide variety of applications such as molecular switches, memory devices, contrast agents in magnetic resonance imaging, thermometry, sensors and spintronics.⁶ Furthermore, it has been pointed out that some SCO compounds can be prepared in form of hybrid thin films for the preparation of molecular devices.⁷

Cooperative SCO compounds with abrupt spin transitions and hysteretic behaviour (memory effect) have attracted notable interest and, even more, when the spin transition is combined synergistically with a second physical property (for example luminescence, electronic transport or ferroelectricity).⁸ High levels of cooperativity can be achieved by the use of bridging ligands in the formation of extended polymeric architectures *via* coordination bonds^{9–12} or by supramolecular assembly of mononuclear centres. In general, these supramolecular lattices are built up by hydrogen bonding.¹³

Significant examples include the family of bis-chelated iron (π) complexes with formula $[Fe(bpp)_2]X_2$ (bpp being the tridentate ligand 2,6-bis(pyrazol-3-yl)pyridine, Chart 1). The bpp ligand possesses imine N atoms that coordinate to the Fe(π)



Chart 1 Molecular structures of bpp and adipate dianion.

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[†]Electronic supplementary information (ESI) available: Tables S1 and S2: Crystallographic data; Fig. S1 and S7: PXRD experiments of **1** under different conditions; Fig. S2–S5: Details of crystal packing; Fig. S6: Thermal variation of crystal cell parameters; Fig. S8: magnetic properties. CCDC 1507864 and 1819792 for **1** at 298 K and 120 K, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt03986a

cation whereas the non-coordinating NH groups are free for hydrogen bonding with the anions or solvate molecules present in the lattice. These interactions are likely to be the reason for the different properties observed in distinct solvatomorphs.^{14,15}

Upon solvent removal, these compounds usually show extremely abrupt transitions close to room temperature and, in addition, they exhibit Light-Induced Excited Spin State Trapping (LIESST) effects at relatively high temperatures.^{16–18}

We started a systematic study of compounds of this type combined with polycarboxylate anions¹⁹ and we focused on the key topic of cooperativity that is directly linked to the rigidity of the building blocks.²⁰ Thus, in a previous comparative work concerning the adipate $(C_6H_8O_4)$ (Chart 1) and terephthalate $(C_8H_4O_4)$ $[Fe(bpp)_2]^{2+}$ salts, we demonstrated the advantage of using rigid hydrogen-bond acceptors. Now we turn our attention to the relevance of the thermal treatment used in the desolvation process. In the present work we have been able to study the structural and magnetic changes that occur after reversible dehydration-rehydration processes in the system [Fe(bpp)₂](C₆H₈O₄)·4H₂O (1·4H₂O) without loss of crystallinity. Normally, the drastic rearrangement of the H-bonded network that occurs upon removal of water results in crystal damage. Indeed, anhydrous $[Fe(bpp)_2]^{2+}$ salts are relatively scarce^{5c,8b,21,22} and only a few of them have been prepared by dehydration of the corresponding hydrated forms.^{8b,22} The present work shows that, if dehydration is performed under vacuum at 400 K, it is possible to obtain a crystalline anhydrous phase (1) that exhibits spin crossover and LIESST effect.

Experimental section

Synthesis

Ligand bpp was prepared by the previously published procedure.²³ All other reagents and solvents were used as received without further purification.

$Ba(C_6H_8O_4) \cdot 0.1C_6H_{10}O_4$

A suspension of adipic acid (1.46 g, 10 mmol) in 5 mL H₂O was combined with 5 mL of a 4 M aqueous solution of KOH. The solution formed was treated with a solution of $BaCl_2 \cdot 2H_2O$ (2.44 g, 10 mmol) in 10 mL H₂O. The mixture was concentrated in a rotatory evaporator until a total volume of 5 mL. Then, a white microcrystalline solid was obtained by filtration. After evaporation of the filtrate, an additional amount of the desired compound was obtained. Total yield: 2.30 g (78%). Found: C, 26.78; H, 2.95. C_{6.6}H₉BaO_{4.4} requires C, 26.78; H, 3.06%; ν_{max}/cm^{-1} 3441, 2943, 2925, 1523, 1460, 1443, 1423, 1411, 1326, 1293, 1208, 1141, 1040, 930, 908, 734, 716, 604, 499.

$[Fe(bpp)_2](C_6H_8O_4)\cdot 4H_2O(1\cdot 4H_2O)$

The synthesis of $1.4H_2O$ was carried out in deoxygenated solvents under an inert atmosphere of N₂. A solution of FeSO₄·7H₂O (0.070 g, 0.25 mmol) in 10 mL MeOH was com-

bined with the ligand bpp (0.106 g, 0.5 mmol). A deep red solution was obtained after complete dissolution of the ligand. After stirring for 1 h, a solution of $Ba(C_6H_8O_4)\cdot 0.1C_6H_{10}O_4$ (71 mg, 0.25 mmol) in 10 mL H₂O was added. Immediately, an orange precipitate (BaSO₄ containing traces of iron complex) was formed and filtered. By slow evaporation of the filtrate, red prisms suitable for X-ray analysis appeared after a few days. It has to be noted that compound $1\cdot 4H_2O$ crystallizes together with some white needles of free ligand. The red crystals could be successfully isolated by hand, yielding 81.5 mg (47%, based on anion). Found: C, 48.45; H, 4.56; N, 19.92. $C_{28}H_{34}FeN_{10}O_8$ requires C, 48.43; H, 4.93; N 20.17%; ν_{max}/cm^{-1} 3422, 3145, 2930, 1617, 1560, 1536, 1500, 1440, 1408, 1353, 1337, 1279, 1213, 1145, 1112, 1069, 891, 809, 764, 617, 492.

$[Fe(bpp)_2](C_6H_8O_4)(1)$

Dehydration of 1·4H₂O was performed by placing a glass tube with the sample in an oil bath and heating at 450 K under vacuum for 2 h. Then, the crystals were suspended in a drop of water and, finally, dehydrated again at 400 K using the same procedure. A sample with poorer crystallinity can be obtained directly from the tetrahydrate after thermal treatment at 400 K. Found: C, 53.28; H, 4.23; N, 21.98. $C_{28}H_{26}FeN_{10}O_4$ requires C, 53.11; H, 4.33; N 22.12%; ν_{max}/cm^{-1} 3122, 3103, 2941, 1612, 1572, 1542, 1461, 1436, 1411, 1353, 1284, 1147, 812, 777, 767.

Characterization techniques

Magnetic susceptibility measurements were performed on polycrystalline samples using a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. Variable temperature measurements were carried out in the temperature range 2-400 K in a magnetic field of 0.1 T. A dehydrated sample of 1 for magnetic measurements was obtained by heating the compound at 400 K in a glass tube under vacuum. Then, the tube was sealed and transferred to the SQUID magnetometer. The temperature sweeping rate was as follows: 2.5 K min⁻¹ (300–400 K), 2.5 K min⁻¹ (400–9 K), 0.4 K min⁻¹ (9-2 K). For photomagnetic measurements, the sample was heated in an oil bath at 400 K for 2 h under vacuum. Then, a thin layer of the anhydrous compound (2.02 mg) was prepared using adhesive tape as the sample holder in order to immobilize the crystals and promote full light penetration, although magnetic measurements indicate some reorientation of the crystallites. After cooling slowly to 10 K under a magnetic field of 0.1 T, irradiation of the sample was performed using a Diode Pumped Solid State Laser DPSS-532-20 from Chylas and coupled via an optical fiber to the cavity of the SQUID magnetometer. Green light (λ = 532 nm, optical power = 3.4 mW cm⁻²) was used since similar related compounds did not show any excitation under red light irradiation.²⁴ The optical fiber was kept 8 cm above the sample and the optical power was measured at the same distance. It was verified that irradiation resulted in no significant change in magnetic response due to heating of the sample. Irradiation was maintained during 280 min. Then, the laser was switched off and the temperature increased at a rate of 0.3 K min⁻¹ to determine the T(LIESST)

value from the minimum of the $\delta(\chi T)/\delta T$ versus *T* curve for the relaxation process.

Mössbauer spectra were collected in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ⁵⁷Co source in a Rh matrix. The velocity scale was calibrated using α -Fe foil. The absorbers were obtained by packing the powdered samples into perspex holders. Isomer shifts are given relative to metallic α -Fe at room temperature. The low temperature spectra were collected using a bath cryostat with the sample immersed in liquid He or He gas for measurements at 4.1 K and above, respectively. The spectra were fitted to Lorentzian lines using a non-linear least-squares method.²⁵

IR transmission measurements of KBr pellets were recorded at room temperature with a Nicolet Avatar 320 FT-IR spectrophotometer in the range $4000-400 \text{ cm}^{-1}$.

CHN elemental analyses were carried out in a CE instruments EA 1110 CHNS analyzer.

Powder X-ray diffraction (PXRD) measurements were collected using Cu K α radiation ($\lambda = 1.54056$ Å) at room temperature in a 2θ range from 2 to 40°. Polycrystalline samples of 1·4H₂O, **1** and rehydrated **1** were lightly ground in an agate mortar and filled into a 0.5 mm borosilicate capillary prior to being mounted and aligned on an Empyrean PANalytical powder diffractometer. The simulated diffractograms were obtained from single crystal X-ray data using the CrystalDiffract software.

Variable-temperature powder X-ray diffraction measurements of **1** were recorded in the temperature range between 300 and 142 K every 20 K, approximately.

Single-crystal X-ray crystallography

Some crystals of $1.4H_2O$ were dehydrated using the procedure described in the Synthesis section. Then, one of them was quickly coated with paratone N oil, suspended on a small fiber loop and placed in a stream of cold nitrogen (120 K) on an Oxford Diffraction Supernova diffractometer equipped with a graphite-monochromated Enhance Mo X-Ray Source ($\lambda = 0.71073$ Å). Another identical single crystal was treated in the same way and placed in a stream of hot nitrogen at 298 K.

The data collection routines, unit cell refinements and data processing were carried out using the CrysAlisPro v38.46 software package (Rigaku, The Woodlands, TX, USA). The structures were solved using SHELXS-97 *via* the WinGX graphical interface,²⁶ and refined using SHELXL-2017.²⁷ H-atoms bonded to C were included at calculated positions and refined with a riding model. H-atoms bonded to N were found in Fourier difference maps and refined using DFIX restraints.

The adipate anion present in the dehydrated sample is disordered between two positions with occupancies of 0.56/0.44 at 120 K and 0.55/0.45 at 298 K. The anisotropic refinement of this disordered anion required the use of DELU, SIMU and DFIX restraints. All non-H atoms were refined anisotropically in both crystal structures. CCDC 1507864 and 1819792† contain the supplementary crystallographic data for 1 at 120 and 298 K, respectively. The volume occupied by adipate dianions in the crystal structure of **1** at 298 K and 120 K was calculated by using the SQUEEZE²⁸ option of PLATON.²⁹ At first, the code was used to check that the crystal structure at both temperatures did not contain any residual solvent accessible void. Next, the coordinates of the adipate anion were removed from the .ins file and an additional refinement step was conducted, generating new files that were introduced into the PLATON software. Then, SQUEEZE was run again to calculate the potential solvent volume.

Unit cell parameters of **1** were measured in the 298–120 K temperature range (with intervals of 20 K) using the same single-crystal specimen used for the data collection at 298 K.

Results and discussion

Influence of thermal treatment on the synthesis of 1

Previous thermogravimetric studies have shown that 1.4H₂O dehydrates in two steps to yield anhydrous **1** at T > 430 K.²⁰ Dehydration of 1·4H₂O performed under vacuum at 453 K for 2 h yielded an essentially amorphous HS material lacking of SCO behaviour. This rehydrates readily to 1.4H2O upon exposure to ambient humidity, recovering its crystallinity. The present work shows that it is possible to obtain a crystalline anhydrous phase of 1 by simply decreasing the temperature of thermal treatment down to 400 K (Scheme 1). Dehydration can be performed directly from the pristine tetrahydrate, yielding a polycrystalline material that is stable in ambient conditions. However, samples with better crystallinity can be obtained from the rehydrated sample as described in the Experimental section. Crystals suitable for X-ray crystal structure determination were thus obtained. The simulated diffractogram obtained from single-crystal data matches that measured on the polycrystalline sample (Fig. S1[†]), confirming the purity of the material and the complete reversibility of the dehydrationrehydration process. Curiously, whereas the amorphous HS sample rehydrates almost instantaneously upon exposure to the open air, this crystalline material is stable even after 6 h at ambient humidity.

It seems then that the combination of several hydration-dehydration cycles can be a valuable tool for the synthesis of other anhydrous $[Fe(bpp)_2]^{2+}$ complexes, a crucial step in the understanding of the role played by water molecules of hydration in SCO properties.



Scheme 1 Spin changes upon reversible dehydration of $1.4H_2O$.

Comparative study of the X-ray crystal structures of $1{\cdot}4H_2O$ and 1

The crystal structure of the tetrahydrate salt $1.4H_2O$ has been reported²⁰ and only some aspects relevant to the comparative analysis will be discussed here. $1.4H_2O$ crystallizes in the monoclinic space group $P2_1/c$. The structure contains only one crystallographically independent LS Fe²⁺ site, with Fe–N bond lengths lying in the range 1.913(11)-1.979(4) Å, and one adipate dianion. The Fe²⁺ cation sits in a distorted octahedral geometry, with the tridentate bpp ligands occupying meridional positions. Strong π - π stacking interactions between adjacent pyrazolyl fragments are found, connecting the [Fe (bpp)₂]²⁺ complexes to form double chains running parallel to the *a* axis (Fig. 1).

Each iron(II) complex is hydrogen-bonded through its noncoordinating NH groups to three adipate anions. Two of them interact with the same bpp ligand, defining intrachain centrosymmetric cyclic dimers, the other bpp ligand being hydrogenbonded to another adipate anion and one water molecule (O1 W). The adipate anions are present in an *anti*, *gauche*, *anti* conformation and are hydrogen-bonded to three $[Fe(bpp)_2]^{2+}$ cations. One of the carboxylate units acts as a bidentate *syn*, *anti* hydrogen-bond acceptor, bridging the double chains in the three directions of the space. The second carboxylate moiety contributes only to the formation of the dimer, and interacts additionally with a water molecule (not shown).

At 298 K, the crystal structure of the anhydrous salt **1** belongs to the monoclinic space group C2/c (Table S1†). Now the structure contains two crystallographically independent Fe²⁺ cations (Fig. 2), denoted Fe1 and Fe2, both sitting on a two-fold axis, and one adipate dianion disordered in two positions, A and B, with occupancy factors of 0.55 and 0.45,



Fig. 1 View of the crystal structure of $1.4H_2O$ along the [101] direction, showing the double chains of $\pi - \pi$ stacked [Fe(bpp)₂]²⁺ complexes bridged by adipate dianions.



Fig. 2 ORTEP view of the crystal structure of **1** at 298 K, showing the two independent $[Fe(bpp)_2]^{2+}$ complexes and the disordered adipate dianion. Thermal ellipsoids are drawn at the 50% probability level. Yellow and green colours highlight adipates A and B, respectively. Dashed lines refer to hydrogen bonds.

respectively. The conformations of both A and B adipate anions differ from that present in the tetrahydrate phase, being gauche, anti, gauche for adipate A and gauche, anti, anti for adipate B (Fig. S2†). The Fe1 site has a distorted octahedral geometry, with Fe1–N bond lengths lying in the 2.111 (2)–2.1849(15) Å range (Table S2†), typical of a HS state. Instead, the Fe2 octahedral environment is more regular and Fe2–N bond distances are considerably shorter (between 1.9154(13) and 1.9671(14) Å), as expected for a LS state. The degree of distortion can be quantified by two independent parameters: (i) the *trans*-N(py)–Fe–N(py) angle φ , defined by the pyridine moieties; (ii) the Σ parameter, given by the sum of deviations from 90° of the 12 *cis* angles of the coordination sphere.³⁰

$$\varSigma = \sum_{i=1}^{12} |90 - \theta_i|$$

The values of this parameter for the Fe1 (Σ = 141.29°) and Fe2 (Σ = 90.49°) sites compare well with those reported for, respectively, HS and LS species.³¹ They indicate a lesser degree of distortion for Fe2, as expected. The φ values (φ = 180.0° and 178.78(9)° for Fe1 and Fe2, respectively) do not allow for comparison because Fe1 sits on a special position with the C_2 axis containing the Fe–N(py) bond (the N(py)–Fe–N(py) fragment is strictly linear).

As observed in $1.4H_2O$, the Fe²⁺ cations are coordinated by two bpp ligands in meridional positions. Now, both ligands are hydrogen-bonded through their NH functions to two adipate anions. There are then four adipate anions in the second coordination sphere of the complexes, arranged in a pseudotetrahedral geometry. In turn, each adipate dianion is hydrogen-bonded to four $[Fe(bpp)_2]^{2+}$ cations, *via* the two carboxylate moieties acting as H-bond acceptors towards Fe1 and Fe2 in a bidentate *syn*, *anti* bridging mode.

The crystal structure can be viewed as built upon twodimensional (4,4) hydrogen-bonded rhombic lattices, with HS Fe1 complexes sitting on the corners and disordered adipate anions occupying the sides of the rhombuses (Fig. 3a). The Fe1–Fe1 distance is 13.6572(5) Å. The layers run parallel to the *ab* plane and alternate along the *c* axis in a ABAB fashion (Fig. 3b). They stack by π - π interactions between adjacent Fe1 complexes, defining zigzag chains that run along the *c* axis, with a Fe1–Fe1 distance of 8.3633(3) Å. Hydrogen-bonded adipate anions occupy the space between the stacks, preventing the extension of π - π interactions in two dimensions observed in terpyridine embrace lattices. The voids within the



Fig. 3 (a) View of the crystal structure of **1** at 298 K along the *c* axis, showing a single rhombic layer of high-spin Fe1 sites connected by adipate anions. Yellow and green colours highlight adipates A and B, respectively. Dashed lines refer to hydrogen bonds. (b) Same view showing the packing of the layers along the *c* axis in an AB arrangement.



Fig. 4 View of the crystal structure of **1** at 298 K, showing the presence of stacks of low-spin Fe2 sites connected by double adipate bridges and $\pi-\pi$ interactions. Yellow and green colours highlight adipates A and B, respectively. Dashed lines refer to hydrogen bonds.

layers are filled (Fig. S3[†]) by zigzag chains of LS Fe2 complexes connected through double adipate bridges and interacting at the same time *via* π - π stacking (Fig. 4). These chains run thus parallel to the Fe1 stacks but have a much shorter intermetallic distance Fe2–Fe2 = 8.1502(2) Å (Fig. S4[†]). Fe1 layers and Fe2 chains are linked to each other by the *syn*, *anti* carboxylate bridges mentioned above. The presence of static disorder in the positions of the adipate anions, yielding unrealistic short values (<2.5 Å in some cases) for H-bond O····N distances, precludes any detailed analysis of the H-bond interactions.

At 120 K, 1 has the same structure than that observed at room temperature (Table S1[†]), with slightly smaller values of cell parameters. The cell volume decrease from the value observed at room temperature ($\Delta V_{SCO} = 103.3 \text{ Å}^3$) is about 1.8%. The disorder of the adipate anions, with similar occupancies for the A and B positions, is still observed, confirming its static character and discarding a thermal motion effect. The coordination geometry of the Fe2 sites remains also very similar, with Fe2-N bond distances in the 1.9161(19)-1.9663 (18) Å range and octahedral distortion parameters ($\Sigma = 89.51^{\circ}$; $\varphi = 178.49(11)^{\circ}$) typical of LS species. Instead, the Fe1–N bond distances (now lying between 2.002(3) and 2.069(2) Å, Table S2[†]) and the Σ parameter (115.65°) decrease considerably with respect to the 298 K values (Fig. S5[†]), being intermediate between those described for HS and LS species,³¹ suggesting a partial SCO. Curiously, the Fe1-Fe1 distance between corners of the 2D rhombic lattice (13.6003(6) Å) decreases as the crystal is cooled (as a result of both thermal contraction and SCO of some Fe1 sites) but this decrease is half that measured for the intrastack Fe2-Fe2 distance (8.0483 (3) Å), despite the fact that the Fe2 spin state remains invariant. This means that, due to the constraints introduced by hydrogen bonding, the contraction of the structure is more pronounced outside the ab plane. Indeed, the intermetallic distance along the parallel Fe1 stacks (8.2513(3) Å) decreases by a similar amount.

The conformation of the adipate anions remains unaltered with respect to that observed at 298 K: *gauche, anti, gauche* and *gauche, anti, anti* for adipates A and B, respectively (Fig. S2†). However, significant changes in torsion angles (more than 20° in some cases) are detected, indicating that the flexible anions are able to accommodate most of the internal pressure result-

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ing from SCO. In fact, the total volume occupied by the adipate anions increases as the sample is cooled from 298 K (1651.8(2) Å³) to 120 K (1740.1(2) Å³). With respect to the unit cell, this means an increase of the relative adipate volume from 29.6% at 298 K to 31.7% at 120 K. This increase compensates partially the contraction of the Fe1 coordination sphere, resulting in the low value $\Delta V_{\rm SCO}$ observed.

Temperature dependence of the unit cell parameters of 1

Lattice cell parameters were measured on a single crystal of 1 at different temperatures between 298 K and 120 K. The thermal variation of the unit cell volume (Fig. 5) shows a monotonic and linear decrease upon cooling that can be fitted to the expression $V(Å^3) = 5401.5 + 0.66T(K)$, affording a volumetric thermal expansion coefficient $\alpha = 118 \times 10^{-6} \text{ K}^{-1}$. This is a rather small value that compares well with the expected contribution resulting solely from thermal contraction. The unit cell parameters a and c decrease also in a linear way on decreasing the temperature, whereas b remains practically constant (Fig. S6[†]). The absence of critical points excludes the possibility of a crystallographic phase transition in the 298-120 K range, in agreement with the strong similarities between the two single crystal structures of 1 discussed in the previous chapter. This has been confirmed by temperaturedependent PXRD. Fig. S7[†] shows clearly the same X-ray pattern at different temperatures between 300 K and 142 K. Only some peaks in the high 2θ region shift continuously to higher values upon cooling due to thermal contraction. The lack of a phase transition, together with the small value of the expansion coefficient, anticipates a rather smooth SCO for this anhydrous phase.

Magnetic properties

Fig. 6 shows the thermal variation of the χT product of 1 (χ = molar magnetic susceptibility; *T* = absolute temperature). Data were obtained from the rehydrated sample by *in situ* dehydra-



Fig. 5 Thermal dependence of the unit cell volume of 1.



Fig. 6 Temperature dependence of the χT product of **1** obtained after dehydration of **1**·4H₂O at 453 K under vacuum (green) or by *in situ* dehydration of rehydrated **1**·4H₂O for 2 h (red) followed by cooling to 2 K (blue).

tion, thus following the same procedure used for the preparation of single crystals for X-ray structure determination. At 300 K, the rehydrated sample is essentially in the expected LS state ($\gamma T = 0.07$ emu K mol⁻¹). Upon heating above 370 K, γT increases abruptly and reaches saturation after keeping the sample at 400 K for 2 h. The value of the magnetic signal at saturation (χT = 1.51 emu K mol⁻¹) matches that expected for 50% of the Fe²⁺ in the HS state, in agreement with the structural data described for the dehydrated material. This is in contrast with the sample obtained by dehydration of 1.4H₂O under vacuum at 453 K, which shows a nearly constant χT value of 2.9 emu K mol⁻¹, close to the one expected for a HS material.²⁰ Further, this value remains constant in the whole temperature range, whereas for the sample dehydrated in situ, it decreases smoothly on cooling to reach a small plateau at around 70 K, where $\chi T \approx 0.60$ emu K mol⁻¹. This corresponds to a fraction of HS centres $\gamma_{\rm HS}$ = 0.2, meaning that a significant residual fraction of HS Fe1 sites (40%) is present at low temperatures. This fraction undergoes zero-field splitting (ZFS) of the quintet ground spin state on further cooling, being responsible of the additional decrease of χT at lower temperatures, to reach a value of 0.25 emu K mol⁻¹ at 2 K. The 60% of Fe1 sites that undergo SCO follow a Boltzmann distribution (Fig. S8[†]) with thermodynamic parameters ($\Delta H = 8.4 \pm 0.2$ kJ mol⁻¹; ΔS = $30 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$) which are low in comparison to other complexes of this family, probably due to the small structural distortions accompanying SCO in this particular case.

Mössbauer spectroscopy

The Mössbauer spectrum of $1.4H_2O$ taken at 295 K (Fig. 7) consists of a single quadrupole doublet. The estimated isomer



Fig. 7 Mössbauer spectra of $1.4H_2O$ (a) and 1 (b) taken at different temperatures. The curves over the experimental points correspond to a single quadrupole doublet (a) or the sum of two quadrupole doublets (high-spin and low-spin Fe^{II}) (b) with parameters given in Table 1.

Table 1 Estimated parameters from the Mössbauer spectra of $1{\cdot}4H_2O$ and 1, taken at different temperatures^a

	Т (К)	IS (mm s ⁻¹)	QS (mm s ⁻¹)	Γ (mm s ⁻¹)	Spin state	I (%)
1 ·4H ₂ O	295	0.29	0.67	0.27	LS	100
1	295	0.30	0.67	0.29	LS	61
		1.01	2.43	0.73	HS	39
1	220	0.34	0.67	0.30	LS	64
		1.02	2.63	0.72	HS	32
1	55	0.39	0.67	0.34	LS	75
		1.09	2.96	0.51	HS	25
1	4	0.39	0.66	0.33	LS	75
		1.11	2.96	0.50	HS	25

^{*a*} IS: Isomer shift relative to metallic α-Fe at 300 K; QS: Quadrupole splitting; *Γ*: Full width at half height; *I*: Relative areas. Estimated errors are $\leq 0.02 \text{ mm s}^{-1}$ for IS, QS and *Γ*, and $\leq 2\%$ for *I*.

shift relative to metallic α -Fe at 300 K, IS (Table 1), is similar to those reported for Fe²⁺ complexes with bpp ligands and lie within the range of low-spin Fe²⁺ isomer shift values.^{16,17,20,32}

The spectrum of the dehydrated salt 1, obtained after heating 1.4H₂O at 400 K under vacuum for 2 h, clearly shows an additional doublet with IS and quadrupole splitting, OS, typical of HS (S = 2) Fe²⁺,^{17,20} in agreement with magnetic susceptibility data. The estimated relative area of the HS signal, $I_{\rm HS}$, is $\approx 39\%$ at 295 K and decreases for lower temperatures down to $\approx 25\%$ at 55 K and 4 K. As explained previously,²⁰ the recoil-free fractions of HS and LS Fe²⁺ are similar at 4 K, and the corresponding $I_{\rm HS}$ and $I_{\rm LS}$ may be considered a good approximation of the fraction of the total Fe atoms in these spin states. As the temperature increases, the recoil-free fraction of LS Fe^{2+} becomes higher than the HS one, and I_{HS} may be slightly lower than the fraction of Fe atoms in this spin state. The increase of $I_{\rm HS}$ with temperature is however fully consistent with the temperature dependence of χT . Further, Mössbauer spectroscopy clearly discards the population of an intermediate spin state (very rare for compounds of this type) or the presence of Fe³⁺ cations.

Photomagnetic properties

The LS-HS photoconversion of the dehydrated complex **1** was investigated in bulk conditions using a SQUID magnetometer connected to a CW optical source. A sample of $1.4H_2O$ was dehydrated *in situ* as described above. Then, the sample was cooled down to 10 K (Fig. 8) and the smooth and partial SCO was reproduced. A residual HS fraction of *ca.* 33% of the Fe1 sites was observed at this temperature. After cooling, the material was irradiated (λ = 532 nm) and an increase of the



Fig. 8 Temperature dependence of χT for **1** upon cooling before irradiation (blue), under irradiation at 10 K (orange) and subsequent heating in the dark at 0.3 K min⁻¹ (red).

magnetic signal in several steps was observed, reaching saturation after 250 min (Fig. S9[†]). Then, light irradiation was stopped and the thermal variation of χT was measured while heating at a rate of 0.3 K min⁻¹, following the standard conditions for a T(LIESST) experiment (Fig. 8). After a small increase of the signal, normally attributed to a zero-field splitting of the S = 2 ground state, χT equals 1.55 emu K mol⁻¹. This indicates that the Fe2 sites are LS even under light irradiation and only the spin states of the Fe1 sites are reversed. On further heating, χT decreases continuously down to a value of 0.5 emu K mol⁻¹ at T = 76 K, corresponding to the HS Fe1 residual fraction of 33% observed before irradiation. The minimum of the derivative $d(\chi T)/dT$ yields a T(LIESST) value of 61 K, similar to that previously reported for the anhydrous terephthalate salt (63 K).²⁰ As it was also observed for this similar compound, the T(LIESST) value falls outside the line $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ expected for $[\text{Fe}(\text{bpp})_2]^{2+}$ complexes.³³ Assuming $T_{1/2} \approx 180$ K and $T_0 = 150$ K, a value of T(LIESST) = 96 K should be observed. This could be due to partial excitation of both iron(II) sites originating a complex relaxation that diverges from a single relaxation process.

Conclusions

The marked dependence of the SCO properties of $[Fe(bpp)_2]^{2+}$ salts on the presence of H₂O molecules of crystallization is due to the strong H-bonding interactions that operate in these structures. Dehydration, thus, causes a strong structural rearrangement of cations and anions, leading to a loss of crystallinity in most cases. In this work, we have shown a mild single-crystal to single-crystal dehydration method that has allowed the characterization of an anhydrous $[Fe(bpp)_2]^{2+}$ salt containing the flexible adipate dianion. A comparison of the crystal structures at low temperature and at ambient conditions illustrates that the adipate dianion accommodates to the change of internal pressure induced by the cations, leading to a very gradual SCO.

Conflicts of interest

There are no conflicts of interest to declare.

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