A two-step spin crossover mononuclear iron(II) complex with a [HS–LS–LS] intermediate phase†

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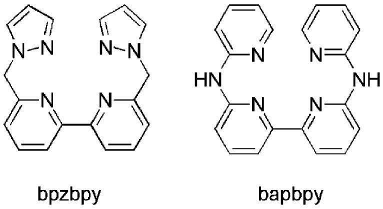
The two-step spin crossover of a new mononuclear iron(II) complex is studied by magnetic, crystallographic and calorimetric methods revealing two successive first-order phase transitions and an ordered intermediate phase built by the repetition of the unprecedented [HS–LS–LS] motif.

The occurrence of spin crossover (hereafter, SCO) between the high-spin (HS) and low-spin (LS) states of $3d^4$–$3d^7$ transition metal ions is appealing because it represents one of the best illustrations of a molecular switch.[1] A remarkable aspect of the SCO phenomenon is the coexistence of short- and long-range interactions between molecules giving rise to cooperative effects, such as hysteresis loops and two-step transitions.[2] Two-step SCO compounds are relatively scarce, and only a few examples of them exhibit hysteresis loop(s).[3,4] In most examples, two-step SCO was observed when there were two crystallographically different ion centers in the HS and/or LS phase. However, two-step transitions were also observed in compounds with crystallographically equivalent metal ions.[3,5–8] In such cases, the two-step SCO may be explained by a competition between antagonistic short-range (inter- or intramolecular) interactions and long-range elastic interactions.[9,10] Experimental evidence for such short-range interactions was firstly observed in the case of the binuclear two-step SCO complex $\{[Fe(bt)(NCS)_2]_2bpym\}$ (bpym = 2,2′-bipyrimidine, bt = 2,2′-bithiazoline), whose intermediate phase (hereafter, IP) appears as a mixture of binuclear molecules in the indistinguishable [HS–LS] and [LS–HS] states.[11] More recently, the long-range ordering of [HS–LS] motifs has been observed for the IP of the mononuclear SCO system $[Fe(pic)_3]Cl_2\cdot EtOH$ (pic = 2-picolylamine), in which the HS : LS ratio is 1 : 1.[12] In the present study, a new two-step SCO mononuclear iron(II) complex is reported, with two hysteresis loops and an ordered IP that is stable over a large temperature range. Unexpectedly, both the X-ray diffraction and magnetic studies show that the population ratio HS : LS of the IP is 1 : 2 rather than 1 : 1.



Scheme 1 Representations of the ligands bpzbpy[13] and bapbpy.

Inspired by earlier investigations on the mononuclear SCO complex $[Fe(bpzbpy)(NCS)_2]$ (see Scheme 1 for bpzbpy),[13] we designed a new rigid N_4-donor ligand, namely *N*-(6-(6-(pyridin-2-ylamino)pyridin-2-yl)pyridin-2-yl)pyridin-2-amine (bapbpy, see Scheme 1), which contains two N–H groups aimed at forming H-bonding networks. Similar to bpzbpy, bapbpy is a rigid, embracing N_4 ligand, which is expected to coordinate at the basal plane of an octahedral iron(II) center, leaving the axial positions for the binding of anions.

The reaction of $Fe(SCN)_2$ with one equivalent of bapbpy in methanol–DMF (20 : 1) produces the SCO complex $[Fe(bapbpy)(NCS)_2]$ (**1**),‡ which was recrystallized from DMF–methanol. Three crystal structures of **1** were determined at 295, 190 and 110 K (phases **I**, **II** and **III**, respectively, see Table 1 and ESI†). As anticipated, the octahedral FeN_6 chromophore is constituted, in the three structures, by the tetradentate ligand in the basal plane, and two axial thiocyanate ions (see Fig. 1 for the molecular geometry in phase **I**).

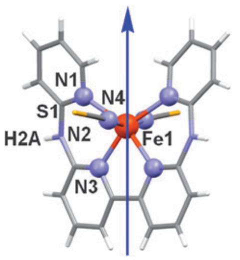


Fig. 1 Asymmetric unit of phase **I** of **1**. The blue arrow indicates the crystallographic twofold axis. One half of **1** is symmetry generated.

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† Electronic supplementary information (ESI) available: Experimental procedures, spectral and analytical data for the ligand bapbpy; X-ray and DSC studies for complex 1; figures illustrating the uncommon structural features for 1. CCDC reference numbers 694533–694535. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811746b

Table 1 Crystallographic data for phases **I**, **II** and **III** of complex **1**

	I	**II**	**III**
Formula	$C_{22}H_{16}FeN_8S_2$	$C_{22}H_{16}FeN_8S_2$	$C_{22}H_{16}FeN_8S_2$
fw	512.40	512.40	512.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$C2/c$	$C\bar{1}$
T/K	295(2)	190(1)	110(1)
a, b, c/Å	15.9263(4) 10.9683(4) 14.2723(3)	15.7348(2) 10.7200(2) 42.3919(5)	15.7337(7) 10.5731(6) 14.1664(6)
α, β, γ/°	90.00 117.457(1) 90.00	90.00 116.565(1) 90.00	93.971(4) 116.104(3) 90.375(5)
V/Å^3	2212.31(11)	6395.64(16)	2109.37(18)
Z, Z'	4, $\frac{1}{2}$	12, 1 + $\frac{1}{2}$	4, 1
D_x/Mg m^{-3}	1.538	1.596	1.613
μ/mm^{-1}	0.90	0.93	0.94
T_{min}, T_{max}	0.713, 0.849	0.663, 0.846	0.762, 0.840
Meas. refls	14 693	35 156	20 861
Indep reflns	2281	5948	4842
$I > 2\sigma(I)$ reflns	1916	4763	4361
R_{int}	0.024	0.035	0.026
θ_{max}/°	26.5	25.5	27.5
$R[F^2 > 2\sigma(F^2)]$,	0.030, 0.078	0.040, 0.086	0.034, 0.086
$wR(F^2)$, S	1.07	1.11	1.21
Refined params	153	456	305
$(\Delta/\sigma)_{max}$	<0.0001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.27, −0.26	0.69, −0.31	0.51, −0.49

At room temperature (phase **I**, $C2/c$), the basal and axial Fe–N bond lengths (Table S1†) are typical for an Fe(II) HS species and comparable to those found for [Fe(bpz-bpy)(NCS)$_2$][13] (see Table S1†). The basal coordination angles vary from 77.34(8) to 113.78(9)° (Table S1†), indicating a strong distortion of the octahedral geometry, which seems to be the results of the small bite angle of the bipyridine moiety [N3–Fe1–N3a = 77.34(8)°] and steric constraints between the pyridine groups N1 and N1a [N1–Fe1–N1a = 113.78(9)°]. The asymmetric unit of phase **I** contains a 1/2 crystallographically independent iron HS center that lies at sites of twofold axial symmetry. In the crystal packing of phase **I** (Fig. S1†), each molecule interacts with two adjacent iron complexes *via* N–H···S hydrogen bonds (Table S2†) and π–π stacking interactions (Table S3†), which both contribute to the building of one-dimensional (hereafter, 1-D) supramolecular chains along [0 0 1].

At intermediate temperatures (190 K, phase **II**, $C2/c$, see Fig. S2A†), the asymmetric unit contains one iron LS center and 1/2 iron HS center (see Fe–N distances, Table S1†). As the transition **I** → **II** occurs, 2/3 of the iron HS centers undergo a HS → LS spin transition, whereas the remaining iron HS centers still occupy twofold symmetry positions. The HS : LS population is found in a 1 : 2 ratio (or 1/2 : 1 ratio) and the IP is characterized by the unusual [HS–LS–LS] state. At 110 K (phase **III**, $C\bar{1}$), the asymmetric unit contains one iron LS center (Fig. S2B and Table S1†) with no imposed symmetry.

The crystal packing remains similar in the three phases (Fig. S4†). They show comparable H bonding and π–π stacking interactions along the 1-D supramolecular chains (Tables S2–S3 and Fig. S3†). The largest structural difference in the phase sequence is found along these chains, which are built of Fe HS centers for phase **I** or Fe LS centers for phase **III**, whereas such chains are built of the repetitive [HS–LS–LS] motif (*i.e.*, there are one LS···LS contact and two HS···LS contacts over three contacts) in phase **II** (Fig. S5†). The long-range order remains in phase **II** since extra Bragg reflections, which do not result from the superimposition of the diffraction pattern of phase **I** with that of phase **III**, are found at intermediate temperatures (Fig. S6†). From these observations, it can be concluded that phase **II** is not a mixture of phases **I** and **III**.

Temperature dependences of the cell dimensions have been determined in the range 160–260 K (see Fig. 2A and ESI†), which notably shows that the IP is stable over a wide temperature range (≈55 K). The variation of the unit cell parameters a, b and c (see Fig. S7†) show that the low-temperature (**II** ↔ **III**) phase transition is anisotropic. Finally, discontinuities in the volume per formula unit (*i.e.*, V/Z) found at the two transition points, as well as two hysteresis cycles, suggest that both phase transitions (**I** ↔ **II** and **II** ↔ **III**) are first order.[14] DSC studies on complex **1** corroborate the two first-order phase transitions, whose occurrences correspond to ΔH and ΔS values of 17 kJ mol^{-1} and 72 J mol^{-1} K^{-1}, and of 9.7 kJ mol^{-1} and 53 J mol^{-1} K^{-1} for the higher- and lower-transitions, respectively (see Fig. S8†).

As expected from the crystal packing in phases **I**, **II** and **III**, which shows supramolecular interactions between the iron(II) centers, and from the variable temperature X-ray diffraction studies, complex **1** shows strongly cooperative spin transition properties. The temperature dependence of the $\chi_m T$ product for a loosely packed polycrystalline sample of **1** is shown in Fig. 2B, where χ_m is the molar magnetic susceptibility and T is the temperature. The magnetic susceptibility data were measured in the range 3–300 K in both cooling and heating modes. The room temperature $\chi_m T$ value of 4.34 cm^3 mol^{-1} K is larger than the spin-only value calculated for a $^5T_2$ ground

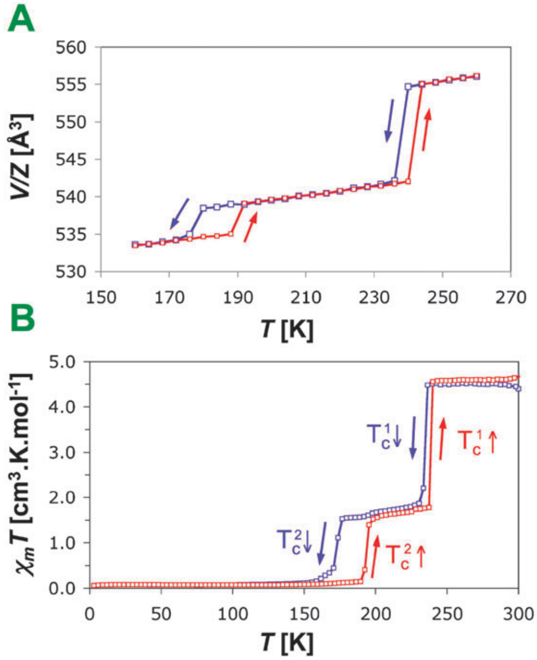

Fig. 2 (A) Temperature dependence of V/Z (the volume per formula unit) of **1** between 160 and 260 K in both cooling and heating modes (±2 K min^{-1}). (B) $\chi_m T$ *vs.* T plot for **1**.

state ($S = 2$) described in an octahedral coordination environment ($\chi_{\mathrm{m}}T = 3.0$ cm^3 mol^{-1} K for $g = 2$). Such an unusually high $\chi_{\mathrm{m}}T$ value has been also observed for the magnetic susceptibility study of the well-known complex [Fe(ptz)$_6$](BF$_4$)$_2$ (ptz = 1-propyltetrazole).[15] This phenomenon is explained by orientational effects of a crystalline sample which will result in effective magnetic moments that do not correspond to the real average magnetic moments. $\chi_{\mathrm{m}}T$ remains constant until 235 K where it drops abruptly to reach a value of 1.8 cm^3 mol^{-1} K at 231 K. This value remains nearly constant down to 177 K where it is exactly 1/3 of its initial value (1.45 cm^3 mol^{-1} K). A second abrupt decrease of $\chi_{\mathrm{m}}T$ is then observed, which is complete below 145 K ($\chi_{\mathrm{m}}T = 0.07$ cm^3 mol^{-1} K).

Remarkably, upon heating (red curve in Fig. 2B) the two transitions occur at different temperatures (*i.e.* $T^{1}{}_{\mathrm{c}}\uparrow = 239$ K while $T^{1}{}_{\mathrm{c}}\downarrow = 235$ K and $T^{2}{}_{\mathrm{c}}\uparrow = 194$ K while $T^{2}{}_{\mathrm{c}}\downarrow = 172$ K) resulting in hysteresis loops of 4 and 22 K for the higher and lower transitions. Overall, variable temperature X-ray diffraction studies, magnetic measurements and differential scanning calorimetry give a consistent view of the spin transitions of compound **1**. The observed hysteresis cycles, as well as the two-step SCO, suggest for such a mononuclear species efficient cooperative effects between adjacent iron(II) centers, as observed along the 1-D supramolecular chains (Fig. S1 and S3†).

In summary, the new bapbpy ligand has been synthesized to favor intermolecular interactions between mononuclear complexes. Its solvent-free iron(II) complex **1**, [Fe(bapbpy)(SCN)$_2$], is a new two-step SCO compound with H-bonding and π–π stacking interactions; steep transitions and hysteresis loops are observed for both HS ↔ IP and IP ↔ LS transitions. Remarkably, complex **1** possesses a unique ordered [HS–LS–LS] intermediate phase that is stable over a wide temperature range. Our undergoing research aims at understanding the observed 1 : 2 HS : LS ratio; we hope that the uncommon features of compound **1** will shine more light on antagonistic short-range and long-range cooperative effects within SCO materials.

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Notes and references

‡ Synthesis of **1**: A yellow suspension of 101 mg of bapbpy (0.30 mmol, see synthesis in the ESI) in 10 mL of methanol was prepared in a vial. 3.2 mL of a 0.1 M methanolic solution of iron(II) bis-thiocyanate was added (0.32 mmol), with 5 mg of ascorbic acid. The vial was closed and the orange suspension was stirred for 16 h. The solid was filtered through a micropore filter, washed with methanol, and dried under vacuum to yield 126 mg of **1** as a rusty powder (83%). IR (cm^{-1}): 3280.4, 3228.9, 3194.8, 3137.2, 3106.2, 2093.9 (SCN), 1629.3, 1582.3, 1533.5, 1486.2, 1457.9, 1442.9, 1429.0, 1237.4, 1226.4, 1177.7, 1163.8, 1009.6, 1002.7, 793.4, 769.8, 732.2, 644.3, 611.9, 517.7, 469.1, 429.8, 415.5, 340.9. ES MS *m*/*z* (calc): 453.8 (454.1, [M − SCN]$^+$). LF Spectroscopy (solid state): $\lambda_{\mathrm{max}} = 393$, 523 nm. $\lambda_{\mathrm{sh}} \approx 800$ nm. Monocrystals suitable for X-ray diffraction study were obtained as follows: 100 mg of the crude powder was dissolved into 20 mL of DMF, affording a dark solution that became red after addition of 5 mg of ascorbic acid. 1 mL aliquots of this solution were pipette-filtered over 1 cm celite into 20 reaction tubes. Degassed methanol was layered on top of these 20 samples, and the 20 tubes were stoppered. Dark-red single crystals were obtained within a week. The single crystals were filtered, washed with methanol and dried under vacuum for 2 h. Yield: 30%. The crystals were not vacuum or air sensitive and therefore could be handled under a normal atmosphere for several weeks. Anal. Calcd for $C_{22}H_{16}FeN_8S_2$: C, 51.57; H, 3.15; N, 21.87; S, 12.52. Found: C, 50.85; H, 3.12; N, 21.38; S, 12.22%.

X-Ray crystallography: see ESI† for further details (data collection, refinement, cell transformations, *T* dependences of the cell dimensions).

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