The first X-ray crystal structure determination of a dinuclear complex trapped in the [low spin–high spin] state: $[Fe^{II}_2(PMAT)_2](BF_4)_4 \cdot DMF$†

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The two metal centres in the doubly 1,2,4-triazole-bridged spin crossover complex $[Fe^{II}_2(PMAT)_2](BF_4)_4 \cdot DMF$ (1·DMF) are trapped in different spin states below ca. 200 K, with no evidence that this particular [LS–HS] species can be converted into the [LS–LS] form at ambient pressure.

The vast majority of known spin crossover (SCO) complexes are mononuclear. Only relatively few are dinuclear[1–7] or trinuclear[8] and the first tetranuclear examples have been described only recently.[9] These oligonuclear complexes feature bridging of the metal ions by heterocycles and this is of interest due to the potential mutual influence of heterocycle-mediated magnetic exchange coupling and SCO behaviour. The doubly pyridazine-bridged complex $[Co^{II}_2(L1)(NCS)_2(SCN)_2]$ (Fig. 1) was the first example of a cobalt complex to exhibit both exchange interactions and SCO.[2,10] The related complex $[Fe^{II}_2(L1)(MeCN)_4](ClO_4)_4$ appeared to be low-spin, as might be expected.[11] Since pyrazole-[3,6,7,12] and especially 1,2,4-triazole-based[13] ligands are well established to have the right ligand field strength to generate SCO complexes of iron(II), we have widened our studies to include the incorporation of these heterocycles into such dinucleating macrocycles[14,15] and related acyclic ligands.[14,16,17]

In dinuclear complexes the SCO of the two metal centres can either occur in a single step, [LS(low spin)–LS] ↔ [HS(high spin)–HS], as was recently observed for the first time in a doubly pyrazolate-bridged diiron(II) complex,[3] or, more commonly, in two steps, [LS–LS] ↔ '[LS–HS]' ↔ [HS–HS], as observed for a range of diiron(II) complexes featuring 2,2′-bipyrimidine (bpym), 4,7-phenanthroline-5,6-diamine (phdia)[1,5] or 3,5-di(2-pyridyl)-pyrazolate (bpypz⁻)[6,7] (examples of which can also show a single step SCO) as the bri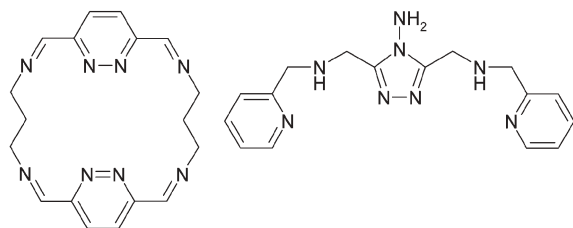dging ligands. In principle, the half-SCO species could consist of either distinct [LS–HS] complexes or a 1 : 1 mixture of [LS–LS] and [HS–HS] complexes.[1,5–7] Magnetic and applied-field Mössbauer data on their half-SCO complexes have led Real, Gütlich and co-workers to predict that they are of the former type, i.e. distinct [LS–HS] complexes, but this has not yet been confirmed by X-ray crystallography.[1,5] In contrast, Kaizaki and co-workers have recently reported that the single crystal X-ray structure determination of the '[LS–HS]' species of their doubly pyrazolate-bridged two-step SCO diiron(II) complex shows that it is of the latter type, i.e. a 1 : 1 mixture of [LS–LS] and [HS–HS] complexes.[7] Here, for the first time, we unambiguously confirm the existence of distinct [LS–HS] entities, in the dinuclear half-SCO species of the doubly 1,2,4-triazole-bridged complex $[Fe^{II}_2(PMAT)_2](BF_4)_4 \cdot DMF$ (1·DMF), by single crystal X-ray diffraction.

Complex 1† was isolated as a pale yellow solid in good yield from the 2 : 2 reaction of PMAT[17] (Fig. 1) with $Fe(BF_4)_2 \cdot 6H_2O$. Recrystallisation from MeCN–DMF gave colourless crystals of 1·DMF which were studied by magnetic susceptibility measurements (Fig. 2). These clearly revealed that at ambient pressure over the accessible temperature range (300–4 K) only the first step, [HS–HS] ↔ '[LS–HS]', of a possible two-step SCO is realised in this system. This transition is both abrupt and complete with $T_{1/2}$ = 224 K. There is a remarkably broad plateau region, at ca. 200–30 K with μ_{eff} = 3.88 μ_B per Fe^{II} centre, over which this half-SCO species is present and it occurs at convenient temperatures for a complete study of the nature of this species. The 3.88 μ_B value is somewhat bigger than the spin-only 1 : 1 '[LS–HS]' value of
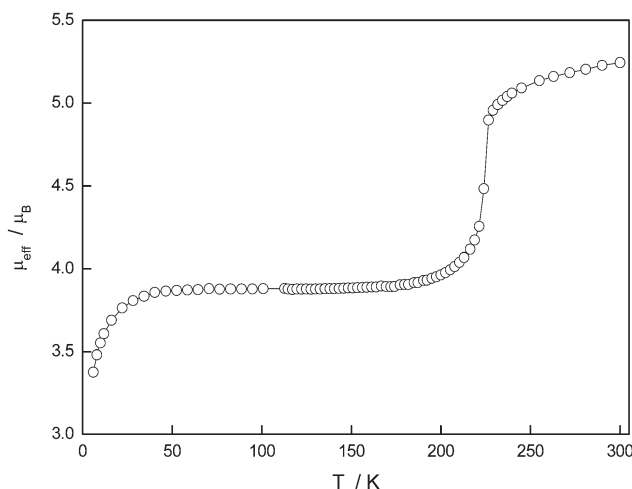

Fig. 1 Pyridazine-based macrocycle L1 (left) and 1,2,4-triazole-based acyclic ligand PMAT (right).

Fig. 2 Plot of the effective magnetic moment per Fe^{II} centre vs. temperature for 1·DMF.

3.47 μ_B because of orbital degeneracy on the HS Fe^{II} centre. No evidence of thermal hysteresis in μ_{eff} was observed. The decrease in μ_{eff} observed in the low temperature region, i.e. below ca. 30 K, is probably due to a combination of zero-field splitting of the HS Fe^{II} centre and low symmetry ligand field splitting effects.[1,5] Similar behaviour was shown by the bpym-bridged half-SCO examples.[5]

Mössbauer data were collected at 82 K (Fig. 3) as this temperature is well within the '[LS–HS]' plateau region. The data can be fitted to 56(1)% HS [IS (isomer shift) = 1.08(1) mm s^{-1}, QS (quadrupole splitting) = 2.39(1) mm s^{-1}] and 44(1)% LS [IS = 0.50(1) mm s^{-1}, QS = 0.26(1) mm s^{-1}]. The HS area is slightly larger than the LS area due to the expected higher recoilless fraction of that state. This is consistent with the presence of a 1 : 1 mixture of HS and LS Fe^{II} centres. However, this does not unambiguously distinguish between the two possible classes of half-SCO species.[5] Therefore, X-ray diffraction†‡ was used to examine a crystal of **1**·DMF at two different temperatures, corresponding to the '[LS–HS]' and [HS–HS] states, to determine the structure of both of these species.

At room temperature†‡ the asymmetric unit consists of one half of the dinuclear complex with the other half generated by a centre of inversion. Each Fe^{II} centre has an N_6 distorted octahedral coordination environment comprising three donor atoms from each of the two PMAT ligands which sandwich the two metal centres. The iron atoms are bridged in the equatorial plane by the two neutral 1,2,4-triazole moieties. The two pyridine rings within a PMAT ligand strand coordinate to axial sites on the same side of the complex and their mean planes intersect at 86.2(2)°. The Fe–N bond lengths [2.116(4)–2.303(5) Å] and cis N–Fe–N angles [75.9(2)–115.9(2)°] are entirely consistent with those expected for HS Fe^{II} centres.

The large plateau region made it straightforward to obtain an X-ray data set corresponding to the half-SCO species and this was
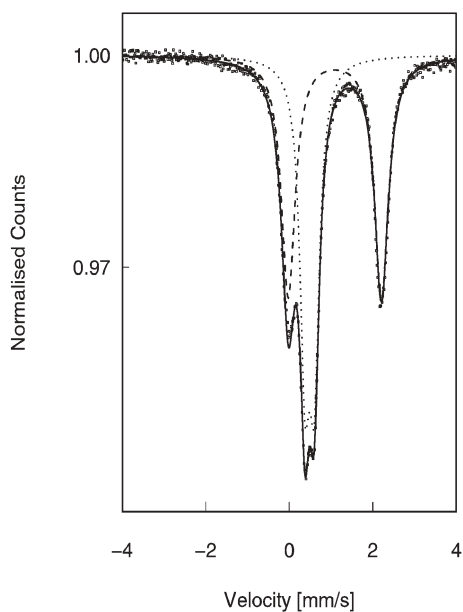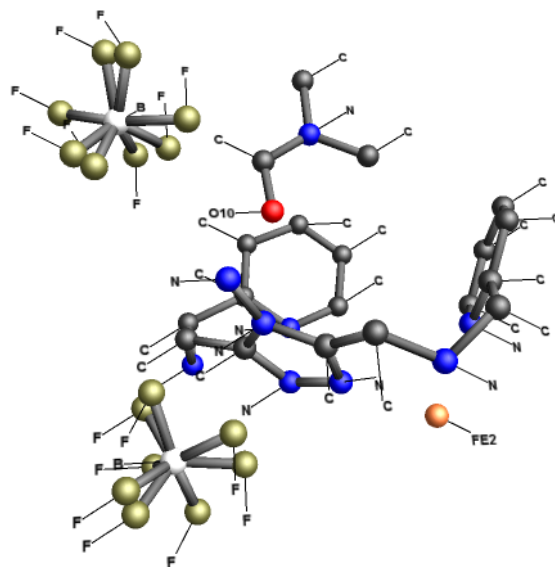
Fig. 4 Perspective view of **1**·DMF at 123 K. The BF_4^- anions, the DMF solvate and all hydrogen atoms, except those bonded to nitrogen atoms, have been omitted for clarity.

collected, on the same crystal, at 123 K (Fig. 4).†‡ The asymmetric unit comprises the entire complex so the two iron atoms are crystallographically independent and indeed exhibit quite different bond lengths and angles. The spin states are readily assigned as Fe(1) being LS [Fe–N 1.934(3)–2.071(4) Å, cis N–Fe–N 81.8(1)–101.1(2)°] and Fe(2) being HS [Fe–N 2.131(3)–2.319(4) Å, cis N–Fe–N 75.1(1)–121.7(1)°]. This corresponds to the localised or trapped, not averaged, half-SCO species, i.e. [LS–HS]. Hence, for the first time the nature of a trapped half-SCO species has been revealed unambiguously by an X-ray crystal structure determination.

The present work has implications for the $\{[Fe^{II}(L)(NCX)_2]_2$-$(\mu$-L$')\}$ series with L$'$ = bpym or phdia, developed by Real, Gütlich and co-workers,[1,5] and the $\{[Fe^{II}(L)(NCX)]_2(\mu$-L$')_2\}$ series with L = py and L$'$ = bpypz$^-$, developed by Kaizaki and co-workers.[6,7] One might predict that in the plateau region of the former series of complexes, with L = L$'$ = bpym and X = Se ($T_{1/2}$ = 120 K), a trapped [LS–HS] state similar to that shown in Fig. 4 occurs. In their two-step SCO compounds with L = bithiazoline, X = S or Se and L$'$ = bpym[5] or phdia[1] the dinuclear [LS–HS] species, at the narrow plateau regions of temperature, are able to change further into [LS–LS] forms as the temperature is lowered. In contrast, the use of the more constrained bis-bidentate L$'$ = bpypz$^-$ ligand, with L = 4-Phpy in axial positions, results in a half-SCO species which is a 1 : 1 mixture of [LS–LS] and [HS–HS] species.[7] In this system the plateau region is very narrow and both the [HS–HS] and the [LS–LS] species can also be observed, at high and low temperatures respectively. Clearly, many structural and electronic factors contribute to these spin changes. In this context it is interesting to note that in **1**·DMF, once the [LS–HS] species has been realised, the complex is locked into it as further lowering of the temperature does not change it into the [LS–LS] form (Fig. 2). This complex is also relatively unusual amongst SCO complexes as

Fig. 3 Mössbauer data for **1**·DMF at 82 K. The solid line is the experimental data, the dashed (LS) and dotted (HS) lines represent the fitting to these data as described in the text.

all of the donor atoms to the two Fe^{II} centres, including the two 1,2,4-triazole bridges between them, are provided by the two PMAT ligands. Although the overall structure at 123 K is very similar in appearance to that at 298 K, the details of the Fe^{II} coordination environments are clearly different, with the localised LS Fe^{II} centre in a compressed, closer-to-octahedral, environment than the HS Fe^{II} centre. The use of a relatively tightly constrained bis-terdentate bridging ligand (PMAT is more tightly constrained than bpypz$^-$) is likely to be a key factor in these observations as structural and electronic changes at one metal site are readily communicated to the other one. In our experience[10,18] it is likely that this effect would be even greater in a suitably designed macrocyclic ligand.

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Notes and references

‡ Crystal data for **1**·DMF at 298 K: colourless, triclinic, space group $P\bar{1}$, a = 10.4819(2), b = 11.3759(2), c = 12.1990(2) Å, α = 63.438(1), β = 72.134(1), γ = 73.886(1)°, V = 1221.39(4) Å^3, Z = 1, $\rho_{calcd.}$ = 1.605 g cm^{-3}, μ = 0.706 mm^{-1}. 20371 Reflections were collected in the range $3 < 2\theta < 56°$ and 5747 independent reflections [R(int) = 0.0611] were used in the structural analysis. The structure was solved by Patterson methods (SHELXS-97)[19] and refined against all F^2 data (SHELXL-97)[20] to $R1$ = 0.0669 [for 3633 $F > 4\sigma(F)$; $wR2$ = 0.2408 and goodness of fit = 1.094 for all 5747 F^2; 420 parameters; all non-hydrogen atoms anisotropic except for the atoms of the disordered DMF; BF$_4^-$ and DMF disorder modelled; coordinates of hydrogen atoms on nitrogen atoms were refined with N–H bonds restrained to have approximately equal bond lengths]. Crystal data for **1**·DMF at 123 K: purple, triclinic, space group $P\bar{1}$, a = 11.2253(1), b = 12.1026(2), c = 20.4672(3) Å, α = 105.919(1), β = 90.564(1), γ = 117.119(1)°, V = 2350.23(6) Å^3, Z = 2, $\rho_{calcd.}$ = 1.669 g cm^{-3}, μ = 0.734 mm^{-1}. 36504 Reflections were collected in the range $2 < 2\theta < 56°$

and the 11118 independent reflections [R(int) = 0.0686] were used in the structural analysis. The structure was solved by Patterson methods (SHELXS-97)[19] and refined against all F^2 data (SHELXL-97)[20] to $R1$ = 0.0672 [for 6773 $F > 4\sigma(F)$; $wR2$ = 0.2387 and goodness of fit = 1.063 for all 11118 F^2; 740 parameters; all non-hydrogen atoms anisotropic; DMF disorder modelled; coordinates of hydrogen atoms on nitrogen atoms were freely refined]. This cell, which is in the standard setting, can be transformed by [0 −1 −1 1 0 0 0 −1 0] into a cell with a = 20.7243, b = 11.2253, c = 12.1026 Å, α = 62.881, β = 71.754, γ = 73.983°, V = 2350.23 Å^3, which corresponds approximately to a doubling of the 298 K cell along the a axis. CCDC 247510 and 247511. See http://www.rsc.org/suppdata/cc/b4/b415891a/ for crystallographic data in .cif or other electronic format.

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