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Structure and magnetism of a new pyrazolate bridged iron(II) spin crossover complex displaying a single HS–HS to LS–LS transition

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The dinuclear iron(II) complex [(pypzH)(NCSe)Fe(μ-pypz)$_2$-Fe(NCSe)(pypzH)].2H_2O displays a single, sharp spin crossover transition between the [HS-HS] and [LS-LS] states and is structurally characterised above and below the $T_{1/2}$ = 225 K value

There is a great revival in studies of iron(II), d^6, spin crossover (SCO) compounds because of the possible applications of their molecular switch properties in areas such as information processing.[1] Such applications require a fundamental understanding of their bistability properties, that is the ability to exist in the high-spin (HS; $t_{2g}^4e_g^2$) and low-spin (LS; t_{2g}^6) states at a particular temperature. This in turn requires an understanding of the cooperativity between the SCO centres in the crystalline state, since this leads to abrupt transitions at the crossover temperature, $T_{1/2}$, and to thermal hysteresis (memory).[2] Little is known on cooperativity in small clusters or extended coordination polymers of Fe(II) compared to monomers.[3] It has been proposed that linking of Fe(II) ions by covalent bridging within a small cluster could lead to enhanced intracluster cooperativity because of the ability to efficiently transmit structural and electronic changes occurring at the Fe centres.[4] Understanding the cooperativity *between* clusters and the synergy, if any, between intracluster magnetic exchange coupling, and the SCO phenomenon are two other fundamental challenges.[5,6]

We have been approaching these problems by designing small clusters as well as extended networks.[7] Most work on dinuclear Fe(II) SCO compounds has been done by Real and Gütlich and their groups.[8,9] A family of bipyrimidine (bpym)-bridged compounds of type [(chel)(NCX)$_2$Fe(μ-bpym)Fe(NCX)$_2$(chel)] has been studied extensively and a common feature to emerge has been the 'two-step' $\chi_M T$ plots in which the intervening plateau is assigned to the presence of [HS–LS] dinuclear species, thus leading to spin changes [HS–HS]↔[HS–LS]↔[LS–LS] occurring between high and low temperatures.[8,9] One such example is when {chel = bithiazoline, X = S} and brief structural data have been given for the [HS–HS] form.[8] The question is posed as to whether all dinuclear compounds will show this two-step behaviour. In this regard, Real *et al.* have observed a very broad, gradual SCO, without a step, in the {chel = 2,2′-dipyridylamine, X = S} derivative, the lack of a step being ascribed to inter-dimer interactions.[10]

Here we show that a new compound, [(pypzH)(NCSe)Fe(μ-pypz)$_2$Fe(NCSe)(pypzH)]·2H_2O (**1**) displays a single, sharp [HS–HS]↔[LS–LS] transition in the $\chi_M T$ *vs.* T plot, at 225 K. The crystal structures of **1** are described at temperatures above and below the $T_{1/2}$ value, and this allows, for the first time, a meaningful structural correlation to be made as a covalent-bridged dinuclear iron(II) complex changes from [HS–HS] to [LS–LS] states. This is the first report of the pypzH ligand, 2-pyrazolylpyridine, forming a dinuclear compound involving a bridge from a deprotonated pyrazole, while leaving a neutral pypzH as chelating 'end' group. A related dipyridyl-pyrazolate ligand has recently been shown to form a dinuclear Fe(II) SCO complex ($T_{1/2}$ = 136 K) but no structural data were given.[11]

Preparing complex **1** is a delicate exercise†, since other intermediate products of type {[Fe(pypzH)$_2$(NCSe)$_2$]$_2$(μ-H_2O)}·2H_2O are readily formed, and this 'pseudo-dimer' compound shows a gradual 'half' SCO transition ($T_{1/2}$ = 125 K) but remains HS when the H-bonded bridging water molecules are removed.[7,12] The structure‡ of **1** was solved at 123 K and 298 K and the dinuclear molecule, numbering scheme and relevant dimensions are shown in Fig. 1.

The structural determination of **1** was initially performed at 123 K‡ then later repeated, on another crystal, at 123 K and 298 K, with all three solutions being isostructural. The repeated 123 K and 298 K refinements gave solutions of higher *R* values of 11 and 10%, respectively, owing to the nature of the crystal. The dinuclear molecule consists of two asymmetric units, with Fe(1)′, N(2)′ and N(3)′ being the symmetry generated equivalents of Fe(1), N(2) and N(3) with the complex located on an inversion centre. The octahedral iron(II) environment of each dimer contains a neutral bidentate pypzH and the negatively charged ions of NCSe and a deprotonated, bridging tridentate pypz ligand. The NCSe ions occupy a *trans* geometry. Within **1**, the pyrazolyl hydrogen of the terminally bound pypzH ligand is H-bonded to the H_2O group with a H(6A)O(1) bond distance of 2.008 Å. The water oxygen O(1) is 3.355(6) Å from Se(1), 3.501(6) Å from Se(1) at ($\frac{1}{2}+x, y, \frac{1}{2}-z$) and the Se···O···Se angle is 115.5(2) °. These data are suggestive of weak hydrogen bonding despite no hydrogens being located during refinement. There is no π–π stacking between dimers. While all crystals of **1** in the bulk product have the molecular structure described, other structural isomers would be possible, in principle.

The isostructural solutions at 123 K and 298 K show that most bond lengths and angles are in close agreement. However, some important differences were observed, most notably concerning the Fe coordination environment. At 123 K and 298 K the respective Fe(1)–Fe(1)′ distances in the dimer are 3.995(5) Å and 4.100(7) Å. The average Fe–N distance at 123 K is 1.995(5) Å increasing to 2.181(7) Å at 298 K. These Fe–N distances are not only indicative of LS Fe–N and HS Fe–N bond distances, but vary by 0.186 Å in agreement with previously observed changes in Fe–N bond lengths

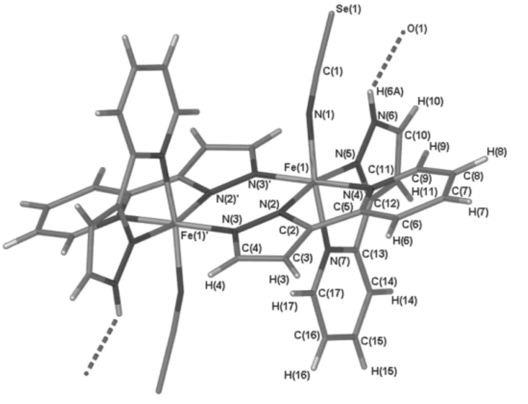

Fig. 1 Structure of [(pypzH)(NCSe)Fe(μ-pypz)$_2$Fe(NCSe)(pypzH)]·2H_2O (**1**) obtained at 123 K.† Atoms marked with a prime are at equivalent positions (1 − *x*, − *y*, 1 − *z*). Pertinent distances and angles are given below.

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occurring during LS to HS spin transitions.[8] Further evidence of the SCO of LS–LS Fe–Fe centres to HS–HS is observed in the expansion of the unit cell volumes, by 9.3%. The increasing Fe–N bond distances at 298 K coincide with a reduction of the NFeN angles of bidentate pypz and pypzH, with N(2)Fe(1)N(4) decreasing from 80.8° to 76.1° and N(7)–Fe(1)–N(5) decreasing from 79.2° to 72.9°. Other notable variations of bond angles between 123 K and 298 K include N(2)Fe(1)N(5) decreasing from 168.5° to 159.5°, N(1)Fe(1)N(7) decreasing from 172.8° to 164.1°, N(1)Fe(1)N(2) increasing from 95.9° to 104.9° and N(2)Fe(1)N(3)′ increasing from 96.06° to 98.17°. Thus, the change from [LS–LS] to [HS–HS] corresponds to a 'breathing out' across the bridge and to the abovementioned, identical structural changes in each FeN_6 chromophore, but with no major change to the dinuclear framework.

The SCO transition in **1** was monitored by magnetic susceptibility measurements. A plot of χ_mT versus temperature is shown in Fig. 2. The χ_mT value at 300 K is 3.09 cm^3 mol^{-1} K (4.97 μ_B per Fe) in agreement with the molecules being in the [HS–HS] state. A sharp crossover occurs at $T_{1/2}$ = 225 K, without any significant thermal hysteresis being observed during cycling up and down in temperature. Below ~180 K there is a very small decrease in χ_mT from 0.298 cm^3 mol^{-1} K (1.54 μ_B) to 0.139 cm^3 mol^{-1} K (1.05 μ_B) at 16 K, before a somewhat more rapid decrease towards 0.061 cm^3 mol^{-1} K (0.70 μ_B), at 2 K. The behaviour below the crossover transition arises from the dinuclear molecules being in the [LS–LS] form, with the non zero χ_mT 'plateau' originating from a combination of 2nd order Zeeman contributions to the LS Fe(II) susceptibilities plus a small Curie-like contribution from any trapped [HS–HS] form. **1** shows a much sharper [HS–HS] to [LS–LS] spin transition than does the recently reported {chel = 2,2′-dipyridylamine, X = S}- bpym compound[10] and does not have the [HS–LS] step in χ_mT noted in the bithiazoline–bpym analogues.[8]

The zero-field Mössbauer spectrum of **1**, at 77 K, shows a well resolved quadrupole doublet, with δ = 0.48(1) mm s^{-1} and ΔE_Q = 0.52(1) mm s^{-1} due to LS iron(II). No HS lines could be detected. The spectrum at 295 K shows a slightly asymmetrical doublet with δ = 0.98(1) mm s^{-1} and ΔE_Q = 1.83(1) mm s^{-1}, values typical of HS Fe(II) centres.

In summary, **1** provides the first dinuclear iron(II) complex in which the spin transition from high- to low-spin states has been followed by crystal structural measurements and in which no step in χ_mT due to [HS–LS] states is observed. The magnetic transition is sharp, with no hysteresis, indicating little cooperativity is occurring between the SCO centres within, or between, dinuclear molecules. Further dinuclear iron(II) examples of the present and related types are being sought.

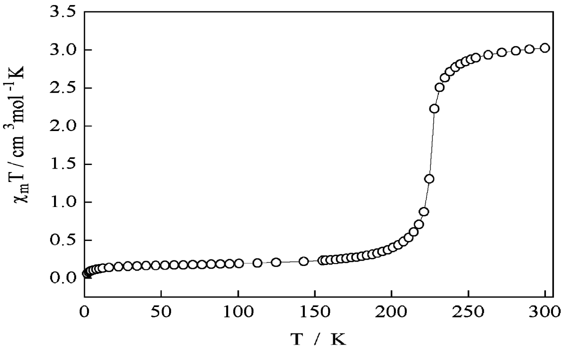

Fig. 2 χ_mT (per Fe) *versus* temperature plot for **1**.

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Notes and references

† All reactions were done under N_2 using standard Schlenk techniques. To a methanolic solution (15 mL) of $[Fe(H_2O)_6](ClO_4)_2$ (153.12 mg, 0.422 mmol) (and a pinch of ascorbic acid to prevent Fe(III) forming) was added a solution of KNCSe (121.6 mg, 0.844 mmol) in the same solvent (15 mL). The mixture was stirred for 15 min., filtered dropwise using a cannula to remove $KClO_4$ into another Schlenk flask containing a solution of pypzH (120 mg, 0.844 mmol) and 3 drops of 1 M NaOH in methanol. Water (2 mL) was then added and the solution was stirred for 1 h at room temperature, then left to slowly evaporate under N_2, overnight, to yield red–orange crystals of (**1**). ν(NC) 2093 cm^{-1} Yield, 22 mg, 9%. Further evaporation of the mother liquor yielded more of **1** but contaminated with yellow–orange crystals of $\{[Fe(pypzH)_2(NCSe)_2]_2(\mu\text{-}H_2O)\}\cdot 2H_2O$.

‡ *Crystal data* for $C_{34}H_{26}Fe_2N_{14}O_2Se_2$ (**1**), M = 932.31, orthorhombic, space group *Pbca*, a = 10.7857(2), b = 17.2422(4), c = 20.1713(5) Å, U = 3751.24(15) Å^3, T = 123(2) K, Z = 4, $F(000)$ = 1856, D_c = 1.651 g cm^{-3}, μ(Mo–K$_\alpha$) = 2.767 mm^{-1}, $2\theta_{max}$ = 28.26°. An orange–red irregular plate (0.22 × 0.22 × 0.05 mm). 38 404 total reflections, 4 635 independent reflections (R_{int} = 0.1019), of which 3 110 were observed [$I > 2\sigma(I)$]. At final convergence R_1 (obs.) = 0.0687, wR_2 (all data) = 0.1887 for 244 parameters, S = 1.160. Highest refined residual peak is 2.87 (1.339 Å from Se(1)). These and the repeat 123 K and 298 K data are in the CIF files. CCDC 220710–220712. See http://www.rsc.org/suppdata/cc/b3/b311818e/ for crystallographic data in .cif or other electronic format.

1 P. Gütlich, Y. Garcia and H. A. Goodwin, *Chem. Soc. Rev.*, 2000, **29**, 419; O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44.
2 P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 20.
3 H. Spiering and N. Willenbacher, *J. Phys.: Condens. Matter*, 1989, **1**, 10089; H. Spiering, T. Kohlhaas, H. Romstedt, A. Hauser, C. Bruns-Yilmaz, J. Kusz and P. Gütlich, *Coord. Chem. Rev.*, 1999, **190–192**, 629.
4 O. Kahn, E. Codjovi, Y. Garcia, P. J. van Koningsbruggen, R. Lapayoudi and L. Sommier, *ACS Symposium Series, Molecule-based magnetic materials*, eds. M. M. Turnbull, T. Sugimoto and L. K. Thompson, 1996, **644**, p. 298.
5 P. Gütlich, *Struct. Bonding*, 1981, **44**, 83; H. Toftlund, *Coord. Chem. Rev.*, 1989, **94**, 67.
6 S. Brooker, D. J. de Geest, R. J. Kelly, P. G. Plieger, B. Moubaraki, K. S. Murray and G. B. Jameson, *J. Chem. Soc., Dalton Trans.*, 2002, 2080.
7 K. S. Murray and C. J. Kepert, in Spin crossover in transition metal compounds, eds. P. Gütlich and H. A. Goodwin, *Topics in Current Chem.*, Springer-Verlag, 2004, in press.
8 J. A. Real, in Transition Metals in Supramolecular Chemistry, ed. J. P. Sauvage, John Wiley and Sons, Ltd., 1999, 53; J. A. Real, A. B. Gaspar, V. Niel and M. C. Muñoz, *Coord. Chem. Rev.*, 2003, **236**, 121.
9 V. Ksenofontov, A. B. Gaspar, J. Real and P. Gütlich, *J. Phys. Chem. B*, 2001, **105**, 12266.
10 A. B. Gaspar, V. Ksenofontov, J. A. Real and P. Gütlich, *Chem. Phys. Lett.*, 2003, **373**, 385.
11 N. Suemura, M. Ohama and S. Kaizaki, *Chem. Commun.*, 2001, 1538.
12 B. A. Leita, J. D. Cashion, B. Moubaraki, K. S. Murray and J. P. Smith, *unpublished data.*