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# An unusual abrupt thermal spin-state transition in $[FeL_2][BF_4]_2$ [L = 2,6-di(pyrazol-1-yl)pyridine]†

**Joanne M. Holland,[a] Judith A. McAllister,[bc] Zhibao Lu,[d] Colin A. Kilner,[a] Mark Thornton-Pett[a] and Malcolm A. Halcrow*[a]**

[a] *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK LS2 9JT. E-mail: M.A.Halcrow@chem.leeds.ac.uk*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
[c] *Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, UK CB3 0HE*
[d] *Centre for Self-Organising Molecular Systems, School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK LS2 9JT*

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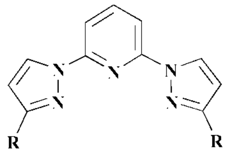
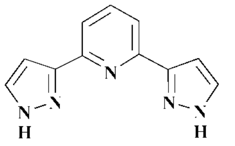
**The complex $[Fe(L^1H)_2][BF_4]_2$ exhibits an abrupt thermal spin-crossover which may be mediated by an order–disorder transition of the $BF_4^-$ anions.**

The spin-crossover phenomenon in Fe(II) complexes continues to be well studied,[1] reflecting their potential applicability as bistable materials for information storage.[2] For such applications, a thermally induced spin-state transition must occur over as small a temperature range as possible, and should exhibit a hysteresis loop.[2] These properties reflect intermolecular cooperativity within the sample, and are most often associated with a concomitant crystallographic phase transition and/or loss of long-range ordering. However, there are isolated examples where this is not the case, and intermolecular cooperativity in a thermal spin–spin transition is instead mediated by covalent pathways,[3] or *via* intermolecular hydrogen-bonding,[4] π–π interactions[5,6] or van der Waals contacts.[7] Following our studies of the electronic structures and solid state fluxionality of $[Cu(L^1R)_2]^{2+}$ (R = H, mesityl),[8–10] we wished to examine the Fe(II) complex chemistry of $L^1R$. This was of particular interest since several salts of $[Fe(L^2)_2]^{2+}$ {a structural isomer of $[Fe(L^1H)_2]^{2+}$} exhibit both thermal and light-induced spin-state transitions, whose physics has been extensively studied.[11]



$L^1R$



$L^2$

Complexation of $Fe(BF_4)_2\cdot 6H_2O$ with 2 mol equivalents of $L^1H$[12] in acetone affords a mustard precipitate of $[Fe(L^1H)_2][BF_4]_2$ **1** in 70% yield, which can be recrystallised from $MeCN–Et_2O$.‡ Variable-temperature magnetic susceptibility measurements§ from polycrystalline **1** demonstrated a transition between high-spin ($S = 2$, $\chi_mT = 3.6–3.7$ cm$^3$ K mol$^{-1}$[13]) and low-spin ($S = 0$, $\chi_mT \leqslant 0.3$ cm$^3$ K mol$^{-1}$[13]) states centred at $T = 259$ K, with a transition width of 3 K and a 3 K hysteresis loop (Fig. 1). This change is reflected in the colour of the compound, which changes sharply from mustard yellow to dark brown upon cooling; this change is reversible upon rewarming to room temperature. Differential scanning calorimetry (DSC) experiments§ of **1** confirmed these results, showing a first-order transition centred at 260 K, with a hysteresis width of 4 K. Values of $\Delta H = 17.2(2)$ kJ mol$^{-1}$ and $\Delta S = 66.2(8)$ J mol$^{-1}$ K$^{-1}$ for the transition were derived from the DSC data.

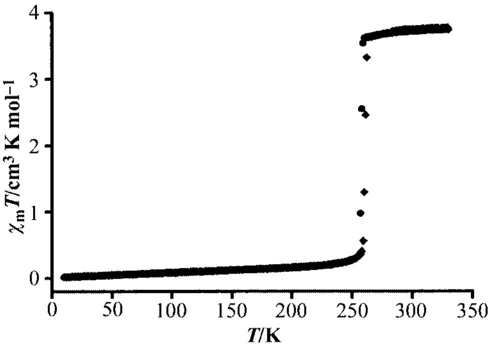


**Fig. 1** Plot of $\chi_mT$ *vs.* $T$ for polycrystalline **1** in cooling (●) and warming (◆) modes.

The temperature of the transition was also confirmed by measuring the crystallographic unit cell in the range 240–300 K, which demonstrated a discontinuity within the range 259–261 K in cooling and warming modes. No hysteresis was detected by this method, although this might reflect the less accurate temperature control at the diffractomer, which is estimated at ±2 K. There is no change in space group ($P2_1$) at these temperatures; rather, the transition is characterised by a decrease of 0.55 Å in the crystallographic $c$-direction, an increase of 0.05 Å in $b$, and an increase of 2.0° in $\beta$ as the temperature is lowered (see ESI†). The decrease in unit cell volume associated with the phase transition (ignoring thermal contraction effects) is 35(5) Å$^3$ or 2.6%, the latter being a typical value for a spin state transition in an Fe(II) complex.[14] The temperature of the crystal can be cycled across the transition several times, although the crystal begins to decay noticeably after *ca.* five cycles.

Four datasets were collected from the complex, at 375, 290, 240 and 150 K.¶ The molecular structures of the complex dication at 290 and 375 K are crystallographically indistinguishable, as are the structures at 240 and 150 K (see ESI†). Therefore, only the structure analyses at 290 and 240 K will be discussed in detail. At both temperatures the six-coordinate Fe(II) ion in **1** has approximate local $D_{2d}$ symmetry, with Fe–N bond lengths that are typical of a high-spin (290 K) and low-spin (240 K) Fe(II) centre (Fig. 2).[15] At 240 K the Fe–N distances are shorter than at 290 K by an average of 0.215(10) Å, which is a typical value for a high- to low-spin transition involving a Fe(II) complex with a hexa-nitrogen donor set.[15] As a result, the average ligand bite angle has increased at 240 K [80.0(3)°] compared to 290 K [73.47(18)°].

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† Electronic supplementary information (ESI) available: tabulated and plotted unit cell dimensions for **1** between 240–300 K; tabulated magnetic susceptibility data between 10–330 K. See http://www.rsc.org/suppdata/cc/b1/b100995h/

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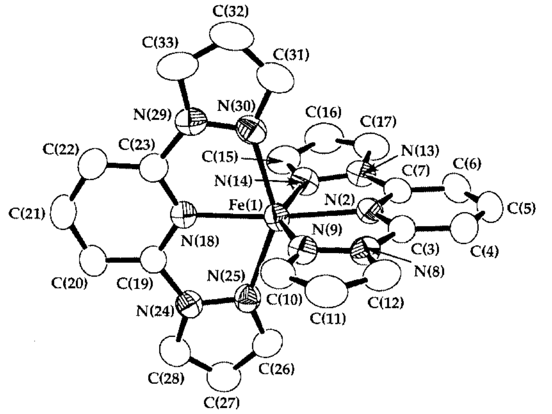

**Fig. 2** View of the $[\mathrm{Fe(L^1H)_2}]^{2+}$ dication in the crystal of **1** at 290 K, showing the atom numbering scheme employed for the complex cation. Thermal ellipsoids are at the 35% probability level. For clarity, all H atoms have been omitted. The complex at 240 K is visually indistinguishable. Selected distances (Å) and angles (°) at 290 K: Fe(1)–N(2) 2.1248(19), Fe(1)–N(9) 2.193(2), Fe(1)–N(14) 2.175(3), Fe(1)–N(18) 2.127(2), Fe(1)–N(25) 2.184(3), Fe(1)–N(30) 2.185(3); N(2)–Fe(1)–N(9) 73.47(8), N(2)–Fe(1)–N(14) 73.65(9), N(2)–Fe(1)–N(18) 173.15(10), N(2)–Fe(1)–N(25) 113.14(9), N(2)–Fe(1)–N(30) 100.21(10), N(9)–Fe(1)–N(14) 147.08(9), N(9)–Fe(1)–N(18) 104.24(8), N(9)–Fe(1)–N(25) 98.46(9), N(9)–Fe(1)–N(30) 92.88(9), N(14)–Fe(1)–N(18) 108.21(9), N(14)–Fe(1)–N(25) 95.95(9), N(14)–Fe(1)–N(30) 91.12(10), N(18)–Fe(1)–N(25) 73.44(9), N(18)–Fe(1)–N(30) 73.31(10), N(25)–Fe(1)–N(30) 146.58(9). Selected distances (Å) and angles (°) at 240 K: Fe(1)–N(2) 1.893(3), Fe(1)–N(9) 1.979(3), Fe(1)–N(14) 1.968(3), Fe(1)–N(18) 1.905(3), Fe(1)–N(25) 1.981(4), Fe(1)–N(30) 1.975(4); N(2)–Fe(1)–N(9) 80.22(14), N(2)–Fe(1)–N(14) 80.05(14), N(2)–Fe(1)–N(18) 178.25(18), N(2)–Fe(1)–N(25) 101.75(15), N(2)–Fe(1)–N(30) 98.34(15), N(9)–Fe(1)–N(14) 160.26(13), N(9)–Fe(1)–N(18) 100.50(14), N(9)–Fe(1)–N(25) 92.92(14), N(9)–Fe(1)–N(30) 92.24(14), N(14)–Fe(1)–N(18) 99.21(14), N(14)–Fe(1)–N(25) 91.57(15), N(14)–Fe(1)–N(30) 90.11(15), N(18)–Fe(1)–N(25) 79.83(15), N(18)–Fe(1)–N(30) 80.06(15), N(25)–Fe(1)–N(30) 159.82(13).

To conclude, we have shown that crystalline **1** undergoes a cooperative spin-state transition centred at 260(1) K, which does not involve a crystallographic phase change. It is not clear what mediates the cooperativity of this transition. However, one possibility is implied by the isomorphous complex $[\mathrm{Cu(L^1H)_2}][\mathrm{BF_4}]_2$ **2**, in which pseudo-Jahn–Teller cooperativity is mediated by rotation of the $\mathrm{BF_4}^-$ anions in the crystal.[10] It is therefore intriguing that there is an apparent change in the anion motion in **1** across the spin-state transition. At 290 K, all F atoms in both $\mathrm{BF_4}^-$ anions are badly disordered, implying that there is essentially free rotation of the near-spherical anions within their lattice cavity. In contrast, at 240 K one F atom in each ion appears to be crystallographically ordered, so that the anions are now disordered by rotation about one B–F bond. Experiments to further define the influence of anion motion on the spin-crossover in **1**, and to determine the magnetic properties of other $[\mathrm{Fe(L^1R)_2}]^{2+}$ complexes, are in progress.

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## Notes and references

‡ *Analytical data* for **1**: Found C, 40.7; H, 2.8; N, 21.2. Calc. for $\mathrm{C_{22}H_{18}B_2F_8FeN_{10}}$: C, 40.5; H, 2.8; N, 21.5%.

§ Susceptibility measurements were carried out in an applied field of 1000 G, with the sample being poised at each temperature for 1 min before measurement. DSC experiments were run using a temperature ramp of 10 °C $\mathrm{min^{-1}}$.

¶ Four datasets were collected for **1** ($\mathrm{C_{22}H_{18}B_2F_8FeN_{10}}$, $M_\mathrm{r}$ = 651.93, monoclinic, $P2_1$, $Z$ = 2).

*Crystal data*: at 375 K: $a$ = 8.5301(3), $b$ = 8.5518(4), $c$ = 19.1757(5) Å, $\beta$ = 94.9043(24)°, $U$ = 1393.70(9) Å$^3$, $\mu$(Mo-K$\alpha$) = 0.628 mm$^{-1}$; 15873 measured reflections, 6039 independent, $R_\mathrm{int}$ = 0.035; $R(F)$ = 0.045, $wR(F^2)$ = 0.120, Flack parameter −0.001(17). The F atoms of both $\mathrm{BF_4}^-$ anions were badly disordered at this temperature. Each anion was modelled using three different disorder orientations, in a 0.50 : 0.25 : 0.25 occupancy ratio. All B–F distances were restrained to 1.37(2) Å, and non-bonded F···F distances within each disorder orientation to 2.24(2) Å. All non-H atoms with occupancy ⩾0.5 were refined anisotropically.

At 290 K: $a$ = 8.4947(2), $b$ = 8.5070(2), $c$ = 19.0535(6) Å, $\beta$ = 95.7050(18)°, $U$ = 1370.07(6) Å$^3$, $\mu$(Mo-K$\alpha$) = 0.639 mm$^{-1}$; 15406 measured reflections, 5442 independent, $R_\mathrm{int}$ = 0.043; $R(F)$ = 0.040, $wR(F^2)$ = 0.110, Flack parameter 0.022(15). Refinement details as for the 375 K structure.

At 240 K: $a$ = 8.4977(3), $b$ = 8.5665(3), $c$ = 18.4299(8) Å, $\beta$ = 98.0931(12)°, $U$ = 3128.25(9) Å$^3$, $\mu$(Mo-K$\alpha$) = 0.659 mm$^{-1}$; 10234 measured reflections, 5538 independent, $R_\mathrm{int}$ = 0.045; $R(F)$ = 0.046, $wR(F^2)$ = 0.124, Flack parameter 0.006(19). Both $\mathrm{BF_4}^-$ anions were disordered by rotation about one B–F bond. The disordered F atoms of the two anions were modelled over three orientations, with 0.50 : 0.25 : 0.25 and 0.40 : 0.30 : 0.30 occupancy ratios. All B–F distances were restrained to 1.39(2) Å, and non-bonded F···F distances within each disorder orientation to 2.27(2) Å. All non-H atoms with occupancy > 0.5 were refined anisotropically.

At 150 K: $a$ = 8.4575(2), $b$ = 8.5233(2), $c$ = 18.3756(4) Å, $\beta$ = 98.2896(13)°, $U$ = 1310.78(5) Å$^3$, $\mu$(Mo-K$\alpha$) = 0.668 mm$^{-1}$; 19914 measured reflections, 5715 independent, $R_\mathrm{int}$ = 0.038; $R(F)$ = 0.031, $wR(F^2)$ = 0.079, Flack parameter −0.009(10). No disorder was detected at this temperature, and no restraints were applied. All non-H atoms were refined anisotropically.

CCDC 158392–158395. See http://www.rsc.org/suppdata/cc/b1/b100995h/ for crystallographic data in .cif or other electronic format.

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