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A stacking spin-crossover iron(II) compound with a large hysteresis†

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An inclusion compound $[Fe(dpp)_2(NCS)_2]\cdot py$ has been prepared and characterized by magnetic and Mössbauer spectral measurements (dpp = dipyrido[3,2-*a*:2′3′-*c*]phenazine and py = pyridine); it shows a spin-crossover behavior with a large hysteresis ($\Delta T_c = 40$ K).

The study of the spin-crossover phenomenon is an important field of magnetochemistry. A variety of iron(II) complexes are known to show a transition from the high-spin state $^5T_2$ ($S = 2$) to the low-spin state $^1A_1$ ($S = 0$) on cooling, upon increasing pressure or by light irradiation.[1–8] Such compounds have attracted much attention since their bistable nature could allow their use as molecular switches in new electronic devices.[9,10] We are interested in investigating the main factors in spin-crossover systems that control abruptness, hysteresis and critical temperature, which are very important for designing molecular switches.

Of the iron(II) systems, $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline) is one of the most throughly studied spin-crossover complexes.[1,11] The influence of a modification of the hydrogen atoms with electron-donating, electron-withdrawing or bulky groups,[1] and by replacing the CH groups with nitrogen atoms has been investigated.[12] However, to our knowledge, no study has been reported so far on the effect of adding an extended aromatic ring. Ligands with extended aromatic rings may be expected to show strong intermolecular π–π interactions to enhance the cooperativity, which has a close relevance to abruptness and thermal hysteresis.[2,3,10] Along this line, we began to use ligands containing a more extended aromatic ring system than phen to study the spin-transition behavior of iron(II) complexes. Here we report the structure and magnetic properties of such a new spin-crossover system $[Fe(dpp)_2(NCS)_2]\cdot py$ (dpp = dipyrido[3,2-*a*:2′3′-*c*]phenazine, py = pyridine).

The complex $[Fe(dpp)_2(NCS)_2]\cdot py$ was prepared by addition of a hot pyridine solution (20 cm^3) of dpp[13] (0.5 mmol) to a hot pyridine solution (80 cm^3) of equimolar $[Fe(py)_4(NCS)_2]$.[14] After filtration, the filtrate was allowed to stand for about 3 months at room temperature to produce the complex as dark violet crystals. All operations were conducted under a nitrogen atmosphere (Found: C, 63.37; H, 3.32; N, 18.83. Calc. for $C_{43}H_{25}FeN_{11}S_2$: C, 63.31; H, 3.09; N, 18.89%).‡

The compound $[Fe(dpp)_2(NCS)_2]\cdot py$ crystallizes in the monoclinic *Pn* space group at room temperature. The crystal structure shows that there is one guest pyridine molecule per iron complex (Fig. 1). Each iron atom is octahedrally co-ordinated to four nitrogen atoms from two dpp bidentate ligands and nitrogen atoms of two NCS ions in a *cis* arrangement. The octahedron geometry is distorted, as Fe–N (CS) bond lengths (2.10 Å on average) are shorter than Fe–N (dpp) (Fig. 1). The Fe–N (dpp) lengths also differ considerably for different dpp ligands (2.17 and 2.23 Å on average). Moreover, the geometric constraints of the bidentate ligands cause significant reduction of the N (dpp)–Fe–N (dpp) bond angles from the ideal 90° value [N(2)–Fe(1)–N(1) 74.1°, N(7)–Fe(1)–N(8) 75.5°]. This distortion of the FeN_6 core from O_h symmetry is also seen in the high-spin phase structure of similar $[FeL_2(NCS)_2]$ (L = phen, bipyridine or 1,4,5,8-tetraazaphenanthrene) complexes.[11,12,16] The NCS groups are almost linear [N(5)–C(19)–S(1) 173.7°], N(6)–C(20)–S(2) 178.0°], whereas the Fe–NC(S) linkages are bent. The two dpp ligands in Fig. 1 are nearly planar, and the largest deviations from the mean planes [C(1)–C(12), N(1)–N(4)] and [C(21)–C(32), N(7)–N(10)] are 0.0378 Å and 0.0292 Å respectively. The dihedral angle between these two planes is 73.0°. Between the nearest $[Fe(dpp)_2(NCS)_2]$ molecules there is a π–π stacking of their dpp ligands with an interplanar distance of 3.50 Å and a dihedral angle of 0.6°, thus forming a column structure along the diagonal of the unit cell (Fig. 2). The solvent pyridine molecule inserts between these columns, with two sets of overlapping dpp ligands around it. The shortest distances from the center of py to the surrounding atoms are 3.452 Å [to C(8′), symmetry transformation $-\frac{1}{2} + x$, $1 - y$, $-\frac{1}{2} + z$] and 3.502 Å [to C(28′), symmetry transformation $-\frac{1}{2} + x$, $1 - y$, $\frac{1}{2} + z$], suggesting a close contact. The dihedral angles between py and the dpp ligands are about 76°.

The temperature dependence of the effective magnetic moment μ_{eff} is illustrated in Fig. 3, showing a $S = 2$ (HS) $\longleftrightarrow$ $S = 0$ (LS) spin-crossover behavior. Fairly abrupt transitions are observed around 123 K in the cooling curve and 163 K in the heating curve, leading to a well shaped hysteresis loop of about 40 K (ΔT_c). This hysteresis feature can be repeated for more than one cycle. The moment at 275 K (5.2 μ_B) is close to the quintet state, while the value at 86 K (1.6 μ_B) is considerably higher than the pure singlet state. It could be due to the presence of some Fe^{III} impurities, which were detected by an EPR signal at liquid-nitrogen temperature. The Mössbauer spectra agree with the magnetic curve. The results show that Fe^{II} ions in $[Fe(dpp)_2(NCS)_2]\cdot py$ at room temperature are in the high-spin state ($\Delta E_q = 2.655$ mm s^{-1}, IS = 0.828 mm s^{-1}, relative to ^{57}Co–Pd) whereas at 80 K they are in the low-spin state ($\Delta E_q = 0.423$ mm s^{-1}, IS = 0.268 mm s^{-1}, relative to ^{57}Co–Pd). A small amount of Fe^{III} (high spin) impurity is present at *ca.* 6 mol% as deduced from analysis of the Mössbauer spectra, an amount which is entirely consistent with the observed effective magnetic moment at 80 K. Note that no $[FeL_2(NCS)_2]$-type spin-crossover compounds have yet shown ΔT_c values larger than 30 K, making $[Fe(dpp)_2(NCS)_2]\cdot py$ a novel example. Until now,

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† *Non-SI unit employed*: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

‡ Crystal data: $C_{43}H_{25}FeN_{11}S_2$, $M = 815.71$, dark violet cubic crystal of dimension 0.23 × 0.28 × 0.34 mm, monoclinic, space group *Pn*, $Z = 2$, $a = 13.381(2)$, $b = 8.708(2)$, $c = 16.301(6)$ Å, $\beta = 104.16(3)°$, $U = 1841.6(9)$ Å^3, $F(000) = 836$, $D_c = 1.471$ g cm^{-1}, μ(Mo-Kα) = 0.573 mm^{-1}, $T = 294$ K. 4202 Reflections collected in the range $1.77 \leqslant \theta \leqslant 25$, 3686 independent data ($R_{int} = 0.06$). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0:[15] $R = 0.0632$, $R' = 0.0845$, goodness of fit = 1.028 for 1704 observed reflections [$I > 2\sigma(I)$]. CCDC reference number 186/837.

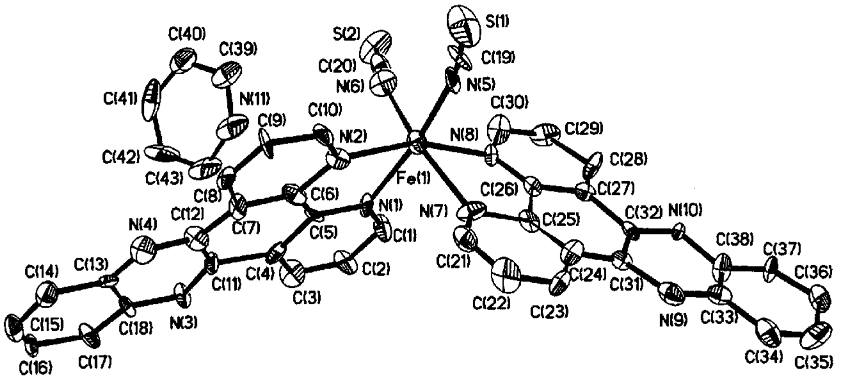

Fig. 1 Molecular structure of $[\mathrm{Fe(dpp)_2(NCS)_2}]\cdot$py. Selected bond lengths (Å) and angles (°): Fe(1)–N(6) 2.090(4), Fe(1)–N(5) 2.104(3), Fe(1)–N(2) 2.165(3), Fe(1)–N(1) 2.186(3), Fe(1)–N(7) 2.227(4), Fe(1)–N(8) 2.237(3), S(1)–C(19) 1.636(4), S(2)–C(20) 1.581(4), N(5)–C(19) 1.114(5), N(6)–C(20) 1.175(5); N(6)–Fe(1)–N(5) 96.4(1), N(6)–Fe(1)–N(2) 99.0(1), N(5)–Fe(1)–N(2) 93.1(1), N(6)–Fe(1)–N(1) 86.1(2), N(5)–Fe(1)–N(1) 167.2(1), N(2)–Fe(1)–N(1) 74.1(1), N(6)–Fe(1)–N(7) 165.8(1), N(5)–Fe(1)–N(7) 87.6(1), N(2)–Fe(1)–N(7) 94.5(1), N(1)–Fe(1)–N(7) 93.1(1), N(6)–Fe(1)–N(8) 90.3(1), N(5)–Fe(1)–N(8) 100.9(1), N(2)–Fe(1)–N(8) 162.3(1), N(1)–Fe(1)–N(8) 91.6(1), N(7)–Fe(1)–N(8) 75.5(1), C(19)–N(5)–Fe(1) 154.3(3), C(20)–N(6)–Fe(1) 149.1(4), N(5)–C(19)–S(1) 173.7(4), N(6)–C(20)–S(2) 178.0(5)

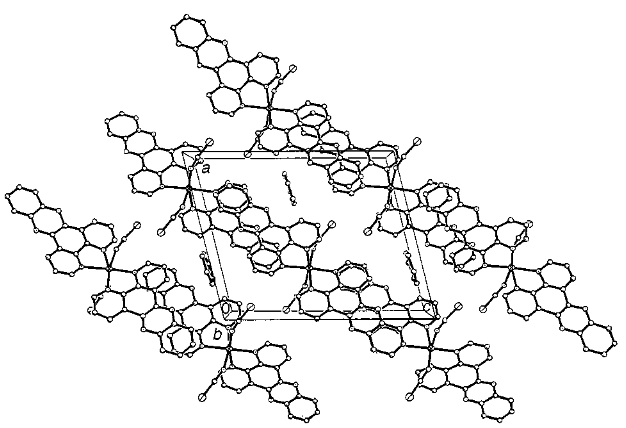

Fig. 2 Crystal packing of $[\mathrm{Fe(dpp)_2(NCS)_2}]\cdot$py

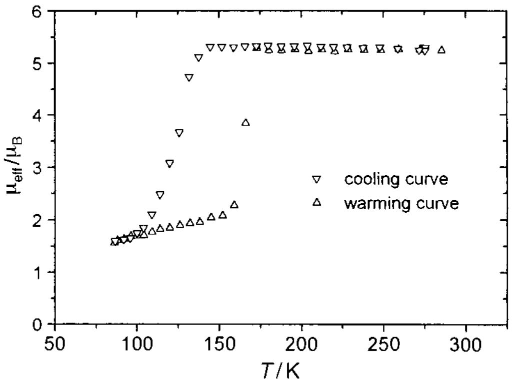

Fig. 3 Temperature dependence of μ_{eff} *versus* T for $[\mathrm{Fe(dpp)_2(NCS)_2}]\cdot$py

the spin-crossover systems with a large hysteresis have been found to contain communication networks of hydrogen bonds or covalent bridges.[1,2,9,17] In our system, only intracolumn π–π stacking and intercolumn van der Waals interactions exist, suggesting that these kinds of supramolecular interactions can also be effective in constructing cooperative spin-crossover systems. Further studies are in progress.

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