## Spin crossover in a heptanuclear mixed-valence iron complex<sup>†</sup>

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The complex  $[Fe^{II}{(CN)Fe^{III}L^5}_6]Cl_2$  consists of a mixedvalence heptanuclear cyanide-bridged unit formed of a Schiffbase pentadentate ligand  $L^5$  and it shows a spin crossover of the peripheral Fe<sup>III</sup> centres.

Mononuclear complexes showing spin crossover (SC), predominantly those of Fe(II), have been studied extensively over a long period and several reviews about this phenomenon have been published.<sup>1</sup> Recently, there has been interest in dinuclear and polynuclear systems where the SC interferes with the magnetic exchange interaction.<sup>2</sup> In addition to numerous dinuclear systems, SC has also been reported for trinuclear, tetranuclear, and some polynuclear systems.<sup>3</sup> Herein we report SC in a mixed-valence heptanuclear cyanide-bridged complex [Fe<sup>II</sup>{(CN)Fe<sup>III</sup>(L<sup>5</sup>)}<sub>6</sub>]Cl<sub>2</sub> formed of a Schiff-base pentadentate blocking ligand L<sup>5</sup>.

The Schiff-condensation of *o*-salicylaldehyde with an aliphatic amine *pet* (1,6-diamino-4-azahexane) at a ratio of 2 : 1 provide the ligand H<sub>2</sub>*salpet* (yellow oil). This ligand is asymmetric, having a propyl- and an ethyl-bridge to the central nitrogen atom: (OH)Ph-CH=N-(CH<sub>2</sub>)<sub>3</sub>-NH-(CH<sub>2</sub>)<sub>2</sub>-N=CH-Ph(OH). Found: C, 70.1; H, 7.12; N, 12.8. Calc. for C<sub>19</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: C, 70.1; H, 7.12; N, 12.9.

The mononuclear precursor [Fe(*salpet*)Cl] was synthesized as follows. A methanol solution of H<sub>2</sub>*salpet* (5 mmol in 15 cm<sup>3</sup>) was combined with a methanol solution of FeCl<sub>3</sub>·6H<sub>2</sub>O (5 mmol in 30 cm<sup>3</sup>) accompanied with a colour change to dark-violet. Then triethylamine (10 mmol) was added. After 30 min of stirring at 50 °C the reacting mixture was cooled to room temperature and a dark-brown crystalline powder precipitated. This was separated by filtration and washed with cold methanol and diethylether. Yield– 85%. Found: C, 54.3; H, 5.10; N, 10.1. Calc. for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>FeCl ( $M_r = 414.69$  g mol<sup>-1</sup>) C, 55.0; H, 5.10; N, 10.1%. IR (KBr,  $\tilde{\nu}$ /cm<sup>-1</sup>): N–H, 3230; C=N, 1631, 1620, 1597. UV-Vis (Nujol,  $\tilde{\nu}$ /cm<sup>-1</sup>) 18000, 24000, 27500, 40000. According to the magnetic susceptibility, magnetization, Mössbauer spectra, and metal– ligand distances this complex is high-spin (S = 5/2).

The mononuclear precursor dissolved in methanol (1 mmol in 50 cm<sup>3</sup>) was combined with a methanol-water solution of  $K_4[Fe(CN)_6]\cdot 3H_2O$  (0.167 mmol in 10 cm<sup>3</sup> of CH<sub>3</sub>OH-H<sub>2</sub>O =

1 : 1). The colour changed from red-violet to blue. The mixture was stirred for 2 h at 50 °C and left to evaporate spontaneously for several days at room temperature. Blue polycrystalline powder was separated by filtration. Yield–90%. Found: C, 55.2; H, 5.01; N, 13.0. Calc. for C<sub>120</sub> H<sub>126</sub>N<sub>24</sub>O<sub>12</sub>Fe<sub>7</sub>Cl<sub>2</sub> ( $M_r = 2558.26 \text{ g mol}^{-1}$ ) C, 56.3; H, 4.96; N, 13.1%. IR (KBr,  $\tilde{\nu}/\text{cm}^{-1}$ ): C=N, 2078 (unsplit).<sup>4</sup> The complex exhibits blue colour, typical of the molecular Prussian-blue analogues; the first absorption occurs at 17000 cm<sup>-1</sup>. The hexacoordination of Fe<sup>II</sup> by CN–Fe<sup>III</sup> is also confirmed by the IR spectra (no splitting of the C≡N band,  $\tilde{\nu} = 2078 \text{ cm}^{-1}$ ) and Mössbauer spectra (the area ratio Fe<sup>III</sup> : Fe<sup>II</sup> ~ 6 : 1, *i.e. ca* 14% of Fe<sup>II</sup> at r.t.). The complex shows a molecular peak in the ESI-mass spectrum: m/z ( $K^{2+}/2$ ) = 1244 g mol<sup>-1</sup>, which matches the composition [K]Cl<sub>2</sub>. Molar mass of [ $K^{2+1}$ ] is 2488 g mol<sup>-1</sup>. K is the heptanuclear molecular dication [Fe<sup>III</sup> {(CN)Fe<sup>III</sup> (*salpet*)}<sub>6</sub>]<sup>2+</sup>.

Single-crystal X-ray diffraction studies of  $[Fe^{II}({CN}-Fe^{II}(salpet))_{6}]Cl_{2}$ ; (hereafter 1) at room temperature revealed the presence of a heptanuclear complex cation  $[Fe^{II}({CN})Fe^{III}(salpet)]_{6}]^{2+}$  and two chloride anions, which are disordered among three positions. The heptanuclear species has an inversion centre (Fig. 1). The Fe1–C bond lengths are in the range 1.879(9)-1.932(10) Å, Fe<sup>II</sup>–C–N bond angles are in the range 177.3(8)-179.3(8)°, which deviate only slightly from linearity; these are similar to only reported  $\{Fe^{II}Fe^{III}_{6}\}$  type complex  $[Fe^{II}({CN})Fe^{III}(saldptm)]_{6}]Cl_{2}\cdot17.25CH_{3}OH$  (saldptm = bis(3-(salicylideneamino)propyl)methylamine, refcode: EKIJUD).<sup>6</sup> The cyanide C–N bond distances are in the range 1.128(9)–1.144(9) Å, and they match other complexes with bridging cyanide bonds.<sup>6,7</sup>



Fig. 1 X-ray structure of the heptanuclear complex  $[Fe^{II}{(CN)Fe^{III}(salpet)}_{\delta}]^{2+}$  (hydrogen atoms omitted for clarity).

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**Table 1** Mössbauer-spectra parameters for the  ${Fe^{II}Fe^{III}}_{6}$  complex 1<sup>a</sup>

T/K	Centre	$\Delta E_Q/\mathrm{mm~s^{-1}}$	$\delta/\mathrm{mm~s}^{-1}$	Area/%	$\chi_{\rm HS}$
20	LS-Fe(III)	2.514	0.103	21.5	0.73
	HS-Fe(III)	1.006	0.297	58.9	
	LS-Fe(II)	[0.15]	-0.057	19.6	
78	LS-Fe(III)	2.475	0.103	29.2	0.66
	HS-Fe(III)	0.951	0.312	57.8	
	LS-Fe(II)	[0.15]	-0.100	13.0	
120	LS-Fe(III)	2.466	0.104	25.3	0.70
	HS-Fe(III)	0.979	0.285	60.8	
	LS-Fe(II)	[0.15]	-0.063	13.9	
150	LS-Fe(III)	2.433	0.100	23.8	0.72
	HS-Fe(III)	0.986	0.275	61.5	
	LS-Fe(II)	[0.15]	-0.019	14.7	
180	LS-Fe(III)	2.452	0.050	12.5	0.85
	HS-Fe(III)	0.901	0.270	73.1	
	LS-Fe(II)	[0.15]	-0.175	14.4	
200	LS-Fe(III)	2.412	0.043	7.7	0.91
	HS-Fe(III)	0.937	0.246	78.6	
	LS-Fe(II)	[0.15]	-0.099	13.7	
300	LS-Fe(III)	_		0	1.00
	HS-Fe(III)	0.876	0.201	72.2	
	LS-Fe(II)	0.154	-0.162	27.8	

<sup>*a*</sup> Estimate for the high-spin mole fraction of Fe(III):  $x_{HS} = A_{HS}/(A_{HS} + A_{LS})$  [under the hypothesis of uniform Debye–Waller factors].

The Fe<sup>III</sup>–N–C bond angles of 165.3(8)–173.8(6)° deviate more from linearity that the analogous bond angles in EKIJUD,<sup>6</sup> but they span the range 150–180° for other complex with bridging cyanide ligands.<sup>7</sup> The distances between Fe<sup>II</sup> and Fe<sup>III</sup> atoms are 5.026(3) (Fe1···Fe4), 5.045(3) (Fe1···Fe2), and 5.055(2) (Fe1···Fe3) Å. The geometry around the peripheral Fe<sup>III</sup> ions is distorted due the nature of *salpet* pentadentate ligand. The bond distances between peripheral Fe<sup>III</sup> and donor atoms are in the range 2.013(10)-2.058(9) Å for Fe<sup>III</sup>–N(cyanide), 1.823(10)-1.960(6) Å for Fe<sup>III</sup>–O(phenolate), 2.020(13)-2.161(9) Å for Fe<sup>III</sup>–N(amine), and 1.832(15)-2.110(8) Å for Fe<sup>III</sup>–N(imine), respectively. However, one pair of Fe<sup>III</sup>–N(cyanide) bonds in *trans* position is shorter than the remaining pairs which indicates that the crystallographic centre Fe4 is more close to the LS state (s = 1/2).

The Mössbauer spectra for the heptanuclear complex (Fig. 2, Table 1) taken at T = 78 K show a coexistence of the low-spin Fe(III) [29%,  $\Delta E_Q = 2.47$ ,  $\delta = 0.10$ ] and of the high-spin Fe(III) [58%,  $\Delta E_Q = 0.95$ ,  $\delta = 0.31$ ], along with the presence of the low-spin Fe(II) [13%,  $\Delta E_Q = 0.15$ ,  $\delta = -0.10$ ]. The Mössbauer parameters are in mm s<sup>-1</sup> (calibrated to  $\alpha$ -Fe at r.t). The central Fe(II) centre remains low-spin over all temperatures studied (20– 300 K). On heating the area-fractions associated with individual quadrupole doublets of six peripheral Fe(III) centres alter in favour of the high-spin Fe(III); the { $\Delta E_Q$ ,  $\delta$ } parameters stay almost constant. This is an unambiguous proof that thermally-induced spin crossover occurs. At T = 200 K the low-spin fraction of Fe(III) almost disappears (less than 8%) and at room temperature it is below a threshold of detection.

Magnetic susceptibility measurements were done using a SQUID magnetometer (Quantum Design) at B = 0.1 T between T = 2 K and 300 K. Raw susceptibility data were corrected for underlying diamagnetism using the set of Pascal constants:  $\chi_{dia} = -18.0 \times 10^{-9}$  m<sup>3</sup> mol<sup>-1</sup> (SI units). The effective magnetic moment (Fig. 3) shows a gradual decrease from the value of  $\mu_{eff} = 14.3 \,\mu_B$  at T = 300 K to  $\mu_{eff} = 11.7 \,\mu_B$  at T = 100 K. Below this temperature



**Fig. 2** Mössbauer spectra at different temperatures for the heptanuclear  $\{\text{Fe}^{II}\text{Fe}^{III}_{6}\}$  complex. From top to bottom: T = 20, 78, 120, 150, 180, 200, and 300 K.



Fig. 3 Magnetic functions for the heptanuclear complex: left—temperature dependence of the effective magnetic moment; right—field dependence of the magnetization (dashed lines are guides for eyes).

the effective magnetic moments stays approximately constant but for T < 30 K it drops down. Six uncoupled Fe(III) centres with the spins s = 5/2 provide a high-temperature limit of  $\mu_{\text{eff}}/\mu_{\text{B}} = g[6s(s + 1)]^{1/2} = 14.5$ . Assuming 4 HS and 2 LS centres ( $x_{\text{HS}} = 0.67$ ), the theoretical value of  $\mu_{\text{eff}} = 12.1 \ \mu_{\text{B}}$  is close to that observed around 100 K. The central Fe(II) coordinated by six cyano ligands stays low-spin (s = 0) and it is magnetically silent. Magnetization taken at 2 K saturates to N > 16 unpaired electrons that probably refer to 3HS+3LS (N = 18).

As the Mössbauer spectra show a coexistence of the lowspin and high-spin Fe(III) centres even at T = 20 K, a more elaborated spin crossover model needs to be developed. In the present case of six magnetoactive Fe(III) centres we are left with seven referential (electronic) states: LLLLLL, LLLLLH (6×), LLLLHH (15×), LLLHHH (20×), LLHHHH (15×), LHHHHH (6×), and HHHHHH separated by six  $\Delta_i$  differences. While the first reference state (six centres of S = 1/2) involves  $2^6 = 64$  magnetic energy levels, the last one (six centres of S = 5/2) involves  $6^6 =$ 46656 magnetic energy levels. Therefore the partition function not only contains a tremendous number (69952) of different terms, but also a large number of parameters ( $\Delta_i$ ,  $g_i$ , and  $J_i$ )

$$Z(B_k) = \sum_{N=0}^{6} {\binom{6}{N}} \cdot \sum_{i=1}^{(2^{6-N} \cdot 6^N)} \exp[-(\Delta_0 + \dots + \Delta_N + \varepsilon_{[L^{6-N} H^N]_{i,k}})/kT]$$

The detected observables (magnetization, magnetic susceptibility, high-spin mole fraction, heat capacity) will involve all these parameters. It is not a realistic target to fix these parameters reliably using the data which are presently available. The estimate that at T = 78 K the complex under study contains *ca* 58% of the high-spin Fe(III) fraction could result from a manifold occupation of the reference states (LLLLLL, LLLLH, LLLLHH, LLLHHH, LLHHHH, LHHHHH, and HHHHHH).<sup>8</sup> This is the raison d'etre why the refinement of the structure cannot reach a better *R*-factor.

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## Notes and references

‡ *Crystallographic data*: X-ray single-crystal data for **1** were collected at room temperature using Oxford Diffraction Gemini R CCD diffractometer with graphite-monochromated Mo-Kα radiation ( $\lambda = 0.7107$  Å). The structure of [Fe<sup>II</sup>{(CN)Fe<sup>III</sup>(*salpet*)}<sub>6</sub>]Cl<sub>2</sub> was solved and refined by SHELX-97 package.<sup>5</sup> Chloride anions are disordered in three positions (one is special position). Crystal data for [Fe<sup>II</sup>{(CN)Fe<sup>III</sup>(*salpet*)}<sub>6</sub>]Cl<sub>2</sub>: C<sub>120</sub>H<sub>126</sub>Cl<sub>2</sub>Fe<sub>7</sub>N<sub>24</sub>O<sub>12</sub>, monoclinic  $P\overline{1}$ , a = 14.443(3), b = 14.480(3), c = 14.842(3) Å,  $\alpha = 105.15(3)$ ,  $\beta = 105.21(3)$ ,  $\gamma = 92.04(3)^{\circ}$ , V =2873.0(10) Å<sup>3</sup>, Z = 1,  $D_c = 1.479$  g cm<sup>-3</sup>,  $\mu = 0.978$  mm<sup>-1</sup>, F(000) =1326, T = 293(2) K,  $2\theta_{max} = 26.4^{\circ}$  (-18  $\leq h \leq 17$ ,-18  $\leq k \leq 18$ ,-16  $\leq l \leq$ 18). Final results (for 692 parameters and 277 restraints) were  $R_1 = 0.1153$ and  $wR_2 = 0.3098$  for 4122 reflections with  $I > 2\sigma(I)$ , and  $R_1 = 0.2325$ ,  $wR_2 = 0.3482$  and S = 1.033 for all 11646 reflections. Reference number is CCDC 633798.

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- 8 Averaged Fe–N (Fe–O) distances in the heptanuclear complex at room temperature are shorter than those in the mononuclear high-spin complex: 2.119 (1.927) versus 2.147 (1.943) Å.