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Isomeric Fe(II) MOFs: from a diamond-framework spin-crossover material to a 2D hard magnet†

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Two Fe(II) coordination polymers formed from isomeric ligands give a diamond-like 3D network exhibiting a gradual SCO and a 2D hard magnet with a large coercive field.

Molecule-based magnetic materials are being investigated for potential applications in fields such as molecular switches, magnetic refrigeration, data storage, and quantum computing.^{1–5} Coordination complexes dominate the field and a large number of magnetic materials have thus been prepared. Although many aspects of their magnetic properties can be rationalized using magnetic models developed for conventional systems, there are some unsolved issues⁶ and certain phenomena such as spin-crossover (SCO),^{5,7} magnetochiral dichroism (MChD)^{8,9} and magnetic semiconductivity^{10–13} are unique to molecule-based systems. While several orbital models describing the nature of the magnetic interactions have been suggested,⁵ as a general rule the much sought-after ferromagnetic coupling is favoured by the presence of orthogonal “magnetic orbitals”,¹⁴ and long-range ordering is promoted by short metal-to-metal electronic pathways.⁵

In a family of 1D chains comprised of $L_2Fe(II)$ complexes (Scheme 1) linked by pyrazine and bipyridine bridges¹⁵ we were able to show that the magnetic coupling was moderated by the electronic effects of ligand substituents X, but the magnitude and nature of these couplings was limited by our complex design. We thus looked to systems which incorporate a bridging ligand and particularly those which would promote orthogonal arrangement of neighbouring units. We consider the pyridine-conjugated Schiff-base systems L^1 or L^2 to be prototypical in this role, but surprisingly no complexes of these ligands have been reported. Here we show that they readily give stable magnetic MOF materials with Fe(II); $[FeL^1_2]_n$ is a diamond-like 3D framework displaying a gradual spin-crossover while

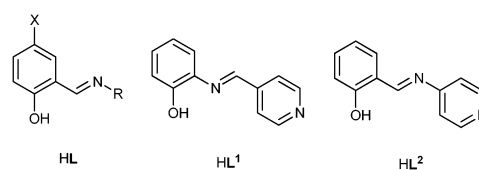
its isomer $[FeL^2_2]_n$ is a 2D framework and a rare example of a molecule-based hard magnet.

Condensation of 2-aminophenol and isonicotinaldehyde in methanol gave HL^1 in high purity.¹⁶ Reaction of the sodium salt with $[FeCl_2(THF)_{1.5}]^{17}$ gave brown $[FeL^1_2]_n$. Single crystals of $[FeL^1_2] \cdot 1\frac{1}{4}(H_2O) \cdot \frac{1}{2}(MeOH)$ were grown from MeOH.†

The crystal contains two independent Fe(II) centres each of which are coordinated by two phenoxymine N–O chelates and two pyridine N atoms from adjacent units [Fig. 1(a)]. The latter occupy *cis* coordination sites with N(4)–Fe(1)–N(4') and N(2)–Fe(2)–N(2') of 84.5(2) and 89.7(2)° respectively. As a result each Fe centre has four nearest neighbours at *ca.* 7.58 and 7.93 Å arranged in a distorted tetrahedron and the extended network is diamond-like [Fig. 1(b)].

There have been various mentions of the unstable Schiff-base HL^2 in the literature, but characterizing data has been presented for it only recently.¹⁸ We found that this compound could be synthesised in high yield by heating salicylaldehyde and 4-aminopyridine to reflux in dry toluene under an inert atmosphere in a Soxhlet extractor fitted with a CaH_2 filled thimble. Treatment of the lithium salt with $[FeCl_2(THF)_{1.5}]$ in dry methanol gave analytically pure and air stable $[FeL^2_2]$ in high yield; the first complex reported of L^2 or of any similar 4-aminopyridine Schiff-base. Single crystals were grown from MeOH/THF (1 : 1).†

Fig. 2(a) shows the repeat unit of $[FeL^2_2]$ which contains one Fe centre. Similar to the situation for $[FeL^1_2]$ each Fe(II) is coordinated by two bidentate N–O ligands and two pyridines of adjacent units, but in contrast the configuration in $[FeL^2_2]$ is all-*trans*. The geometry is close to octahedral with chelate N(1)–Fe(1)–O(1) angle of 85.24(14)° and other *cis* angles close to 90°. These molecular units are assembled *via* pyridine coordination to give a planar rhombic array of Fe atoms [Fig. 2(b)] with Fe–Fe–Fe angles of 83.93 and 97.07°. In contrast to L^1 the rigid structure of L^2 dictates that nearest

Scheme 1 Schiff-base proligands; HL^1 and HL^2 are isomeric.

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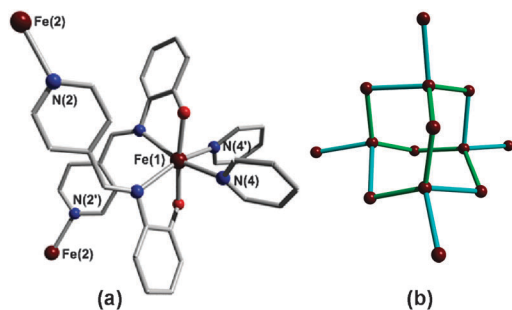


Fig. 1 X-ray structure of $[\text{FeL}^1_2] \cdot 1\frac{1}{4}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{MeOH})$: (a) the complex unit at Fe(1) [Fe(2) is similar]; (b) the corresponding diamond-like network with Fe–Fe distances of 7.93 Å (turquoise) and 7.58 Å (green). Hydrogen atoms omitted for clarity.

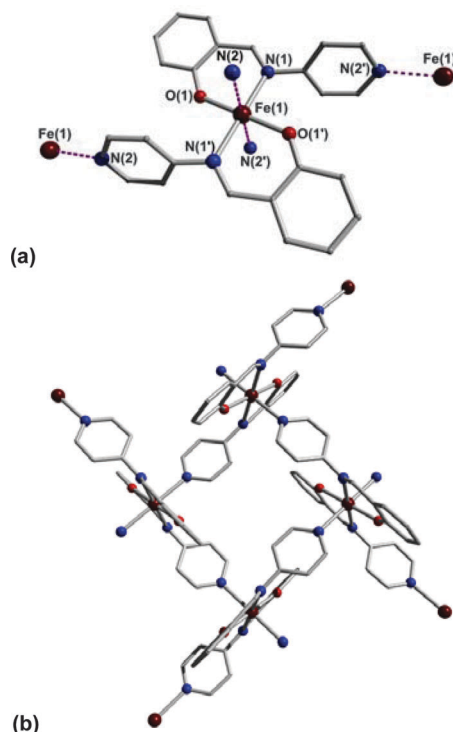


Fig. 2 X-ray structure of $[\text{FeL}^2_2]$: (a) the repeat unit; (b) 2D array of orthogonal complexes. Hydrogen atoms omitted for clarity.

neighbour coordination units (Fe···Fe distance 7.44 Å) are arranged almost orthogonally; the angle between xy planes [*i.e.* Fe(1), N(1,1'), O(2,2')] of adjacent coordination units is *ca.* 86.0°. These xy planes all form an angle of *ca.* 72.0° to the Fe atom plane. The mutual arrangement of the layers is described in ESI.

The curve of molar magnetic susceptibility (χ_M) \times temperature (T) against T for $[\text{FeL}^1_2]$ is shown in Fig. 3. The general form of the data indicates that the Fe(II) ion undergoes a spin state transition as the temperature changes. The $\chi_M T$ increases sharply from 2 K to 25 K, likely due to a zero field splitting, but then rises more gradually to a value of *ca.* 2.90 cm³ K mol^{−1} at 320 K. This value is lower than expected if all the Fe(II) centres were in the high spin state (>3.0 cm³ K mol^{−1} since Fe(II) typically has g -values significantly greater than 2). Therefore the spin transition is incomplete. While this behaviour could result from

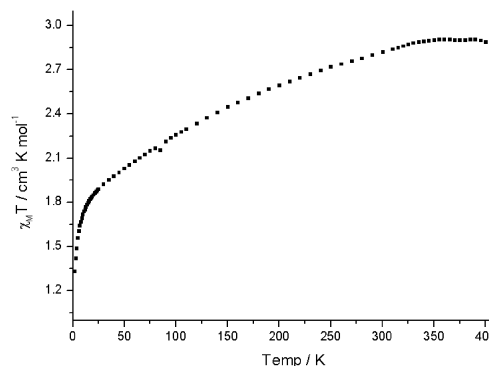


Fig. 3 $\chi_M T$ vs. T curve of $[\text{FeL}^1_2]$ measured at 1000 Oe.

antiferromagnetic interactions, the Mössbauer spectrum is consistent with a mixture of spin states, with low spin ($S = 0$, 65%) and high spin ($S = 2$, 35%) Fe(II) at 80 K (see ESI).^{19,20} As the bulk magnetic data gives a value for $\chi_M T$ of 2.16 cm³ K mol^{−1} at 80 K, this would correspond to an average g value of 2.87, which is certainly high but not unreasonable for Fe(II) in distorted octahedral environments (*vide infra*).

Spin crossover Fe(II) systems in imine N -rich environments are well known, and sharp transitions are frequently observed in mononuclear complexes and some 1D chains.^{7,21–23} Here the gradual nature of the spin state change is probably due in the main to constraints imposed on structural changes by the 3D framework, and possibly in part to the coexistence of two slightly different Fe(II) environments.

The magnetic properties of $[\text{FeL}^2_2]$ are strikingly different, as shown in the plots of χ_M vs. T (see ESI) and $\chi_M T$ vs. T (Fig. 4). In the high temperature regime the magnetic susceptibility data obey the Curie–Weiss law with $C = 2.93$ cm³ K mol^{−1} and $\Theta = +9.9$ K. $\chi_M T$ is *ca.* 3.17 cm³ K mol^{−1} at 300 K, which is consistent for an isolated high spin Fe(II) centre with $g > 2.0$. This $\chi_M T$ value rises dramatically from *ca.* 10 K and reaches a maximum of 44.4 cm³ K mol^{−1} at *ca.* 5 K. This suggests that $[\text{FeL}^2_2]$ undergoes long range magnetic ordering at that temperature. This was confirmed by measurements on warming the sample after cooling in zero field (ZFCW), followed by measuring on cooling in a field (FCC) from 2–25 K using a field of 1000 Oe. These two curves diverge at a T_C of 5.3 K (Fig. 5).

The hysteresis curve for $[\text{FeL}^2_2]$ (Fig. 6) at 1.8 K indicates magnetic saturation at *ca.* 2000 Oe. While the coercive field for

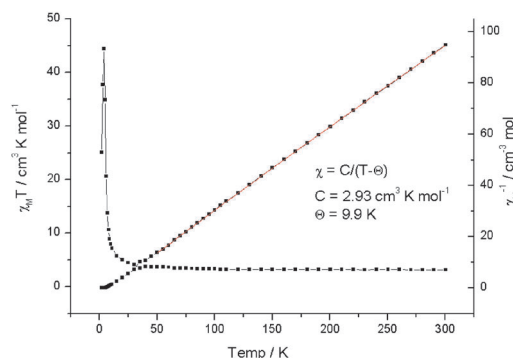


Fig. 4 $\chi_M T$ and χ_M^{-1} vs. T for $[\text{FeL}^2_2]$ measured at 1000 Oe.

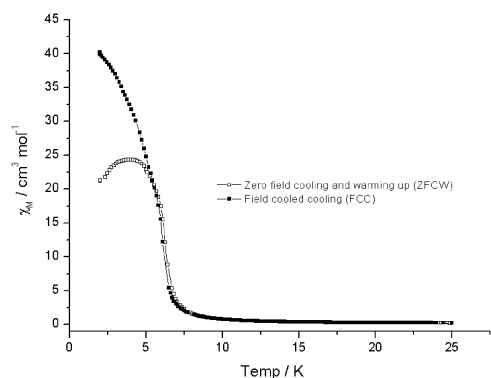


Fig. 5 ZFCW and FCC M vs. T curves for $[\text{FeL}^2]$ measured at 1000 Oe.

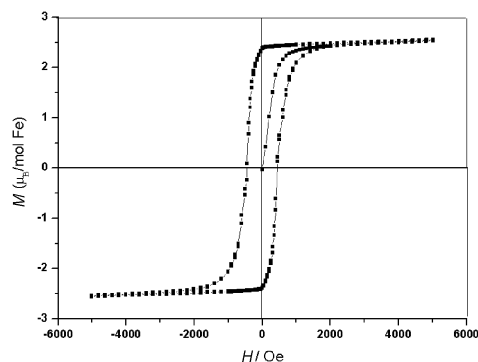


Fig. 6 M vs. H curve at 1.8 K for complex $[\text{FeL}^2]$ showing ferromagnetic hysteresis.

the compound of 467 Oe is smaller than for some room temperature permanent magnets such as SmCo_5 (44 kOe) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (19 kOe), such hard magnetism even at low temperatures is unusual in molecular systems where a few examples of very large coercivities have been observed.^{24,25}

In conclusion, while the more flexible L^1 system gives a diamond-like 3D network exhibiting gradual spin-crossover, the geometry of the now readily available L^2 favours a 2D framework and orthogonal arrangement of adjacent metal centres, leading to^{5,26–30} a rare molecular example of a hard ferromagnet. While these are the first complexes of either ligand, L^1 and L^2 can be used with a range of metals. The behaviour and versatility of L^2 in particular gives us the opportunity to modulate steric and electronic properties to affect intermetallic coupling and inter-layer interactions to further understand the structure/property relationships and to pursue higher T_C systems.

Notes and references

† Crystal data for $[\text{FeL}^1] \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{MeOH})$: $\text{C}_{24}\text{H}_{22.50}\text{FeN}_4\text{O}_{3.75}$, $M = 488.82$, tetragonal, $a = 19.3307(2)$ Å, $b = 19.3307(2)$ Å, $c = 27.7612(8)$ Å, $V = 10373.7(3)$ Å³, $T = 100(2)$ K, space group $I\bar{4}2d$, $Z = 16$, 23 628 reflections measured, 3577 independent reflections ($R_{\text{int}} = 0.0795$). The final R_1 values were 0.0553 ($I > 2\sigma(I)$).

The final $wR(F^2)$ values were 0.1291 ($I > 2\sigma(I)$). The final R_1 values were 0.1068 (all data). The final $wR(F^2)$ values were 0.1407 (all data).

Crystal data for $[\text{FeL}^2]$: $\text{C}_{24}\text{H}_{18}\text{FeN}_4\text{O}_2$, $M = 450.27$, orthorhombic, $a = 9.9499(6)$ Å, $b = 11.0634(5)$ Å, $c = 19.3835(9)$ Å, $V = 2133.73(19)$ Å³, $T = 100(2)$ K, space group $Pbca$, $Z = 4$, 11 020 reflections measured, 2026 independent reflections ($R_{\text{int}} = 0.1488$). The final R_1 values were 0.0830 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1831 ($I > 2\sigma(I)$). The final R_1 values were 0.1027 (all data). The final $wR(F^2)$ values were 0.1936 (all data).

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