ChemComm

Crystal structure and metamagnetic property of a 2-D layered complex, $[Fe^{II}(N_3)_2(pyz)]_n$ (pyz = pyrazine)†

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Received (in Cambridge, UK) 27th June 2000, Accepted 2nd October 2000
First published as an Advance Article on the web

In crystals of $[Fe^{II}(N_3)_2(pyz)]_n$ (pyz = pyrazine), two adjacent Fe^{2+} ions are bridged *via* two μ-1,1-N_3^- ligands along the *c* axis to afford ferromagnetically coupled linear chains, which are bridged *via* μ-pyrazine ligands along the *b* axis to afford 2-D antiferromagnetically coupled layers; these competitive magnetic couplings lead to the occurrence of metamagnetic behavior.

Recently, several groups have shown interest in 1-D[1a,2] and 2-D[1b,c,3,4] molecular-based magnetic materials with alternating ferro- and antiferro-magnetic interactions, which may lead to the occurrence of metamagnetic behavior. The azido ligand, N_3^-, is a good candidate for designing these materials owing to its versatile bridging mode, *i.e.* μ-1,3, μ-1,1 and (rarely) μ-1,1,1. The former can couple spins antiferromagnetically, while the latter two can usually couple spins ferromagnetically.[5] The utilization of combinations of azido and other nitrogen-containing ligands (such as bipyrimidine,[1b,c,3] 2,2′-bipyridine,[1a] 4,4′-dimethylbipyridine,[2] *N,N*-diethyl-*N′*-methylethylenediamine,[4] *etc.*) had led to several such materials. Following the above strategy, Miller and coworkers prepared a 2-D layered complex $Mn(N_3)_2(pyz)$ (pyz = pyrazine) **1**,[6] which exhibited ferro- and antiferro-magnetic interactions *via* μ-1,1-N_3^- and μ-pyz ligands, respectively. However, this complex did not show any indication of metamagnetic behavior. We attribute this to the rather weak magnetic interactions and very low Neél temperature, T_N (≈ 2 K). Substituting Mn^{2+} ions with Fe^{2+} ions, we have succeeded in isolating single crystals of $[Fe^{II}(N_3)_2(pyz)]_n$ **2** by a slow diffusion method.‡ Although **1** and **2** are almost isostructural, the magnitude of both the magnetic interactions and T_N of **2** is significantly increased by *ca.* one order with respect to **1** and metamagnetic behavior was observed.

In crystals of **2**,§ each Fe^{2+} ion resides on the symmetry center of a tetragonally elongated octahedron: the basal plane is defined by four azido-N atoms, and the two axial sites are occupied by two pyz-N atoms (Fig. 1). The Fe–N1 and Fe–N2 bond distances are 2.196(6) and 2.180(3) Å, respectively. The former is slightly shorter than Fe^{II}–N_{pyz} [2.246(2) Å] reported previously,[7] while the latter is in the range of those found in two ferrous azide complexes [2.132(2)–2.240(2)[1a] and 2.118(2)–2.201 (3) Å[1c]]. According to bond valence sum (BVS) theory,[8] the BVS around each iron atom is estimated as 2.2, in accord with the valence of the Fe^{2+} ion. In the layer, two adjacent iron atoms are bridged *via* two μ-1,1-N_3^- ligands along the *c* axis to afford an extended linear chain. The Fe–N2–Fe bond angle is 99.8(2)°, and the shortest Fe···Fe distance is 3.336 Å. The N2, N3 and N4 atoms of the azido ligand are almost collinear with a bond angle of 179.5(6)°. Interestingly, the azido ligands do not reside in the Fe–N–Fe–N plane but form alternating angles of *ca.* 16° up and down to the plane, respectively, leading to the length of the *c* axis being twice the shortest Fe···Fe distance. The chains are bridged *via* μ-pyz ligands along the *b* axis to afford an extended 2-D layer. The pyz ring is vertical to this layer, thus the shortest Fe···Fe distance *via* μ-pyz ligand is equal to the length of the *b* axis (7.201 Å). The layers are arranged in an orderly manner along the *a* axis to complete the solid-state structure of the crystal (see Graphical abstract). It is noticeable that two adjacent layers are displaced by half a repeat unit along the *b* axis, which effectively prevents steric hindrance between the interlayer azido ligands and favors the closer packing. The shortest interlayer Fe···Fe distance is 8.408 Å.

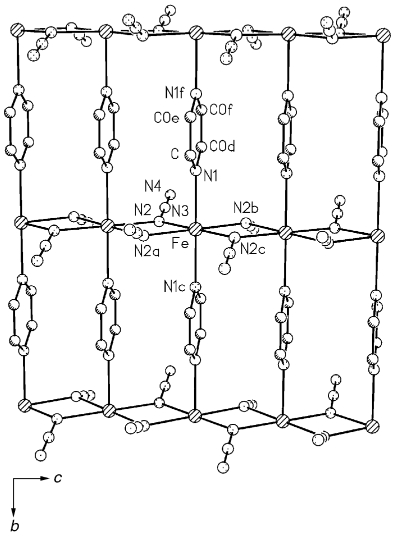

Fig. 1 Layer structure of $[Fe^{II}(N_3)_2(pyz)]_n$ (view along *a* axis). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe–N1 2.196(6), Fe–N2 2.180(3), N1–C 1.334(5), C–C0e 1.385(9), N2–N3 1.201(7), N3–N4 1.125 (6); N1–Fe–N2 90.79(7), N2–Fe–N2a 80.15 (19), C–N1–C0d 115.5(5), C–N1–Fe 122.3(3), N1-C-C0e 122.3(3), N2–N3–N4 179.5(6), N3–N2–Fe 127.97(10) (symmetry codes: a −*x*, *y*, 0.5−*z*; b *x*, −*y*, *z*−0.5; c −*x*, −*y*, −*z*; d −*x*, *y*, *z*; e *x*, 1−*y*, −*z*; f −*x*, 1−*y*, −*z*).

The dc variable temperature magnetic susceptibility of **2** was measured in the range 2–298 K at H_{dc} = 1 T. The value of χ_mT at room temperature is *ca.* 4.1 emu K mol^{-1} (Fig. 2), which is larger than the expected spin-only χ_mT value (3.0 emu K mol^{-1}) for an Fe^{2+} ion but similar to that of another ferrous azide complex (4.2 emu K mol^{-1}).[1c] This is mainly due to the fact that the orbital contribution is not negligible.[9] Upon cooling, χ_mT increases rapidly to a maximum value of 8.18 emu K mol^{-1} at 30.8 K, which is a typical feature of ferromagnetic interactions. Upon further cooling to 2 K, χ_mT drops sharply, indicative of the occurrence of antiferromagnetic interactions. Owing to lack of theoretical models, we were unable to perform a global fit. However, an estimation was made by fitting χ_m data above 30 K to the 1D-Fisher model with molecular field corrections.[10] The results are J/k = 6.1(2) K, zJ'/k = −1.19(3) K, g = 2.12(2) with a final agreement factor $R = 1.3 \times 10^{-4}$ [$R = \sum(\chi_m^{obs} - \chi_m^{calc})^2/\sum(\chi_m^{obs})^2$], in which the Landé-*g* factor is identical to that of a ferrous pyrazine complex,[7] and J and zJ' correspond to the ferro- and antiferro-magnetic interactions *via* μ-1,1-N_3^- and μ-pyz ligands, respectively. These two values are much larger than those of **1** [0.61(4) and −0.48(3) K, respectively].[6]

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† Electronic supplementary information (ESI) available: ac susceptibility measurements. See http://www.rsc.org/suppdata/cc/b0/b005137n/

DOI: 10.1039/b005137n

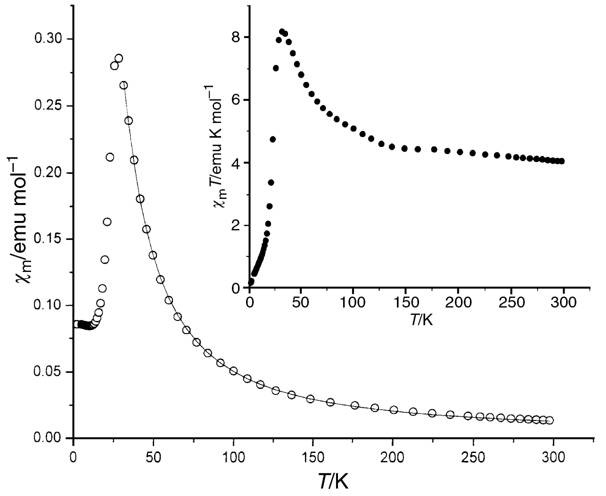

Fig. 2 Dc χ_m *vs.* T plot for $[Fe^{II}(N_3)_2(pyz)]_n$ at H_{dc} = 1 T over the temperature range 2–298 K. The solid line corresponds to the fit to the theoretical expression. The inset shows the χ_mT *vs.* T plot.

Attempts to extend this model to the lower temperature region were not successful. The reason is that the 1D-Fisher model is an isotropic Heisenberg model and neglects zero-field-splitting (ZFS) effects as well as any extended 3-D ordering. However, ours may be best described as an anisotropic Ising model, and ZFS effects and 3-D ordering are operative below 30 K.

ac Susceptibilities were also measured with no spin-glass behavior being observed. All real parts under different frequencies show a common broad maximum at *ca.* 27 K, indicative of short-range antiferromagnetic ordering. The actual long-range ordering temperature, T_N, may be slightly lower than 27 K.[6] Although **2** shows global antiferromagnetic behavior, there are very important ferromagnetically coupled linear chains comprised of Fe^{2+} ions *via* μ-1,1-N_3^- ligands along the *c* direction. These competitive couplings imply the occurrence of metamagnetic behavior.

The isothermal magnetization curve performed at 1.8 K over the applied field range 0–6 T shows a characteristic sigmoidal form (Fig. 3), which is a typical feature of metamagnetic behavior. Upon decreasing the applied field, the magnetization curve decreases along a different route (see inset to Fig. 3), leading to a small remnant magnetization (RM) at H = 0 T, *ca.* 260 emu G mol^{-1}. The existence of the small RM is in accord with the nonzero χ_m (*ca.* 0.086 emu mol^{-1}) below 10 K (Fig. 2), which was also found in other molecular-based metamagnets.[1c,4,11] We attribute the RM and nonzero χ_m (< 10 K) to the presence of spin canting, which is confirmed by the fact that the magnetization is hard to be saturated (Fig. 3, only *ca.* 70% of saturation is attained at a very high field, 6 T).

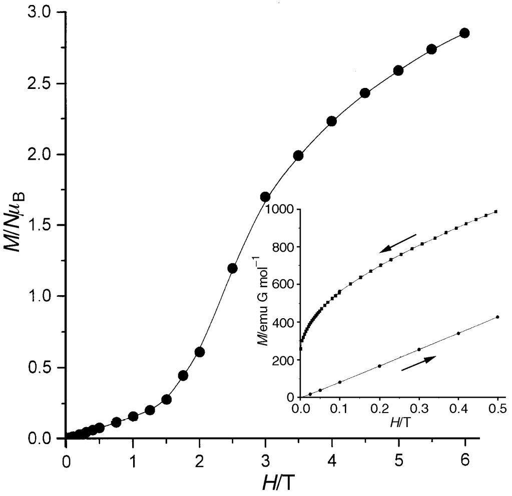

Fig. 3 Isothermal magnetization curves for $[Fe^{II}(N_3)_2(pyz)]_n$ at T = 1.8 K over the applied field range 0–6 T.

The canting of spin may originate from ZFS effects, which often occur in ferrous-ion-containing materials.[7,9] However, the origin of the metamagnetic behavior is still under investigations in our lab.

This work was supported by grants (Nos. 29871003 and 29733080) from the National Natural Science Foundation of the People's Republic of China. We gratefully acknowledge Prof. Song Gao in the Department of Chemistry, Peking University for magnetic measurements and helpful discussions.

Notes and references

‡ A solution of $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (0.39 g, 1.0 mmol) dissolved in distilled water (7 ml) was layered in a test tube with a solution of NaN_3 (0.13 g, 2.0 mmol) and pyrazine (0.16 g, 2.0 mmol) dissolved in distilled water (7 ml) and ethanol (2 ml). After diffusion for *ca.* one month, dark red plate-like crystals, suitable for single crystal X-ray diffraction, were precipitated in 39% yield (based on Fe). Calc. for $C_4H_4FeN_8$: C, 21.84; H, 1.833; N, 50.94. Found: C, 21.75; H, 1.47; N, 51.02%. Selected IR absorptions (KBr pellet, cm^{-1}): ν_{as}(azido) 2098s, 2064s; ν_s(azido) 1327m.

§ *Crystal data* for $C_4H_4FeN_8$: M = 219.98, orthorhombic, space group *Cmcm*, a = 15.197(3), b = 7.2010(10), c = 6.6720(10) Å, U = 730.1(2) Å^3, Z = 4, D_c = 2.001 Mg m^{-3}, μ(Mo-Kα) = 2.024 mm^{-1}, T = 293(2) K. The data were collected on a Rigaku AFC6S diffractometer over the θ range 3.13–26.47°. 431 Reflections were collected of which 364 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods using SHELXS-97, and refined with SHELXL-97. All nonhydrogen atoms were refined anisotropically, while all hydrogen atoms were located from differential Fourier maps. The final agreement factor R [$I > 2\sigma(\sigma I)$] = 0.0647, wR (all data) = 0.1741 and GOF = 1.101.

CCDC 182/1799. See http://www.rsc.org/suppdata/cc/b0/b005137n/ for crystallographic files in .cif format.

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