

# Mn<sup>II</sup>(N<sub>3</sub>)<sub>2</sub>(pyrazine). A 2-D layered structure consisting of ferromagnetically coupled 1-D {Mn(μ-1,1-N<sub>3</sub>)<sub>2</sub>}<sub>n</sub> chains

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Received (in Bloomington, IN, USA) 20th April 1999, Accepted 21st June 1999

Mn(N<sub>3</sub>)<sub>2</sub>(pyz) (pyz = pyrazine) consists of ferromagnetically coupled linear chains of {Mn(N<sub>3</sub>)<sub>2</sub>}<sub>n</sub> comprised of μ-1,1-azido bridges together with μ-pyz ligands to afford 2-D planar layers.

In the last decade several families of molecule-based magnets have emerged,<sup>1</sup> including examples that exhibit ordering temperatures, *T*<sub>c</sub>, in excess of 300 K.<sup>2,3</sup> For the latter high-*T*<sub>c</sub> materials, both diamagnetic (cyanide) and paramagnetic ligands (tetracyanoethylene, TCNE) have been used to organize transition metal centers into 3-D networks. To better interpret magnetic properties of complex 3-D solids, reduced-dimensional structures, *i.e.* 1- and 2-D, are preferred to develop the necessary theoretical models. Recently, we have exploited the coordination chemistry of the dicyanamide ligand, [N(CN)<sub>2</sub>]<sup>-</sup>, which has produced a rich variety of polymeric architectures<sup>4</sup> with *T*<sub>c</sub> values as high as 47 K.<sup>5</sup>

The azido ligand, N<sub>3</sub><sup>-</sup>, unlike cyanide can bond two metal ions symmetrically either μ-1,1 through a terminal nitrogen which typically couple spins ferromagnetically, or μ-1,3 through both terminal nitrogens which couple spins antiferromagnetically.<sup>6</sup> Several monomeric,<sup>7</sup> dimeric<sup>8</sup> and polymeric<sup>9</sup> species typically with combinations of azido and pyridine-type ligands have been utilized to assemble a plethora of framework structures. NMe<sub>4</sub>[Mn(N<sub>3</sub>)<sub>3</sub>] is the only material where the metal coordination sphere contains only 1,3-N<sub>3</sub><sup>-</sup> bridging ligands,<sup>9a</sup> while the others possess μ-1,3- or a mixture of μ-1,1- and μ-1,3-azido linkages, *i.e.* there are no characterized examples of polymeric solids that consist solely of μ-1,1-N<sub>3</sub><sup>-</sup> bridging units. Hence, expecting ferromagnetic coupling, we sought to synthesize and structurally and magnetically characterize the first such example. Herein, we report the crystal structure and magnetic properties of Mn<sup>II</sup>(N<sub>3</sub>)<sub>2</sub>(pyz), **1** (pyz = pyrazine).

The reaction of MnCl<sub>2</sub>, NaN<sub>3</sub> and pyrazine in aqueous media leads to the formation of yellow plates of Mn(N<sub>3</sub>)<sub>2</sub>(pyz)<sup>†</sup> suitable for single crystal X-ray diffraction.<sup>‡</sup> Each Mn<sup>II</sup> ion is octahedrally coordinated to four different N<sub>3</sub><sup>-</sup> ligands and two axial pyrazine ligands. In turn, each N<sub>3</sub><sup>-</sup> ligand is μ-1,1-bound to two Mn<sup>II</sup> metal centers. The MnN<sub>6</sub> octahedron is markedly distorted, with Mn–N<sub>azido</sub> distances ranging from 2.198(12) to 2.270(14) Å (averaging 2.235 Å) and two equivalent Mn–N<sub>pyz</sub> distances of 2.299(4) Å while *cis*-N–Mn–N angles range from 80.1(4) to 101.2(5)°. The Mn<sup>II</sup>–N bond distances found for the MnN<sub>4</sub> equatorial plane are typical of azide coordination while the longer Mn–N<sub>pyz</sub> distances are similar to those found in Mn[N(CN)<sub>2</sub>]<sub>2</sub>(pyz).<sup>4b</sup> The N–N distances of the azido ligand range from 1.091(18) to 1.248(17) Å (averaging 1.170 Å) and reflects typical double bond character, and as such, N(1)–N(2)–N(3) and N(4)–N(5)–N(6) bond angles are 178.5(14) and 179.4(13)°, respectively. Interestingly, the azide ligands do not reside within the Mn–N–Mn–N plane but form angles of 19.2(8) and 15.4(7)°. The solid consists of 1-D {Mn(N<sub>3</sub>)<sub>2</sub>}<sub>n</sub> linear chains linked *via* μ-pyz ligands to afford an extended 2-D layered network, Fig. 1, with intranetwork Mn⋯Mn separations of 3.412 (*via* azide) and 7.385 Å (*via* pyz) while the shortest internetwork Mn⋯Mn separation is 8.412 Å.

The magnetic susceptibility of **1** was measured between 2 and 300 K in a 1 kOe dc field upon warming. Above 10 K the data can be least-squares fit to the Curie-Weiss expression,  $\chi^c = g(T - \theta)$ , with  $g = 2.037(1)$  and  $\theta = 5.51(3)$  K, Fig. 2, indicative of ferromagnetic coupling between the Mn<sup>II</sup> metal sites joined *via* the μ-1,1-N<sub>3</sub><sup>-</sup> ligands. The Lande-*g* value is in good agreement with the literature.<sup>9c</sup>  $\chi T$  has a value of 4.63 emu K mol<sup>-1</sup> at 300 K, slightly larger than the expected value (4.38 emu K mol<sup>-1</sup>) for isolated  $S = 5/2$  Mn<sup>II</sup> ions and due to ferromagnetic coupling increases gradually upon cooling to *ca.* 50 K. Below this temperature,  $\chi T$  increases to a maximum value of 9.7 emu K mol<sup>-1</sup> at 5 K due to rapidly increasing ferromagnetic correlations between adjacent spin carriers. Upon cooling to 2 K,  $\chi T$  decreases quickly due to interchain antiferromagnetic interactions through the bridging pyrazine ligands. To determine the exchange parameters *via* each bridge type,  $\chi T$  was fit to the  $S = 5/2$  Fisher chain model,  $\chi_{1-D}$ ,<sup>10</sup> [eqn. (1)] in conjunction with an additional mean-field correction term,  $\chi_{MF}$ , [eqn. (2)] assuming  $z = 2$ ,<sup>11</sup> where  $N$  is Avogadro's number,  $\mu_B$  is the Bohr magneton,  $k_B$  is the Boltzmann constant and  $z$  is the number of nearest neighbours. The best least squares fit parameters gave  $g = 2.037(3)$ ,  $J/k_B = 0.61(4)$  K, and  $J'/k_B$

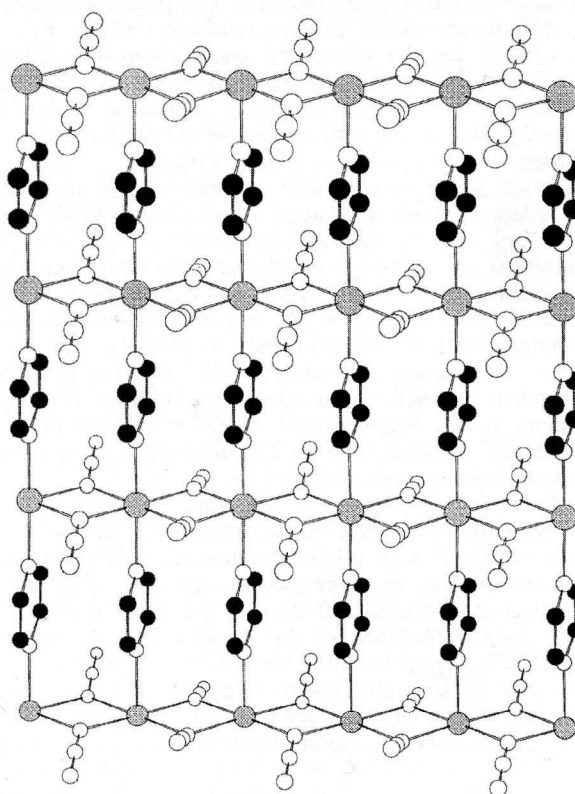


Fig. 1 Crystal structure of Mn(N<sub>3</sub>)<sub>2</sub>(pyz) showing a single 2-D layer. The shaded, open and filled spheres represent Mn, N and C, respectively. Hydrogen atoms have been omitted for clarity.

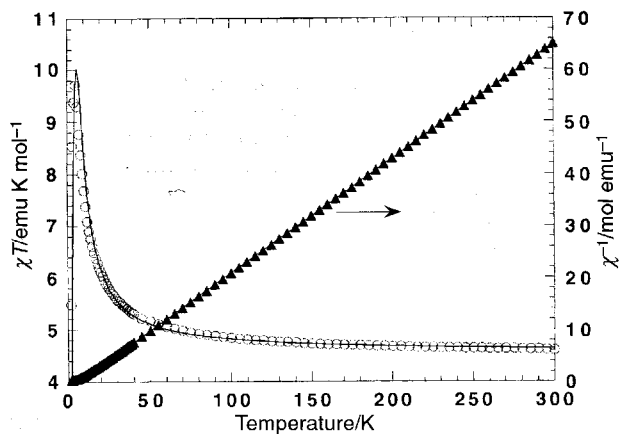


Fig. 2 Temperature-dependence of  $\chi T$  (○) and the reciprocal molar magnetic susceptibility,  $\chi^{-1}$  (▲) for  $\text{Mn}(\text{N}_3)_2(\text{py}_2)$ . The heavy line denotes the theoretical fit of the data to eqn. (1) and (2).

=  $-0.24(3)$  K for ferro- and antiferro-magnetic interactions via the azide and pyrazine ligands, respectively.

$$\chi_{1-D} = \frac{Ng^2\mu_B^2 S(S+1)}{3k_B T} \cdot \frac{1+u(K)}{1-u(K)}$$

$$\text{where } u(K) = \coth K - 1/K \text{ and } K = \frac{2JS(S+1)}{k_B T} \quad (1)$$

$$\chi_{\text{MF}} = \frac{\chi_{1-D}}{[1 - \chi_{1-D}(2zJ'/Ng^2\mu_B^2)]} \quad (2)$$

Weak ferromagnetic coupling is anticipated when the Mn–N–Mn bridge angles are appreciably less than  $103\text{--}104^\circ$ .<sup>12</sup> These angles are  $97.9(5)$  and  $101.2(5)^\circ$  for **1** and hence suggest ferromagnetic coupling. Bridge angles approaching  $105^\circ$  give rise to strong ferromagnetic coupling due to accidental orthogonality of the magnetic  $d_{yz}$  orbital as shown by EHMO (extended Huckel molecular orbital) calculations.<sup>13</sup> By comparison, Mn–N–Mn angles of  $104.6$  and  $101.0^\circ$ , respectively, lead to  $J/k_B = 3.5$  K for the dinuclear complex  $(\text{N}_3)_2[\text{Mn}(\text{terpy})_2(\text{X})_2]$  (terpy = 2,2':6',2''-terpyridine; X =  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ )<sup>14</sup> and  $13.8$  K for the alternating chain compound  $[\text{Mn}(\text{bipy})(\text{N}_3)_2]_n$ .<sup>13</sup> A significantly reduced angle of  $84.2^\circ$  was reported for 2-D  $[\text{Ni}(\text{N}_3)_2(\text{tmeda})]_n$  (tmeda =  $N,N,N',N'$ -tetramethylethylenediamine) which yielded antiferromagnetic exchange ( $-9.9$  K) via the  $\mu\text{-}1,1\text{-N}_3^-$  bridge.<sup>15</sup>

A broad maximum indicative of short-range antiferromagnetic ordering was observed at  $2.7$  K using low field  $M(T)$  ( $H_{\text{dc}} \leq 50$  Oe) and ac susceptibility measurements. For low dimensional solids, the actual ordering temperature lies below the maximum as elucidated by Fisher<sup>10</sup> from plots of  $d\chi T/dT$ , and for  $\text{Mn}(\text{N}_3)_2(\text{py}_2)$ ,  $T_N \approx 2$  K. Specific heat measurements are better suited to unambiguously identify  $T_N$  and are in progress. According to ac susceptibility,  $\chi''(T)$  is frequency independent suggesting a non-glassy ground state. A shallow minimum at  $3$  K was observed in  $\chi''(T)$ , with the onset of spontaneous magnetization near  $2$  K and suggests the presence of a weak ferromagnetic ground state.

Isothermal magnetization experiments performed at  $2$  K show behavior typical of a soft ferromagnet as coercivity was not observed. Below *ca.*  $6$  kOe, the magnetization rises rapidly where a decrease in slope occurs, reaching a saturation magnetization,  $M_s$ , of  $23530$  emu Oe mol<sup>-1</sup> at  $50$  kOe. This value is comparable, although slightly reduced, to the expected value of  $27925$  emu Oe mol<sup>-1</sup> for isolated  $S = 5/2$  ions.

The authors gratefully acknowledge the ACS-PRF (Grant #30722-ACS) and the U.S. Department of Energy (Grant #DE-FG03-93ER45504) for support of this work.

## Notes and references

† A  $3$  mL aqueous solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  ( $1.6$  mmol,  $0.3169$  g) was mixed with a  $\text{H}_2\text{O}$  solution ( $3$  mL) containing  $\text{NaN}_3$  ( $3.2$  mmol,  $0.2080$  g) and pyrazine ( $1.6$  mmol,  $0.1281$  g) affording small plate-like crystals suitable for X-ray diffraction. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu_s(\text{azido}) = 2098\text{s}, 2049\text{m}$  and  $\nu_{\text{as}}(\text{azido}) = 1328\text{m}$ .

‡ Crystal data for  $\text{C}_4\text{H}_4\text{MnN}_8$ :  $M = 219.09$ , monoclinic  $Cc$ ,  $a = 16.3458(17)$ ,  $b = 7.3848(5)$ ,  $c = 6.8236(7)$ ,  $\beta = 112.032(4)^\circ$ ,  $U = 763.53(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.906$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.690$  mm<sup>-1</sup>,  $T = 200.0(1)$  K. The data were collected on an Enraf-Nonius KappaCCD diffractometer. Of 1230 data ( $8 < 2\theta < 62^\circ$ ), 928 were observed [ $I > 2\sigma(I)$ ]. The structure was solved by direct methods using SIR97 and refined with SHELXL-97. All nonhydrogen atoms were refined anisotropically, while all hydrogen atoms were located but not refined,  $R(F) = 0.0625$ ,  $R(wF) = 0.1659$ , and  $\text{GOF} = 1.038$ . CCDC reference number 182/1298. See <http://www.rsc.org/suppdata/cc/1999/1479/> for crystallographic files in .cif format.

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Communication 9/03406D