$Mn^{II}(N_3)_2$(pyrazine). A 2-D layered structure consisting of ferromagnetically coupled 1-D $\{Mn(\mu\text{-}1,1\text{-}N_3)_2\}_n$ chains

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$Mn(N_3)_2$(pyz) (pyz = pyrazine) consists of ferromagnetically coupled linear chains of $\{Mn(N_3)_2\}_n$ 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,[1] including examples that exhibit ordering temperatures, T_c, in excess of 300 K.[2,3] For the latter high-T_c 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, $[N(CN)_2]^-$, which has produced a rich variety of polymeric architectures[4] with T_c values as high as 47 K.[5]

The azido ligand, N_3^-, 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.[6] Several monomeric,[7] dimeric[8] and polymeric[9] species typically with combinations of azido and pyridine-type ligands have been utilized to assemble a plethora of framework structures. $NMe_4[Mn(N_3)_3]$ is the only material where the metal coordination sphere contains only 1,3-N_3^- bridging ligands,[9a] 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_3^- 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 $Mn^{II}(N_3)_2$(pyz), **1** (pyz = pyrazine).

The reaction of $MnCl_2$, NaN_3 and pyrazine in aqueous media leads to the formation of yellow plates of $Mn(N_3)_2$(pyz)[†] suitable for single crystal X-ray diffraction.[‡] Each Mn^{II} ion is octahedrally coordinated to four different N_3^- ligands and two axial pyrazine ligands. In turn, each N_3^- ligand is μ-1,1-bound to two Mn^{II} metal centers. The MnN_6 octahedron is markedly distorted, with Mn–N_{azido} distances ranging from 2.198(12) to 2.270(14) Å (averaging 2.235 Å) and two equivalent Mn–N_{pyz} distances of 2.299(4) Å while *cis*-N–Mn–N angles range from 80.1(4) to 101.2(5)°. The Mn^{II}–N bond distances found for the MnN_4 equatorial plane are typical of azide coordination while the longer Mn–N_{pyz} distances are similar to those found in $Mn[N(CN)_2]_2$(pyz).[4b] 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 $\{Mn(N_3)_2\}_n$ 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, $\chi \propto g/(T - \theta)$, with $g = 2.037(1)$ and $\theta = 5.51(3)$ K, Fig. 2, indicative of ferromagnetic coupling between the Mn^{II} metal sites joined *via* the μ-1,1-N_3^- ligands. The Lande-*g* value is in good agreement with the literature.[9c] χT has a value of 4.63 emu K mol^{-1} at 300 K, slightly larger than the expected value (4.38 emu K mol^{-1}) for isolated $S = 5/2$ Mn^{II} ions and due to ferromagnetic coupling increases gradually upon cooling to *ca.* 50 K. Below this temperature, χT increases to a maximum value of 9.7 emu K mol^{-1} at 5 K due to rapidly increasing ferromagnetic correlations between adjacent spin carriers. Upon cooling to 2 K, χT decreases quickly due to interchain antiferromagnetic interactions through the bridging pyrazine ligands. To determine the exchange parameters *via* each bridge type, χT was fit to the $S = 5/2$ Fisher chain model, $\chi_{1\text{-}D}$,[10] [eqn. (1)] in conjunction with an additional mean-field correction term, χ_{MF}, [eqn. (2)] assuming $z = 2$,[11] where N is Avogadro's number, μ_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

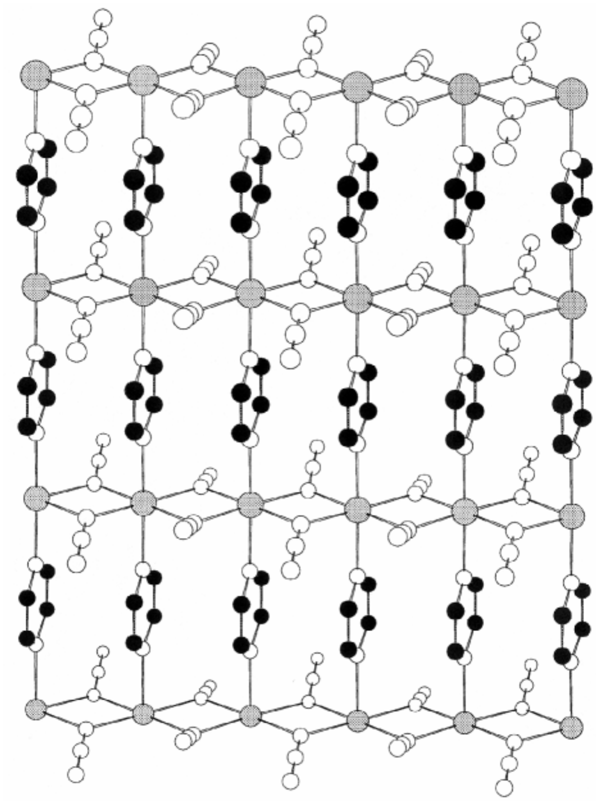

Fig. 1 Crystal structure of $Mn(N_3)_2$(pyz) showing a single 2-D layer. The shaded, open and filled spheres represent Mn, N and C, respectively. Hydrogen atoms have been omitted for clarity.

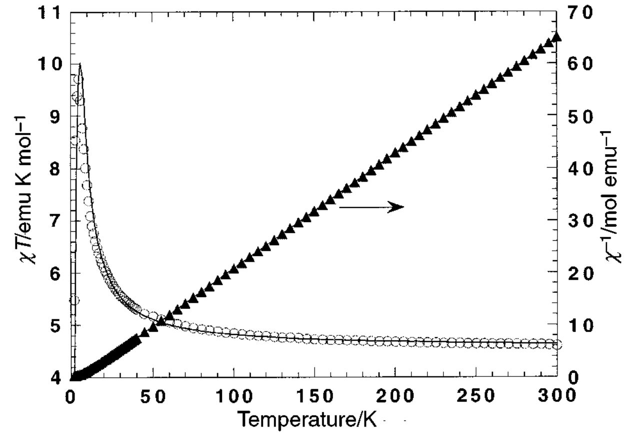

Fig. 2 Temperature-dependence of χT (○) and the reciprocal molar magnetic susceptibility, χ^{-1} (▲) for $Mn(N_3)_2(pyz)$. The heavy line denotes the theoretical fit of the data to eqn. (1) and (2).

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

$$\chi_{1-D} = \frac{Ng^2\mu_B{}^2S(S+1)}{3k_BT} \bullet \frac{1+u(K)}{1-u(K)};$$

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

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

Weak ferromagnetic coupling is anticipated when the Mn–N–Mn bridge angles are appreciably less than 103–104°.[12] These angles are 97.9(5) and 101.2(5)° for **1** and hence suggest ferromagnetic coupling. Bridge angles approaching 105° 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.[13] By comparison, Mn–N–Mn angles of 104.6 and 101.0°, respectively, lead to J/k_B = 3.5 K for the dinuclear complex $(N_3)_2[Mn(terpy)_2]_2(X)_2$ (terpy = 2,2′:6′,2″-terpyridine; X = ClO_4^-, PF_6^-)[14] and 13.8 K for the alternating chain compound $[Mn(bipy)(N_3)_2]_n$.[13] A significantly reduced angle of 84.2° was reported for 2-D $[Ni(N_3)_2(tmeda)]_n$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) which yielded antiferromagnetic exchange (−9.9 K) *via* the μ-1,1-N_3^- bridge.[15]

A broad maximum indicative of short-range antiferromagnetic ordering was observed at 2.7 K using low field $M(T)$ ($H_{dc} \leq 50$ Oe) and ac susceptibility measurements. For low dimensional solids, the actual ordering temperature lies below the maximum as elucidated by Fisher[10] from plots of $d\chi T/dT$, and for $Mn(N_3)_2(pyz)$, $T_N \approx 2$ 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^{-1} at 50 kOe. This value is comparable, although slightly reduced, to the expected value of 27925 emu Oe mol^{-1} for isolated $S = 5/2$ ions.

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Notes and references

† A 3 mL aqueous solution of $MnCl_2 \cdot 4H_2O$ (1.6 mmol, 0.3169 g) was mixed with a H_2O solution (3 mL) containing 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, cm^{-1}): ν_s(azido) = 2098s, 2049m and ν_{as}(azido) = 1328m.

‡ *Crystal data* for $C_4H_4MnN_8$: M = 219.09, monoclinic *Cc*, a = 16.3458(17), b = 7.3848(5), c = 6.8236(7), β = 112.032 (4)°, U = 763.53(12) Å^3, Z = 4, D_c = 1.906 Mg m^{-3}, μ(Mo-Kα) = 1.690 mm^{-1}, T = 200.0 (1) K. The data were collected on an Enraf-Nonius KappaCCD diffractometer. Of 1230 data ($8 < 2\theta < 62°$), 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 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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