

# Structure and magnetic properties of $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyrazine})$ . An antiferromagnet with an interpenetrating 3-D network structure

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$\text{Mn}[\text{N}(\text{CN})_2]_2(\text{pyz})$  (pyz = pyrazine) orders antiferromagnetically at low temperature and possesses intralayer  $\mu\text{-NCNCN}$  and interlayer  $\mu\text{-pyz}$  ligands that form a pseudo- $\text{ReO}_3$  interpenetrating network structure.

The synthesis of multidimensional network structures is at the forefront of modern research due to their ability to design as well as control a wide range of architectures.<sup>1</sup> Likewise, the study of molecule-based magnets due to their potential for exhibiting cooperative magnetic behavior is being widely investigated.<sup>2</sup> Polydentate cyanocarbons have been utilized extensively to assemble transition metals into 1-, 2- and 3-D arrays.<sup>3</sup> Tetracyanoethylene, TCNE, has been used to link  $\text{Mn}(\text{porphyrin})$  into 1-D chains<sup>4</sup> and when reacted with  $\text{V}(\text{C}_6\text{H}_6)_2$  yields a 3-D polymeric ferrimagnet with a critical temperature far exceeding room temperature.<sup>5</sup> Work has focused on diamagnetic  $[\text{N}(\text{CN})_2]^-$  due to its ability to bond to multiple transition metal sites.<sup>6</sup> Tricoordinate dicyanamide forms rutile-structured ferromagnets with  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  with  $T_c$ 's ranging from 9 K (Co) to 21 K (Ni) while isostructural  $\text{Mn}^{\text{II}}$  orders antiferromagnetically below 16 K.<sup>7,8</sup> In addition to  $\text{M}[\text{N}(\text{CN})_2]_2$  complexes, octahedral complexes of  $\text{M}[\text{N}(\text{CN})_2]_2\text{-L}_2$  (L = Lewis base) stoichiometry can be prepared. Owing to the polydentate character of  $[\text{N}(\text{CN})_2]^-$  numerous structural motifs can be constructed. Herein we report the single crystal structure and magnetic properties of  $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$  (pyz = pyrazine).

Reaction of  $\text{MnCl}_2$ ,  $\text{Na}[\text{N}(\text{CN})_2]$ , and pyrazine in  $\text{H}_2\text{O}$ -EtOH results in the formation of small pale yellow crystals of  $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$  whose structure was solved by X-ray diffraction.<sup>†</sup> The structure consists of infinite  $\text{MNCNCN}$ -linked  $\text{Mn}[\text{N}(\text{CN})_2]_2$  layers bridged by pyrazine affording pseudo-cubic frameworks, Fig. 1, similar to  $\text{ReO}_3$ . Furthermore, owing to the combination of the large separation between Mn atoms and the small ligand sizes, large cavities are formed which can accommodate a second interpenetrating lattice.

Each octahedral  $\text{Mn}^{\text{II}}$  is bonded to four different  $[\text{N}(\text{CN})_2]^-$  ligands in the  $ab$ -plane and two different pyrazine bridges along  $c$ . Each  $[\text{N}(\text{CN})_2]^-$  is  $\mu$ -bonded to two  $\text{Mn}^{\text{II}}$ 's through the terminal CN's. The  $\text{Mn}^{\text{II}}$  octahedron is tetragonally elongated

from  $O_h$  symmetry with Mn–N distances ranging from 2.173(7) Å (dicyanamide N's) to 2.299(9) Å (pyrazine N's) and average 2.236 Å while *cis*-N–Mn–N' bond angles range from 83.5(3) to 92.3(6)°. The dicyanamide ligand displays nearly ideal  $C_{2v}$  symmetry with C≡N bond distances averaging 1.145 Å typical for this ligand.<sup>9</sup> The C≡N–Mn bond angles deviate appreciably from linearity and range from 142.6(9) to 164.9(13)°. The intranetwork Mn···Mn separations are 7.351 (through the pyrazine bridge), 8.678, and 8.803 Å, which exceed the shortest Mn···Mn internetwork separation of 6.282 Å. For comparison,  $\text{Zn}[\text{N}(\text{CN})_2]_2$  features a 2-D layered structure with only  $\mu\text{-N}\equiv\text{C}$  linkages similar to  $\text{Mn}[\text{N}(\text{CN})_2]_2(\text{pyz})$ , however due to the tetrahedral  $\text{Zn}^{\text{II}}$  centers, the layers are markedly buckled and pack in a staggered fashion.<sup>10</sup> The pyrazine ligands reside in noncoplanar orientations with a dihedral angle of 43.1° relative to the "cube" faces. Thermogravimetric analysis reveals a sharp weight loss at  $\approx 230$  °C corresponding to the loss of one pyrazine per formula unit (Calc. 30.0; obs. 29.9). To the best of our knowledge this is the only structurally characterized unsubstituted pyrazine  $\text{Mn}^{\text{II}}$  complex.

Several 2-D materials such as  $\text{Co}(\text{pyz})_2(\text{NCS})_2$  feature  $\mu\text{-pyz}$  ligands that organize paramagnetic metal centers into square grids.<sup>11</sup> Interestingly, the only example of a 3-D network solid consisting of pyz bridges is diamagnetic  $[\text{Ag}(\text{pyz})_3][\text{SbF}_6]$  which also possesses a  $\text{ReO}_3$ -like structure.<sup>12</sup>

The 2 to 300 K temperature dependence of the magnetic susceptibility,  $\chi$ , of  $\text{Mn}[\text{N}(\text{CN})_2]_2(\text{pyz})$  was measured and fit by the Curie–Weiss expression,  $\chi \propto (T - \theta)^{-1}$ , with  $g = 2.01$  and  $\theta = -3.6$  K indicative of finite antiferromagnetic coupling between the  $\text{Mn}^{\text{II}}$  metal sites, Fig. 2. At 300 K the effective moment is  $5.90 \mu_B$ , in excellent agreement with the expected value ( $5.92 \mu_B$ ) for isolated  $S = 5/2$   $\text{Mn}^{\text{II}}$  ions and due to antiferromagnetic coupling decreases at lower temperature. A similar material,  $\text{Mn}[\text{N}(\text{CN})_2]_2(\text{py})_2$ , also has  $\mu\text{-NCNCN}$  bridges and weaker antiferromagnetic coupling is observed ( $\theta = -1.8$  K) suggesting enhanced spin coupling *via* the pyrazine linkages.<sup>13</sup> To elucidate the exchange coupling through the  $\text{NCNCN}$  and  $\text{pyz}$  linkages,  $\chi$  was also fit to a 2-D ( $\chi_{2D}$ ) antiferromagnet model derived by Rushbrooke and Wood<sup>14a</sup> with  $g = 2.01$  and  $J/k_B = -0.18(1)$  K.<sup>14b</sup> To account for the residual 3-D interactions an additional mean-field correction ( $\chi_{\text{MF}}$ )<sup>14c,d</sup> was included, eqn. (2), also with  $g = 2.01$  and  $J'/k_B = -0.21(1)$  K.

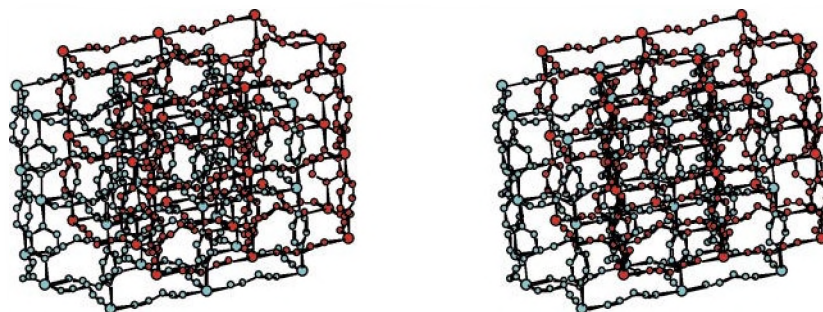
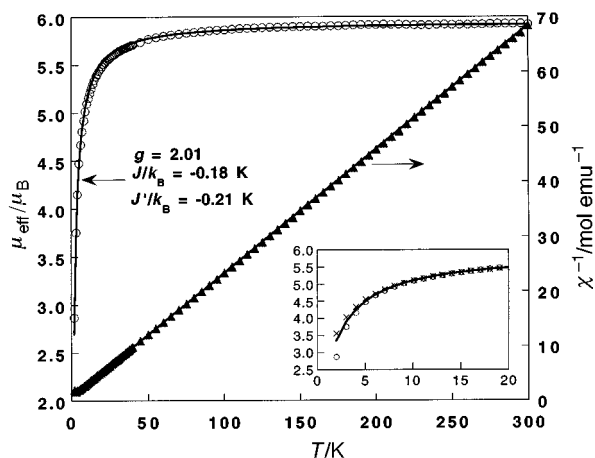
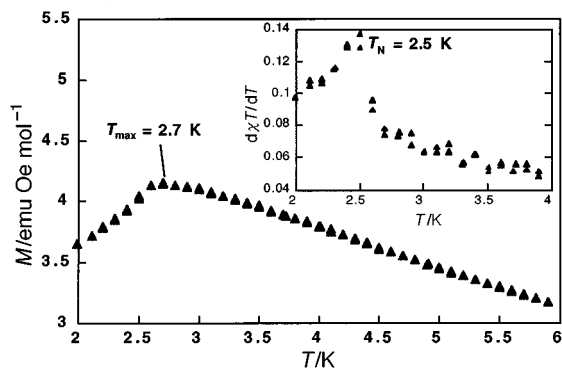


Fig. 1 Stereoview of the crystal structure of  $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$  illustrating the interpenetrating pseudo- $\text{ReO}_3$  frameworks.



**Fig. 2** Temperature dependence of effective magnetic moment ( $\mu_{\text{eff}}$ ) and the reciprocal molar magnetic susceptibility ( $\chi^{-1}$ ) for  $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$ . The data was fit to the expression derived by Rushbrooke and Wood<sup>14a</sup> for a 2-D antiferromagnet (—) with  $S = 5/2$ ,  $g = 2.01$  and  $J/k_{\text{B}} = -0.18$  K. Interlayer exchange was determined to be  $J'/k_{\text{B}} = -0.21$  K. A low temperature comparison to the Curie-Weiss law ( $\times$ ) with  $g = 2.01$  and  $\theta = -3.6$  K is also shown (inset).



**Fig. 3** Zero-field and field-cooled magnetization as a function of temperature for  $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$  taken in a 50 Oe applied dc magnetic field on warming.  $T_{\text{N}} = 2.5$  K as determined from the plot of  $d\chi(T)/dT$ , inset.

$\chi_{2\text{D}} =$

$$\frac{2.91Ng^2\mu_{\text{B}}^2}{k_{\text{B}}T[1 + C_1x + C_2x^2 + C_3x^3 + C_4x^4 + C_5x^5 + C_6x^6]} \quad (1)$$

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

$J$  is assigned to coupling within the layers *via* the NCNCN bridges and  $J'$  is assigned to coupling between the layers *via* the pyrazine bridges. The zero field splitting is typically negligible for high spin  $\text{Mn}^{\text{II}}$  and is ignored. Evidence of long-range antiferromagnetic ordering is demonstrated by a cusp in  $M(T)$  at 2.7 K, Fig. 3. The actual magnetic ordering temperature occurs just below the maximum and can be determined from a plot of  $d\chi(T)/dT$ , Fig. 3 inset.<sup>16</sup> Additionally, zero-field and field-cooled magnetization experiments carried out in small applied magnetic fields ( $H \leq 50$  G) fail to show bifurcation unlike  $\alpha\text{-Mn}[\text{N}(\text{CN})_2]_2$ .<sup>8</sup> Field-dependent magnetization measurements performed at 2 K to 5 T demonstrate behavior typical of an ordered antiferromagnet. The magnetization rises nearly linearly to approximately 19 000 emu Oe mol<sup>-1</sup> (at 3 T) and then decreases reaching a final value of 26 600 emu Oe mol<sup>-1</sup> (at 5 T). This value is only slightly less than the expected value of 27 925 emu Oe mol<sup>-1</sup> expected for  $S = 5/2$   $\text{Mn}^{\text{II}}$ .

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## Notes and references

† A 5 mL aqueous solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (1.7 mmol, 0.3373 g) was mixed with a 1:1  $\text{H}_2\text{O}$ -EtOH solvent mixture (10 mL) containing  $\text{Na}[\text{N}(\text{CN})_2]$  (3.4 mmol, 0.3034 g) and pyrazine (1.7 mmol, 0.1360 g) affording immediate precipitation of a pale yellow powder (90%). Small crystals suitable for X-ray diffraction were grown from the filtrate solution upon standing at room temperature for 2 weeks.  $\nu_{\text{CN}}$  (Nujol): 2170s, 2180s, 2193s (sh), 2236m, 2248m, 2311m, 2325m and 2357w  $\text{cm}^{-1}$ .

‡ Crystal data for  $\text{C}_8\text{H}_4\text{MnN}_8$ :  $M = 267.13$ , monoclinic,  $P2_1/n$ ,  $a = 7.3514(11)$ ,  $b = 16.865(2)$ ,  $c = 8.8033(12)$  Å,  $\beta = 90.057(2)^\circ$ ,  $U = 1091.4(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.626$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.199$  cm<sup>-1</sup>,  $T = 198(2)$  °C. Of 4518 data ( $4 \leq 2\theta \leq 57^\circ$ ), 1556 were independent ( $R_{\text{int}} = 0.0928$ ), and 1019 were observed [ $I > 2\sigma(I)$ ]. Two nitrogen atoms in two different cyano groups were positionally disordered 70:30 and 60:40. CCDC reference number 186/1201. See <http://www.rsc.org/suppdata/dt/1998/3705/> for crystallographic files in .cif format.

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