

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- 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.¹ Likewise, the study of molecule-based magnets due to their potential for exhibiting cooperative magnetic behavior is being widely investigated.² Polydentate cyanocarbons have been utilized extensively to assemble transition metals into 1-, 2- and 3-D arrays.³ Tetracyanoethylene, TCNE, has been used to link $\text{Mn}(\text{porphyrin})$ into 1-D chains⁴ 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.⁵ Work has focused on diamagnetic $[\text{N}(\text{CN})_2]^-$ due to its ability to bond to multiple transition metal sites.⁶ Tricoordinate dicyanamide forms rutile-structured ferromagnets with Co^{II} and Ni^{II} with T_c 's ranging from 9 K (Co) to 21 K (Ni) while isostructural Mn^{II} orders antiferromagnetically below 16 K.^{7,8} 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 MnCl_2 , $\text{Na}[\text{N}(\text{CN})_2]$, and pyrazine in H_2O - EtOH results in the formation of small pale yellow crystals of $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})^\dagger$ whose structure was solved by X-ray diffraction.[‡] The structure consists of infinite MNCNCNM -linked $\text{Mn}[\text{N}(\text{CN})_2]_2$ layers bridged by pyrazine affording pseudo-cubic frameworks, Fig. 1, similar to 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 Mn^{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 μ -bonded to two Mn^{II} 's through the terminal CN's. The Mn^{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 $cis\text{-N-Mn-N'}$ bond angles range from 83.5(3) to 92.3(6)°. The dicyanamide ligand displays nearly ideal C_{2v} symmetry with $\text{C}\equiv\text{N}$ bond distances averaging 1.145 Å typical for this ligand.⁹ The $\text{C}\equiv\text{N-Mn}$ 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 Zn^{II} centers, the layers are markedly buckled and pack in a staggered fashion.¹⁰ 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 $\approx 230^\circ\text{C}$ 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 Mn^{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.¹¹ 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 ReO_3 -like structure.¹²

The 2 to 300 K temperature dependence of the magnetic susceptibility, χ , 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 Mn^{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 $S = 5/2$ Mn^{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.¹³ To elucidate the exchange coupling through the NCNCN and pyz linkages, χ was also fit to a 2-D (χ_{2D}) antiferromagnet model derived by Rushbrooke and Wood^{14a} with $g = 2.01$ and $J/k_B = -0.18(1)$ K.^{14b} To account for the residual 3-D interactions an additional mean-field correction (χ_{MF})^{14c,d} was included, eqn. (2), also with $g = 2.01$ and $J'/k_B = -0.21(1)$ K.

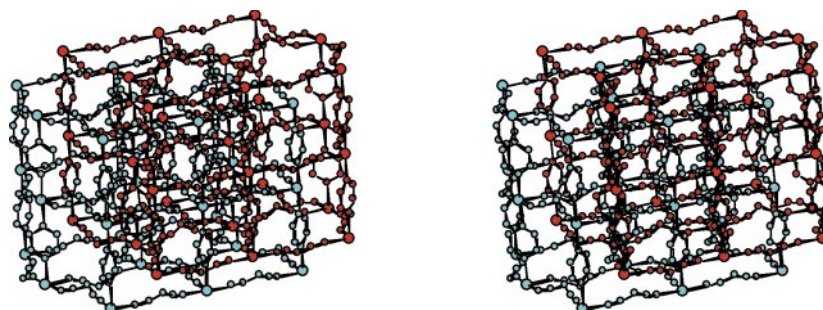


Fig. 1 Stereoview of the crystal structure of $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$ illustrating the interpenetrating pseudo- ReO_3 frameworks.

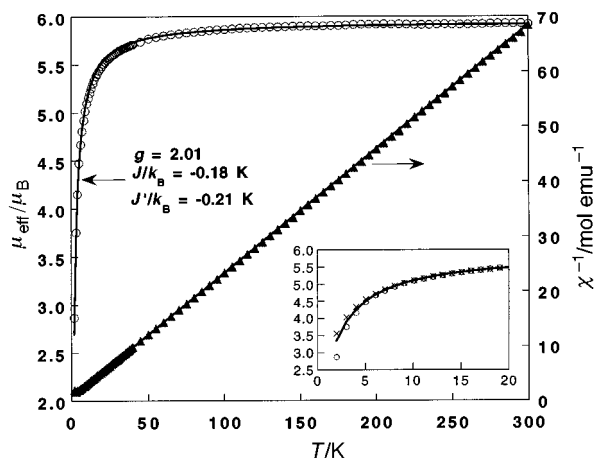


Fig. 2 Temperature dependence of and effective magnetic moment (μ_{eff}) and the reciprocal molar magnetic susceptibility (χ^{-1}) for $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$. The data was fit to the expression derived by Rushbrooke and Wood^{14a} for a 2-D antiferromagnet (—) with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

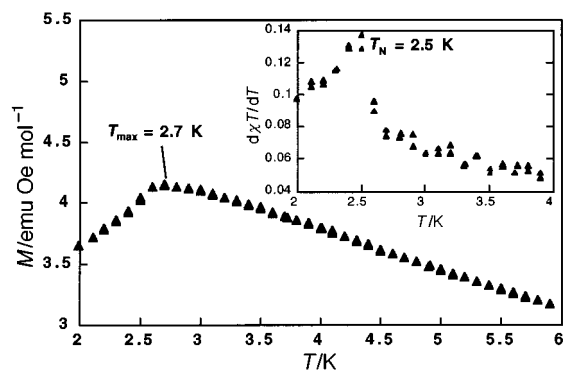


Fig. 3 Zero-field and field-cooled magnetization as a function of temperature for $\text{Mn}^{\text{II}}[\text{N}(\text{CN})_2]_2(\text{pyz})$ taken in a 50 Oe applied dc magnetic field on warming. $T_N = 2.5$ K as determined from the plot of $d\chi(T)/dT$, inset.

$\chi_{2D} =$

$$\frac{2.91 N g^2 \mu_B^2}{k_B T [1 + C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + C_5 x^5 + C_6 x^6]} \quad (1)$$

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

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 Mn^{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.¹⁶ Additionally, zero-field and field-cooled magnetization experiments carried out in small applied magnetic fields ($H \leq 50$ G) fail to show bifurcation unlike $\alpha\text{-Mn}[\text{N}(\text{CN})_2]_2$.⁸ 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⁻¹ (at 3 T) and then decreases reaching a final value of 26 600 emu Oe mol⁻¹ (at 5 T). This value is only slightly less than the expected value of 27 925 emu Oe mol⁻¹ expected for $S = 5/2$ Mn^{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 H_2O -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. ν_{CN} (Nujol): 2170s, 2180s, 2193s (sh), 2236m, 2248m, 2311m, 2325m and 2357w 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, $\beta = 90.057(2)^\circ$, $U = 1091.4(3)$ Å³, $Z = 4$, $D_c = 1.626$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 1.199$ cm⁻¹, $T = 198(2)$ °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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