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Novel 1-D Coordination Polymers Containing μ-$[N(CN)_2]^-$ Bridging Ligands. Structure and Magnetic Properties of $Mn[N(CN)_2]_2L$ (L = 2,2'-Bipyridine, 4,4'-Bipyridine)

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One-dimensional coordination polymers consisting of $\{Mn[N(CN)_2]_2\}_\infty$ structural units have been characterized. Incorporation of 2,2'-bipyridine and 4,4'-bipyridine affords zigzag and cylindrical chain structures, respectively; weak antiferromagnetic coupling is also observed. 4,4'-bipyridine unexpectedly binds as a monodentate ligand.

Keywords: coordination polymers; antiferromagnetic coupling; dicyanamide

INTRODUCTION

Crystal engineering of novel network structures is an area of increasing multidisciplinary interest.[1] Numerous architectures with extended 1-, 2- and 3-D bonding interactions have been synthesized and characterized,[2] which frequently have interesting physical properties such as conductivity[3a] and magnetism.[3b] Dicyanamide, $[N(CN)_2]^-$, being a polydentate ligand, is particularly suitable for coordination to transition metals and several novel structural motifs have been reported.[4] Three-coordination of $[N(CN)_2]^-$ to Co and Ni yields noninterpenetrating rutile-like structures which order ferromagnetically below 8.7 and 19.7 K, respectively,[5] while bidentate-coordination to tetrahedral Zn yields a buckled 2-D layered structure[6].

Several solid state structures have been assembled using dicyanamide in conjunction with other coordinating organic ligands such as imidazole[7] and

substituted-pyridines.[8] Reaction of Mn^{II}, $[N(CN)_2]^-$, and pyrazine in aqueous solution affords a novel interpenetrating ReO_3-like network which undergoes antiferromagnetic ordering at 2.5 K.[9] Herein we report the structures and magnetic properties of two novel 1-D coordination polymers consisting of $\{Mn[N(CN)_2]_2L\}_\infty$ (L = 2,2'-bipyridine, $Mn[N(CN)_2]_2$(2,2'-bipy), **1**, 4,4'-bipyridine, $Mn[N(CN)_2]_2$(4,4'-bipy)•$3/2H_2O$, **2**.

Reaction of $MnCl_2$, $Na[N(CN)_2]$, and L in a water/ethanol or water/acetone solvent mixture, results in the formation of yellow and colorless crystals upon slow solvent evaporation of **1** and **2**, respectively,[10] whose structures were solved by single crystal X-ray diffraction.[11] One-dimensional zigzag chains comprised of μ-NCNCN ligands are found in **1** while cylindrical tubes consisting of cross-linking μ-NCNCN ligands are observed in **2**.

In **1**, octahedral Mn^{II} centers are bonded to only two nearest-neighbors. The coordination sphere consists of four N's of $[N(CN)_2]^-$ and two N's of chelated 2,2'-bipyridine, Figure 1. The monoclinic *C2/c* unit cell contains four discrete molecules. Metal-dicyanamide nitrogen distances are 2.195 (3) and 2.230 (4) Å for Mn-N(2) and Mn-N(3), respectively. The chelated 2,2'-bipyridine ligand features slightly longer Mn-N(1) distances of 2.258 (3) Å. The Mn^{II} octahedron possesses a distorted coordination environment with bond angles ranging from 86.50(13) to 102.60(17)° for N(2)-Mn-N(3)#1 and N(2)-Mn-N(2)#1, respectively. Each dicyanamide ligand coordinates two Mn^{II} centers via μ-N≡C-N-C≡N linkages while retaining pseudo-C_{2v} symmetry with C(21)≡N(2) and C(31)≡N(3) bond distances averaging 1.136 Å. Incorporation of chelating amines such as 2,2'-bipyridine was deliberate in an attempt to design and assemble a 1-D zigzag chain motif. In the extended lattice, 1-D chains pack in-registry along the *a*-axis affording discrete buckled 2-D sheets, Figure 2.

The distorted octahedral Mn^{II} coordination sphere of **2** consists of four N's of $[N(CN)_2]^-$, one 4,4'-bypridine nitrogen and an oxygen *trans* to the 4,4'-bypridine, Figure 3. Two unique chains exist in the structure but possess essentially identical characteristics, thus only one of them will be described. One-dimensional cylindrical tubes are formed via cross-linking μ-NCNCN

ligands, Figure 4. The four Mn-N(dicyanamide) bond distances range from 2.187 (6) to 2.213 (7) Å and average 2.20 Å, consistent with other Mn^{II}-N bond distances. Due to the bulk size of 4,4'-bipyridine and close proximity of *ortho*-hydrogens to the coordinated metal center, Mn-N(8) is

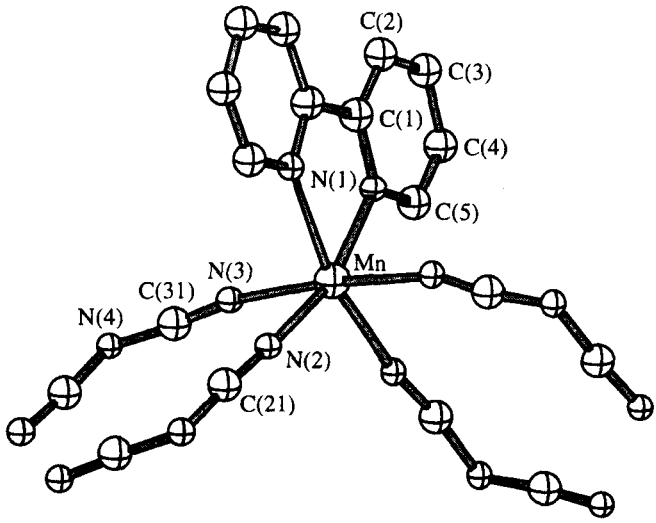

Figure 1. Local coordination about Mn^{II} in **1** depicting the atom labeling scheme. Selected bond distances [Å] and angles [°]: Mn-N(1) 2.258(3), Mn-N(2) 2.195(3), Mn-N(3) 2.230(4), C(1)-N(1) 1.342(4) C(21)-N(2) 1.141(4), C(31)-N(4) 1.282(5), C(21)-N(4) 1.297(5), N(2)-Mn-N(3)#1 86.50(13), N(2)-Mn-N(3) 90.26(13), N(3)#1-Mn-N(1) 94.60(11), N(2)-Mn-N(2)#1 102.60(17), N(3)#1-Mn-N(3) 174.81(18), N(1)-Mn-N(2)#1 164.19(12).

longer at 2.263 (4) Å. The coordinated H_2O molecule is disordered over two positions [O(1) and O(1)'] and were refined as 1/2 occupancy. Mn-O(1) and Mn-O(2) bond distances are 2.309 (9) and 2.220 (11), respectively, suggesting a weakly bound water molecule. A single water of solvation [O(3)] is located on the two-fold axis near O(1) and O(1)'. The dicyanamide ligand possesses pseudo-C_{2v} symmetry with C≡N bond distances ranging from 1.111 (10) to 1.140 (10) Å. Remaining $[N(CN)_2]^-$ C≡N bond distances are

much longer and range from 1.280 (12) to 1.308 (12) Å. Furthermore, *cis*-N-Mn-N' bond angles display a slight distortion from 90° and range from 85.1 (2) to 92.9 (2)°. The smallest N-Mn-O(1) and N-Mn-O(1)' bond angles deviate appreciably from 90° and are 78.9 (4) and 76.9 (4)°, respectively. The 4,4'-bipyridine rings are

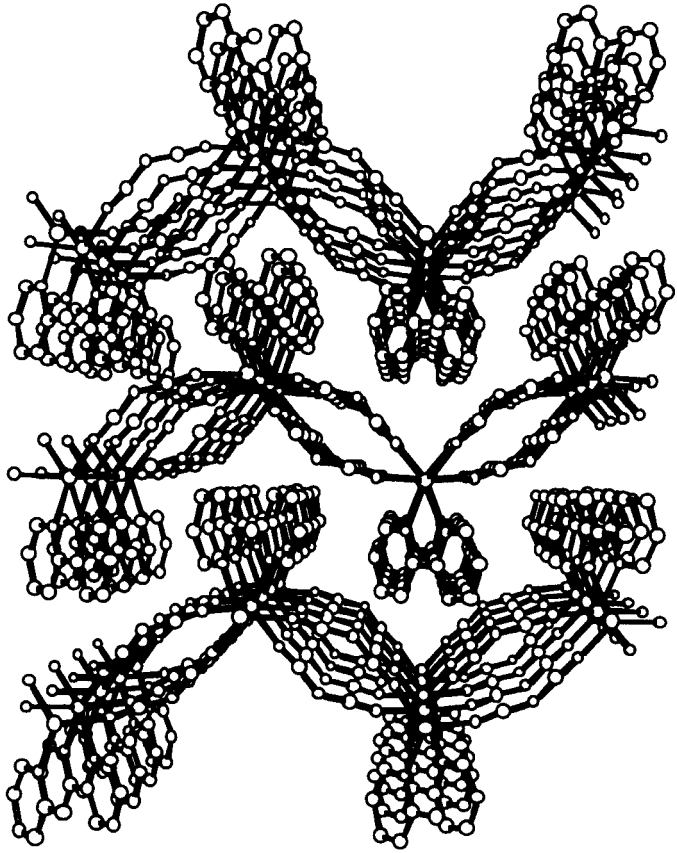

FIGURE 2. Packing diagram of the 1-D chains in **1** generating the 2-D layered network.

slightly twisted out-of-plane by 10.8°. The chains are isolated from one another by the monodentate 4,4'-bipyridine ligands. To the best of our knowledge, **2** is the first coordination compound to exhibit monodentate 4,4'-bipyridine.

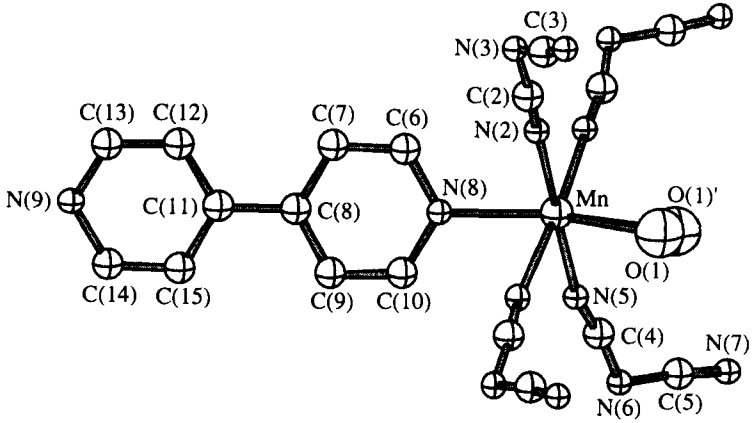

FIGURE 3. The Mn^{II} coordination sphere for **2** showing the atom-labeling diagram. Selected bond distances [Å] and angles [°]: Mn-N(2) 2.187(6), Mn-N(4) 2.206(7), Mn-N(7) 2.213(7), Mn-N(8) 2.263(4), Mn-O(1) 2.309(9), Mn-O(2) 2.220(11), C(2)-N(2) 1.137(9), C(4)-N(5) 1.140(9), C(2)-N(3) 1.280(12), N(2)-Mn-N(4) 89.4(2), N(5)-Mn-N(7) 91.3(2), N(4)-Mn-O(1) 104.5(4), N(8)-Mn-O(1)' 163.3(4), N(2)-Mn-N(5) 178.9(3), N(4)-Mn-N(7) 176.4(3).

The magnetic susceptibility, χ, of **1** and **2** have been measured and can be fit to the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$, with g-values of 2.00 and θ-values of -3.6 and -4.4 K for **1** and **2**, respectively consistent with weak antiferromagnetic coupling between nearest-neighbor Mn^{II} centers in each. The room temperature effective moments for **1** and **2** are 5.87 and 5.92 μ_B, respectively, in excellent agreement with the spin-only value expected for uncoupled S = 5/2 Mn^{II}. Due to antiferromagnetic coupling each compound displays a rapid decrease in the moment below 50 K. In order to elucidate the intrachain interactions, the data was also fit to the 1-D Heisenberg chain model

derived by Fisher[12] with isotropic g-values of 2.00 and exchange constants of -0.17 and -0.24 K, respectively, Figure 5. Long-range magnetic ordering is not observed in either material down to 2 K although the onset of a maximum in χ is noted in **1**.

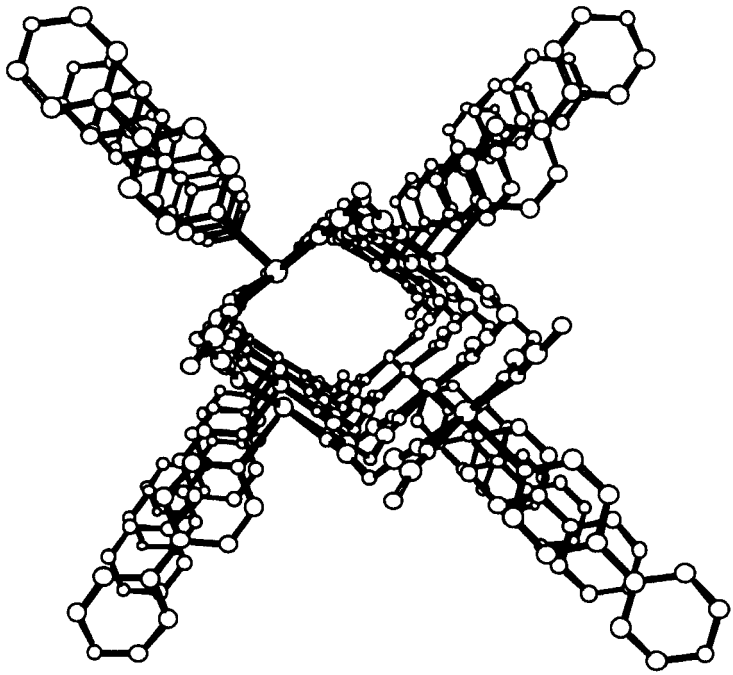

FIGURE 4. Perspective view of the 1-D cylindrical tube of **2** down the *z*-axis. The coordinated and lattice water molecules are not shown for clarity.

Conclusion

Two new 1-D coordination polymers have been synthesized and characterized by single crystal structure determination and magnetic susceptibility. Use of $[N(CN)_2]^-$ in conjunction with Mn^{II} and bipyridine derivatives have yielded 1-D structural motifs with the composition $Mn[N(CN)_2]_2L$ (L = 2,2'-bipy and 4,4'-bipy). Zig-zag chains and cylindrical tubes were found for the 2,2'-bipy

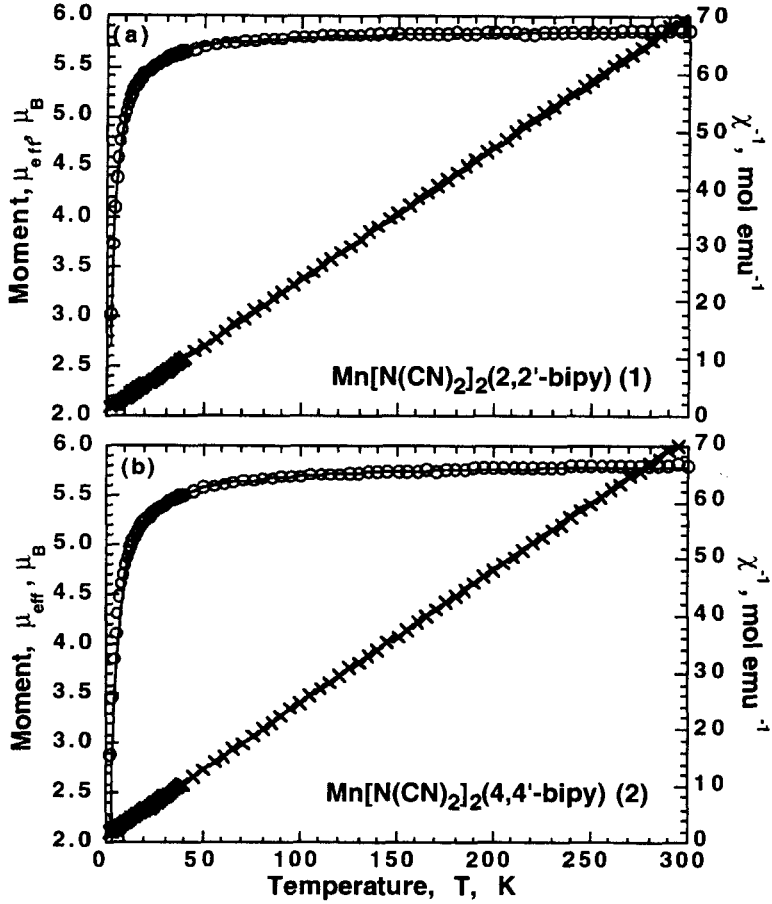

FIGURE 5. Temperature dependence of the effective magnetic moment (o) and reciprocal molar magnetic susceptibility (x) for compounds **1** and **2**. Heavy lines denote fits to the Fisher 1-D chain model with J/k_B = -0.17 and -0.24 K for **1** and **2**, respectively. Data was taken in a 1000 Oe dc magnetic field upon warming.

and 4,4-bipy analogs, respectively. Weak antiferromagnetic interactions between Mn centers via the $[N(CN)_2]^-$ ligand was observed with no 3-D

ordering above 2 K. Similar bis-dicyanamide complexes were reported at this meeting by M. Kurmoo and K. Murray.

Acknowledgments

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[10] (a) $Mn[N(CN)_2]_2$(2,2'-bipy), **1.** A 5-mL aqueous solution of $MnCl_2{\bullet}4H_2O$ (1.36 mmol, 0.2686 g) was added slowly to a stirring 15 mL H_2O/EtOH solvent mixture containing $Na[N(CN)_2]$ (2.71 mmol, 0.2413 g) and 2,2'-bipyridine (1.35 mmol, 0.2115 g). A yellow microcrystalline powder precipitated immediately and was collected via vacuum filtration and dried *in vacuo* over P_2O_5 (0.4187 g, 89 %). υ_{CN} (Nujol): 2414 w, 2304 m, 2232 m, 2205 s, and 2169 S cm^{-1}. Anal. Calc'd for $C_{14}H_8N_8Mn$: C, 48.99 ; H, 2.34 ; N, 32.65. Found: C, 48.90; H, 2.31; N, 32.73. (b) $Mn[N(CN)_2]_2$(4,4'-bipy)$\bullet 3/2H_2O$, 2. A 5 mL aqueous solution of $MnCl_2{\bullet}4H_2O$ (1.42 mmol, 0.2818 g) was added slowly to a stirring 10 mL H_2O/Me_2CO solvent mixture containing $Na[N(CN)_2]$ (2.87 mmol, 0.2558 g) and 4,4'-bipyridine (1.43 mmol, 0.2226 g). A pale peach microcrystalline powder precipitated immediately and was collected via vacuum filtration and dried *in* vacuo over P_2O_5 (0.4577 g, 94 %). υ_{CN} (Nujol): 2415 w, 2303 m, 2242 m, and 2178 S cm^{-1}. Anal. Calc'd for $C_{28}H_{22}N_{16}O_3Mn_2$: C, 45.42 ; H, 2.99 ; N, 30.27. Found: C, 45.40; H, 2.98; N, 30.18.

[11] (a) *Crystal Data* for $C_{14}H_8MnN_8$, **1:** $M = 343.22$, monoclinic *C2/c*, $a = 6.6769(3)$ Å, $b = 17.2008(2)$ Å, $c = 13.0142(4)$ Å, $\beta = 90.110\ (2)°$, $U = 1494.65(8)$ Å^3, $Z = 4$, $D_c = 1.525$ Mg/m^3, μ(Mo-K$_\alpha$) = 0.895 mm^{-1}, $T = 173\ (2)$ K. The data was collected on a standard Siemens P4/CCD diffractometer. Of 3096 data ($4 < 2\theta \leq 52°$), 1343 were independent ($R_{int} = 0.0364$), and 692 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined using the Siemens SHELXTL© (Version 5.0) Software Package. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions, R(F) = 0.0514, R(wF) = 0.1218, GOF = 1.742. The X-ray data was deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-102608. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ [fax: (+44) 1223–336–033; email deposit@ccdc.cam.ac.uk]. (b) *Crystal Data* for $C_{28}H_{22}N_{16}O_3Mn_2$, **2**: $M = 740.50$, orthorhombic *Iba2*, $a = 22.378(6)$ Å, $b = 22.517(5)$ Å, $c = 13.519(5)$ Å, $U = 6812(3)$ Å^3, $Z = 8$, $D_c = 1.444$ Mg/m^3, μ(Mo-K$_\alpha$) = 0.797 mm^{-1}, $T = 291\ (2)$ K. The data was collected on a standard Enraf-Nonius CAD4 automated diffractometer. Of 3135 data ($5 \leq 2\theta \leq 50°$), 3135 were independent ($R_{int} = 0.0000$), and 3008 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined using the Siemens SHELXTL97© Software Package. Disordered water molecules with O(1), 0(2), O(1)′ and O(2)′ atoms were refined as 0.5 occupancy each. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions, R(F) = 0.0384, R(wF) = 0.0861, GOF = 1.033. All illustrations were drawn with *Crystal Maker*©.

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