Polish J. Chem., **78**, 343–348 (2004) **INORGANIC CHEMISTRY**

Synthesis, Crystal Structure and Magnetic Properties of $[Mn(L)_2(N(CN)_2)_2]$, a One-Dimensional Systems with End to End Single Dicyanamide Bridges (L = 4-Cyanopyridine N-Oxide)

by Q.-H. Zhao[1], Y.-Q. Liu[1,2] and R.-B. Fang[2*]

[1]*Department of Chemistry, Yunnan University, Kunming 650091, P. R. China*
[2]*School of Pharmacy, Yunnan University, Kunming 650091, P. R. China*

(Received November 3rd, 2003)

A new 1-D polymeric coordination compound $[Mn(L)_2(N(CN)_2)_2]$ (L = 4-cyanopyridine N-oxide) has been synthesized and characterized. The crystal structure of this compound was determined by X-ray diffraction analysis. In the crystal structure, the $[Mn(L)_2]^{2+}$ units are linked by $[N(CN)_2]^-$ μ-bridging ligands to form one dimensional structure. The manganese ions display four coordination, with two terminal N atoms of different $[N(CN)^2]^-$ ligands and two O atoms of different 4-cyanopyridine N-oxide ligands. Analysis of variable temperature magnetic susceptibility (2–300 K) indicates that the polymer shows weak antiferromagnetic interaction.

Key words: manganese(II) compound, dicyanamide, crystal structure, magnetic properties

Richness topology and related physical properties of polymeric coordination compounds constitute a hot subject of research [1–3]. Dicyanamide (dca) bridged polynuclear systems are a fast growing research, due to the large variety of topologies and potentially useful properties that may be obtained from the ligand [4]. It is a remarkable versatile building block for the construction of supramolecular architectures, since it may act as a uni-, bi-, tri-, and an unusual μ_4 coordination, where one nitrile nitrogen binds to two metal atoms. Many extended coordination polymers have been reported, for example: 3-D for $M^{II}[N(CN)_2]_2$ (M = Cu, Co, Ni, Mn, Pb) [5–7], 2-D for $Zn[N(CN)_2]_2$ [8] and 1-D for $[Mn[N(CN)_2]_2 \cdot 2(py)]$ and $[Mn[N(CN)_2]_2(DMF)_2]$ [9]. Some of them display unusual magnetic properties including long-range ferromagnetic ordering and hard magnetic behavior. On the other hand, the 4-cyanopyridine N-oxide was used as a bridging ligand in $[Cd(L)_2] \cdot 2H_2O$ [10], an unprecedented three-dimensional network. Taking advantage of both 4-cyanopyridine N-oxide and the dicyanamide to coordinate transition metals, we report here the synthesis, X-ray crystal structure and magnetic properties of the one dimensional polymeric compound with formula $[Mn(L)_2(N(CN)_2)_2]$ (L = 4-cyanopyridine N-oxide), where the dicyanamide anion also bridged metal ions in an end-to-end fas-

---

[*] Author for correspondence.

hion ($\mu_{1,5}$). So far, very few 1-D chain of $[N(CN)_2]^-$ metal complexes with dipyridyl ligands have been reported [4,11–14].

EXPERIMENTAL

Materials and physical measurements: Elemental analysis of carbon, hydrogen and nitrogen were carried out on Elementar Cario EL elemental analyzer. The IR spectrum was taken on a Thermo-Nicolet AVATAR FT-IR360 spectrophotometer. Variable temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Synthesis of the complex: All reagents were commercial grade materials, used as received. $Na[N(CN)_2]$ was purchased from Aldrich Company. 4-Cyanopyridine N-oxide was prepared according to the literature [15].

$[Mn(L)_2(N(CN)_2)_2]$: A methanolic solution (10 cm^3) of $MnCl_2{\cdot}4H_2O$ (98.96 mg, 0.5 mmol) was added to a stirred methanolic solution (10 cm^3) of $NaN(CN)_2$ (89.03 mg, 1 mmol), 4-cyanopyridine-N-oxide (120 mg, 1 mmol) was added dropwise with stirring. Well-shaped crystals of $[Mn(L)_2(N(CN)_2)_2]$ were separated from the mother liquor and covered with plastic paper by slow evaporation at room temperature after two weeks. (Yield: 60%). Anal. Calcd. for $C_{16}H_8N_{10}O_2Mn$: C, 44.98; H, 1.89; N 32.78; Found: C, 45.12; H, 2.05; N, 32.31%. IR (KBr disk) cm^{-1} (ν_{sym}(C≡N) 2187; ν_{sym} (C≡N) 2252; ν_{sym} (C–N) 900; ν_{sym} (C–N) 1371, ν(N–H) 3478, ν(N→O) 1208.

X-ray measurements and structure determination: A colourless crystal (0.23 × 0.23 × 0.05 mm^3) was selected and mounted on a glass fiber. All measurements were made on a CCD area detector, equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The data were collected at room temperature including 7295 reflections in the $2.09° < \theta < 29.98°$ range, including 2504 independent reflections ($R_{int} = 0.0271$). A summary of the crystallographic data is given in Table 1.

Table 1. Summary of the crystallographic data for $[Mn(L)_2(N(CN)_2)_2]$.

Empirical formula	$C_{16}H_8N_{10}O_2Mn$
Formula weight	427.24
Temperature	223(2) K
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	6.9498(7)
b (Å)	19.511(2)
c (6)	7.2273(8)
α (°)	90.00
β (°)	116.568(2)
γ (°)	90.00
Z	11
Density (g/cm^3)	1.619
$F(000)$	430
θ range for data collection	2.09–29.98°
Ranges of indices h, k, l	–9/7, –27/27, –7/9
μ (mm^{-1})	0.792
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0418$, $wR_2 = 0.0499$
R indices (all data)	$R_1 = 0.1026$, $wR_2 = 0.1069$

The structure was solved by direct methods using the SHELXS-97 program [16]. All non-hydrogen atoms were refined anisotropically. The H atoms were located from molecular geometry and included in the final refinement. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [17] and the goodness-of-fit on F^2 was 1.061. Maximum and minimum peaks in the final difference Fourier synthesis were 0.739 and –0.395 e Å^{-3}.

RESULTS AND DISCUSSION

Crystal structure: An ORTEP plot of the complex is shown in Fig. 1. The selected bond lengths and angles for complex are presented in Table 2. The crystal structure (Fig. 2) contains well isolated chains of manganese atoms by means of single end-to-end dicyamide bridges. Each manganese atom is four-coordinated by means of two O atoms [Mn(1)–O(1): 2.2018(13) Å; Mn(1)–O(1A): 2.2018(13) Å] belonging to the 4-cyanopyridine-N-oxide ligand and two terminal N atoms of different $[N(CN)_2]^-$ ligands [Mn(1)–N(3): 2.1898(16) Å; Mn(1)–N(3A): 2.1898(16) Å]. $[N(CN)_2]^-$ has pseudo C_{2v} symmetry with average C–N and N≡C bond lengths of 1.306 Å and 1.144 Å, respectively, as commonly observed in $[N(CN)_2]^-$ anions [18–27]. The Mn–N≡C angles of 146.06(15) and 159.42(15)° deviate from linearity, while N–C≡N angles (mean value 175.8°) are linear. Each $[N(CN)_2]^-$ is coordinated to two Mn(II) atoms *via* the two nitrile nitrogens, and the distance between two Mn(II) atoms linked by $[N(CN)_2]^-$ is equal to 7.227 Å.

Magnetic properties: The temperature dependence of the magnetic susceptibility was measured between 2–300 K, with an applied field of 1 T. The magnetic behavior of the compound is presented in Fig. 3 in the form of plot of $\chi_M T$ *versus* T. The $\chi_M T$ value at room temperature is 4.29 cm^3 K mol^{-1}, which is lower than the spin-only value expected for a non-coupled high-spin S = 5/2 spin system (4.37 cm^3 K mol^{-1}). When the temperature is lowered, the $\chi_M T$ values remain constant down to *ca.* 50 K, then decrease rapidly to 3.2 cm^3 K mol^{-1} at 4.4 K. There are two contributions to such

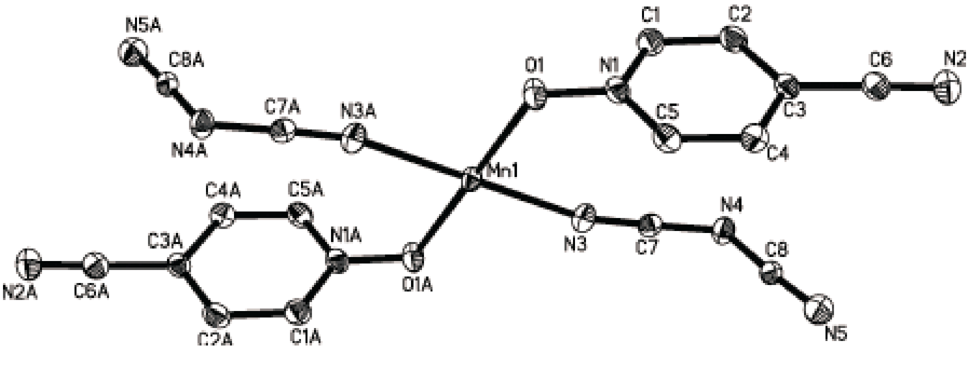

Figure 1. ORTEP drawing with 30% thermal ellipsoid probability showing atom labeling of $[Mn(L)_2(N(CN)_2)_2]$.

behavior for a manganese(II), (d^5) system, zero-field splitting of the short range antiferromagnetic coupling. The splitting of the singe-ion $^6A_{1g}$ state by spin-orbit coupling in zero-field is expected to be very small and will be ignored. The short range antiferromagnetic coupling was simulated by use of a 1-D Heisenberg chain model, developed by Fisher and applied commonly to manganese(II) chain system [28].

$$H = -2J\hat{S}_i\hat{S}_{i+1};\ \chi_M = \frac{Ng^2\beta^2 S(S+1)}{3kT}\cdot\frac{1+u}{1+u};\ u = \coth\left[\frac{2JS(S+1)}{kT}\right] - \frac{kT}{2JS(S+1)}$$

The best fit parameters are $J_1 = -0.75\ \text{cm}^{-1}$, $g = 1.98$ and $R = 2.8\times10^{-3}$ (R is the agreement factor defined as $R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$). The very small values of J indicate, that weak antiferromagnetic intrachain interactions are mediated by the dicyanamide bridge.

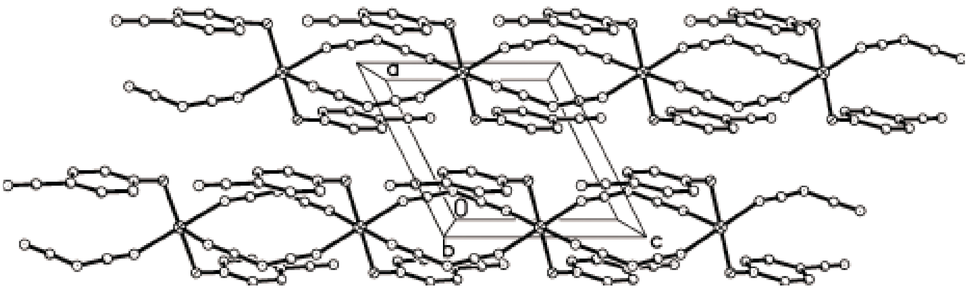

Figure 2. The unit cell of compound $[Mn(L)_2(N(CN)_2)_2]$.

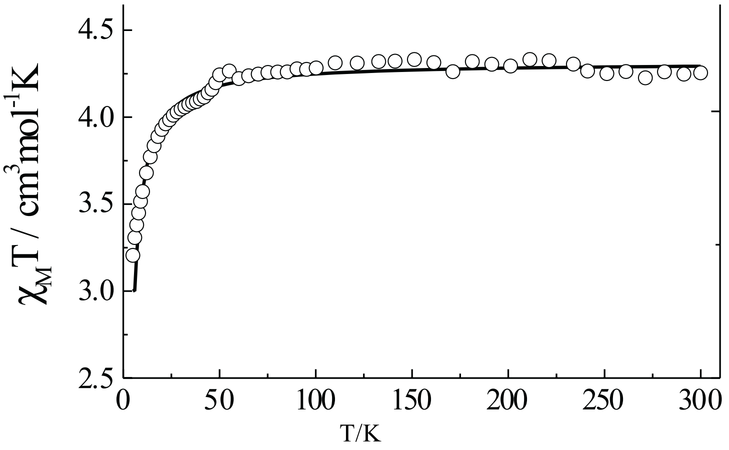

Figure 3. Plot of $\chi_M T$ and χ_M for $[Mn(L)_2(N(CN)_2)_2]$ *versus T*.

Table 2. Selected bond lengths (Å) and angles (°).

Mn(1)–N(3)	2.1898(16)	O(1)–N(1)	1.3222(19)
Mn(1)–N(3A)	2.1898(16)	N(4)–C(8)	1.306(2)
Mn(1)–O(1)	2.2018(13)	N(5)–C(8)	1.144(2)
Mn(1)–O(1A)	2.2018(13)	N(3)–C(7)	1.154(2)
N(4)–C(7)	1.306(2)		
O(1)–Mn(1)–N(3)	88.92(5)	N(3)–Mn(1)–N(3A)	180.00(9)
O(1A)–Mn(1)–N(3A)	88.92(5)	O(1)–Mn(1)–O(1A)	180.00(6)
O(1)–Mn(1)–N(3A)	91.08(5)	N(1)–O(1)–Mn(1)	118.85(10)
O(1A)–Mn(1)–N(3)	91.08(5)	C(7)–N(3)–Mn(1)	159.42(15)
N(3)–C(7)–N(4)	175.94(19)	C(7)–N(4)–C(8)	117.25(15)

Symmetry transformations used to generate equivalent atoms: A x, y, $z+1$.

Supporting information. Detailed crystallographic data, atomic position parameters, bond lengths and angles in CIF format in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-222306 for complex. (Copy of this information may be obtained free of charge *via* e-mail:deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the Natural Science Foundation of Yunnan Province (No: 2003E0012M; 2002FXX05), Natural Science Foundation of Yunnan University under the Grant (No: 2002Z001GC) and Natural Science Foundation of Educational Committee of Yunnan Province (No: 0111158).

REFERENCES

1. Hoskins B.F. and Robson R., *J. Am. Chem. Soc.*, **112**, 1456 (1990).
2. Batten S.R. and Robson R., *Angew. Chem., Int. Ed.*, **37**, 1461 (1998).
3. Kutasi A.M., Batten S.R., Moubaraki B. and Murray K.S., *J. Chem. Soc., Dalton Trans.*, 819 (2002).
4. Claramunt A., Escuer A., Mautner F.A., Sant N. and Vicente R., *J. Chem. Soc. Dalton Trans.*, 2627 (2000).
5. Batten S.R., Jensen P., Moubaraki B., Murray K.S. and Robson R., *Chem. Commun.*, 439 (1998).
6. Jensen P., Batten S.R., Moubaraki B. and Murray K.S., *J. Chem. Soc., Dalton Trans.*, 3712 (2002).
7. Shi Y.J., Chen X.T. and Li Y.Z., *New J. Chem.*, **26**, 1711 (2002).
8. Batten S.R., Jensen P., Kepert C.J. and Kurmoo M., *Chem. Commun.*, 177 (1999).
9. Martin S., Barandika M.G., Cortes R., Larramendi J.I.R., Lezama L. and Rojo T., *J. Chem. Soc. Dalton Trans.*, 4275 (2002).
10. Zheng C.G., Xie Y.L., Xiong R.G. and You X.Z., *Inorg. Chem. Commun.*, **8**, 405 (2001).
11. Sun B.W., Gao S., Ma B.Q., Niu D.Z. and Wang Z.M., *J. Chem. Soc., Dalton Trans.*, 4187 (2000).
12. Sun B.W., Gao S., Ma B.Q. and Wang Z.M., *Inorg. Chem. Commun.*, **4**, 72 (2001).
13. Batten S.R., Jensen P., Kepert C.J., Kurmoo M., Moubaraki B., Murray K.S. and Price D.J., *J. Chem. Soc. Dalton Trans.*, 2987 (1999).
14. Dasna I., Golhen S., Qouahab L., Pena O., Guillevic J. and Fettouhi M., *J. Chem. Soc. Dalton Trans.*, 129 (2000).
15. Ochial E., *J. Org. Chem.*, **13**, 534 (1953).

16. Sheldrick G.M., SHELXS-97, *Program for X-ray Crystal Structure Determination*, University of Göttingen, Germany, 1990.
17. Sheldrick G.M., SHELXL-97, *Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
18. Manson J.L., Kmety C.R., Huang Q.-Z., Lynn J.W., Bendele G.M., Pagola S., Stephens P.W., Liable-Sands L.M., Rheingold A.L., Epstein P.W. and Miller J.S., *Chem. Mater.*, **10**, 2552 (1998).
19. Manson J.L., Buschmann W.E. and Miller J.S., *Angew. Chem.,Int. Ed.*, **37**, 783 (1998).
20. Manson J.L., Campana C. and Miller J.S., *Chem. Commun.*, 151 (1998).
21. Potocnak I., Dunaj-Jurco M., Miklos D. and Jager J., *Acta Cryst., Sect. C*, **52**, 1653 (1996).
22. Potocnak I., Dunaj-Jurco M., Miklos D., Kabesova M. and Jager J., *Acta Cryst., Sect. C*, **51**, 600 (1995).
23. Chow Y.M., *Inorg. Chem*., **10**, 1938 (1971).
24. Britton D. and Chow Y.M., *Acta Cryst., Sect. B*, **33**, 607 (1997).
25. Britton D., *Acta Cryst., Sect. B*, **46**, 2297 (1990).
26. Chow Y.M. and Britton D., *Acta Cryst., Sect. B*, **31**, 1934 (1975).
27. Mrozinski J., Hvastijova M. and Kohout J., *Polyhedron*, **11**, 2867 (1992).
28. Fisher M.E., *Am. J. Phys*., **32**, 343 (1964).