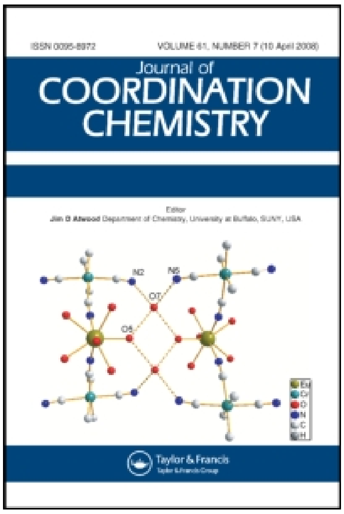

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Syntheses, crystal structures and magnetic study of two binuclear manganese(II) complexes with aromatic N-oxide as bridging ligand

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Syntheses, crystal structures and magnetic study of two binuclear manganese(II) complexes with aromatic N-oxide as bridging ligand

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Two new binuclear complexes, $[Mn_2(\mu\text{-}dmpo)_2(SCN)_4(H_2O)_2]$ (**1**) (where *dmpo* = 3,5-dimethylpyridine N-oxide), $[Mn_2(\mu\text{-}po)_2(H_2O)_6I_2]I_2$ (**2**) (where *po* = pyridine N-oxide), have been synthesized and their crystal structures determined by X-ray crystallography. Complexes **1** and **2** crystallize in monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 8.8836(18)$ Å, $b = 15.450(3)$ Å, $c = 15.484(3)$ Å, $\beta = 91.020(3)^\circ$ for **1**, and $a = 8.8352(13)$ Å, $b = 17.927(3)$ Å, $c = 8.3338(12)$ Å, $\beta = 103.765(2)^\circ$ for **2**. In each binuclear complex two Mn(II) were bridged by two 3,5-dimethylpyridine N-oxides or by two pyridine N-oxides and the distances between the bridged Mn(II) ions are 3.599 Å for **1** and 3.552 Å for **2**. Variable temperature (4–300 K) magnetic measurements were performed for **1** and the susceptibility data were fitted by using a binuclear Mn(II) magnetic coupling formula producing the $2J = -2.17\,\text{cm}^{-1}$.

Keywords: Magnetism; Crystal structure; Binuclear complex; Aromatic N-oxide

1. Introduction

Magnetism of multi-nuclear complexes has attracted considerable attention for understanding biological function of some metallic proteins and preparing molecular-based magnets [1].

It is well known that the bridging ligand is a major factor in magnetic coupling properties in bridging metallic ions. Complexes with aromatic N-oxide compounds as bridging ligands have exhibited interesting magnetic coupling properties. For example, the complexes with pyrazine-1,4-dioxide and its derivatives as bridging ligands display stronger magnetic interactions than complexes with pyrazine and its derivatives as bridging ligands [2–5]. We are interested in magneto-structure studies of multi-nuclear complexes with pyridine N-oxide and its derivatives as bridging ligands and have synthesized a few such complexes [6, 7] and studied their magnetism. In this article we present the crystal structures of two complexes and the magnetic study of **1**.

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2. Experimental

2.1. *Preparation*

3,5-Dimethylpyridine N-oxide and pyridine N-oxide were prepared from the 3,5-dimethylpyridine and pyridine, respectively, by the literature method [8]; other chemicals were analytical grade and used without further purification.

Preparation of $[Mn_2(\mu\text{-}dmpo)_2(SCN)_4(H_2O)_2]$ (**1**): $Mn(ClO_4)_2 \cdot 6H_2O$ (0.2539 g, 0.701 mmol), *dmpo* (0.0875 g, 0.711 mmol) and NaNCS (0.1203 g, 1.48 mmol) were dissolved in 5 mL H_2O, and then the three solutions were mixed together and stirred for a few minutes. Colorless single crystals were obtained after the solution was allowed to stand for three weeks at room temperature. Anal. Calcd for $C_{32}H_{40}Mn_2N_8O_6S_4$ (Fw: 870.84): C, 44.13; H, 4.63; N, 12.87; Mn, 12.62%. Found: C, 44.34; H, 4.93; N, 12.54; Mn, 12.08%.

Yellowish single crystals of $[Mn_2(\mu\text{-}po)_2(H_2O)_6I_2]I_2$ (**2**) were prepared the same way as **1** except *dmpo* and NaNCS were replaced by *po* and NaI. Anal. Calcd for $C_{10}H_{22}I_4Mn_2N_2O_8$ (Fw: 915.78): C, 13.11; H, 2.42; N, 3.06; Mn, 12.00%. Found: C, 13.35; H, 2.71; N, 3.45; Mn, 12.43%.

2.2. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin-Elmer 240 instrument. Variable-temperature magnetic susceptibility measurement was performed using a crushed single crystal sample in the temperature range of 4–300 K with a SQUID magnetometer and applied magnetic field of 3 K Oe. The data were corrected for magnetism of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

2.3. *X-ray crystal structure determination*

The single crystal of **1** or **2** was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25°C was carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD, using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was performed to the raw intensities by using the SADABS program [9]. Corrections for *Lp* factor was applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms from H_2O were located in a difference map, other hydrogen atoms were placed in calculated positions, and all were refined as riding atoms. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). The deposition numbers of the crystals at the CCDC are 266582 for **1** and 265079 for **2**. The relevant structure parameters were given in table 1 and selected bond distances and associated angles are listed in table 2.

Table 1. Crystal data and structure refinement.

	1	**2**
Empirical formula	$C_{32}H_{40}Mn_2N_8O_6S_4$	$C_{10}H_{22}I_4Mn_2N_2O_8$
CCDC deposit no.	266582	265079
Formula weight	870.84	915.78
Temperature (K)	298	298
Crystal size (mm^3)	0.50 × 0.35 × 0.21	0.20 × 0.15 × 0.09
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.8836(18)	8.8352(13)
b (Å)	15.450(3)	17.927(3)
c (Å)	15.484(3)	8.3338(12)
β (°)	91.020(3)	103.765(2)
Volume (Å^3)	2124.9(7)	1282.0(3)
Z	2	2
Density (calculated) (Mg m^{-3})	1.361	2.372
Absorption coefficient (mm^{-1})	0.839	5.833
$\theta_{\min}$, $\theta_{\max}$ (°)	1.86; 26.00	2.27; 25.50
Completeness (%)	0.995 ($\theta = 26.00°$)	0.995 ($\theta = 25.50°$)
Goodness-of-fit on F^2	1.003	1.101
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0385$; $wR_2 = 0.1037$	$R_1 = 0.0306$; $wR_2 = 0.0769$
R indices (all data)	$R_1 = 0.0537$ $wR2 = 0.1106$	$R_1 = 0.0348$ $wR_2 = 0.0788$
$(\Delta/\sigma)_{\max}$	0.001	0.001
Largest diff. peak and hole (e Å^{-3})	0.279, −0.294	0.918, −1.010

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

1					
Mn1–N2	2.116(2)	Mn1–N3	2.129(2)	Mn1–O3	2.2072(15)
Mn1–O2	2.2078(14)	Mn1–O1	2.2523(17)	Mn1–O2A	2.2127(14)
2					
Mn1–I1	2.8284(9)	Mn1–O2	2.167(4)	Mn1–O3	2.179(4)
Mn1–O1	2.183(4)	Mn1–O4	2.186(3)	Mn1–O4A	2.214(3)
1					
N2–Mn1–N3	105.19(9)	N2–Mn1–O3	94.34(7)		
N3–Mn1–O3	91.82(8)	N2–Mn1–O2	90.62(7)		
N3–Mn1–O2	164.17(7)	O3–Mn1–O2	87.84(6)		
N2–Mn1–O1	100.54(8)	N3–Mn1–O1	95.53(8)		
O3–Mn1–O1	161.04(6)	O2–Mn1–O1	80.36(6)		
N2–Mn1–O2A	160.72(8)	N3–Mn1–O2A	93.36(7)		
O3–Mn1–O2A	79.62(6)	O2–Mn1–O2A	71.00(5)		
O2A–Mn1–O1	82.52(6)				
2					
O2–Mn1–O3	170.32(16)	O2–Mn1–O1	84.59(15)		
O3–Mn1–O1	87.03(16)	O2–Mn1–O4	89.88(14)		
O3–Mn1–O4	96.56(15)	O1–Mn1–O4	161.17(14)		
O2–Mn1–I1	94.20(13)	O3–Mn1–I1	92.41(10)		
O1–Mn1–I1	103.16(11)	O4–Mn1–I1	95.18(9)		
O2–Mn1–O4A	88.61(15)	O4A–Mn1–I1	167.22(9)		
O3–Mn1–O4A	86.49(14)	O1–Mn1–O4A	89.51(14)		
O4–Mn1–O4A	72.34(14)				

Symmetry codes: O2A: $-x+1$, $-y+1$, $-z$; O4A: $-x+1$, $-y$, $-z+2$.

3. Results and discussion

3.1. *Infrared spectrum*

For **1** the strong and sharp peaks at 2077 and 2055 cm^{-1} come from vibrations of SCN^-, and the peaks at 1636, 1614 and 1457 cm^{-1} may be attributed to the vibrations of the C=N and C=C bonds of pyridine.

3.2. *Crystal structure*

3.2.1. Crystal structure 1. Figure 1 shows the coordination diagram of **1** with atom numbering scheme and table 2 gives the data dealing with the coordinated bond lengths and the associated angles. Mn1 has a distorted octahedral coordination, formed by two N atoms from two thiocyanate terminal ligands and four O atoms from two *dmpo* bridged ligands and one H_2O molecule and one *dmpo* terminal ligand. Figure 1 also displays that the binuclear unit is constructed by two *μ-dmpo* bridged ligands, and in the unit the separation distance of the two Mn(II) ions is 3.599 Å. In addition, there are hydrogen bonds between neighbor binuclear units as shown in table 3.

3.2.2. Crystal structure 2. Figure 2 shows the coordination diagram of **2** with atom numbering scheme and table 2 gives the data dealing with the coordinated bond lengths and associated angles. Mn1 atom assumes a distorted octahedral MnO_5I coordination geometry, in which five O atoms are from three H_2O molecules and two *po* bridged ligands. The separation distance of the two Mn(II) ions in the binuclear unit is 3.552 Å close to that of **1**. Table 3 shows that in this crystal there are hydrogen bonds between

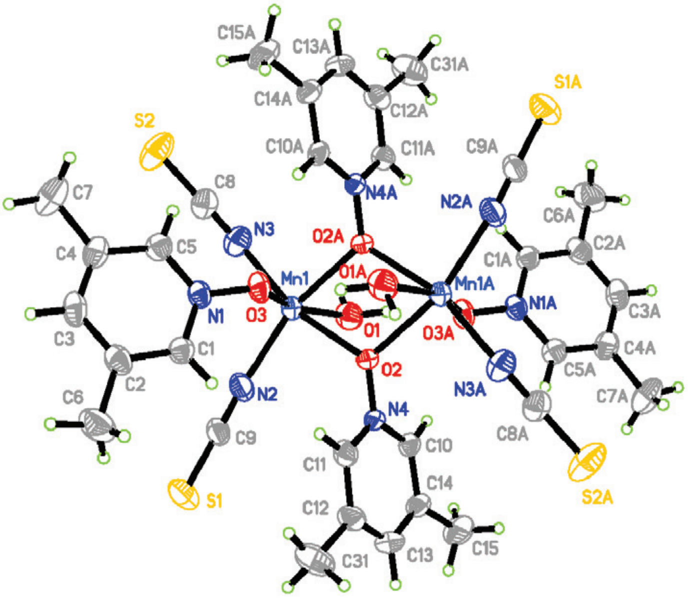

Figure 1. Coordination diagram with the atom numbering scheme for **1**.

Table 3. Hydrogen bond lengths (Å) and angles (°).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
1				
O1–H4···O3^{i}	0.90	2.05	2.898(2)	157.4
O1–H5···S2^{ii}	0.88	2.75	3.3535(19)	126.8
2				
O1–H5···I2^{iii}	0.78	2.76	3.509(4)	160.3
O1–H6···I2^{iv}	0.70	2.81	3.496(4)	167.7
O3–H1···I1^{v}	0.65	2.97	3.579(4)	158.1
O3–H2···I2^{vi}	0.92	2.69	3.578(4)	162.8
O2–H3···I1^{vii}	0.68	2.88	3.557(4)	173.9

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+2, -y+1, -z$; (iii) $-x+1, y-1/2, -z+3/2$; (iv) $-x+1, -y, -z+1$; (v) $-x+2, -y, -z+2$; (vi) $-x+1, -y, -z+2$; (vii) $-x+1, -y, -z+1$.

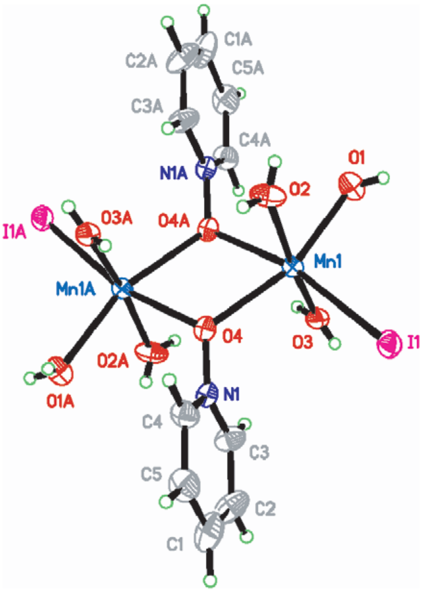

Figure 2. Coordination diagram with the atom numbering scheme for **2**.

the uncoordinated I$^-$ anion and the coordinated H_2O molecules, and between the coordinated I$^-$ anion and the coordinated H_2O molecules, which made the neighbor complexes connect each other and led to formation of a supermolecular one-dimensional chain in the *c* axis.

3.3. *Magnetism*

Figure 3 shows plots of $\chi_{\rm mol}$ *versus* T and $\mu_{\rm eff}$ *versus* T for **1**. The magnetic moment value per binuclear Mn(II) at 300 K is 8.09 μ_B, smaller than 8.37 μ_B of uncoupled binuclear Mn(II) at room temperature; the magnetic moments go down with

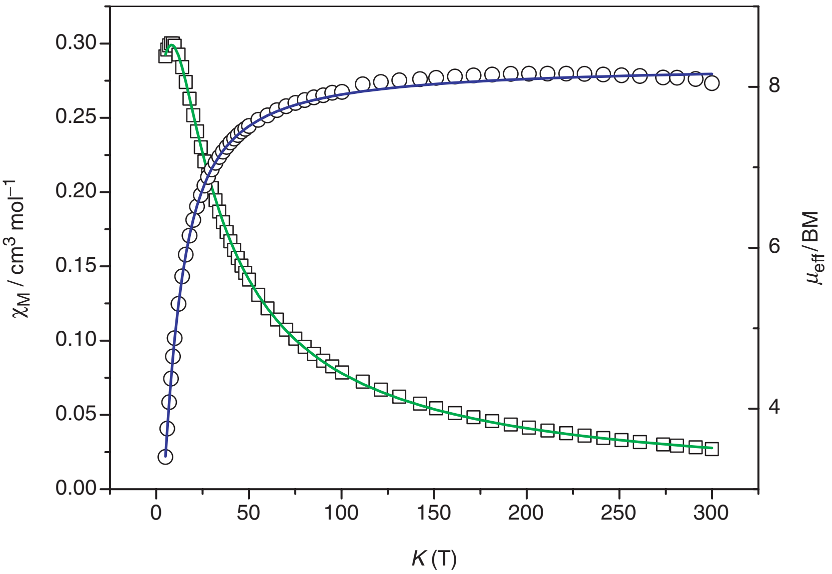

Figure 3. Plots of χ_M (open black square for experimental value, green curve for theoretical value) *vs. T*, and μ_{eff} (open black circle for the experimental values, blue curve for theoretical value) *vs. T* for **1**.

temperature and reach a minimum of $1.45\,\mu_B$ at 4.96 K. The formula of binuclear Mn(II) [10] fits the experimental data, as shown in figure 3, and gives the best fit parameters: $2J = -2.17\,\mathrm{cm}^{-1}$, $g = 1.98$ and the agreement factor $R = 1.75 \times 10^{-5}$ [R is defined as $R = \Sigma\,(\chi_{obsd} - \chi_{Calcd})^2/(\chi_{obsd})^2$]. The $2J = -2.17\,\mathrm{cm}^{-1}$ indicates that there is a very weak magnetic coupling between the bridged Mn(II) ions.

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