



**SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES
OF MONONUCLEAR $[\text{Mn}(2,2'\text{-BIPYRIMIDINE})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2$
AND POLYNUCLEAR $[\text{Mn}(2,2'\text{-BIPYRIMIDINE})(\text{NO}_3)_2]$
COMPLEXES**

D. M. HONG

Tzu-Chi Junior College of Nursing, Hualien, Taiwan

and

H. H. WEI* and L. L. GAN

Department of Chemistry, Tamkang University, Tamsui, Taiwan

and

G. H. LEE and YU WANG

Department of Chemistry, National Taiwan University, Taipei, Taiwan

(Received 12 July 1995; accepted 20 October 1995)

Abstract—Two new complexes $[\text{Mn}(\text{bpym})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2$ (**1**) and $[\text{Mn}(\text{bpym})(\text{NO}_3)_2]$ (**2**) (bpym = 2,2'-bipyrimidine) have been prepared and characterized by spectroscopic and X-ray diffraction methods. Compound **1** consists of a mononuclear $[\text{Mn}(\text{bpym})_2(\text{H}_2\text{O})_2]^{2+}$ unit in which the manganese atom shows a distorted elongated octahedral coordination with two bpym nitrogens and two H_2O oxygens forming a *cis* configuration. The structure of compound **2** is made up of an infinite zigzag bpym-bridged polymeric chain with $[\text{Mn}(\text{bpym})(\text{NO}_3)_2]$ units, in which the manganese atom has seven coordination with four nitrogen atoms of two bpym ligands and three oxygen atoms of monodentate NO_3^- and bidentate NO_3^- anions. The intermetallic distance of $\text{Mn} \cdots \text{Mn}$ is 6.234(2) Å. The temperature dependence of the magnetic susceptibility of **2** reveals the presence of a one-dimensional Heisenberg antiferromagnetic chain with $J = -0.93 \text{ cm}^{-1}$. Published by Elsevier Science Ltd.

The coordination chemistry of manganese has achieved remarkable progress in the last decade due to the increased recognition of this metal's role in biological systems and also to molecular magnetism.^{1–6} The molecular design of models, to mimic mono-, bi- and polynuclear biologically active centres, and the synthesis of new molecular magnetic materials are among the driving forces of this interdisciplinary research field.^{1–9} In this context, we tried to prepare the mononuclear and

polynuclear Mn^{II} complexes by using the 2,2'-bipyrimidine (bpym) ligand.

Bpym can act as a chelate or a bischelate with metal atom. Recently, the studies on the structural characterization and magnetic measurements of bpym-bridged first transition-metal ions have been reported.^{10–15} It has been demonstrated that the design of one-, two- and three-dimensional networks of the bpym-bridged M^{II} complexes depending on both the M^{II} : bpym molar ratio and the nature of the counter ions.^{10–14} In this respect we thought that such a flexibility of the M^{II} -bpym system, could be used to design the expected mono-,

* Author to whom correspondence should be addressed.

bi- and polynuclear Mn^{II} complexes with different counter ions. We have recently prepared and characterized a centrosymmetric binuclear complex [Mn₂(bpym)(H₂O)₆(SO₄)₂] with an antiferromagnetic interaction between two Mn^{II} atoms.¹⁵ In this binuclear complex, bpym as a bridging ligand and the counter-ions SO₄²⁻ as monodentate are coordinated with the Mn^{II} atom. In the present work we report on the preparation, structural determination and magnetic characterization of two new mono- and polynuclear Mn^{II} complexes of the formula [Mn(bpym)₂(H₂O)₂][ClO₄]₂ (**1**) and [Mn(bpym)(NO₃)₂] (**2**), respectively. The purpose of this work was to clarify the role of the counter ions, X of Mn^{II} X_n (*n* = 1, 2), on the molecular design of mono- or polynuclear Mn^{II} complexes with the bpym ligand.

EXPERIMENTAL

Materials

2,2'-Bipyrimidine (bpym), manganese(II) nitrate hexahydrate and manganese(II) perchlorate hexahydrate were purchased from commercial sources and used as received.

Preparation of complexes

[Mn(bpym)₂(H₂O)₂][ClO₄]₂ (**1**) and [Mn(bpym)(NO₃)₂] (**2**) were synthesized by mixing an aqueous solution of the corresponding manganese(II) salt (2 mmol, 20 cm³) and an ethanolic solution of bpym (1 mmol, 10 cm³). The resulting yellow-green crystals of **1** (90% yield) and light-brown crystals of **2** (80% yield) were filtered off, air dried and characterized initially by elemental analysis, and also by single-crystal X-ray diffraction analysis. Found: C, 29.8; H, 3.2; N, 17.5. Calc. for C₁₆H₂₀N₈MnO₁₂Cl₂ (**1**): C, 29.9; H, 3.1; N, 17.5%. Found: C, 28.5; H, 1.8; N, 24.9. Calc. for C₈H₆N₆MnO₆ (**2**): C, 28.5; H, 1.8; N, 24.9%.

Crystal structure determination

Crystallographic data for the complexes **1** and **2** were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation at 25°C. Crystallographic parameters and pertinent refinement results are summarized in Table 1. The structures were solved by the heavy-atom method and subsequent difference-Fourier maps followed by full-matrix least-squares refinement. The ORTEP plots of the molecules are shown in Figs 1 (**1**) and 2 (**2** with a manganese environment). Figure 3 shows the polymer chain

structure of **2**. Selected interatomic distances and angles are listed in Tables 2 and 3 for complexes **1** and **2**, respectively. Complete crystal data, components of the anisotropic temperature factors, atomic positional parameters, and structure factors are deposited as supplementary material.

Physical measurements

IR spectra were recorded on a Bio-Rad FTS-40 FTIR spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ region. X-band EPR spectra at 300 K for the complexes in powder and in deoxygenated aqueous solution were recorded on a Bruker ESS-106 spectrometer. Temperature dependence of magnetic susceptibilities of the polycrystalline samples were measured between 4 and 300 K at a field 10 KG using a Quantum Design Model MPMS computer-controlled SQUID magnetometer. Corrections for the diamagnetism of complexes **1** and **2** were estimated from Pascal's constants.

RESULTS AND DISCUSSION

IR spectra

The most important aspects concerning the IR spectra of **1** and **2** deal with the possibility to distinguish between the chelating and bis-chelating coordination modes of bpym. The observed IR spectra of **1** shows the presence of a very asymmetric doublet at 1574s and 1560s cm⁻¹ (ring stretching mode of bpym) for **1** (chelating bpym), whereas it appears as a strong absorption as a quasi-symmetric doublet at 1577 cm⁻¹ in complex **2**, which has been observed for the structurally characterized complex **2** containing bis-chelating bpym.^{10–12} IR spectra also allow the determination of the coordination modes of NO₃⁻. The absorption bands of **2** at 1459s, 1380s and 820 cm⁻¹ are assigned to bidentate NO₃⁻ and those at 1420s, 1317m and 837 cm⁻¹ are assigned to monodentate NO₃⁻, respectively.¹⁶

Description of the structures

The structure of **1** is made up of cationic mononuclear [Mn(bpym)₂(H₂O)₂]²⁺ unit (Fig. 1) and two ClO₄⁻ ions. The manganese atom has a six-coordinate MnN₄O₂ chromophore with distorted octahedral coordination; it is bound to four nitrogen atoms of bpym [averaged Mn–N = 2.254(3) Å] and two oxygen atoms of H₂O [averaged Mn–O: 2.161(3) Å] in a *cis* position with respect to the two bpym ligands.

X-ray structural analysis of **2** revealed that the manganese(II) atom has a seven-coordination (Fig.

Table 1. Crystallographic data for **1** and **2**

	1	2
Formula	C ₁₆ H ₂₀ N ₈ MnO ₁₂ Cl ₂	C ₈ H ₆ N ₆ MnO ₆
Formula weight	642.22	337.11
Diffractometer	Nonius	Nonius
Space group	Monoclinic <i>C</i> 2/ <i>c</i>	Orthorhombic <i>P</i> <i>bca</i>
<i>a</i> (Å)	24.915(8)	10.886(2)
<i>b</i> (Å)	7.761(3)	13.188(4)
<i>c</i> (Å)	17.289(7)	15.518(6)
β (°)	131.71(3)	
<i>V</i> (Å ³)	2495.7(16)	2228(1)
<i>Z</i>	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.709	2.010
γ (Mo- <i>K</i> _α) (Å)	0.7107	0.71069
<i>F</i> (000)	1311	1355
Unit-cell detection; no; 2 θ range	25, (16.36–23.12)	25, (14.76–22.50)
Scan type	θ -2 θ	θ -2 θ
2 θ scan width (°)	2(0.60 + 0.35 tan θ)	2(0.65 + 0.35tan θ)
2 θ range (°)	50	50
μ (Mo- <i>K</i> _α) (cm ⁻¹)	12.203	11.810
Crystal size (mm)	0.4 × 0.50 × 0.50	0.1 × 0.20 × 0.20
Temperature (K)	298	298
No. of uniqueness reflections	2193	1953
No. of observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1757	1299
<i>R</i> , <i>R</i> _w	0.040, 0.039	0.036, 0.035
GoF	1.11	2.56
Minimized function	$\Sigma w F_o - F_c ^2$	$\Sigma F_o - F_c ^2$
<i>g</i> (second extinction coefficient) × 10 ⁴	4.8(3)	9.3(1)
(Δ/σ) _{max}	0.0039	0.0085
($\Delta\rho$) _{min,max} (e Å ⁻³)	-0.400, 0.450	0.350, -0.390
Computation program	NRCVAX ¹⁸	NRCVAX ¹⁸

^a*R* = $[\Sigma |F_o - F_c|/F_o]$. *R*_w = $[\Sigma w |F_o - F_c|^2 / \Sigma w (|F_o|^2)]^{1/2}$; $\sigma^2(F_o)$ from counting statistics.

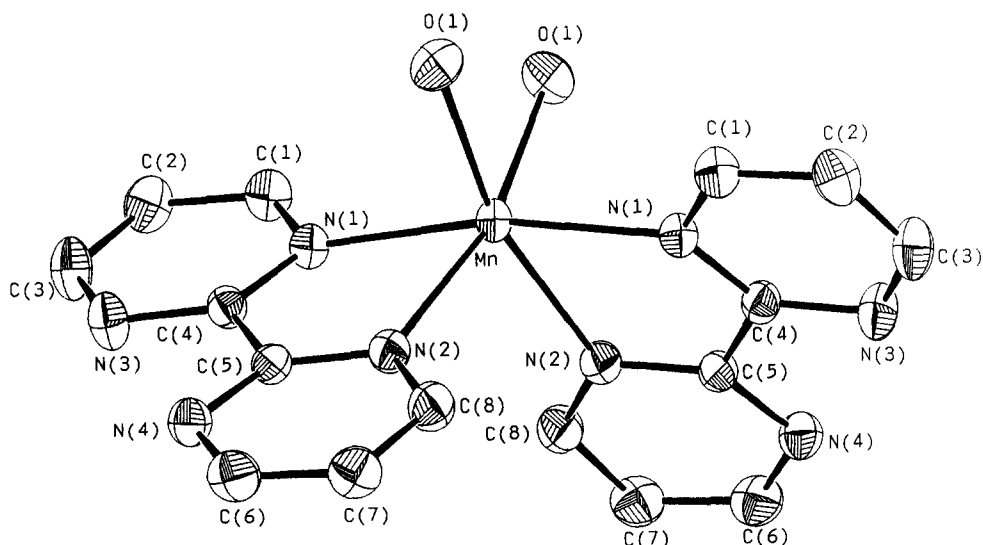


Fig. 1. ORTEP drawing of [Mn(bpym)₂(H₂O)₂]²⁺ (**1**) with numbering scheme and vibrational ellipsoids at the 30% probability level.

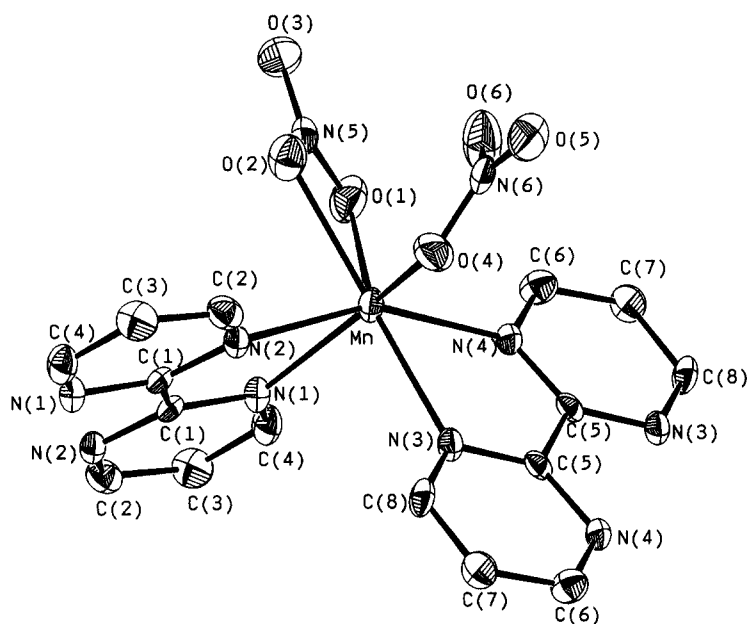


Fig. 2. ORTEP drawing of the seven-coordinated $[\text{Mn}(\text{bpym})(\text{NO}_3)_2]$ (**2**) with numbering scheme and vibrational ellipsoids at the 30% probability level.

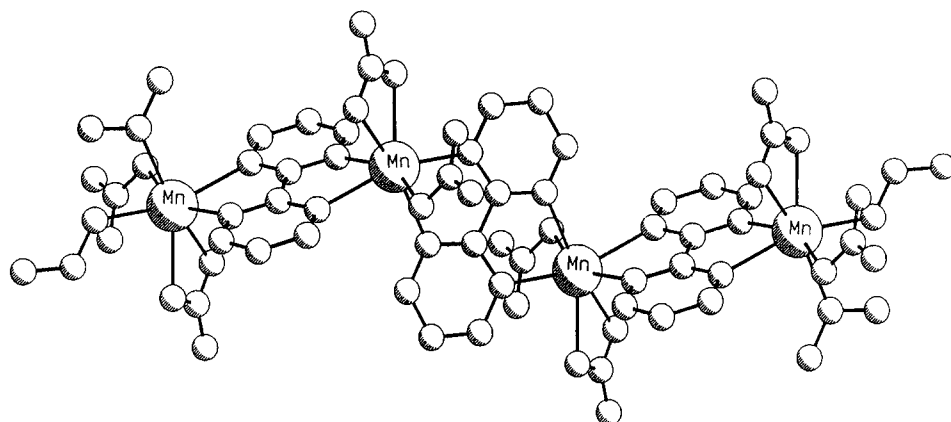


Fig. 3. View of a one-dimensional chain formed by $[\text{Mn}(\text{bpym})(\text{NO}_3)_2]$ (**2**).

2) MnN_4O_3 chromophore with distorted capped octahedral coordination. Manganese is bonded to four nitrogen atoms [averaged $\text{Mn}-\text{N} = 2.350(4)$ Å] of two bpym and three oxygen atoms of monodentate NO_3^- [$\text{Mn}-\text{O} = 2.197$ Å] and bidentate NO_3^- [$\text{Mn}-\text{O} = 2.388(4)$ and $2.311(4)$ Å] anions, the remaining two nitrogen atoms of each bpym ligand being bound to the other Mn^{II} ions. As a result, the Mn^{II} ions, NO_3^- ions and bpym ligands form a zigzag one-dimensional polymeric chain structure (Fig. 3). All the atoms of bpym ring are almost coplanar and the dihedral angle of the planes are $71.6(2)^\circ$ to each chelating bpym ring. The resulting $\text{Mn}\cdots\text{Mn}$ distance is $6.234(2)$ Å, which is longer than $5.345(2)$ Å of the previously reported

binuclear $[\text{Mn}_2(\text{bpym})(\text{H}_2\text{O})_6(\text{SO}_4)_2]$ complex.¹⁵ Thus, this distance makes a weak magnetic interaction. It is worthy of note that the averaged $\text{Mn}-\text{N}$ bond distance of **2** [$2.350(4)$ Å] is significantly longer compared with that of **1** [$2.254(3)$ Å]. We explain this effect as a weaker bonding of $\text{Mn}-\text{N}$ in bischelating bpym-bridged complex **2**.

Magnetic properties

X-band EPR spectra of the polycrystalline powder and in aqueous solution at 298 K for **1** and **2** show singlets ($g = 1.98$ for **1** and 1.99 for **2**) and a hyperfine sextet ($A = 90.42$ G for **1** and 90.38 G for **2**). We used the value $g = 1.99$ to fit the curve

Table 2. Selected interatomic bond distances (Å) and angles (°) for **1**

Mn—N(1)	2.255(3)	Mn—N(2)	2.253(3)
Mn—O(1)	2.161(3)		
N(1)—Mn—N(1)	168.74(11)	N(1)—Mn—N(2)	72.83(10)
N(1)—Mn—N(2)	99.63(10)	N(1)—Mn—O(1)	94.45(10)
N(1)—Mn—O(1)	93.96(10)	N(2)—Mn—N(2)	98.62(11)
N(2)—Mn—O(1)	165.44(10)	N(2)—Mn—O(1)	90.37(10)
O(1)—Mn—O(1)	83.32(10)	Mn—N(1)—C(1)	126.66(22)
Mn—N(1)—C(4)	116.14(20)	Mn—N(2)—C(5)	126.19(23)

Table 3. Selected interatomic bond distances (Å) and angles (°) for **2**

Mn—N(1)	2.322(4)	Mn—N(2)	2.386(4)
Mn—N(3)	2.353(4)	Mn—N(4)	2.342(4)
Mn—O(1)	2.342(4)	Mn—O(2)	2.388(4)
Mn—O(4)	2.197(4)		
N(1)—Mn—N(2)	69.38(14)	N(1)—Mn—N(3)	94.15(14)
N(1)—Mn—N(4)	100.67(14)	N(1)—Mn—O(1)	80.30(13)
N(1)—Mn—O(2)	96.44(14)	N(1)—Mn—O(4)	151.22(13)
N(2)—Mn—N(3)	89.30(13)	N(2)—Mn—N(4)	156.24(13)
N(2)—Mn—O(1)	119.08(13)	N(2)—Mn—O(2)	78.05(13)
N(2)—Mn—O(4)	83.09(14)	N(3)—Mn—N(4)	69.47(13)
N(3)—Mn—O(1)	145.90(13)	N(3)—Mn—O(2)	159.41(13)
N(3)—Mn—O(4)	76.75(14)	N(4)—Mn—O(1)	78.49(13)
N(4)—Mn—O(2)	125.31(13)	N(4)—Mn—O(4)	101.44(14)
O(1)—Mn—O(2)	53.88(12)	O(1)—Mn—O(4)	122.16(13)
O(2)—Mn—O(4)	85.57(13)		

of the temperature dependence of molar magnetic susceptibility of **2**.

The effective magnetic moments of **1** at 300 and 4 K are 5.87 and 5.45 μ_B , respectively, and are near the spin-only value of 5.90 μ_B usually observed for high-spin Mn^{II} complexes ($S = 5/2$); thus indicating the absence of significant intermolecular magnetic interactions of the manganese ions in this complex. The observed effective magnetic moment 5.65 μ_B at 300 K for **2** is slightly lower than the spin-only value of 5.90 for $S = 5/2$ and it decreases regularly to 2.70 μ_B at 4 K, indicating that the metal ions are not magnetically isolated in **2**.

The molar susceptibility χ increased steadily with decreasing temperature, reaching a maximum at *ca* 5 K and then decreased (Fig. 4). The product χT of the molar susceptibility and temperature exhibits a continuous decrease upon cooling, with $\chi T = 4.0$ at 300 K and an extrapolated value that vanishes when T approaches zero. This behaviour is characteristic of an intramolecular antiferromagnetic interaction between two high-spin Mn^{II} ions through the bpm ligand in this polymer chain.

We have attempted to reproduce theoretically the experimental susceptibility in this one-dimensional regime by use of the expression calculated by

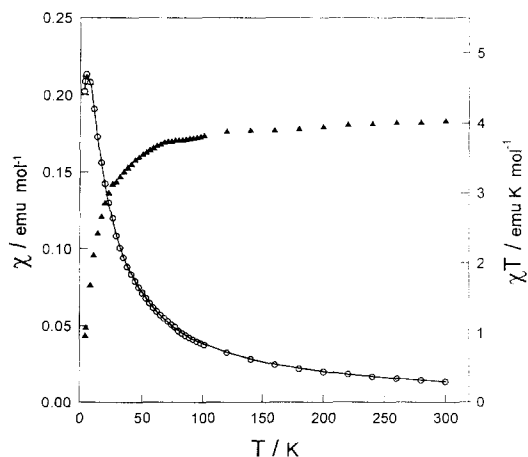


Fig. 4. Temperature dependence of molar magnetic susceptibility χ and χT for compound **2** (solid line is the best-fitted curve).

Fischer for a classical-spin Heisenberg chain,^{13,17} scaled to a real spin $S = 5/2$:

$$\chi = [2Ng^2\mu_B^2 S(S+1)/3kT](1-\nu)/(1+\nu),$$

where $\nu = -\coth K + 1/K$, $K = JS(S+1)/kT$, and the exchange Hamiltonian is written as $-JS_i S_j$. A very close agreement with experiment is obtained with $J = -0.93 \text{ cm}^{-1}$ and $g = 1.99$ (solid line of Fig. 4). In the present case the magnetic data can be described without considering the interchain magnetic ordered state, due to this effect being too weak to be detectable over the reported temperature range.

As a final comment, we emphasize that this study gives a new example of molecular design of the simple one-dimensional chain of seven-coordinated Mn^{II} with two coordination types of NO_2^- ions. In addition, the molecular design of mono-, bi- or polynuclear Mn^{II} complexes with 2,2'-bipyrimidine ligand is dependent on the nature of counter-ions (X) of $\text{Mn}^{\text{II}}(\text{X})_n$ ($n = 1, 2$) salts.

Acknowledgement—We thank the National Science Council of Taiwan for the financial support of this research work.

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