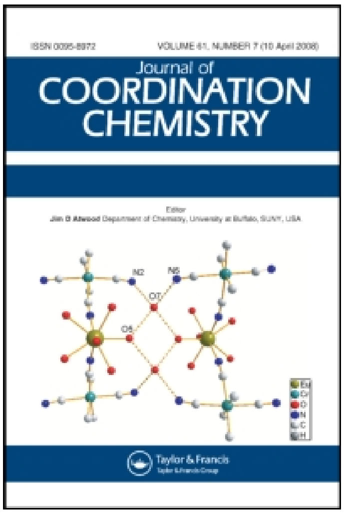

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Synthesis, crystal structure and magnetic properties of a dinuclear manganese(III) tetradentate Schiff-base complex

Yuhua Feng[a,b]; Jinxia Xu[a]; Daizheng Liao[a]; Shiping Yan[a]; Zonghui Jiang[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China [b] Department of Chemistry, Tonghua Normal University, Tonghua 134002, P.R. China

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Synthesis, crystal structure and magnetic properties of a dinuclear manganese(III) tetradentate Schiff-base complex

YUHUA FENG†‡, JINXIA XU†, DAIZHENG LIAO*†,
SHIPING YAN† and ZONGHUI JIANG†

†Department of Chemistry, Nankai University, Tianjin 300071, P.R. China
‡Department of Chemistry, Tonghua Normal University, Tonghua, 134002, P.R. China

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A dinuclear manganese(III) tetradentate Schiff-base complex, $[Mn_2(salophen)_2(4,4'\text{-bipy})_3](BPh_4)_2$ (**1**) (salophen = *N*,*N*′-*o*-phenylene-*bis*(salicylideneaminato)), has been synthesized and structurally characterized. Compound **1** crystallized in the triclinic, $P\bar{1}$ space group, $a = 13.431(4)$, $b = 13.791(4)$, $c = 13.886(4)$ Å, $\alpha = 73.599(5)^\circ$, $\beta = 80.410(6)^\circ$, $\gamma = 71.241(5)^\circ$, $V = 2328.3(12)$ Å^3. Complex **1** contains two Mn(salophen) moieties bridged by 4,4′-bipy to form a dinuclear unit, with two terminal 4,4′-bipy ligands. Variable temperature magnetic susceptibility (2–300 K) shows very weak ferromagnetic interactions between the Mn(III) ions.

Keywords: Crystal structure; Magnetic properties; Dinuclear manganese(III) complex; Tetradentate Schiff-base

1. Introduction

Manganese(III) coordination polymers have interesting structural, electronic and magnetic properties. Manganese(III) salen type Schiff-base compounds, with a high-spin ground state and an apparent magnetic anisotropy of six-coordinate Mn(III) due to Jahn–Teller distortion, is one ideal candidate as a paramagnetic building block for expanded structures with magnetic properties [1–4]. Tetradentate salen type Schiff-base ligands occupy four equatorial coordination sites of the six-coordinate paramagnetic cation, leaving axial positions to be occupied by bridging ligands that can link adjacent paramagnetic metal centers to form dinuclear or extended 1D structures. Structures and magnetic properties of manganese(III) salen type Schiff-base complexes have been studied, but reports on Mn(III)(salophen) complexes (salophen = *N*,*N*′-*o*-phenylene-*bis*(salicylideneaminato)) are rare. Most reported Mn(III)(salophen) complexes are mononuclear with various apical ligands [5–14]. There are only a limited number of dinuclear [14] and 1D chain structures [9, 15, 16].

Herein, we report the synthesis, crystal structure, and magnetic properties of a dinuclear Mn(III) salophen Schiff-base complex, $[Mn_2(salophen)_2(4,4'\text{-bipy})_3](BPh_4)_2$ (**1**), which represents the first dinuclear structure based on Mn(III)(salophen) units.

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*Corresponding author. Email: liaodz@nankai.edu.cn

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Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{59}H_{46}BMnN_5O_2$
Formula weight	922.76
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	
a	13.431(4)
b	13.791(4)
c	13.886(4)
α	73.599(5)
β	80.410(6)
γ	71.241(5)
Volume (Å^3)	2328.3(12)
Z, Calculated density (Mg m^{-3})	2, 1.316
Absorption coefficient (mm^{-1})	0.335
$F(000)$	962
Crystal size (mm^3)	$0.24 \times 0.20 \times 0.16$
θ range for data collection (°)	1.53–25.02
Limiting indices	$-15 \le h \le 12$, $-16 \le k \le 11$, $-16 \le l \le 15$
Reflections collected/unique	12126/8179 [R(int) = 0.0301]
Completeness to $\theta = 25.02$	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.724846
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8179/0/613
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.1040$
R indices (all data)	$R_1 = 0.0839$, $wR_2 = 0.1235$
Largest diff. peak and hole (e Å^{-3})	0.203 and −0.287

2. Experimental

2.1. *Materials and physical measurements*

All reagents were analytical grade and used as received from commercial sources without further purification. Salophen and Mn(salophen)Cl were prepared according to the literature method [17, 18]. The infrared spectrum was obtained on a Bruker Tensor 27 Fourier transform infrared in the 4000–400 cm^{-1} region, using KBr pellets. Elemental analysis for C, H and N were carried out on a Perkin–Elmer elemental analyzer model 240. Variable temperature magnetic susceptibilities were measured on a SQUID magnetometer between 2 and 300 K in a magnetic field of 1000 Oe. The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants.

2.2. *X-ray crystallography*

Single crystal X-ray diffraction data were collected on a AapexII CCD area detector equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods and refined by full-matrix least squares on F^2 by SHELX-97 [19]. A summary of crystal data and structure refinements for **1** is provided in table 1. Selected bond lengths and angles are listed in table 2.

Table 2. Bond lengths [Å] and angles [°] for **1**.

Mn(1)–O(1)	1.8604(17)	N(1)–C(8)	1.425(3)
Mn(1)–O(2)	1.8814(18)	N(2)–C(14)	1.304(3)
Mn(1)–N(2)	1.985(2)	N(2)–C(13)	1.432(3)
Mn(1)–N(1)	1.996(2)	N(3)–C(25)	1.323(4)
Mn(1)–N(3)	2.326(2)	N(3)–C(21)	1.333(3)
Mn(1)–N(5)	2.413(2)	N(4)–C(29)	1.306(4)
O(1)–C(1)	1.333(3)	N(4)–C(28)	1.322(5)
O(2)–C(20)	1.328(3)	N(5)–C(35)	1.321(3)
N(1)–C(7)	1.303(3)	N(5)–C(31)	1.330(3)
O(1)–Mn(1)–O(2)	92.39(8)	C(20)–O(2)–Mn(1)	128.30(17)
O(1)–Mn(1)–N(2)	175.30(8)	C(7)–N(1)–C(8)	122.4(2)
O(2)–Mn(1)–N(2)	92.05(8)	C(7)–N(1)–Mn(1)	123.45(19)
O(1)–Mn(1)–N(1)	93.60(8)	C(8)–N(1)–Mn(1)	113.84(16)
O(2)–Mn(1)–N(1)	173.77(8)	C(14)–N(2)–C(13)	121.2(2)
N(2)–Mn(1)–N(1)	82.01(8)	C(14)–N(2)–Mn(1)	124.70(19)
O(1)–Mn(1)–N(3)	88.08(8)	C(13)–N(2)–Mn(1)	113.82(15)
O(2)–Mn(1)–N(3)	89.38(8)	C(25)–N(3)–C(21)	116.1(2)
N(2)–Mn(1)–N(3)	90.45(8)	C(25)–N(3)–Mn(1)	118.20(18)
N(1)–Mn(1)–N(3)	92.52(8)	C(21)–N(3)–Mn(1)	125.70(19)
O(1)–Mn(1)–N(5)	87.93(8)	C(29)–N(4)–C(28)	114.8(3)
O(2)–Mn(1)–N(5)	92.87(8)	C(35)–N(5)–C(31)	115.3(2)
N(2)–Mn(1)–N(5)	93.36(8)	C(35)–N(5)–Mn(1)	128.15(18)
N(1)–Mn(1)–N(5)	85.64(8)	C(31)–N(5)–Mn(1)	116.52(19)
N(3)–Mn(1)–N(5)	175.50(7)	N(2)–C(14)–C(15)	125.9(3)
C(1)–O(1)–Mn(1)	128.91(18)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+2$.

Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Centre with CCDC reference number 643367.

2.3. *Synthesis of [Mn_2(salophen)$_2$(4,4′-bipy)$_3$](BPh_4)$_2$ (1)*

To a solution of [Mn(salophen)Cl] (80 mg, 0.2 mmol) in 10 mL of methanol was added a solution of 4,4′-bipy (31 mg, 0.2 mmol) in 10 mL methanol. The resulting solution was stirred at room temperature for 15 min and then $NaBPh_4$ (70 mg, 0.2 mmol) in 5 mL methanol was added. Dark brown solution was stirred for 5 min and filtered and the clear brown solution stood for one month at room temperature to form dark brown crystals suitable for X-ray structure analysis of [Mn_2(salophen)$_2$(4,4′-bipy)$_3$](BPh_4)$_2$. The crystals were collected by filtration, washed with a minimum methanol and water, and dried *in vacuo*. Yield 110 mg, 60% based on Mn(III). Anal. Calcd for $C_{59}H_{46}BMnN_5O_2$ (%): C, 76.73; H, 4.99; N, 7.59. Found: C, 76.58; H, 5.34; N, 7.84. IR (KBr): $\nu_{C=N}$ 1635, 1605 cm^{-1}.

3. Results and discussion

3.1. *Crystal structures of* 1

In the unsymmetric unit of **1**, there is only one crystallographically independent Mn with square-bipyramidal six-coordination (figure 1). The equatorial plane of Mn(III)

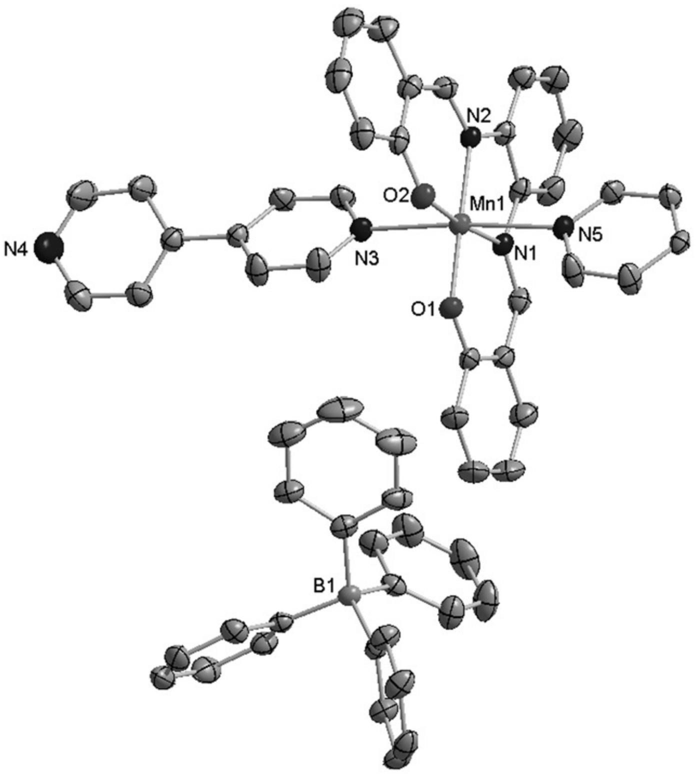

Figure 1. ORTEP diagram for **1** with partial atom labeling (30% ellipsoids) (H atoms have been omitted for clarity).

has two nitrogens and two oxygens of the salen with bond distances of Mn(1)–O(1) 1.8604(2), Mn(1)–O(2) 1.8814(2), Mn(1)–N(1) 1.985(2), Mn(1)–N(2) 1.996(2) Å. The two axial positions are occupied by two nitrogens from 4,4′-bipy with bond distances of Mn(1)–N(3) 2.326(2), Mn(1)–N(5) 2.413(2) Å. These Mn–N distances are significantly longer than observed in the equatorial planes, consistent with the Jahn–Teller elongation of high spin d^4 Mn(III) in the axial direction.

There are two modes of coordination for 4,4′-bpy in **1** (figure 2), bridging, which links two Mn(III)(salophen)$^+$ units into a dinuclear structure, and terminal coordination. The configurations of 4,4′-bipy in these coordination modes are different. In the bridging 4,4′-bipy, the two pyridine rings are coplanar, forming a conjugated system, while in the terminally coordinated 4,4′-bipy, the dihedral angle of the two pyridine rings is 36.5°. This is very similar to that reported in the literature [20]. Figure 3 shows the packing of **1** (view along *b* direction).

3.2. *Magnetic properties of* 1

The magnetic susceptibility of **1** was measured from 2 to 300 K at an external magnetic field strength of 1000 Oe. As shown in figure 2, the value of $\chi_M T$ at room temperature is 6.02 cm^3 mol^{-1} K, close to that expected for uncorrelated spins (6 cm^3 mol^{-1} K, if *g* is

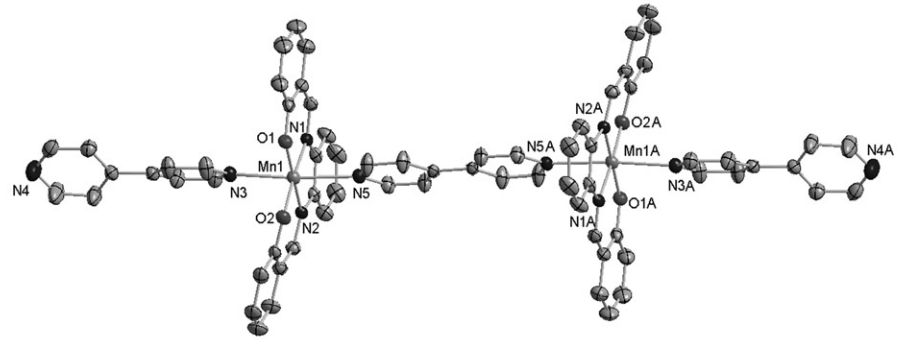

Figure 2. Dinuclear structure of **1** with partial atom labeling (30% ellipsoids) (H atoms have been omitted for clarity).

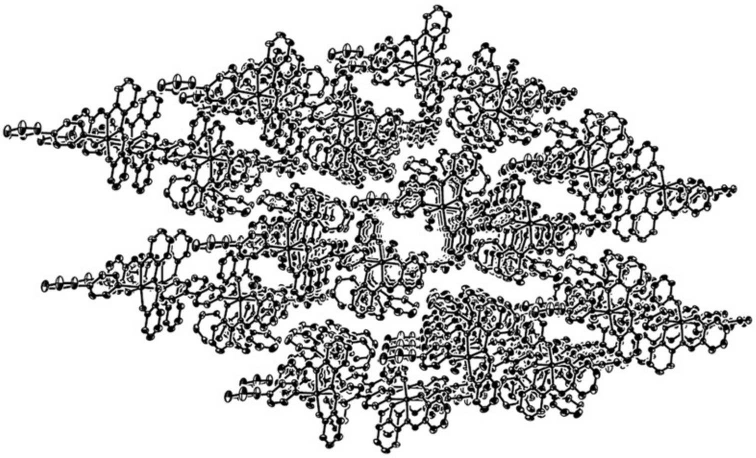

Figure 3. The packing mode of **1** (view along *b* direction).

equal to 2). These values increase slowly to $6.13\,\mathrm{cm^3\,mol^{-1}\,K}$ when cooling down to 19 K, indicating the very weak ferromagnetic interactions between Mn(III) ions through the bridging 4,4′-bipy ligand. Below 19 K, the $\chi_M T$ decreases sharply to a value of $4.14\,\mathrm{cm^3\,mol^{-1}\,K}$ at 2 K. The decrease of $\chi_M T$ in the low temperature region may be due to zero-field splitting of the ground state of the Mn(III) ion or very weak Mn(III)–Mn(III) magnetic interactions.

The susceptibility data were fitted by a dinuclear formula including single ion zero-field splitting (D) of $\mathrm{Mn^{III}}$ based on the Hamiltonian: $\hat{H} = -2J\hat{S}_1\hat{S}_2$; the equations are:

$$
\begin{aligned}
\chi_{bi} &= \frac{2Ng^2\beta^2}{KT}\frac{A}{B} \\
A &= 16\exp(-28D/3KT) + 9\exp(-7D/3KT) + 4\exp(8D/3KT) + \exp(17D/3KT) \\
&\quad + 14\exp(-8J/KT) + 5\exp(-14J/KT) + \exp(-18J/KT) \\
B &= \exp(20D/3KT) + 2\exp(-28D/3KT) + 2\exp(-7D/3KT) + 2\exp(8D/3KT) \\
&\quad + 2\exp(17D/3KT) + 7\exp(-8J/KT) + 5\exp(-14J/KT) \\
&\quad + 3\exp(-18J/KT) + \exp(-20J/KT)
\end{aligned}
$$

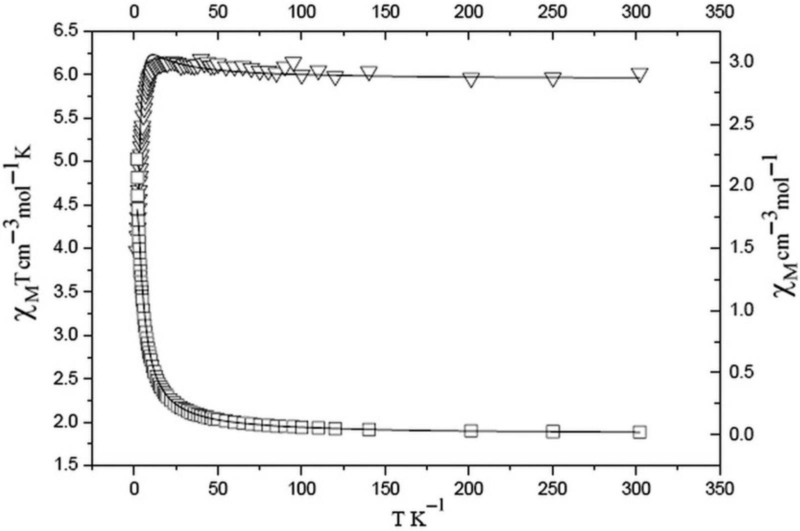

Figure 4. Temperature dependence of $\chi_M T$ for 1 at 1000 Oe.

The best agreement between the calculated and experimental values of the susceptibility was found with $g = 1.99$, $J = 0.4\,\text{cm}^{-1}$, $D = -0.29\,\text{cm}^{-1}$, $R = 8.5 \times 10^{-3}$. This fit is indicated in figure 4 as a solid line. The J value is similar to one reported in the literature [21].

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