

氰根和酚氧桥联 M(II)-Mn(III)(M=Ru 和 Os) 二维配合物的合成、结构与磁性

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摘要: 基于六氰根构筑单元 $[M(II)(CN)_6]^{4-}$ 与 $[Mn(III)(salen)]^+$ 模块反应合成了 2 个新型酚氧和氰根混合桥联的 M(II)-Mn(III) 配合物 $\{[Mn(III)(salen)]_4[Mn(III)(salen)(H_2O)]_2[M(II)(CN)_6]\}(ClO_4)_2 \cdot 2H_2O$ (M=Ru (1), Os (2), $salen^{2-}$ =双水杨酰胺乙基负离子)。单晶衍射结果表明: 它们是结构类似的二维化合物, 其中氰根桥联的七核 $[Mn(III)_6M(II)]^{2+}$ 单元进一步通过双酚氧桥相互连接构成二维层状结构。磁性研究表明: 2 个化合物通过酚氧桥均呈现反常的反铁磁耦合, 基于自旋哈密顿算符 $\hat{H} = -2J_{MnMn}\hat{S}_{Mn1}\hat{S}_{Mn2}$ 拟合得到它们的磁耦合常数分别是 $J = -0.340 \text{ cm}^{-1}$ (1) 和 -0.561 cm^{-1} (2)。

关键词: 双金属配合物; 氰根桥联; 酚氧桥连; 反铁磁耦合

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Syntheses, Crystal Structures and Magnetic Properties of Cyanide- and Phenolate-Bridged Two-Dimensional M(II)-Mn(III) (M=Ru and Os) Complexes

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Abstract: Two new M(II)-Mn(III) complexes $\{[Mn(III)(salen)]_4[Mn(III)(salen)(H_2O)]_2[M(II)(CN)_6]\}(ClO_4)_2 \cdot 2H_2O$ (M=Ru (1) and Os (2)) ($salen^{2-}$ =*N,N'*-ethylenebis(salicylideneaminato)dianion) have been synthesized based on $[Mn(III)(salen)]^+$ segment and hexacyanide-containing building blocks $[M(II)(CN)_6]^{4-}$. Single crystal X-ray diffraction analyses show that both complexes are isostructurally two-dimensional (2D) structures in which cyanide-bridged heptanuclear $[Mn(III)_6M(II)]^{2+}$ units are linked together by double phenolate bridges. Magnetic studies show that they are abnormal antiferromagnetic through the double phenolate bridges with the magnetic coupling constant $J = -0.340 \text{ cm}^{-1}$ for 1 and -0.561 cm^{-1} for 2 based on the spin exchange Hamiltonian $\hat{H} = -2J_{MnMn}\hat{S}_{Mn1}\hat{S}_{Mn2}$. CCDC:1447244, 1; 1447245, 2.

Keywords: dimetallic complex; cyanide-bridged; phenolate-bridged; antiferromagnetic coupling

0 Introduction

The design and synthesis of new coordination complexes with excellent magnetic, optical and adsorptive properties have received much attention in the past several decades^[1-16]. Up to date, a large number

of complexes with different topological structures have been obtained through the rational design and selection of metal ions, bridging groups and ligands. Among the many famous bridging groups, cyanide group plays an important role because the topological structures of cyanide-bridged complexes can be

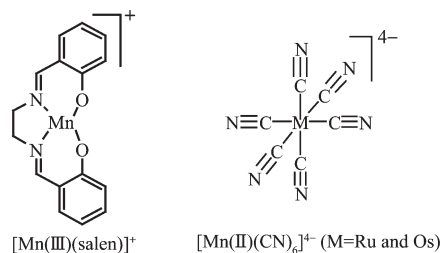
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relatively readily controlled and anticipated through changing the number and position of cyanide group and the charge number of the cyanide-containing blocks. Although there are several tens of cyanide-containing building blocks for cyanide-bridged complexes, the central metal ions are mainly focused on the 3d metal ions such as Fe(II), Fe(III), Cr(III) or Ni(II) et al^[17-25]. The cyanide-bridged complexes based on cyanide-containing building blocks containing 4d and 5d metal ions are relatively limited^[1,5,8,10-11,15].

Corresponding to cyanide-containing metal ions, the selection of another functional metal centers is also very important for the assembly of interesting functional complexes. High-spin $[\text{Mn(III)}(\text{salen})]^+$ segment and its derivatives as known magnetic carriers have been extensively employed for new magnetic materials^[12-16,26-28], and a variety of polynuclear, 1D chains^[11,15], 2D networks^[2,4,29-30] complexes which exhibit ferro-, antiferro-, ferri- or metamagnetic behaviors have been reported. Recently, we synthesized two new 2D cyanide- and phenolate-bridged M(II)-Mn(III) complexes based on $[\text{Mn(III)}(\text{salen})]^+$ segment and $[\text{M(II)}(\text{CN})_6]^{4-}$ (M=Ru and Os) building blocks (Scheme 1). Herein, we report the synthesis, crystal structures and magnetic properties of two new complexes $\{[\text{Mn(III)}(\text{salen})]_4 [\text{Mn(III)}(\text{salen})(\text{H}_2\text{O})_2][\text{M(II)}(\text{CN})_6]_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (M=Ru (**1**) and Os (**2**), $\text{salen}^{2-}=\text{N,N}'\text{-ethylenebis(salicylideneaminato)dianion}$).



Scheme 1 Building blocks for complexes **1** and **2**

1 Experimental

1.1 Materials and physical measurements

Elemental analyses (C, H and N) were carried out on an Elementar Vario El. The infrared spectra of solid samples on KBr pellets were recorded on a Nicolet 7199B FT-IR spectrophotometer in the regions of 4 000 ~400 cm^{-1} . The powder XRD data were

measured on a Bruker D8 Advance X-ray diffractometer equipped with a Cu $K\alpha$ radiation ($\lambda=0.154\ 18\ \text{nm}$, cathode voltage=40 kV, cathode current=30 mA, $2\theta=5^\circ\sim 50^\circ$). Variable-temperature magnetic susceptibilities of powder samples were measured on a Quantum Design MPMS SQUID magnetometer in the applied field of 1 000 Oe. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascal's constants.

All of the reactions were carried out under an air atmosphere, and all chemicals and solvents used in the synthesis were reagent grade without further purification. $[\text{Mn}(\text{salen})]\text{ClO}_4$ was available from our previous work^[31]. $\text{K}_4[\text{Ru}(\text{CN})_6]$ and $\text{K}_4[\text{Os}(\text{CN})_6]$ were prepared by the literature methods^[32].

Caution! KCN is hypertoxic and hazardous. Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities with care.

1.2 Preparation of complexes **1** and **2**

The two complexes were prepared using one similar procedure. Therefore, only the synthesis of complex **1** was detailed as a typical representative. A methanol/MeCN (1:1, V/V, 10 mL) solution of $[\text{Mn}(\text{salen})]\text{ClO}_4$ (0.4 mmol) was carefully layered onto a methanol/ H_2O (1:4, V/V, 10 mL) solution of $\text{K}_4[\text{Ru}(\text{CN})_6]$ (0.1 mmol). After the mixture stood for a few weeks in a dark room, dark brown block single crystals suitable for X-ray diffraction were obtained. Then they were filtered, washed with 1:1 (V/V) methanol-water and dried at room temperature.

Complex 1: Yield: 58%. Anal. Calcd. for $\text{C}_{102}\text{H}_{92}\text{N}_{18}\text{O}_{24}\text{Cl}_2\text{Mn}_6\text{Ru}$ (%): C, 49.85; H, 3.75; N, 10.26. Found (%): C, 49.62; H, 3.84; N, 10.05. Main IR frequencies (KBr disk, cm^{-1}): 2 050 (m, $\nu_{\text{C}\equiv\text{N}}$), 1 087 (m, ν_{ClO_4}).

Complex 2: Yield: 60%. Anal. Calcd. for $\text{C}_{102}\text{H}_{92}\text{N}_{18}\text{O}_{24}\text{Cl}_2\text{Mn}_6\text{Os}$ (%): C, 48.10; H, 3.62; N, 9.90. Found (%): C, 47.86; H, 3.74; N, 9.80. Main IR frequencies (KBr disk, cm^{-1}): 2 038 (m, $\nu_{\text{C}\equiv\text{N}}$), 1 087 (m, ν_{ClO_4}).

1.3 Single-crystal X-ray diffraction data collection and structure refinement

Single-crystal X-ray diffraction data of complexes

1 and **2** were collected on Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The structures were solved by the direct method and refined by full-matrix least squares (SHELX-2014) on F^2 ^[33]. Hydrogen atoms were added geometrically and refined using a riding model. Images were created by using

DIAMOND program. There is no hydrogen bond acceptor for one hydrogen atom of coordinated water molecule in two complexes, which may be due to steric effect of relatively large salen²⁻ ligand as well as the release of some solvent molecules. The crystal data for the two complexes are given in Table 1.

CCDC: 1447244, **1**; 1447245, **2**.

Table 1 Crystal data and structure refinement parameters for complexes **1** and **2**

	1	2
Empirical formula	C ₁₀₂ H ₉₂ N ₁₈ O ₂₄ Cl ₂ Mn ₆ Ru	C ₁₀₂ H ₉₂ N ₁₈ O ₂₄ Cl ₂ Mn ₆ Os
Formula weight	2 455.55	2 544.68
Crystal size / mm	0.16×0.14×0.12	0.10×0.08×0.08
Temperature / K	123(2)	123(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.349 4(3)	1.341 8(3)
b / nm	1.356 3(3)	1.356 6(3)
c / nm	1.587 3(3)	1.582 1(3)
α / (°)	73.63(3)	73.66(3)
β / (°)	73.42(3)	73.32(3)
γ / (°)	87.85(3)	87.91(3)
V / nm ³	2.668 5(9)	2.644 3(9)
Z	1	1
D_c / (g·cm ⁻³)	1.528	1.598
$F(000)$	1 250	1 282
θ range for data collection / (°)	3.05~25.00	3.05~25.00
Reflection collected, unique	26 266, 9 294	26 360, 9 220
R_{int}	0.051 9	0.037 1
Reflection with $I>2\sigma(I)$	8 210	8 656
Goodness-of-fit on F^2	0.965	0.993
R_1 [$I>2\sigma(I)$]	0.064 5	0.047 9
wR_2 (all data)	0.164 0	0.120 3

2 Results and discussion

2.1 Crystal structures of complexes **1** and **2**

The X-ray crystal analysis reveals that both complexes crystallize in the triclinic $P\bar{1}$ space group and they are isostructural. Firstly, a $[\text{M(II)}(\text{CN})_6]^{4-}$ anion connects axially six $[\text{Mn(III)}(\text{salen})]^+$ cations through its six cyanide bridges to form centrosymmetric heptanuclear $[\text{Mn(III)}_6\text{M(II)}]^{2+}$ cationic units as depicted in Fig.1. Then, the heptanuclear $[\text{Mn(III)}_6\text{M(II)}]^{2+}$ cationic units are connected together by double phenolate bridges from four sides, giving two-dimensional (2D)

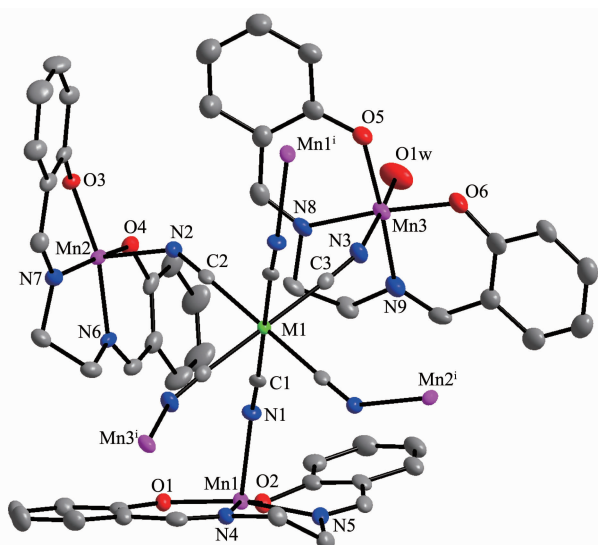
layer-like structures (Fig.2). The measured XRD patterns on powder samples of complex **1** and **2** are consistent well with the calculated data based on their single crystal structures (Fig.3), indicating the two samples have high purity. Selected bond distances and angles of the two complexes are listed in Table 2.

For the cyanide-containing metal centers, the coordination environments of the two complexes are the same and relatively simple. The central Ru(II) or Os(II) metal ions is coordinated by six carbon atoms of cyanide groups. The M-C bond lengths are very similar (0.204 2(5)~0.204 6(5) nm) although the two

Table 2 Selected bond distances (nm) and angles ($^{\circ}$) of complexes **1** and **2**

	1	2		1	2
Mn(1)-N(1)	0.217 0(4)	0.216 8(4)	Mn(2)-N(2)	0.217 6(4)	0.215 4(4)
Mn(1)-N(4)	0.198 6(4)	0.198 1(4)	Mn(2)-N(6)	0.198 5(4)	0.197 7(4)
Mn(1)-N(5)	0.200 2(4)	0.199 4(4)	Mn(2)-N(7)	0.200 1(4)	0.199 2(4)
Mn(1)-O(1)	0.188 8(4)	0.187 6(4)	Mn(2)-O(3)	0.191 1(4)	0.191 2(3)
Mn(1)-O(2)	0.190 1(4)	0.189 8(4)	Mn(2)-O(4)	0.187 7(4)	0.187 7(4)
Mn(1)-O(2) ⁱ	0.271 5(4)	0.271 9(4)	Mn(2)-O(3) ⁱⁱ	0.261 5(4)	0.260 3(4)
Mn(3)-N(3)	0.223 7(5)	0.222 6(4)	M(1)-C(1)	0.204 3(5)	0.204 2(5)
Mn(3)-N(8)	0.199 9(5)	0.199 4(5)	M(1)-C(2)	0.204 5(5)	0.204 4(5)
Mn(3)-N(9)	0.199 6(5)	0.199 2(5)	M(1)-C(3)	0.204 6(5)	0.204 5(5)
Mn(3)-O(5)	0.190 9(4)	0.191 1(4)	M(1)⋯Mn(1)	0.509 5(5)	0.509 5(5)
Mn(3)-O(6)	0.188 4(4)	0.188 3(4)	M(1)⋯Mn(2)	0.507 2(5)	0.504 4(5)
Mn(3)-O(1w)	0.232 4(4)	0.233 3(5)	M(1)⋯Mn(3)	0.518 2(5)	0.516 5(5)
N(1)-Mn(1)-O(2) ⁱ	169.8(4)	169.9(4)	N(3)-Mn(3)-O(1w)	171.78(15)	171.71(17)
Mn(1)-N(1)-C(1)	142.9(4)	142.9(4)	Mn(3)-N(3)-C(3)	144.8(4)	144.4(4)
Mn(1)-O(2)-Mn(1) ⁱ	95.1(4)	95.2(4)	N(1)-C(1)-M(1)	176.9(4)	176.9(4)
N(2)-Mn(2)-O(3) ⁱⁱ	172.5(4)	172.5(4)	N(2)-C(2)-M(1)	176.7(4)	171.1(4)
Mn(2)-N(2)-C(2)	141.4(4)	141.0(4)	N(3)-C(3)-M(1)	177.1(5)	177.7(4)
Mn(2)-O(3)-Mn(2) ⁱⁱ	97.0(4)	96.5(4)			

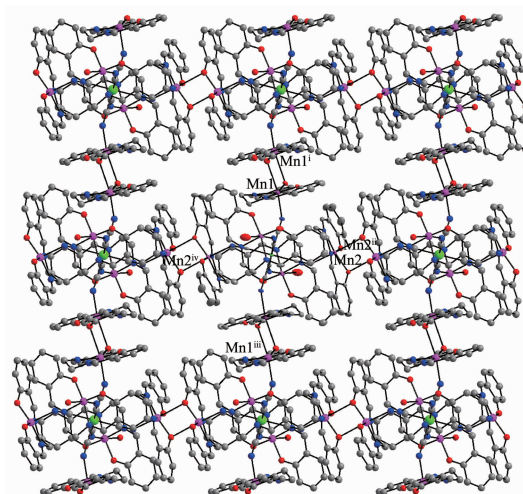
M=Ru for **1** and Os for **2**; Symmetry codes: ⁱ 1-x, 2-y, 1-z; ⁱⁱ 2-x, 1-y, 1-z.



Free water molecules, balanced anions and all the hydrogen atoms have been omitted for clarity; Symmetry codes: ⁱ 1-x, 1-y, 1-z

Fig.1 Molecular structures of complexes with 30% probability ellipsoids (M=Ru (**1**) and Os (**2**))

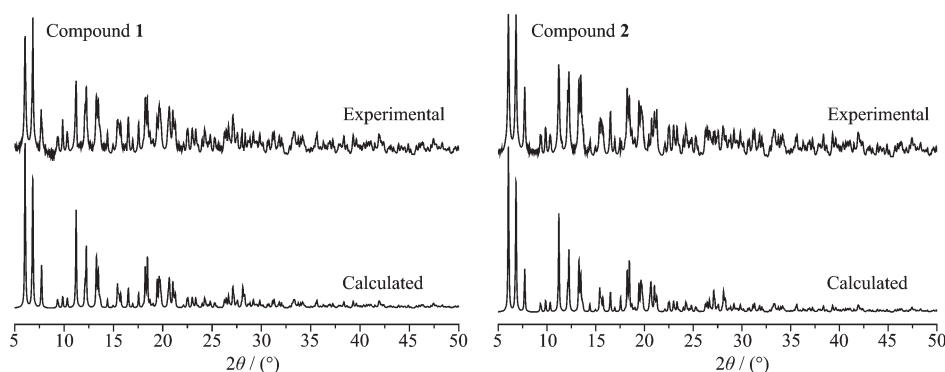
metal centers are different periodic elements of the same family, which can be compared to the bond parameters of their building blocks $[M(II)(CN)_6]^{4-}$ [32].



Free water molecules, balanced anions and all the hydrogen atoms have been omitted for clarity; Symmetry codes: ⁱ 1-x, 2-y, 1-z; ⁱⁱ 2-x, 1-y, 1-z; ⁱⁱⁱ x, -1+y, -z; ^{iv} -1+x, y, z

Fig.2 2D layer-like structures of complexes **1** and **2**

The M-C≡N linkages are almost collinear with the angles from 176.7(4) $^{\circ}$ to 177.7(4) $^{\circ}$, which are similar to other 3d metal cyanide-containing building blocks^[17-25]. The intramolecular Mn(III)-M(II) separations through the cyanide bridges locate within 0.504 4 ~ 0.518 2 nm.

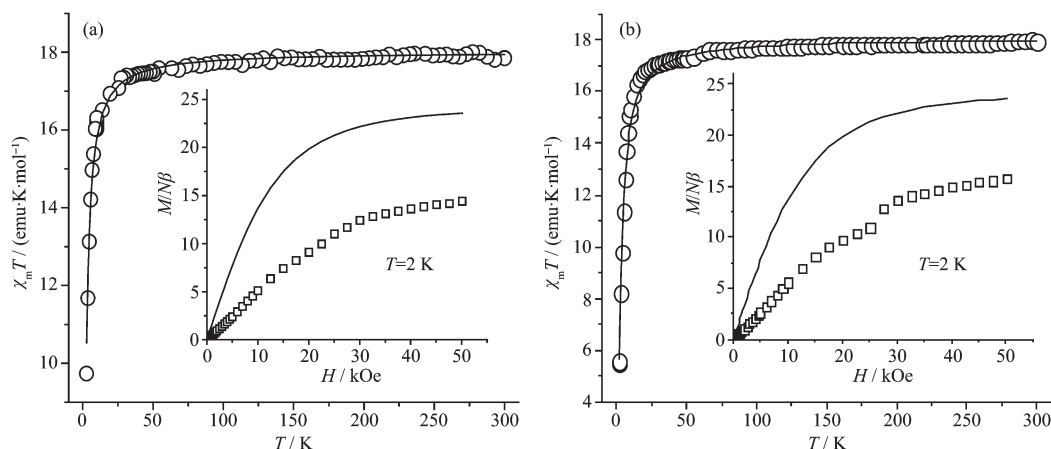
Fig.3 XRD patterns for powder samples of complexes **1** and **2**

There are three independent Mn(III) ions in complexes **1** and **2**. Mn(1) and Mn(2) ions have the same coordination environments. The Mn(1) and Mn(2) ions severally form $[Mn(III)(NC)(salen)(\mu-O_{phenolate})_2Mn(III)(NC)(salen)]$ linkages by double phenolate bridges between the neighboring $[Mn(III)_6M(II)]^{2+}$ units, giving one-dimensional (1D) chains, respectively, along the *a* and *b* directions. Then complexes **1** and **2** lead to 2D layer-like structures, which can be widely observed among the $[Mn(III)(salen)]^+$ Schiff base derivatives^[24,27,29-30]. Mn(1) and Mn(2) centers are surrounded by N_2O_2 atoms set from tetradentate $salen^{2-}$ ligand in the equatorial plane, a N atom from the cyanide bridge and a O atom from the neighboring $[Mn(III)(salen)]^+$ moiety in two axial positions, giving rise to an elongated octahedral coordination geometry. The Jahn-Teller elongation axis in the Mn(1) and Mn(2) octahedron lies along the axial direction, and the Mn-N_{cyanide} bond distances range from 0.215 4(4) to 0.217 0(5) nm. The Mn-O_{phenolate} bond distances range from 0.260 3(4) to 0.271 9(5) nm, which are significantly shorter than those of the reported double phenolate-bridged Mn(III) complexes^[1,5,15,35]. The Mn-N \equiv C bond angles are normal bent ($141.0(4)^\circ \sim 142.9(4)^\circ$) for Mn(1) and Mn(2) ions. The N_{cyanide}-Mn-O_{phenolate} bond angles are nearly linear ($169.8(4)^\circ \sim 172.5(4)^\circ$). The bridged Mn(1)-O(2)-Mn(1a) and Mn(2)-O(3)-Mn(2b) angles are also very similar within the range of $95.1(4)^\circ \sim 97.0(4)^\circ$ for the two complexes. The adjacent metal-metal distances through the cyanide bridge distribute in a narrow range from 0.504 4(4) to 0.509 5(4) nm for Mn(1)···M and Mn(2)···M.

The Mn(3) ion also has an elongated octahedral coordination geometry in which the equatorial plane sites are occupied by N_2O_2 atoms set from the tetradentate $salen^{2-}$ ligand and the two axial sites are coordinated by a nitrogen atom from the cyanide bridge and an oxygen atom from the coordinated water molecule. The Mn(3)-N_{cyanide} lengths are 0.223 7(5) nm for **1** and 0.222 6(4) nm for **2**. The Mn(3)-O(1w) bond distances are 0.232 4(5) nm for **1** and 0.234 4(5) nm for **2**, respectively, which are obviously shorter than the Mn-O_{phenolate} bond distances of Mn(1) and Mn(2). The Mn(3)-N \equiv C bond angles for bridging linkages are in a bent fashion with the angles of $144.8(4)^\circ$ for **1** and $144.4(4)^\circ$ for **2**. The N(3)-Mn(3)-O(1w) bond angles are $171.78(15)^\circ$ for **1** and $171.71(17)^\circ$ for **2**, which are similar with Mn(1) and Mn(2) ions. The intramolecular Mn(3)···M distances are 0.518 2(5) nm for **1** and 0.516 5(5) nm for **2**, which are longer than those of the above Mn(1)···M and Mn(2)···M.

2.2 Magnetic properties

Magnetic properties of the two complexes were measured in the temperature range of 2~300 K under an external magnetic field of 1 000 Oe, as shown in Fig.4. Obviously, there are very similar magnetic properties for the two complexes. The $\chi_m T$ values for complexes are in the range of 17.01~17.08 $emu \cdot K \cdot mol^{-1}$ at room temperature, which is nearly equal to the paramagnetic response of the six isolated high-spin Mn(III) cations based on $S=2$ and $g=2.00$. With the temperature decreasing, the $\chi_m T$ values remain nearly constant until the temperature decreases to 50 K and then sharply drop to their lowest values of 9.73



Inset: Field dependence of magnetization at 2.0 K; Line represent the Brillouin function that corresponds to six non-interaction Mn(III) ions based on $g=2.00$

Fig.4 Temperature dependences of $\chi_m T$ for the complexes **1** (a) and **2** (b) measured under an applied field of 1 000 Oe

$\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **1** and $5.48 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **2** at 2 K, respectively, which indicate there are overall antiferromagnetic interactions for the complexes. On the other hand, the magnetic susceptibilities of two complexes conform well to Curie-Weiss law in the range of 10~300 K and give a negative Weiss constant $\theta = -1.38 \text{ K}$, Curie constant $C = 17.99 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **1** and $\theta = -2.19 \text{ K}$, $C = 18.58 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **2**. Moreover, the field dependence of the magnetizations of complexes **1** and **2** is significantly lower than the corresponding Brillouin curve for the six Mn(III) cautions with $S=2$ and $g=2.00$ (Inset of Fig.4). On the basis of these above data, the overall antiferromagnetic interaction in the two complexes can be concluded.

According to their crystal structures of the two complexes, it can be seen that the main magnetic coupling contribution takes place in the adjacent double phenolate-bridged Mn(III) dimers and the isolated Mn(III) ions. The magnetic exchanges for the two types of dimers $[\text{Mn(III)}]_2$ and $[\text{Mn(III)}]_2$ in the two

complexes are nearly the same because their bond parameters are very similar. In order to quantitatively interpret these data, calculations based on the expression Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}}\hat{S}_{\text{Mn(a)}}$ for the magnetic susceptibility (χ_d) of the Mn(III) dimer were performed, where J is the exchange coupling constant between Mn(III) ions via phenolate bridges. And due to the symmetry of the structures of complexes, the final molar magnetic susceptibility ($\chi_m(\text{Mn}_2\text{Mn})$) can be calculated in the formula 2. In addition, the experimental curves of complexes **1** and **2** have been simulated as shown in Fig.3. The best fit gave the parameters of $g=2.00$, $J=-0.340 \text{ cm}^{-1}$ for **1** and $g=2.03$, $J=-0.561 \text{ cm}^{-1}$ for **2**. If considering the single ion zero-field splitting (D) of Mn(III), the best fitting parameters are $g=1.99$, $J=-0.192 \text{ cm}^{-1}$ and $D=-0.342 \text{ cm}^{-1}$ for **1**, and $g=2.01$, $J=-0.243 \text{ cm}^{-1}$ and $D=-0.384 \text{ cm}^{-1}$ for **2** based on the method of the literature^[34]. The negative J values support the overall antiferromagnetic coupling for the two complexes.

$$\chi_d = \frac{2Ng^2\beta^2}{kT} \left[\frac{14\exp(-8x) + 5\exp(-14x) + \exp(-18x) + 30}{7\exp(-8x) + 5\exp(-14x) + 3\exp(-18x) + \exp(20x) + 9} \right] \quad (1)$$

$$x = \frac{J}{kT}$$

$$\chi_m = 2 \left[\chi_d + \frac{2Ng^2\beta^2}{3kT} S_{\text{Mn}}(S_{\text{Mn}} + 1) \right] \quad (2)$$

Table 3 Specific structural parameters of selected dimeric Mn(III) Schiff bases and their magnetic nature

Complex	$d(\text{Mn-O bridging}) / \text{nm}$	$d(\text{Mn-O}(i)) / \text{nm}$	$\angle \text{Mn-O-Mn}(i) / (^{\circ})$	Magnetism ^a	J / cm^{-1}	Ref.
[Mn(saltmen)(O ₂ CCH ₃) ₂ ·2CH ₃ CO ₂ H]	0.189 1(1)	0.281 3(5)	99.57	F	1.35	[1]
[Mn(saltmen)(N ₃) ₂]	0.186 3(4)	0.319 0(2)	98.39	F	0.60	[1]
[(Tp)Fe(CN) ₃] ₂ [Mn(acphen)] ₂	0.190 4(3)	0.232 2(3)	98.52(14)	F	0.85	[5]
[(Tp)Fe(CN) ₃] ₂ [Mn(5-Bracphen)] ₂	0.190 8(4)	0.241 8(4)	99.17(17)	F	1.30	[5]
[(Tp)Fe(CN) ₃] ₂ [Mn(salen)] ₂ ·6H ₂ O	0.191 3(2)	0.241 1(2)	100.23(9)	F	0.55	[5]
[Mn(naphtmen)(Cl)] ₂	0.189 2(5)	0.350 5(5)	94.2(2)	F	0.38	[35]
[Mn(saltmen)(NCS)] ₂	0.187 2(2)	0.344 1(2)	96.24(8)	F	0.55	[35]
[Mn(saltmen)(H ₂ O)] ₂ (ClO ₄) ₂	0.190 9(2)	0.243 4(2)	101.58(10)	F	1.79	[35]
[Mn(saltmen)] ₄ [Fe(CN) ₆]ClO ₄	0.190(1)	0.285(1)	100.1(5)	F		[2]
[Mn(salen)(H ₂ O)] ₂ (ClO ₄) ₂	0.190 1(5)	0.241 2(6)	100.58(22)	F	6.30	[36]
[Mn(saltmen)(ReO ₄)] ₂	0.191 3(4)	0.245 9(4)	98.5(2)	F	2.65	[37]
[Mn(5-Clsalen)(N ₃) ₂]	0.190 7(2)	0.267 1(2)	99.93(7)	F		[38]
[Mn(salacen)(H ₂ O)] ₂ (ClO ₄) ₂	0.191 2(3)	0.230 5(2)	103.4(1)	AF	-1.68	[39]
[Mn(saldmen)(N ₃) ₂]	0.191 2(4)	0.237 5(5)	101.83	AF	-0.55	[40]
[Mn(5-Brsalen)(CH ₃ OH)] ₂ (ClO ₄) ₂	0.190 8(3)	0.239 5(3)	99.85	AF	-0.45	[1]
[Mn(salen)(NCS)] ₂	0.188 0(6)	0.275 0(6)	98.7(2)	AF	-0.44	[41]
1^b	0.190 6(4)	0.266 5(4)	96.1(4)	AF	-0.340	This work
2^b	0.190 0(4)	0.266 1(4)	96.7(4)	AF	-0.561	This work

^a F=ferromagnetic coupling, AF=antiferromagnetic coupling; ^b Bond parameters are average bond distances and angles for **1** and **2**.

Most of the complexes of Mn(III) dimer bridged by phenolate oxygen atoms exhibit the ferromagnetic coupling with few exceptions. Nevertheless, the two complexes in this paper present the abnormal antiferromagnetic coupling. Table 3 summarized the pertinent bond distances and angles of the dimeric cores with the magnetic pathway through the phenolate linkages and the estimated magnetic parameters. The published paper once has reported the magneto-structural correlation of such magnetic systems and concluded one the empiric correlation between magnetic coupling constants of two Mn(III) ions through phenolate bridge and Mn-O_{phenolate} distance, that is $J = 4.572 - 11.868x$ (x is the Mn-O_{phenolate} distance in the range of 0.24~0.37 nm)^[35]. According to this empiric correlation, the magnetic coupling should be ferromagnetic with J value of 1.467 cm⁻¹ for **1** and 1.483 cm⁻¹ for **2**. However, both of the complexes herein are all practically antiferromagnetic. In addition, several other examples also deviate from the above expression as shown in Table 3. From the limited examples in Table 3, the Mn-O_{phenolate} distance is only one key factor for the final magnetic nature. The full

establishment of magneto-structural correlation for this system needs further investigations in the future.

3 Conclusions

In summary, two new cyanide- and phenolate-bridged M(II)-Mn(III) complexes based on [Mn(III)(salen)]⁺ and 4d/5d metal cyanide-containing [M(II)(CN)₆]⁴⁻ (M= Ru and Os) building blocks have been successfully prepared and characterized. The complexes have similar single crystal structures in which the cyanide-bridged heptanuclear [Mn(III)₆M(II)]²⁺ units are further linked by phenolate bridges from four sides to form 2D layer-like structures. Magnetic investigations reveal that the two complexes show abnormally overall antiferromagnetic coupling for double phenolate-bridged Mn(III) systems. The magnetic susceptibilities of the two complexes have been fitted by the Mn₂ dimer model together with the contribution from the isolated Mn(III) ion.

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