

Cyanide- and Phenoxo-Bridged Heterobimetallic Fe(III)-Mn(III) Coordination Polymer: Synthesis, Crystal Structures and Magnetic Properties

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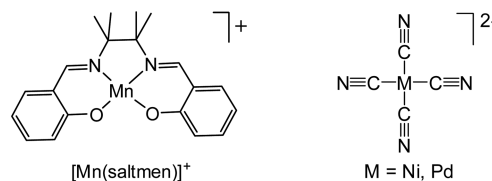
Two two-dimensional cyanide- and phenoxo-bridged heterometallic M(II)-Mn(III) (M = Ni, Pd) coordination polymers $\{[\text{Mn}(\text{saltmen})_4[\text{Ni}(\text{CN})_4]\}(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $\{[\text{Mn}(\text{saltmen})_4[\text{Pd}(\text{CN})_4]\}(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (**2**) ($\text{saltmen}^{2-} = N,N'-(1,1,2,2\text{-tetramethylethylene})\text{bis}(\text{salicylideneaminato})\text{dianion}$) have been obtained by using $\text{K}_2[\text{M}(\text{CN})_4]$ as building blocks and a salen-type Schiff-base manganese(III) compound as assembling segment. Single X-ray analysis reveals their isostructural cyanide-bridged MMn_4 pentanuclear cationic structure. The four Schiff base manganese units of the pentanuclear entity are self-complementary through the phenoxo oxygen atoms from the neighboring complex, therefore forming cyanide- and phenoxo-bridged 2D sheet-like structure. Investigation over magnetic susceptibilities reveals the overall ferromagnetic coupling between the adjacent Mn(III) ions bridged by the phenoxo oxygen atoms with $J = 2.13$ and 2.21 cm^{-1} for complexes **1** and **2**, respectively.

Key Words : Cyanide-bridged, Heterometallic, Crystal structure, Magnetic property

Introduction

Molecule-based magnetic materials have attracted much attention owing to their potential applications in magnetic devices in the past three decades. In particular, as one of the most famous magnetic transferring groups, cyanide-bridged magnetic complexes have been actively studied not only because of their various structure types ranging from discrete polynuclear compounds, one-dimensional chains, two- and three-dimensional networks but also more importantly for the growing interest in the field of molecular magnetism covering high- T_C magnets,^{1,2} photomagnets,³⁻⁵ spin cross-over,^{6,7} chiral magnets,⁸⁻¹² single-molecule magnets (SMMs),¹³⁻¹⁵ and singlechain magnets (SCMs).¹⁶⁻¹⁸

Moreover, due to their facile preparation and large spin state ($S = 2$) as well as the usually negative magnetic anisotropy of the central Mn(III) ions, Mn(III) quadridentate Schiff bases containing N_2O_2 equatorial salen-type ligands with enhanced Jahn-Teller effects have been frequently utilized as anisotropic ingredient to fabricate cyanide-bridged magnetic system. Thus far, many manganese(III)-salen-based cyanide-bridged magnetic complexes showing a rich variety of structures and interesting magnetic properties have been prepared.¹⁹ Interested also in this type of magnetic system, we have reported some cyanide-bridged heterometallic complexes based on polycyanidemetalates and schiff base manganese(III) compounds containing bicompartimental Schiff base ligands, in which several ones show interesting metamagnet property.²⁰ To throw further light on the systems of schiff base Manganese(III) compounds with different types of cyanide-containing precursors, we investigated the reactions of $[\text{Mn}(\text{saltmen})(\text{H}_2\text{O})_2]\text{ClO}_4$ ($\text{saltmen}^{2-} = N,N'$ -



Scheme 1. The starting materials used.

(1,1,2,2-tetramethylethylene)bis(salicylideneiminato) dianion) (Scheme 1) with $\text{K}_2[\text{M}(\text{CN})_4]$ (M = Ni, Pd) (Scheme 1), resulting in two cyano and phenoxo oxygen atom mixed-bridged two-dimensional heterobimetallic complexes. The synthesis, crystal structures and magnetic properties of $\{[\text{Mn}(\text{saltmen})_4[\text{Ni}(\text{CN})_4]\}(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $\{[\text{Mn}(\text{saltmen})_4[\text{Pd}(\text{CN})_4]\}(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (**2**) will be described in this paper.

Experimental

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the $4000\text{--}400 \text{ cm}^{-1}$ region. Variable-temperature magnetic susceptibility was performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

General Procedures and Materials. All the reactions were carried out under an air atmosphere and all chemicals and solvents used in the synthesis were reagent grade without further purification. $[\text{Mn}(\text{saltmen})(\text{H}_2\text{O})_2]\text{ClO}_4$ were prepared according to the previous works.²¹

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.

These two complexes were synthesized by similar procedures and both of them were obtained by a three layers diffusion method. A solution containing $K_2[Ni(CN)_4]$ (0.1 mmol, 24 mg) or $K_2[Pd(CN)_4]$ (0.1 mmol, 34 mg) dissolved in 5 mL H_2O was laid in the bottom of a tube, upon which a mixture solvent of water, acetonitrile and methanol with a ratio of 1:2:1 was carefully added. Then, a solution of $[Mn(\text{saltmen})(H_2O)_2]ClO_4$ (0.2 mmol, 102.6 mg) in 5 mL CH_3CN/CH_3OH (2:1, V/V) was carefully added to the top of the mixture solvent layer above formed. About ten days later, dark-brown single crystals suitable for X-ray diffraction were obtained, collected by filtration and dried in air.

Complex 1: Yield 60.9 mg, 63.5%. Anal. Calcd. for $C_{85}H_{94}Cl_2Mn_4N_{12}NiO_{18}$: C, 53.14; H, 4.93; N, 8.75. Found: C, 52.96; H, 4.71; N, 9.03. Main IR bands (cm^{-1}): 2126 (s, $\nu_{C\equiv N}$), 1630, 1614 (vs, $\nu_{C=N}$), 1098 (vs, $\nu_{Cl=O}$).

Complex 2: Yield 58.7 mg, 59.4%. Anal. Calcd. for $C_{86}H_{93}Cl_2Mn_4N_{13}O_{17}Pd$: C, 52.22; H, 4.74; N, 9.21. Found: C, 51.89; H, 4.60; N, 9.59. Main IR bands (cm^{-1}): 2124 (s, $\nu_{C\equiv N}$), 1627, 1615 (vs, $\nu_{C=N}$), 1095 (vs, $\nu_{Cl=O}$).

X-ray Data Collection and Structure Refinement. Single crystals of all the complexes for X-ray diffraction analyses with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoK α sealed tube ($\lambda = 0.71073 \text{ \AA}$) at 293 K, using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced as fixed contributors and assign-

ed isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$, and their coordinates were allowed to ride on their respective carbons using SHELXL97. The CIF tables of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 983784 and 983785, respectively. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. The reactions between $[Mn(\text{saltmen})(H_2O)_2]ClO_4$ and $K_2[M(CN)_4]$ ($M = Ni, Pd$) with a molar ratio of 1:2 afforded not neutral cyanide-bridged complexes containing trinuclear M_2Mn core, but gave two cyanide-bridged compounds containing MMn_4 pentanuclear cationic entity with the free ClO_4^- anions acting balance ions. The cyanide-bridged MMn_4 entity can be further linked into phenoxo-bridged 2D sheet depending on the self-complementary of the phenoxo oxygen atoms from the neighboring complexes by coordinating to the Mn(III) ion. The structures of these two complexes are similar to the previously reported examples resulted from the reactions of $[Mn(\text{saltmen})(H_2O)_2]ClO_4$ with $K_3[Fe(CN)_6]$, $Na_2[Fe(CN)_5NO]$, $K_2[Fe(CN)_5(1-MeIm)]$ (1-Methylimidazole) or $K_3[Cr(CN)_5(NO)]$,²¹⁻²³ indicated that this type of manganese Schiff base compounds are very favor of forming phenoxo oxygen-bridged structure. The two cyanide-bridged heterometallic complexes have been characterized by IR spectroscopy. In their IR spectra, the single peak at about 2125 cm^{-1} can be assigned to the bridging cyanide groups. Observation of a strong broad peak centered at ca. 1100 cm^{-1} suggests the presence of ClO_4^- anions.

Crystal Structures of Complexes 1 and 2. Some important structural parameters for complexes **1** and **2** are collected in Table 2. The cationic pentanuclear structure for complexes **1** and **2** and their two-dimensional sheet-like structure are shown in Figures 1 and 2, respectively.

As can be found in Table 2, both of these two complexes are isostructural and crystallize in tetragonal space group $I4/m$, containing four independent units in the unit cell. The structure of these two complexes can be characterized as 2D network, which is comprised by the cationic layer of $\{[Mn(\text{saltmen})]_4[M(CN)_4]\}^{2+}$ including two basic building units, namely the dimeric $[Mn_2(\text{saltmen})_2]^{2+}$ cation and the $[M(CN)_4]^{2-}$ anion, the balanced ClO_4^- anions and the solvent molecules. The parameters around the M(II) ion (Table 2) involved in a perfect square plane is almost same to those found in $K_2[M(CN)_4]$, indicating that the coordination of the cyanide group to the Mn(III) ion has no obvious influence on the geometry of the M(II) ion. In the dimeric Mn_2 units, both Mn(III) centers are surrounded by two N and two O atoms of the saltmen ligand in the equatorial plane, one axial N atom derived from $[M(CN)_4]^{2-}$ unit and one axial O atom derived from the neighboring $[Mn(\text{saltmen})]^{2+}$ moiety, therefore forming an octahedral coordination sphere. As shown in Table 2, the average distances between the Mn atom and the

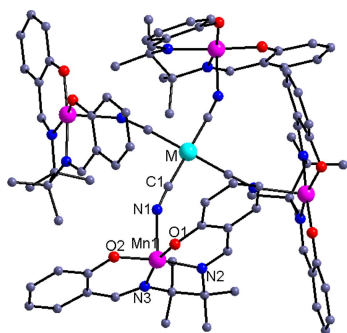
Table 1. Crystallographic data for complexes **1** and **2**

	1	2
Chemical formula	$C_{85}H_{94}Cl_2Mn_4N_{12}NiO_{18}$	$C_{86}H_{93}Cl_2Mn_4N_{13}O_{17}Pd$
Fw	1921.09	1977.79
Crystal system	Tetragonal	Tetragonal
Space group	$I4/m$	$I4/m$
$a/\text{\AA}$	18.6022(16)	18.6992(10)
$b/\text{\AA}$	18.6022(16)	18.6992(10)
$c/\text{\AA}$	27.858(5)	27.936(4)
α/deg	90	90
β/deg	90	90
γ/deg	90	90
$V/\text{\AA}^3$	9640(2)	9768.2(15)
Z	4	4
Completeness	97.9%	98.2%
$F(000)$	3976	4064
θ/deg	2.13 to 25.02	1.54 to 25.02
GOF	1.008	0.984
$R_1[I > 2\sigma(I)]$	0.0652	0.0574
wR_2 (all data)	0.1883	0.1677

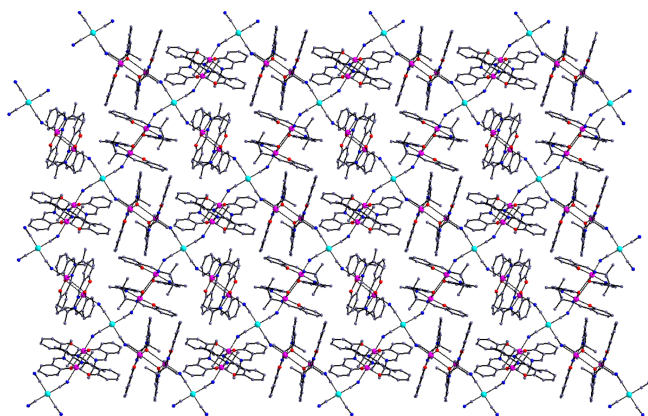
Table 2. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	2
M1-C1	1.856(6)	1.981(6)
Mn1-N1	2.206(5)	2.216(5)
Mn1-N2	1.970(4)	1.976(4)
Mn1-N3	1.969(4)	1.972(4)
Mn1-O1	1.872(4)	1.881(3)
Mn1-O2	1.869(4)	1.864(3)
Mn1-O1#1	2.870(3)	2.724(1)
C1-N1-Mn	156.3(5)	155.5(4)
N1-C1-M	175.4(5)	176.0(5)
C1#2-M1-C1	178.8(4)	178.7(3)

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

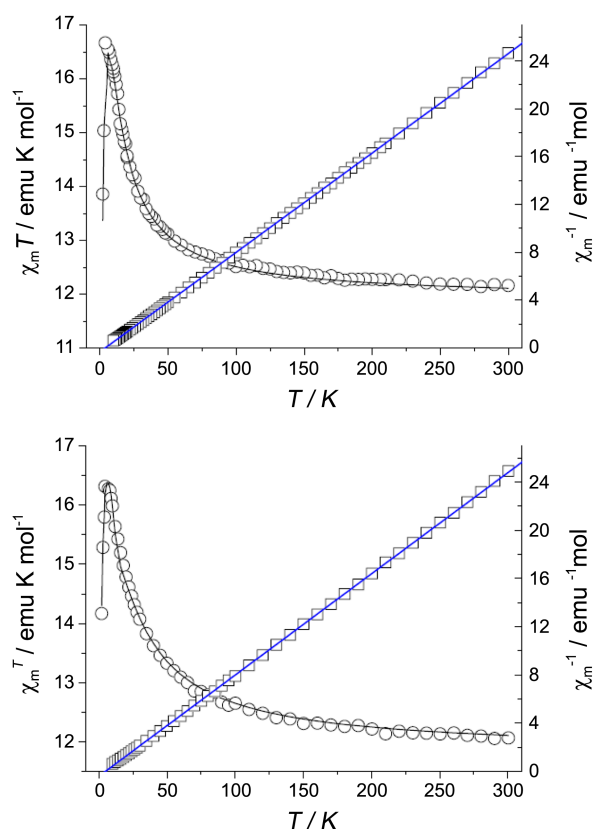
**Figure 1.** The representative pentanuclear cationic structure of complexes **1** and **2**. The balanced ClO_4^- ions, the solvent molecules and all the H atoms are omitted for clarity.

N, O atoms of the Schiff-base ligand in complexes **1** and **2** are 1.970, 1.871 Å and 1.974, 1.863 Å, respectively, while the Mn-N_{cyanide} and Mn-O_{phenoxo}(axial) bond lengths are 2.206(5), 2.870(3) Å and 2.216(5), 2.724(1) Å, clearly indicating the elongation octahedron surrounding the Mn(III) ion, typically accounting for the well known Jahn-Teller effect. The Mn-O(axial)-Mn bond angles are about 100°, and the

**Figure 2.** The two-dimensional sheet-like structure of complexes **1** and **2**. The balanced ClO_4^- ions, the solvent molecules and all the H atoms are omitted for clarity.

intermolecular phenoxo oxygen-bridged Mn^{III}-Mn^{III} distance are 3.681 and 3.566 Å, for the latter which are markedly shorter than the intramolecular Mn^{III}-Mn^{III} separation through diamagnetic $[\text{M}(\text{CN})_4]^{2-}$ with the values of 5.091 and 5.211 Å.

Magnetic Properties of Complexes 1 and 2. The magnetic properties of compounds **1** and **2** have been investigated in the range of 1.8-300 K under the external magnetic field of 2000 Oe, where, $\chi_m T$ is the magnetic susceptibility per Mn₄ unit. The $\chi_m T$ vs T and χ_m^{-1} vs T curves for complexes **1** and **2** are presented in Figure 3. At room temperature, the values of the $\chi_m T$ product are about 12.1 emu mol⁻¹ K for these two complexes, which corresponds for four high spin manganese(III) ions with $S = 2$. Upon cooling, the $\chi_m T$ values gradually increases reach a maximum value of 16.31 and 16.66 emu mol⁻¹ K for complexes **1** and **2** at about 4 K before decreasing down to about 14 emu mol⁻¹ K at 1.8 K. The rapid decrease of $\chi_m T$ at low temperature may be due to the weak magnetic interaction between $[\text{Mn}(\text{saltmen})]^+$ moieties possibly through the diamagnetic $[\text{M}(\text{CN})_4]^{2-}$ and/or the zero-field splitting effect of the Mn(III) ions in axially elongated octahedral surroundings. The magnetic susceptibility obeys Curie-Weiss law in the range of 10-300 K, and affords positive Weiss constant $\theta = 2.35$ K, Curie constant $C = 12.06$ emu K mol⁻¹ and $\theta = 2.47$ K, Curie constant $C = 11.91$ emu K mol⁻¹ for complexes **1** and **2**, respectively. The change tendency of the $\chi_m T$ and the positive Weiss constant primarily indicated the ferromagnetic coupling in these two

**Figure 3.** $\chi_m T$ vs T and χ_m^{-1} vs T curves for complex **1** (top) and complex **2** (bottom). The solid lines represent to the best fit curves.

complexes.

Considering that the long distance between the two Mn(III) ions bridged by the diamagnetic $[\text{M}(\text{CN})_4]^{2-}$ ion, the magnetic coupling are mainly caused by the biphenolate-bridged Mn_2 dimer. The magnetic susceptibility data for these two complexes were simultaneously fitted by the following spin Hamiltonian:²⁴

$$H = -2JS_1S_2 + D(S_{z, \text{Mn1}}^2 + S_{z, \text{Mn2}}^2)$$

The first term refers to the exchange interaction between the manganese(III) ions within the supramolecular dimer. The second terms take into account the zero field splitting (ZFS) effects for the two manganese ions ($D_1 = D_2 = D$). In view of the axially elongated structure around Mn(III), a negative sign is expected for D ;²⁶ therefore, D was constrained to negative values in our calculations. The magnetic susceptibilities have been numerically calculated using the MAGPACK program, giving the best set of parameters $J = 2.13 \text{ cm}^{-1}$, $D = -0.98 \text{ cm}^{-1}$, $g = 2.01$ and $J = 2.21 \text{ cm}^{-1}$, $D = -1.01 \text{ cm}^{-1}$, $g = 2.02$ for complexes **1** and **2**, respectively. These results are basically comparable to those found in the reported examples containing also phenolate-bridged Mn_2 dimer.^{22,24,26,27}

Similar to that for the reported manganese Schiff dimers,^{22,24,26,27} the magnetic coupling between the phenoxo-bridged Mn(III) ions in complexes **1** and **2** is ferromagnetic. The ferromagnetic exchange in these types of systems can be understood with the consideration of the arrangement of d -orbitals of the Mn(III) ion. As has been known, the electronic configuration of the Mn(III) ion in an elongated Jahn–Teller distortion is $(d_{xy})^1$, $(d_{yz})^1$, $(d_{xz})^1$ and $(d_{z^2})^1$ with a $^5\text{B}_1$ ground state.²⁸ The methyl groups of saltmen²⁻ act as electronic donor and enhances the Jahn–Teller orbital splitting. Therefore, the ferromagnetic exchange interaction between Mn(III) ions could be mainly the result of the d_{z^2} and the d_{π} orbitals (d_{xy} , d_{yz} and d_{xz} orbitals) orthogonality.^{26,27}

Conclusion

In summary, two new heterobimetallic cyanide- and phenoxo-bridged coordination polymers have been synthesized with tetracyanidemetalates and manganese(III) schiff base compound as building blocks. The structural characterization reveals their cyanide-bridged MMn_4 cationic nature and the extended biphenolate-bridged 2D sheet-like structure. Investigation over their magnetic properties reveals ferromagnetic coupling between the biphenolate-bridged Mn_2 dimer.

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