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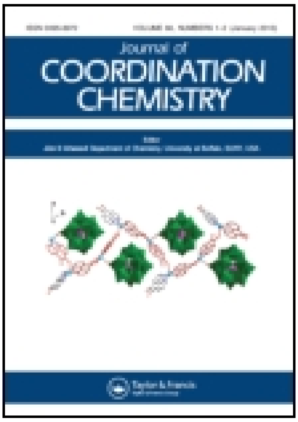

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Structures and magnetism of two manganese crowns assembled with 2,4-dihydroxyacetophenone oxime

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Structures and magnetism of two manganese crowns assembled with 2,4-dihydroxyacetophenone oxime

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Reactions of 2,4-dihydroxyacetophenone oxime with manganese salts yielded two manganese crowns, $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(HCOO)(MeOH)_5]\cdot MeOH$ (**1**) and $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(CH_3COO)(MeOH)_5]\cdot MeOH$ (**2**) (4-OH-Me-saoH$_2$=2,4-dihydroxyacetophenone oxime). Both compounds possess $[Mn^{III}{}_3(\mu_3\text{-}O)]^{7+}$ cores which contain 9-MC-3 metallacrown (MC) rings with the repeating pattern [–Mn–N–O–]. However, the difference in the structures of both compounds is coordinated carboxylates. In **1** and **2**, the MC molecules are connected with each other through intermolecular hydrogen bonds, generating similar 3-D supramolecular networks. Magnetic properties reveal that in **1** and **2** the metal ions exhibit ferromagnetic exchange coupling.

Keywords: $[Mn^{III}{}_3(\mu_3\text{-}O)]^{7+}$ core; 9-MC-3 metallacrown; Magnetic properties; 2,4-Dihydroxyacetophenone oxime

1. Introduction

In 1989, Pecoraro reported the synthesis and characterization of metallacrown (MC) compounds, $[VO(shi)(MeOH)]_3$ and $\{Mn^{II}(OAc)_2[Mn^{III}(shi)_4](DMF)_6\}\cdot 2DMF$ [1]. Since then, many researchers have studied such compounds owing to their intrinsic magnetism [2–4]. MCs, which are inorganic structural and functional analogs to crown ethers, are a new class of metallamacrocyclic molecules [5] with a wide range of potential applications, such as catalysis [6], selective separation agents [7, 8], recognition agents [9], and single-molecule magnets [10]. Many structural types of MCs have been reported, such as 9-MC-3, 12-MC-4, 15-MC-5, 24-MC-8, etc. [11–13]. They can also be utilized as building blocks to construct 1-D, 2-D, and 3-D coordination polymers [14].

Oxime acids have been reported to construct MCs [15]. Phenolic oximes have gained renewed attention owing to their propensity to generate polynuclear compounds, in which both the oximate and the phenolate bridge. A series of phenolic oximes (HsaoH$_2$,

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Me–saoH_2, Et–saoH_2, etc.) have been explored to construct 9-MC-3 MCs [16], especially manganese crowns, for example, $[Mn^{III}{}_3O(Et{-}sao)_3(MeOH)_3](ClO_4)$ consists of a 9-MC-3 manganese crown ring, which is capped by a ClO_4^- in a $\eta^1:\eta^1:\eta^1:\mu_3$ fashion [16g]. Some of them exhibit single-molecule magnetic behavior [16b–16f,16k], for example, $[Mn^{III}{}_3O(Et{-}sao)_3(O_2CPh(Cl)_2)(MeOH)_3(H_2O)]$ is a low nuclearity single-molecule magnet with anisotropy barrier $U_{eff} \sim 51$ K, which is almost the largest effective barrier [16f]. However, manganese clusters with 2,4-dihydroxyacetophenone oxime have remained unreported. In this manuscript, we report syntheses and structures of two manganese crowns based on this ligand, $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(HCOO)(MeOH)_5]\cdot MeOH$ (**1**) and $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Mesao)_3\ (CH_3COO)(MeOH)_5]\cdot MeOH$ (**2**). Both compounds possess similar $[Mn^{III}{}_3(\mu_3\text{-}O)]^{7+}$ cores which contain 9-MC-3 MC rings with the repeating pattern [–Mn–N–O–]. In **1** and **2**, the MC molecules are connected into similar 3-D supramolecular networks through intermolecular hydrogen bonds. Magnetic properties reveal that the metal ions exhibit ferromagnetic exchange coupling in **1** and **2**.

2. Experimental

2.1. *Materials and physical measurements*

All manipulations were performed under aerobic conditions using materials as received (reagent grade). 2,4-Dihydroxyacetophenone oxime was synthesized by reaction of 2,4-dihydroxyacetophenone with hydroxylamine and sodium acetate in a mixture of MeOH/H_2O, as described in the literature [17]. Elemental analyses (C, H, N) were performed by a Perkin-Elmer 2400 elemental analytical instrument. IR spectra were recorded as KBr pellets on a Nicolet-460 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Structures were characterized by a Bruker Smart-1000 CCD diffractometer. Variable-temperature direct current (dc) magnetic susceptibility measurements down to 2.0 K were carried out on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 0.1 T dc magnet.

***Caution*!** Although we encountered no problems, care should be taken when using the potentially explosive perchlorates.

2.2. *Synthesis*

2.2.1. Preparation of $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(HCOO)(MeOH)_5]\cdot MeOH$ (1). A solution of $Mn(ClO_4)_2\cdot 6H_2O$ (181 mg, 0.5 mmol) and 2,4-dihydroxyacetophenone oxime (83.5 mg, 0.5 mmol) in MeOH was treated with a molar equivalent of MeONa and stirred for 1 h to form a black solution. After filtration the solution was left to evaporate slowly and black block X-ray quality crystals were formed after one week. Yield: 30% (based on $Mn(ClO_4)_2\cdot 6H_2O$). $C_{31}H_{46}Mn_3N_3O_{18}$ (913.53): calcd C 40.76, H 5.08, N 4.60; found C 40.13, H 4.67, N 4.27. IR(KBr, cm^{-1}): 3423(s), 1617(s), 1529(m), 1436(w), 1384(w), 1369(w), 1333(w), 1300(w), 1251(m), 1177(m), 1158(w), 1122(w), 1070(s), 1037(m), 992 (s), 963(m), 851(w), 808(w), 763(m), 736(w), 669(s), 612(m), 535(m), 479(w), 444(w).

2.2.2. Preparation of $[Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(CH_3COO)(MeOH)_5]\cdot MeOH$ (2). A similar procedure to **1** was followed, except that $Mn(CH_3COO)_2\cdot 4H_2O$ was used instead. Yield: 36.83% (based on $Mn(CH_3COO)_2\cdot 4H_2O$). $C_{32}H_{48}Mn_3N_3O_{18}$ (927.55): calcd C 41.44, H 5.22, N 4.53, found C 40.27, H 4.79, N 4.06. IR(KBr, cm^{-1}): 3397.6(m), 1604.7(s), 1529.5(s), 1433.3(m), 1384.2(w), 1369.0(w), 1332.5(w), 1304.1(w), 1252.0(m), 1178.3(m), 1152.7(w), 1070.3(m), 1037.9(m), 992.0(s), 964.0(w), 851.6(w), 808.0(w), 765.5(w), 669.9(s), 612.4(w), 536.2(w), 479.3(w), 444.3(w).

2.2.3. X-ray structural studies. Data of the compounds were obtained on a Bruker Smart-1000 CCD diffractometer using graphite-monochromated Mo K_α radiation. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 crystallographic software package [18, 19]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The refinement details and selected bond distances and angles of **1** and **2** are listed in tables 1 and 2, respectively.

3. Results and discussion

3.1. *Syntheses*

The syntheses were performed under aerobic conditions with reactions of Mn^{2+} salts and 2,4-dihydroxyacetophenone oxime in a molar ratio of 1 : 1 in basic methanol solution. All Mn ions are +3, indicating Mn^{II} was oxidized by atmospheric O_2 and the oxidation process was base-assisted [16a, 20]. The Mn^{2+} and Na^+ salts have large influences on the

Table 1. Details of the crystal parameters, data collection, and refinement for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{31}H_{46}Mn_3N_3O_{18}$	$C_{32}H_{48}Mn_3N_3O_{18}$
Formula weight	913.53	927.55
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*
Unit cell dimensions		
a (Å)	8.4810(8)	8.5170(8)
b (Å)	42.080(3)	42.440(4)
c (Å)	12.7191(13)	12.6151(11)
a (°)	90	90
b (°)	117.160(2)	117.120(2)
c (°)	90	90
V (Å^3)	4038.7(6)	4058.5(6)
Z	4	4
D_{calc} (Mg m^{-3})	1.502	1.518
F(0 0 0)	1888	1920
θ Range (°)	2.31–25.02	2.32–25.02
Index ranges	$-10 \leq h \leq 9$,	$-8 \leq h \leq 10$,
	$-49 \leq k \leq 33$,	$-50 \leq k \leq 50$,
	$-15 \leq 1 \leq 15$	$-14 \leq 1 \leq 15$
Measd./unique	20,019/7048	16,518/6897
(R_{int}) reflns.	0.0615	0.1308
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.1005$	$R = 0.1186$
	w$R = 0.2197$	w$R = 0.2547$
R indices (all data)	$R = 0.1273$	$R = 0.1620$
	w$R = 0.2330$	w$R = 0.2754$
GOF on F^2	1.127	1.126

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

1					
Mn(1)–O(10)	1.884(5)	Mn(2)–O(10)	1.897(6)	Mn(3)–O(10)	1.896(5)
Mn(1)–O(2)	1.889(5)	Mn(2)–O(5)	1.878(6)	Mn(3)–O(8)	1.901(6)
Mn(1)–O(7)	1.928(6)	Mn(2)–O(1)	1.944(5)	Mn(3)–O(4)	1.916(6)
Mn(1)–N(1)	2.002(7)	Mn(2)–N(2)	2.009(7)	Mn(3)–N(3)	2.010(7)
Mn(1)–O(15)	2.266(6)	Mn(2)–O(16)	2.249(6)	Mn(3)–O(17)	2.255(7)
Mn(1)–O(11)	2.325(7)	Mn(2)–O(12)	2.297(6)	Mn(3)–O(14)	2.340(6)
Mn(1)–O(10)–Mn(3)	119.2(3)	Mn(1)–O(10)–Mn(2)	120.9(3)	Mn(3)–O(10)–Mn(2)	118.4(3)
2					
Mn(1)–O(10)	1.893(6)	Mn(2)–O(10)	1.890(6)	Mn(3)–O(10)	1.875(6)
Mn(1)–O(8)	1.882(7)	Mn(2)–O(2)	1.877(6)	Mn(3)–O(5)	1.864(7)
Mn(1)–O(1)	1.912(7)	Mn(2)–O(4)	1.951(6)	Mn(3)–O(7)	1.929(7)
Mn(1)–N(3)	2.001(8)	Mn(2)–N(1)	2.006(7)	Mn(3)–N(2)	1.995(8)
Mn(1)–O(15)	2.258(7)	Mn(2)–O(16)	2.255(7)	Mn(3)–O(17)	2.273(7)
Mn(1)–O(13)	2.356(7)	Mn(2)–O(11)	2.304(7)	Mn(3)–O(14)	2.323(7)
Mn(3)–O(10)–Mn(2)	121.0(3)	Mn(3)–O(10)–Mn(1)	118.6(3)	Mn(2)–O(10)–Mn(1)	119.1(3)

resulting structures. Formate ($HCOO^-$) in **1** may be the result of oxidation of CH_3OH [20].

3.2. *Crystal structures of [$Mn_3(\mu_3$-O)(4-OH-Me-sao)$_3$(HCOO)(MeOH)$_5$]·H_2O (1)*

As shown in figure 1(a), **1** crystallizes in the monoclinic space group *P2(1)/c* and the asymmetric unit consists of three doubly deprotonated 2,4-dihydroxyacetophenone oxime ligands, three Mn ions, one μ_3-O, one formate, five coordinated methanols, and one free methanol. The oxidation states of Mn ions were confirmed by a combination of charge balance, bond-valence sum (BVS) calculations, and bond-length considerations (table 3) [21–23]. The trinuclear compound contains a $[Mn^{III}{}_3(\mu_3\text{-O})]^{7+}$ oxo-centered core, in which the three manganeses are bridged by the central oxygen 0.133 Å below the [Mn_3] plane. The three Mn-O^{2-} bonds range from 1.884(5) to 1.897(6) Å, comparable with those of reported compounds containing similar cores [24–27]. The three oximates $\eta^1:\eta^1:\eta^1:\mu$ using their –N–O– oxime moieties span each edge of the [Mn_3] plane forming a 9-MC-3 MC ring with the repeating pattern [–Mn–N–O–]. The Mn–N–O–Mn torsion angles are 37.5(2)°, 41.3(4)°, and 40.0(7)°, respectively. The other coordination sites of the three metal centers are furnished by formate and two MeOH on the "upper" triangular [Mn_3] plane and three MeOH on the "lower" triangular [Mn_3] plane, constructing an octahedral coordination geometry around each Mn^{III}. The average bond lengths of Mn–O/N are 1.926 (3)–1.932(6) Å in the equatorial plane and 2.273(6)–2.298(1) Å at the axial position, close to those of other manganese complexes [16, 28], displaying a classical Jahn–Teller (JT) elongation. These JT axes are approximately parallel and perpendicular to the [Mn_3] triangular plane.

O–H···O hydrogen bonding interactions connect these clusters into 3-D supramolecular networks (figure 1(b)), similar to that of [Mn(H_2bptc)(2,2'-bpy)$_2$]·H_2O [29]. Three MeOH on the "lower" triangular face (O15, O16, and O17) interact with uncoordinated oxygen O13 of $HCOO^-$ on the "upper" triangular face of another molecule, linking adjacent clusters into 1-D chains along the *a* axis. These chains are connected with each other through O–H···O hydrogen bonding interactions between lattice methanols (O18) and oximate oxygens O2 as well as the uncoordinated phenolic hydroxyl O9, forming 2-D supramolecular layers. Adjacent 2-D supramolecular layers are linked into 3-D supramolecular

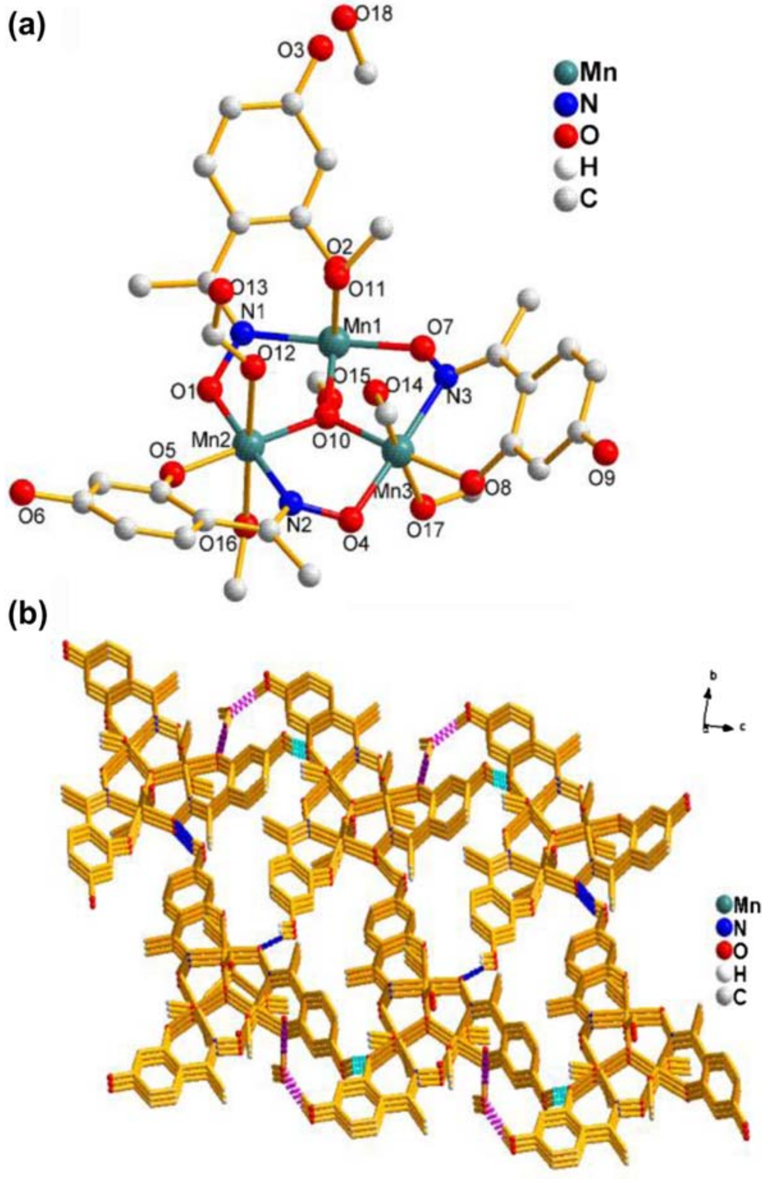

Figure 1. The molecular structure (a) and 3-D network structure (b) of **1**.

networks by O–H···O hydrogen bonds (O3–H···O8 and O6–H···O1). The data of these hydrogen bonds are collected in table 4.

3.3. *Crystal structures of [$Mn_3(\mu_3\text{-}O)(4\text{-}OH\text{-}Me\text{-}sao)_3(CH_3COO)(MeOH)_5$]·MeOH (2)*

Compound **2** crystallizes in the monoclinic space group *P2(1)/c* and is also a 9-MC-3 MC (figure 2(a)). Acetate takes place of formate. The central oxygen (O10) is 0.129 Å below

Table 3. BVS calculations for **1** and **2**.

		2+	3+	4+
1	Mn1	3.216411	2.977307	3.068347
	Mn2	3.207430	2.968346	3.060151
	Mn3	3.132503	2.898971	2.988684
2	Mn1	3.237867	2.997104	3.088913
	Mn2	3.216467	2.977052	3.068574
	Mn3	3.160382	2.988841	3.147424

Table 4. Data of hydrogen bonds of **1** and **2**.

	D–H···A	d(H···A) (Å)	∠DHA (°)	d(D···A) (Å)
1	O(15)–H(15)···O(13) #3	1.962	175.43	2.780
	O(16)–H(16)···O(13) #3	1.878	165.35	2.679
	O(17)–H(17)···O(13) #3	1.991	159.26	2.773
	O(3)–H(3)···O(8) #1	1.938	161.60	2.729
	O(6)–H(6)···O(1) #5	1.931	161.15	2.720
	O(9)–H(9)···O(16) #2	1.771	166.74	2.576
	O(18)–H(18)···O(2) #4	2.000	170.63	2.812
2	O6–H6···O8 #2	1.980	164.99	2.780
	O9–H9···O18 #1	1.797	176.57	2.616
	O3–H3···O8 #5	1.938	160.21	2.736
	O15–H15···O12 #4	1.907	167.82	2.714
	O16–H16···O12 #4	1.922	165.81	2.725
	O17–H17···O124	1.978	158.54	2.758
	O18–H18···O5 #3	2.029	171.69	2.843

Symmetry transformations used to generate equivalent atoms for **1**: #1 $x, y, z+1$; #2 $x, y, z-1$; #3 $x+1, y, z$; #4 $x-1, y, z$; #5 $x-1, -y+1/2, z-1/2$; for **2**: #1 $x, y, z+1$; #2 $x, y, z-1$; #3 $x+1, y, z$; #4 $x-1, y, z$; #5 $x+1, -y+1/2, z+1/2$.

the triangular [Mn_3] plane. The torsion angles are 43.6(9)°, 38.3(9)°, and 39.7(2)°. In **2**, adjacent molecules are also connected with each other by intermolecular hydrogen bonds to form a 3-D supramolecular network (figure 2(b)).

3.4. *Magnetic studies*

Variable-temperature, solid-state dc magnetic susceptibility measurements were carried out on both polycrystalline samples in a field of 0.1 T and a temperature range of 2–300 K. As plotted in figure 3, different coordinated carboxyl in both complexes has little effect on magnetic properties. Both **1** and **2** exhibit ferromagnetic coupling exchanges within the metal centers. The $\chi_M T$ values of **1** and **2** are almost the same. At room temperature, the values of $\chi_M T$ are 9.72 (**1**) and 10.00 $cm^3 mol^{-1} K$ (**2**), comparable to those of analogous 9-MC-3 manganese crowns [16], and increase steadily as the temperature decreases, reaching maximum values of 16.99 (**1**) and 17.43 $cm^3 mol^{-1} K$ (**2**), and then drop to 11.26 (**1**) and 12.3 $cm^3 mol^{-1} K$ (**2**) at 2.0 K, respectively. The $\chi_M T$ values at room temperature are larger than expected for three non-interacting Mn(III) centers with $g = 2.0$ (9.00 $cm^3 mol^{-1} K$) [27], which may indicate that ferromagnetic interactions may have occurred at room temperature. The decrease at low temperature may be assigned to the Zeeman effect, zero-field splitting, and/or intermolecular interactions.

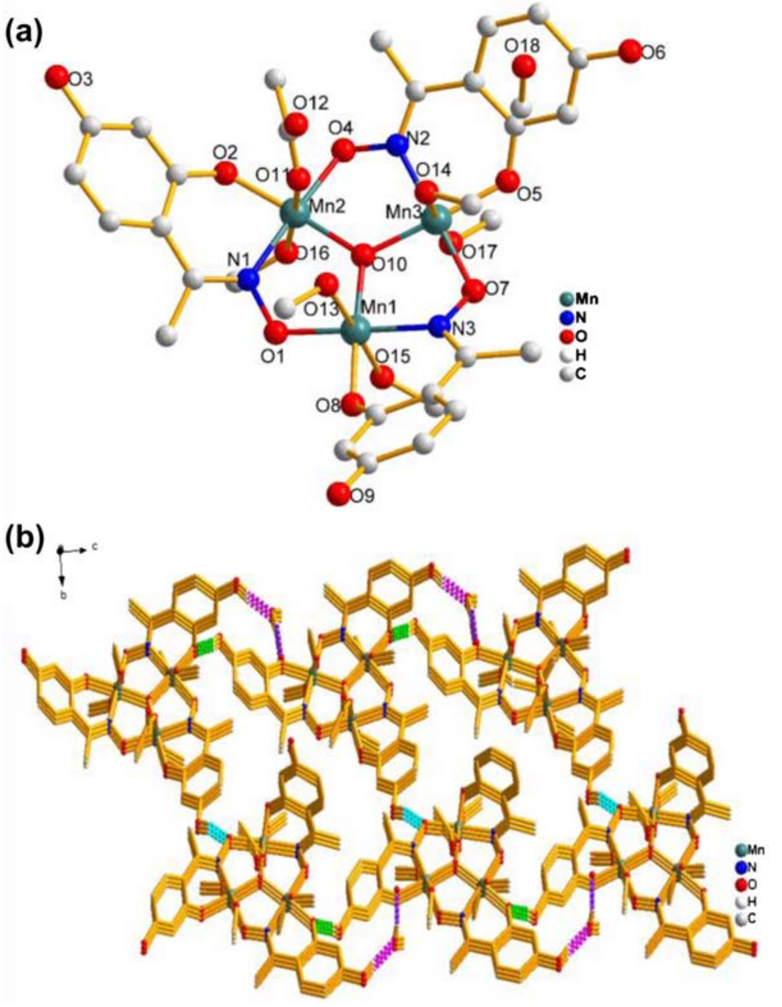

Figure 2. The molecular structure (a) and 3-D network structure (b) of **2**.

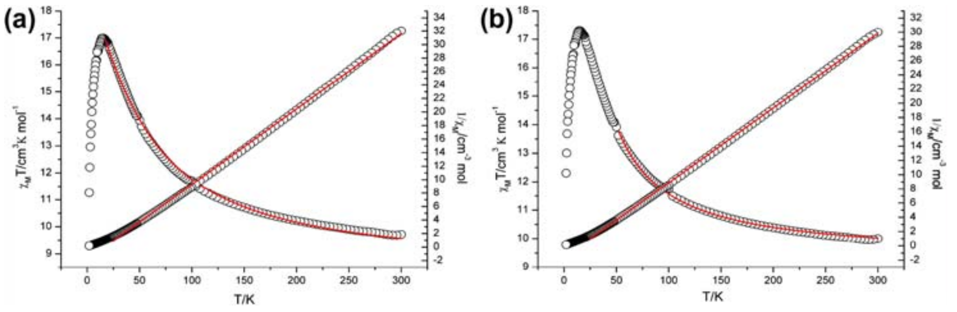

Figure 3. (a)–(b) Plots of $\chi_M T$ and $1/\chi_M$ vs. T for **1** and **2**; the solid lines represent the best theoretical fit of the data.

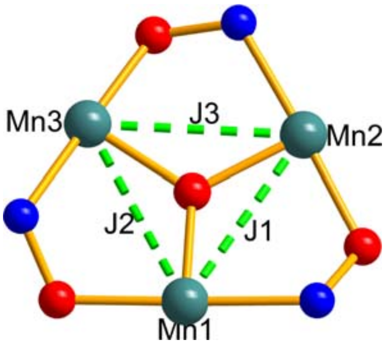

Figure 4. The magnetic coupling interactions within the 9-MC-3 unit.

In order to have a better estimation of the exchange coupling parameters, the experimental magnetic data were successfully simulated. For **1** and **2**, the interactions between adjacent molecules are very weak, and only the intramolecular coupling interactions are considered. The Heisenberg spin Hamiltonian was written as (figure 4):

$$\hat{H} = -2J_1\hat{S_1}\hat{S_2} - 2J_2\hat{S_1}\hat{S_3} - 2J_3\hat{S_2}\hat{S_3} \tag{1}$$

The best fits are $J_1 = 0.12\,\text{cm}^{-1}$, $J_2 = J_3 = 0.96\,\text{cm}^{-1}$, and $g = 1.96$, with $R = 1.8 \times 10^{-4}$ for **1**, while $J_1 = J_2 = J_3 = 0.25\,\text{cm}^{-1}$, and $g = 2.0$, with $R = 2.7 \times 10^{-5}$ for **2**. The magneto-structural relations for analogous [$\text{Mn}^{\text{III}}{}_6$] compounds have been well established [30]. The coupling is largely dependent upon the Mn–O–N–Mn torsion angles; the ferromagnetic exchange interaction is attributed to Mn–O–N–Mn torsion angles above the "magic area" of 30.4°–31.3° [15, 27, 31], whereas antiferromagnetic interaction arises from the Mn–O–N–Mn torsion angle below the *magic area*. That is, when the Mn–O–N–Mn torsion angle is larger than ca. 31.3°, $J > 0$ (*F*), and if the Mn–N–O–Mn torsion angle is lower than ca. 30.4°, then $J < 0$ (AF) [16 h]. For **1** and **2**, the Mn–O–N–Mn torsion angles are 38.0–44.0 with ferromagnetic coupling existing. Of course, other interactions such as those between adjacent 9-MC-3 along the chain also have influence on the coupling, and the resulting ferromagnetic interactions should be the synergistic effect of both of them.

4. Conclusion

We have described the structures and magnetic properties of two manganese MCs assembled from 2,4-dihydroxyacetophenone oxime. Both compounds possess 9-MC-3 MC rings with the repeating pattern [–Mn–N–O–]. In **1** and **2**, the MC molecules are connected with each other by intermolecular hydrogen bonds into similar 3-D supramolecular networks. It is difficult to understand the relationship between structures and magnetic properties in these trinuclear manganese complexes since all contributions to the exchange must be considered, such as ligand type, bond length and angles, weak interactions between molecules, etc. The magneto-structural investigations of the two complexes indicate the Mn–O–N–Mn torsion angles within the MCs play a dominant role in the magnetic coupling consistent with earlier work on analogous [Mn_6] compounds.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition numbers CCDC-834672 for **1** and 838577 for **2**. The data may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, via Fax (+44 1223 336033) or email (deposit@ccdc.cam.ac.uk).

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