

TRINUCLEAR MIXED-VALENT MANGANESE COMPLEX WITH NON-SCHIFF-BASE TETRADENTATE LIGAND SHOWING A FERROMAGNETIC COUPLING

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Abstract. Mixed-valent trinuclear manganese complex with *N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethyl-1,2-ethanediamine (H_2hdde), $[Mn_3(hdde)_2(CH_3CO_2)_2(CH_3O)_2]$, was synthesized. The X-ray crystal structure analysis revealed that compound is a trinuclear manganese complex with linearly arrangement of $Mn^{III}-Mn^{II}-Mn^{III}$, where two manganese ions of each $Mn^{II}-Mn^{III}$ pair are bridged by μ -phenolato-oxygen of $hdde^{2-}$ ligand, μ -methanolato-oxygen, and μ -acetato ion. Temperature dependence of magnetic susceptibilities showed an increase of magnetic moment as the temperature lowers in the range of 300–6 K and a decrease below 6 K. The magnetic analysis based on Heisenberg model yielded ferromagnetic coupling ($J = 2.62 \text{ cm}^{-1}$) between Mn^{III} and Mn^{II} ions.

Keywords: manganese complex, mixed-valent complex, magnetic property, ferromagnetic interaction.

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Introduction

There is a growing interest in the chemistry of manganese complexes with organic ligands [1-8]. Among organic ligands, Schiff-base ligands are very popular and have been often used to synthesize manganese complexes, because the combination of the oxygen and nitrogen donor atoms is favourable for binding manganese(II)/(III) ions [1,7]. For example, tetradentate N_2O_2 Schiff-base $salen^{2-}$ ligand ($H_2salen = \text{disalicylideneethylenediamine}$) affords a number of manganese(III) complexes of $[Mn(salen)X]$ ($X = \text{monovalent anion}$) type. Manganese(III) complexes with chiral $salen^{2-}$ are known as useful catalysts for organic synthesis [9]. Introduction of a functional group to organic ligands is usually easy for Schiff-base ligands and this is another reason for a large number of reports on Schiff-base manganese complexes. Many manganese complexes have been also reported as potential model compounds for the oxygen-evolving complex (OEC) of photosystem II (PSII) in green plants [6,10-12], in which the existence of tetranuclear manganese site in the S_0-S_4 states is widely accepted [13,14]. Our group has also been engaged in synthetic work of some manganese complexes with organic ligands [15-19]. In this study we have introduced a non-Schiff-base type tetradentate ligand, *N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethyl-1,2-

ethanediamine (H_2hdde), having a similar frame to the Schiff-base $salen^{2-}$ ligand (Figure 1).

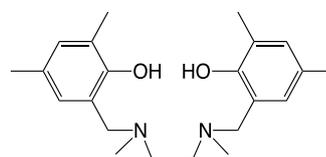


Figure 1. Non-Schiff-base tetradentate ligand (H_2hdde).

Using this ligand, our group has prepared a tetranuclear and a hexanuclear nickel(II) complexes, $[Ni_4(hdde)_2(CH_3COO)_4]$ and $[Ni_6(hdde)_3(OH)_4(NO_3)_2(H_2O)_2]$, where the former has antiferromagnetic coupling with an eight-membered cyclic tetranuclear nickel core, whereas the latter possesses ferromagnetic coupling with a hexanuclear nickel core [20]. Therefore, an interesting feature for manganese complex with this ligand was expected and an investigation of manganese complexes with H_2hdde has been started. A mixed-valence trinuclear manganese complex was obtained. A search in the Cambridge Structural Database (Version 5.38, November 2016) showed that, an analogous trinuclear manganese complex with $hdde^{2-}$ ligand, $[Mn_3(hdde)_2(C_2H_5CO_2)_2(CH_3O)_2] \cdot H_2O$, has been already reported [21]. The reported complex was

obtained in two-step reaction of H₂hdde with manganese perchlorate and successive sodium propionate, while the one-pot reaction has been used by us in order to obtain the complex. Here we report the synthesis and characterization of the trinuclear manganese complex with H₂hdde compared to the reported compound.

Experimental

Synthesis

All reagents were commercially available and used without further purification. The *N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethyl-1,2-ethanediamine (H₂hdde) was synthesized according to the published method [22].

[Mn₃(hdde)₂(CH₃CO₂)₂(CH₃O)₂]-CH₃OH (I)

60 mg (0.25 mmol) of manganese(II) acetate tetrahydrate were added to a solution of H₂hdde (17 mg, 0.05 mmol) in 5 cm³ methanol while stirring. 8 drops (0.08 mmol) of triethylamine were added to this solution while stirring. The resulting solution was heated for 1 h and then filtered, the filtrate was left several days to give dark purple crystals. The crystals were collected and dried under a vacuum. Yield, 7.0 mg (26% based on H₂hdde). Anal. found: C, 56.17%; H, 7.27%; N, 5.05%. Calc. for C₅₁H₇₆Mn₃N₄O₁₁: C, 56.40%; H, 7.05%; N, 5.16%. IR(KBr): $\nu_{\text{as}}(\text{CO}_2^-)$ 1568, $\nu_{\text{s}}(\text{CO}_2^-)$ 1415 cm⁻¹. Diffuse reflectance spectrum: λ_{max} : 248, 291, 364sh, 533 (⁵B_{1g}→⁵E_g), 655sh (⁵B_{1g}→⁵B_{2g}), 985 (⁵B_{1g}→⁵A_{1g}) nm.

[Mn₃(hdde)₂(CH₃CO₂)₂(CH₃O)₂]-H₂O (I')

The complex I' was also prepared by using manganese(III) acetate instead of manganese(II) acetate in the same way as **1**. Yield, 3.5 mg (13% based on H₂hdde). Anal. found: C, 55.82%; H, 7.07%; N, 5.08%. Calc. for C₅₀H₇₄Mn₃N₄O₁₁: C, 56.02%; H, 6.96%; N, 5.23%. IR(KBr): $\nu_{\text{as}}(\text{CO}_2^-)$ 1568, $\nu_{\text{s}}(\text{CO}_2^-)$ 1415 cm⁻¹. Diffuse reflectance spectrum: λ_{max} : 248, 291, 364sh, 539 (⁵B_{1g}→⁵E_g), 655sh (⁵B_{1g}→⁵B_{2g}), 988 (⁵B_{1g}→⁵A_{1g}) nm.

Measurements

Elemental analyses were performed using a Thermo Finnigan FLASH EA 1112 series CHNO-S analyzer.

Infrared spectra were recorded on a JASCO MFT-2000 FT-IR spectrometer in the range of 4000–600 cm⁻¹.

Electronic spectra were recorded on a Shimadzu UV-Vis-NIR spectrophotometer Model UV-3100 in the range of 200–1500 nm.

Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID

susceptometer operating at a magnetic field of 0.5 T in the range of 4.5–300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The values of effective magnetic moment were calculated from the equation $\mu_{\text{eff}} = \sqrt{8\chi_{\text{M}}T}$, where χ_{M} is the molar magnetic susceptibility per mole of trinuclear manganese unit.

X-ray crystallography: X-ray diffraction data were collected on a Bruker CCD X-ray diffractometer (SMART APEX, USA) using graphite-monochromated MoK α radiation at 123 K. Crystal data and details concerning data collection are given in Table 1.

Table 1

Crystallographic data and structure refinement.	
[Mn ₃ (hdde) ₂ (CH ₃ CO ₂) ₂ (CH ₃ O) ₂]-CH ₃ OH (I)	
Parameter	Value
Formula	C ₅₁ H ₇₆ Mn ₃ N ₄ O ₁₁
Formula mass	1085.97
Temperature, <i>T</i> (K)	123
Crystal system	Orthorhombic
Space group	<i>Pca</i> 2 ₁
<i>a</i> (Å)	23.573(3)
<i>b</i> (Å)	20.057(2)
<i>c</i> (Å)	22.415(2)
Unit-cell volume, <i>V</i> (Å ³)	10598(2)
Formula per unit cell, <i>Z</i>	8
Density, <i>D</i> _{calcd} (g cm ⁻³)	1.361
<i>D</i> _{obsd} (g cm ⁻³)	1.28
Crystal size (mm)	0.10 × 0.15 × 0.34
Absorption coefficient, μ (mm ⁻¹)	0.765
θ range (°)	1.33–28.54
No. of reflections	65993
No. of unique reflections	23266
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] [*]	<i>R</i> 1 = 0.0669, <i>wR</i> 2 = 0.114
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0994, <i>wR</i> 2 = 0.126
Goodness-of-fit on <i>F</i> ²	1.070

$$^*R1 = \sum(|F_o| - |F_c|) / \sum|F_o|;$$

$$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

The structure was solved by direct methods, and refined by full-matrix least-squares methods. The hydrogen atoms were inserted in their calculated positions and included in the least-squares calculation using a riding-atom model. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package [23,24]. Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1549836. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223336033; e-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk/data_request/cif).

Results and discussion

The synthesis of a trinuclear complex was achieved by 1:5 molar ratio reaction of the non-Schiff-base ligand (H_2hdde) and manganese(II) acetate tetrahydrate in methanol. When manganese(III) acetate dihydrate has been used as metal source, the same compound in a lower yield was isolated. In the case of 1:1 or 1:2 molar ratio reactions, it was possible to obtain the same compound, but in lower yields. The analytical data of these compounds afforded a chemical formula with mixed-valent Mn(III)-Mn(II)-Mn(III) complex, $[Mn_3(hdde)_2(CH_3CO_2)_2(CH_3O)_2]$. The infrared spectra of the complexes show a sharp band at 1568 and 1415 cm^{-1} , respectively, which can be assigned to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching vibration bands of the acetato ligand. The Δ value of $\nu_{as}(CO_2^-) - \nu_s(CO_2^-)$, 153 cm^{-1} , is in the ranges of those of the bridging-acetato complexes, suggesting a *syn-syn* bridging of the acetato ligand [25,26].

Single crystals suitable for the X-ray structure analysis were obtained from the methanol solution of **1** and the crystal structure was determined by the X-ray diffraction method. In the crystal, the asymmetric unit consists of two trinuclear manganese molecules $[Mn_3(hdde)_2(CH_3CO_2)_2(CH_3O)_2]$ and two methanol molecules. The structure drawn by ORTEP program for one of the two trinuclear complexes is shown in Figure 2. Selected bond distances are listed in Table 2.

The two trinuclear complexes have a similar trinuclear structure. In each complex, the two $hdde^{2-}$ ligands act as a tetradentate chelate in

a *cis- α* fashion [27] to bind a terminal manganese atom (Mn1 (Mn4) and Mn3 (Mn6)), which is connected to the central manganese atom (Mn2 (Mn5)) by a phenolato-oxygen of $hdde^{2-}$, a methanolato-oxygen and a *syn-syn* bridging acetato-oxygen atoms to form a linear array of the three manganese atoms (Mn1...Mn2 3.1719(16) Å, Mn2...Mn3 3.1827(16) Å, Mn1...Mn2...Mn3 144.90(4)°; Mn4...Mn5 3.1795(15) Å, Mn5...Mn6 3.1884(15) Å, Mn4...Mn5...Mn6 146.35(4)°).

Table 2

Selected bond lengths for complex 1.			
$[Mn_3(hdde)_2(CH_3CO_2)_2(CH_3O)_2] \cdot CH_3OH$			
Bond	Bond length (Å)	Bond	Bond length (Å)
Mn1...Mn2	3.1719(16)	Mn3-N3	2.303(6)
Mn2...Mn3	3.1827(16)	Mn3-N4	2.169(6)
Mn4...Mn5	3.1795(15)	Mn4-O11	1.868(5)
Mn5...Mn6	3.1884(15)	Mn4-O12	1.932(5)
Mn1-O1	1.875(5)	Mn4-O15	2.205(5)
Mn1-O2	1.932(5)	Mn4-O19	1.907(5)
Mn1-O5	2.181(5)	Mn4-N5	2.194(6)
Mn1-O9	1.918(3)	Mn4-N6	2.357(6)
Mn1-N1	2.180(6)	Mn5-O12	2.240(5)
Mn1-N2	2.316(6)	Mn5-O13	2.267(4)
Mn2-O2	2.242(5)	Mn5-O16	2.140(5)
Mn2-O3	2.265(5)	Mn5-O17	2.127(5)
Mn2-O6	2.168(5)	Mn5-O19	2.159(5)
Mn2-O7	2.185(5)	Mn5-O20	2.154(5)
Mn2-O9	2.138(5)	Mn6-O13	1.942(5)
Mn2-O10	2.148(5)	Mn6-O14	1.880(5)
Mn3-O3	1.941(5)	Mn6-O18	2.165(5)
Mn3-O4	1.886(5)	Mn6-O20	1.913(5)
Mn3-O8	2.198(5)	Mn6-N7	2.317(6)
Mn3-O10	1.915(5)	Mn6-N8	2.183(6)

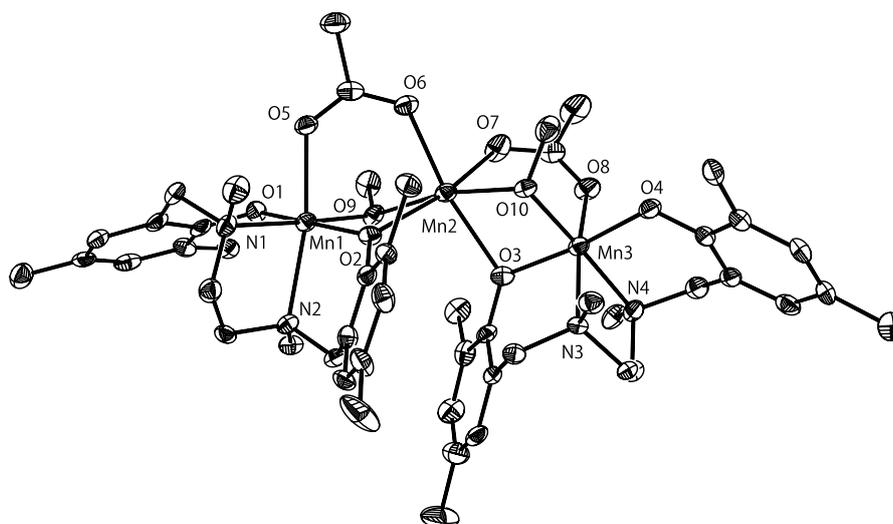


Figure 2. ORTEP drawing of one trinuclear molecule of **1**, showing the thermal ellipsoids at 50% probability level. Hydrogen atoms and solvents were omitted for clarity.

The terminal manganese atoms adopt an elongated octahedral geometry with two amino-nitrogen (Mn-N 2.303(6)—2.357(6) Å; 2.169(6)—2.194(6) Å) and two phenolato-oxygen atoms (Mn-O(terminal) 1.868(5)—1.886(5) Å; Mn-O(bridging) 1.932(5)—1.942(5) Å) from the hdde^{2-} ligand, acetato-oxygen (Mn-O 2.165(5)—2.205(5) Å), and methanolato-oxygen atoms (Mn-O 1.907(5)—1.918(5) Å), suggesting the pseudo Jahn-Teller effect due to the manganese(III) oxidation state. On the other hand, the central manganese atom adopts a distorted octahedral geometry with the two bridging phenolato-oxygen atoms of the two hdde^{2-} ligands (Mn-O 2.240(5)—2.267(5) Å), two bridging acetato-oxygen atoms (Mn-O 2.127(5)—2.185(5) Å), and two bridging methanolato-oxygen atoms (Mn-O 2.138(5)—2.159(5) Å).

The generally longer bond distances compared with those of the terminal manganese atoms suggest the manganese(II) oxidation state of the central manganese atom. This structure is similar to that of $[\text{Mn}_3(\text{hdde})_2(\text{C}_2\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{O})_2]\cdot\text{H}_2\text{O}$ [21]. Stabilization of the mixed-valent Mn(III)-Mn(II)-Mn(III) state may be due to the combination of the donor atoms containing

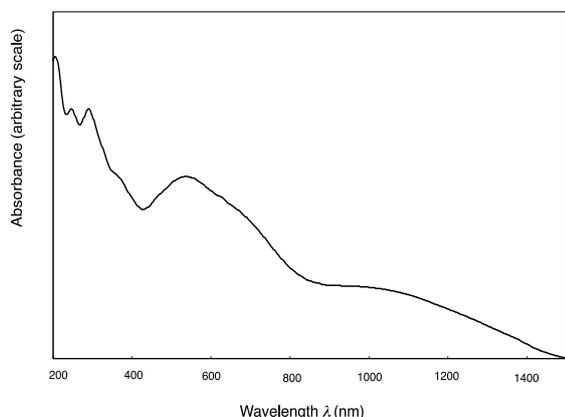


Figure 3. Diffused reflectance spectrum of **1**.

The decrease in the value below 6 K may be due to the zero-field-splitting of manganese ions and/or intermolecular interaction. In this case, the magnetic data can be analyzed by the Van Vleck equation [32] for the $(S_1 = 2)-(S_2 = 5/2)-(S_3 = 2)$ spin system with the spin Hamiltonian $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J'S_1 \cdot S_3$, assuming the equivalent intramolecular interaction (J) between the terminal Mn(III) and

the phenolato-oxygen atoms of the non-Schiff-base ligands, which prefer the higher oxidation state [16].

The diffused reflectance spectrum of **1** is shown in Figure 3. The complex shows two strong bands (248, 291 nm) and a shoulder band at 364 nm in the UV region, three broad bands at 533 nm, 655 nm (shoulder) and 985 nm in the visible and NIR regions. The band at 364 nm can be assigned to LMCT band from the phenolato-oxygen to the manganese d orbital [16, 28-31]. The three bands in the visible region can be assigned to $d-d$ transitions (${}^5B_{1g} \rightarrow {}^5E_g$, ${}^5B_{1g} \rightarrow {}^5B_{2g}$, and ${}^5B_{1g} \rightarrow {}^5A_{1g}$), confirming the elongated octahedral coordination environment of the manganese(III) atom [28].

The temperature dependence of magnetic susceptibility and magnetic moment per trinuclear molecule for **1** is shown in Figure 4. The magnetic moment of **1** is $9.43 \mu_B$ at 300 K. This value is larger than the spin-only value of $9.11 \mu_B$ calculated for non-interacting two high-spin Mn(III) ($S = 2$) and one manganese(II) ($S = 5/2$) centers with $g = 2$. The magnetic moment increases with lowering the temperature, reaching a maximum value of $13.27 \mu_B$ at 6 K, and then decreases to $13.07 \mu_B$ at 4.5 K.

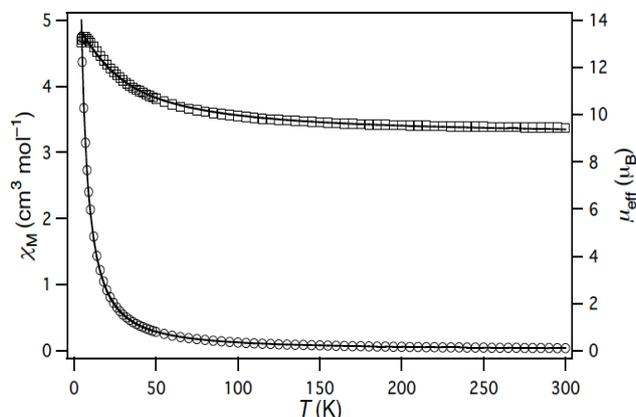


Figure 4. Temperature dependence of magnetic susceptibility (○) and magnetic moment (□) of **1**. Solid lines are fitting curves with the parameters $g = 1.99$, $J = 2.62 \text{ cm}^{-1}$, $J' = -1.04 \text{ cm}^{-1}$.

the central Mn(II) ions and the intramolecular interaction (J') between the terminal Mn(III) ions. A theoretical magnetic susceptibility equation was obtained by applying the Kambe vector-coupling method [33] and Van Vleck equation and used to fit the magnetic data. The magnetic parameters obtained from the fitting procedure are $g = 1.99$, $J = 2.62 \text{ cm}^{-1}$, $J' = -1.04 \text{ cm}^{-1}$. If the magnetic interaction between the terminal manganese ions

is neglected, the fitting parameters become $g = 2.01$, $J = 1.84 \text{ cm}^{-1}$, $J' = 0 \text{ cm}^{-1}$, $\theta = -0.58 \text{ K}$, where θ was introduced to consider the intermolecular interaction. The negative θ value goes with the positive J value in the latter case. These results suggest that the magnetic interaction within the trinuclear unit is weakly ferromagnetic as a whole. So far, several trinuclear Mn(III)-Mn(II)-Mn(III) complexes with linear arrangements were reported [34-45]. Most of these complexes show weak antiferromagnetic interaction between the manganese ions ($J = -0.13$ — -18.8 cm^{-1}) and the ferromagnetic interaction was found in only few compounds [37,44]. In this regard, it is interesting that the related manganese complex $[\text{Mn}_3(\text{hdde})_2(\text{C}_2\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{O})_2] \cdot \text{H}_2\text{O}$ was reported as antiferromagnetic compound ($J = -0.13 \text{ cm}^{-1}$) [21], although the molecular structure is similar to that of the reported here complex. The important bridging angles for magnetic interaction of this complex [Mn1-O9-Mn2 102.8(2)°, Mn2-O10-Mn3 103.0(2)°, Mn4-O19-Mn5 102.7(2)°, Mn5-O20-Mn6 103.1(2)° for the methanolato-bridges; Mn1-O2-Mn2 98.66(19)°, Mn2-O3-Mn3 98.1(2)°, Mn4-O12-Mn5 99.0(2), Mn5-O13-Mn6 98.21(19)° for the phenolato-bridges] are similar to those of $[\text{Mn}_3(\text{hdde})_2(\text{C}_2\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{O})_2] \cdot \text{H}_2\text{O}$ Mn-O-Mn 102.61(9)° and 102.70(8)° for the methanolato-bridges; Mn-O-Mn 97.19(8)° and 99.00(8) for the phenolato-bridges. The magnetic and electronic spectral properties of the sample **1'** are also almost identical with those of **1**.

Conclusions

In this study, a mixed-valent trinuclear manganese complex $[\text{Mn}_3(\text{hdde})_2(\text{CH}_3\text{CO}_2)_2(\text{CH}_3\text{O})_2] \cdot \text{CH}_3\text{OH}$ was prepared and confirmed the linear trinuclear arrangement based on the X-ray crystal structure. The mixed-valence state is consistent with the crystal structure, electronic spectra, and variable-temperature magnetic data. Interestingly, the complex showed a weak ferromagnetic coupling contrary to the antiferromagnetic behaviour of the related trinuclear manganese complex $[\text{Mn}_3(\text{hdde})_2(\text{C}_2\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{O})_2] \cdot \text{H}_2\text{O}$. The reason why this difference occurred is unclear at present. Very subtle change in the crystal structures may influence the magnetic properties of these complexes.

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