

Studies on binuclear hydroxo/carboxylato-bridged manganese(III) complexes and a mononuclear manganese(III) complex involving salen type ligands

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Abstract

Synthesis of six hydroxo-bridged binuclear manganese(III) complexes of formulae $[\text{MnL-X-MnL}](\text{ClO}_4)$ [$\text{X} = \text{OH}$ ($1-6$)] along with a mononuclear manganese(III) complex (7) $[\text{Mn}(\text{L})(\text{L}')(\text{MeOH})_2]$ [$\text{HL}' = 2$ -(2-hydroxyphenyl)benzimidazole] and two carboxylate-bridged binuclear manganese(III) complexes (8) and (9) are described. The complexes have been characterized by the combination of i.r., u.v.-vis spectroscopy, magnetic moments and by their redox properties. The electronic spectra of all the complexes exhibit almost identical features consisting of two d-d bands at *ca.* 550 and 600 nm, one MLCT band at *ca.* 400 nm, together with two $\pi-\pi^*$ intra-ligand transitions at *ca.* 250 nm and *ca.* 300 nm. Room temperature magnetic data range from $\mu = 2.7-3.0$ BM indicates some superexchange between the binuclear metal centers *via* bridging hydroxo/carboxylato groups. The X-ray crystal structure of the binuclear complex (5) revealed that it has a symmetric $\text{Mn}^{\text{III}}\text{N}_2\text{O}_2$ core bridged by a hydroxyl group. The X-ray analysis of the mononuclear complex (7) showed that the manganese-center possesses a distorted octahedral geometry. Electrochemical properties of hydroxo-bridged manganese(III) complexes ($1-6$) show identical features consisting of an irreversible and a quasi-reversible reduction corresponding to the $\text{Mn}_2^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$ couples in the voltammogram. It was found that electron withdrawing substituents on the ligand result in easier reduction. Complex (7) displays an irreversible reduction at 0.08 V and a reversible oxidation at 0.45V assignable to the $\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}}$ reduction and $\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{IV}}$ oxidation, respectively. The carboxylate-bridged compound (8) exhibits two irreversible oxidations at 0.4 and 0.6 V, probably due to $\text{Mn}_2^{\text{III}} \rightarrow \text{Mn}^{\text{III}}\text{Mn}^{\text{IV}} \rightarrow \text{Mn}^{\text{IV}}\text{Mn}^{\text{IV}}$ oxidations and shows a quasi-reversible reductive wave at -0.85 V, tentatively assigned to $\text{Mn}_2^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ reduction.

Introduction

There is a considerable amount of interest in the synthesis of manganese complexes of salen type ligands due to their rich manganese chemistry [1–5]. A large number of salen and salen type (chiral) ligands have been prepared to investigate steric, electronic and overall structural effects on their catalytic activity [6–15]. Attempts have also been made to synthesize binuclear/polynuclear complexes with the aim of understanding the effect of the second metal ion on the catalytic activity. Furthermore, it is very important to investigate the function of manganese in some bimetallic metalloproteins [16–25]. Although considerable advances have been made in understanding the manganese-core structure, a good deal remains to be done to fully understand the function of manganese in metalloproteins. We have examined the electrochemical aspect of a series of complexes in an attempt to understand its ability to act as electroactive redox catalysts. Our goal of

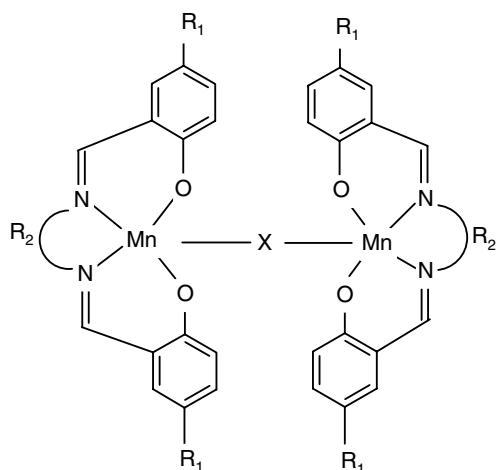
research is to get a series of complexes with a diverse range of redox potentials for any specific application. Moreover, it helps to study the chemistry of manganese involving different oxidation states. We have, therefore, undertaken a comprehensive study on a series of tetradentate ligands derived from salicylaldehyde and bromosalicylaldehyde with different amines and report the syntheses, structure and electrochemistry of these new complexes (Table 1).

Experimental

Reagents and instruments

Ligands were synthesized by the direct method [17, 34]. Manganese fumarate was prepared by a known method [26a]. The piperinium salt of terephthalic acid was prepared by the literature method [26b, c]. All reagent grade chemicals and solvents used for the syntheses were commercially available and were used without further purification.

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Scheme 1.

TEAP was made as per the literature [27]. Elemental analyses were made on a Perkin-Elmer 2400II elemental analyzer. Electrochemical studies were carried out using EG&G PARC VersaStat II potentiostat with three-electrode configuration consisting of a PARC glassy carbon working electrode, saturated calomel electrode as an auxiliary electrode, Ag/AgCl as the reference electrode and $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$ as the supporting electrolyte in MeCN solution under a dry N_2 atmosphere at a different scan rate. Data were collected using 'Echem' software supplied by PARC. For electrochemical and spectral measurements, HPLC grade solvents were used. All the electrochemical potentials were calibrated against a ferrocene–ferrocenium couple of value 0.44 V under this condition. Electronic spectra were obtained using a JASCO 7850 Spectrophotometer. I.r. spectra were recorded on a JASCO FT/IR-460 Spectrometer with samples prepared as KBr pellets. Room temperature magnetic susceptibility measurements were carried out by a PAR 155 model calibrating against $[\text{HgCO}(\text{NCS})_4]$.

Crystal structure determination and structural refinement of (5) and (7)

The crystal data of (5) and (7) are summarized in Table 2. Intensity data of a dark burgundy primitive

Table 1. List of complexes

Complex	R ₁	R ₂	X
(1) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	H	1,2	OH
(2) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	Br	1,2	OH
(3) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	H	1,3	OH
(4) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	Br	1,3	OH
(5) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	H	oph	OH
(6) $[\text{Mn}_2(\text{L})_2(\mu\text{-OH})(\text{ClO}_4)]$	Br	oph	OH
(7) $[\text{Mn}(\text{L})(\text{L}')](\text{MeOH})_2$	H	oph	–
(8) $[\text{Mn}_2(\text{L})_2(\mu\text{-terephthalate})] \cdot 4\text{H}_2\text{O}$	Br	1,2	OOC
(9) $[\text{Mn}_2(\text{L})_2(\mu\text{-fumarate})] \cdot 4\text{H}_2\text{O}$	H	oph	OOC

[HL' = 2-(2-hydroxyphenyl)benzimidazole].

unit cell (5) was measured with a Rigaku AFC6S diffractometer with graphite $\text{Mo-K}\alpha$ radiation at 299.2 K . Cell constants and an orientation matrix for data collection, were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $9.13 < 2\theta < 28.91^\circ$. The structure was solved by direct methods [29] with the program DIRDIF94 [28]. A purple prism primitive crystal (7) was measured by the Bruker P₄/CCD system at $193(2) \text{ K}$. The structure was solved by direct methods [29] and expanded using Fourier techniques [28]. The refinement was performed using SHELXL-97 [30].

Synthesis of the complexes

Complexes (1–6)

To a solution of 1 mmol ligand in MeOH (15 cm^3) was added 1 mmol of manganese triacetate $[\text{Mn}(\text{O}_2\text{CMe})_3 \cdot 2\text{H}_2\text{O}]$. The suspension was stirred at room temperature for 2 h . The resulting brown solution was filtered and to the filtrate was added a MeOH solution (5 cm^3) of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (4 mmol). A brown microcrystalline solid precipitate was collected after slow evaporation from MeOH . Yield ranges from 50–60%.

Complex (7)

We have followed the similar method as above. After addition of $[\text{Mn}(\text{O}_2\text{CMe})_3 \cdot 2\text{H}_2\text{O}]$ to the ophsal ligand, the mixture was boiled under reflux for 4 h and then filtered to remove undissolved substances. The crystalline compound separated during slow solvent evaporation. Yield = 30%.

Complex (8)

To a solution of ligand (1 mmol) in ($\text{CHCl}_3 + \text{MeOH}$) (15 cm^3) mixed solvent was added $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in MeOH (10 cm^3) and stirred at room temperature for 2 h . To the solution piperidinium terephthalate (169 mg , 0.5 mmol) in (10 cm^3) of MeOH was added and the mixture was boiled under reflux for 2 h . The resulting brown solution was filtered after cooling and the reddish brown microcrystalline compound was collected after slow evaporation of the MeOH . Yield = 65%.

Complex (9)

To a solution of ligand (1 mmol) in MeOH (15 cm^3) was added $[\text{Mn}(\text{fumarate})_n]$ (1 mmol) in the solid state and the mixture was refluxed for 4 h . After cooling, the resulting brown solution was filtered and the reddish brown microcrystalline compound was collected after slow evaporation of MeOH . Yield = 60%.

All the perchlorate salts reported here are potentially explosive and therefore should be handled with care.

Table 2. Crystallographic data for complexes (5) and (7)

Complex	(5)	(7)
Empirical formula	C ₄₀ H ₃₀ N ₄ O ₉ Mn ₂ Cl	C ₃₅ H ₃₁ N ₄ O ₅ Mn
Formula weight	856.03	642.58
Crystal color, habit	dark burgandy, rectangular	purple, prism
Crystal		
Dimensions (mm)	0.20 × 0.20 × 0.40	0.30 × 0.30 × 0.20
Crystal system	orthorhombic	Monoclinic
<i>a</i> (Å)	14.469(7)	9.8042(11)
<i>b</i> (Å)	13.67(1)	16.2648(18)
<i>c</i> (Å)	18.659(4)	18.729(2)
α (°)	90	90
β (°)	90	91.264(2)
γ (°)	90	90
<i>V</i> (Å ³)	3691(3)	2985.8(6)
Space group	P _{cca} (#54)	P2 ₁ /n (#14)
<i>Z</i> value	4	4
μ (MoK α)(mm ⁻¹)	0.8	0.493
<i>T</i> (max), <i>T</i> (min)	1.000, 0.925	0.9078, 0.8661
<i>F</i> ₀₀₀	1748	1336
Index ranges	0 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 17, -24 ≤ <i>l</i> ≤ 0	-12 ≤ <i>h</i> ≤ 12, -20 ≤ <i>k</i> ≤ 20, -23 ≤ <i>l</i> ≤ 23
Data/restraints/parameters	2149/0/236	6132/0/499
<i>R</i> ₁ ; <i>R</i> _w	0.091, 0.097	0.048, 0.126
Max and min		
Peak in difference map	1.30 and -1.13	0.93, -0.26
(e Å ⁻³)		
GOF on <i>F</i> ²	4.58	1.02

Results and discussion

Synthesis

All the manganese(III) hydroxo-bridged binuclear complexes (1–6) have been prepared by the direct reaction of corresponding ligands with manganese(III) acetate. The benzimidazole unit manganese(III) complex was formed after refluxing the solution for 4 h. During refluxing, a portion of the complex probably hydrolyzed to salicylaldehyde and *o*-phenylene diamine, which undergoes further condensation to form the imidazole derivative, and finally it formed complex (7). A carboxylate-bridged complex (8) was obtained by the reaction of the ligand, carboxylate salt and Mn(ClO₄)₂ · 6H₂O and the complex (9) was made by the reaction of solid Mn(fumarate)_n with the ligand.

Infrared spectra, conductance data and magnetic moments

The analytical data of the complexes, along with their room temperature magnetic moment data, are given in Table 3. The i.r. spectra of all the complexes have several prominent bands. A strong band at *ca.* 1605 cm⁻¹ is assigned to the ν (C=N) stretching vibration. Additional strong bands at *ca.* 1585, 1532 and 1450 cm⁻¹ have been previously assigned to ν (C=C, phenyl ring), ν (C=N + C=C + C=O) and stretching vibrations respectively [31]. The perchlorate complexes (1–6) show a number of strong and broad bands with peaks at *ca.* 1106 and 1128 cm⁻¹ that are indicative of the presence of non-coordinated perchlo-

rate. In addition to the above bands, binuclear complexes (1–6) exhibit a strong band at *ca.* 760 cm⁻¹ indicating OH group bridging [32]. The ν_a (COO) and ν_s (COO) bands of the terephthalate complex (8) appear at *ca.* 1454 and 1310 cm⁻¹ and for complex (9) show at *ca.* 1481 and 1350 cm⁻¹, respectively which support a bridging carboxylate [32]. A broad absorption of most of the complexes at *ca.* 3430 cm⁻¹ is due to ν (H₂O) vibrations. The conductance data for complexes (1–6) indicate 1:1 electrolytes at room temperature. Room temperature magnetic moments of (1–6, 8 and 9) fall in the 2.7–3.0 BM range (per Mn atom) adding support to the high spin electronic configuration and also indicating a weak magnetic interaction between the two S = 2 configurations. The room temperature magnetic moment of (7) is 5.1 BM indicating a spin-only value for a high spin d⁴ configuration.

Table 3. Analytical data and magnetic moments for complexes

Complex	Found (Calcd.)%			μ_{eff} (BM)
	C	H	N	
(1)	50.5(50.6)	3.7(3.8)	7.3(7.3)	2.9
(2)	35.8(35.7)	2.3(2.3)	5.3(5.2)	2.8
(3)	51.9(51.8)	4.1(4.1)	7.0(7.1)	2.9
(4)	37.1(37.0)	2.6(2.6)	5.1(5.0)	2.8
(5)	56.0(56.1)	3.4(3.5)	6.6(6.5)	2.7
(6)	41.1(41.0)	2.0(2.1)	4.7(4.7)	2.9
(7)	65.3(65.4)	4.8(4.8)	8.8(8.7)	5.1
(8)	40.2(40.2)	3.1(3.0)	4.6(4.7)	2.7
(9)	57.2(57.1)	4.2(4.1)	6.1(6.1)	2.8

Electronic spectra

The electronic spectrum of all of the binuclear complexes shows (Table 4) a similar trend and exhibits two strong absorption bands at *ca.* 250 nm and *ca.* 300 nm, probably due to $\pi \rightarrow \pi^*$ intra-ligand transitions. In addition to this, they also show a band at *ca.* 400 nm which is assigned as the phenolate oxygen to the manganese(III) [O(p_π) \rightarrow Mn(d_{π^*})] ligand-to-metal charge transfer transition [33]. Moreover, all the complexes show two bands/shoulders at *ca.* 550 and 600 nm in the visible region attributable to the d–d transitions. The mononuclear complex (7) shows some identical features consisting of two visible bands at *ca.* 600 and 560 nm and some u.v. bands at 435, 345 and 260 nm.

Electrochemistry

The redox properties of all of the complexes have been investigated by cyclic voltammetry using a glassy carbon electrode. The experiments were carried out at room temperature in MeCN solution using 0.1 mol dm⁻³ Et₄NClO₄ as supporting electrolyte. The ligands are electro-inactive from +1.54 to -1.5 V [22, 34a, 35]. The electrochemical properties of all the hydroxo-bridged dinuclear manganese(III) complexes (1–6) have mostly identical features (Table 5). All the complexes exhibit an irreversible and a quasi-reversible reductive wave

Table 4. Electronic spectral data for complexes

Complex	u.v.–vis [$\lambda_{\max}(\text{nm})$] / $\epsilon(\text{M}^{-1} \text{cm}^{-1})$
(1)	600(592), 550(815), 430(8 230), 340(23 870), 250(30 000)
(2)	610(495), 540(935), 430(9 230), 350(24 870), 250(32 000)
(3)	600(518), 540(768), 440(9 330), 330(23 000), 250(31 130)
(4)	600(526), 550(915), 435(8 550), 340(23 500), 260(31 230)
(5)	600(612), 550(950), 445(9 200), 340(23 500), 240(31 200)
(6)	610(610), 550(815), 430(10 210), 350(20 470), 250(32 500)
(7)	600(478), 560(900), 435(10 030), 345(22 250), 260(30 540)
(8 ^a)	600(528), 560(750), 440(8 000), 340(21 500), 265(31 580)
(9 ^a)	610(654), 560(867), 445(9 870), 340(20 580), 250(32 420)

^ain DMF. The rest are in MeOH

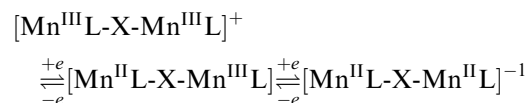
Table 5. Electrochemical data for complexes

Complex	$E_{1/2}^a(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ / $[\Delta E]$ (V)	$E_{1/2}^a(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ / $[\Delta E]$ (V)	$E_{1/2}^a(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ / $[\Delta E]$ (V)	$E_{1/2}^a(\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}})$ / $[\Delta E]$ (V)
(1)	-0.21 ^b	-0.50(0.10) ^b		
(2)	-0.10 ^b	-0.36(0.10) ^b		
(3)	-0.19 ^b	-0.45(0.09) ^b		
(4)	-0.08 ^b	-0.37(0.19) ^b		
(5)	-0.21(0.04)	-0.33(0.06) ^b		
(6)	0.06(0.11)	-0.16(0.08) ^b		
(7)	–	–	0.08 ^b	0.45(0.07)
(8)	-0.85(0.09)	–		
(9)	–	–		

^a $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ V, $\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$ V where E_{pa} and E_{pc} are anodic peak potential and cathodic peak potential, respectively.

^b are irreversible peak potentials. The rest are quasi-reversible and reversible peak potential, respectively.

tentatively assigned to $\text{Mn}_2^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$ according to the equation



The irreversible and quasi-reversible peaks remain unchanged in quality over the 20, 50, 100, 200, 500 mV s⁻¹ scan rate under identical conditions. The irreversible reductive wave indicates that the Mn^{II}Mn^{III} mixed-valent species are unstable under these conditions. In a more positive potential range, no oxidative response was observed. The one-electron-transfer for the above redox couples have been proved by comparison of current height with the cyclic voltammograms of a known complex [Fe(bipy)₃]⁺² under identical conditions. It is interesting to note that the electrochemical data of (1–6) show a perceptible substituent effect on the redox potential (Figure 1). A comparison of the potential data (Table 5) reveals that the complexes involving an electron-withdrawing ligand environment influences easier reductions. It is also clear from the electrochemical data of (1–6) that the effect of potential is insignificant with the change of flexibility from a greater flexible-(CH₂)₃-chain to a more rigid -(CH₂)₂-chain [36]. Complex (7) exhibits an irreversible reduction at +0.08 V and a reversible oxidation at 0.45 V ($\Delta E_{\text{p}} = 70$ mV) assignable to the Mn^{III} \rightarrow Mn^{II} reduction and Mn^{III} \rightarrow Mn^{IV} oxidation. The carboxylate-bridged complex (8) shows two irreversible oxidations at *ca.* +0.4 V and *ca.* +0.6 V probably attributable to Mn₂^{III} \rightarrow Mn^{III}Mn^{IV} \rightarrow Mn^{IV}Mn^{IV} oxidations, and a quasi-reversible reduction at -0.85 V due to Mn₂^{III} \rightarrow Mn^{II}Mn^{III} reduction.

Crystallography and description of the structures of (5) and (7)

Complex (5) [Mn₂(L)₂(μ -OH)(ClO₄)]

The crystal structure of (5) consists of discrete dimanganese complex cations and perchlorate anions (Figure 2). The selected bond distances and angles have been

mentioned in Table 6. Each manganese(III) center is coordinated by two nitrogen atoms and two oxygen atoms from one ligand unit and each manganese(III) unit is bridged by an oxygen atom from a hydroxo group forming square-pyramidal geometry. The two phenolic oxygen atoms and two imine nitrogen atoms are located in the *cis* position [35b], which is opposite to the related dimanganese(IV) structure [17d]. A 2-fold symmetry axis is present through the bridging hydroxo group. The Mn–O–Mn bridging angle (148.0°) and Mn...Mn bond distance (3.918 Å) are much higher than the similar types of compounds [17d]. Similarly the Mn(1)–O(3) bond distance [2.038 Å(3)] is higher than the normal Mn–O bond distance [17d]. Interestingly, the two Mn–N and Mn–O bond lengths for the equatorial positions are very similar [Mn–N(1) = 1.97 Å (1) and Mn–N(2) = 1.96 Å(1)] and [Mn(1)–O(1) = 1.874(8) Å and Mn(1)–O(2) = 1.867(8) Å] which is shorter than other Mn(III)–O–Mn(III) binuclear complexes [35c]. The two manganese units form similar geometry which is consistent with the cyclic voltammogram data where two manganese(III) centers reduced to the manganese(II) oxidation state within a very short potential range.

Complex (7) [MnL(L')(MeOH)₂]

The structural data of complex (7) has revealed that the central manganese(III) exhibits a distorted octahedral geometry. An ORTEP representation of the complex is shown in Figure 3 and selected inter atomic distances and angles listed in Table 6. The N₂O₄ donor set, coming from the ligand itself, forms an equatorial plane;

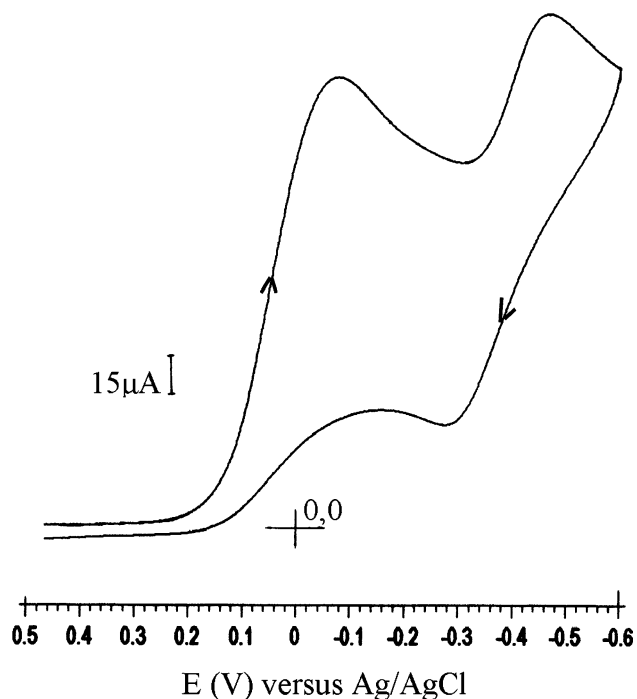


Fig. 1. Cyclic voltammogram of (4) [Mn₂L₂(μ-OH)(ClO₄)] in MeCN with 0.1 mol dm⁻¹ Et₄NClO₄ as supporting electrolyte (working electrode, Glassy-Carbon; reference electrode, Ag/AgCl; scan rate 100 mV s⁻¹).

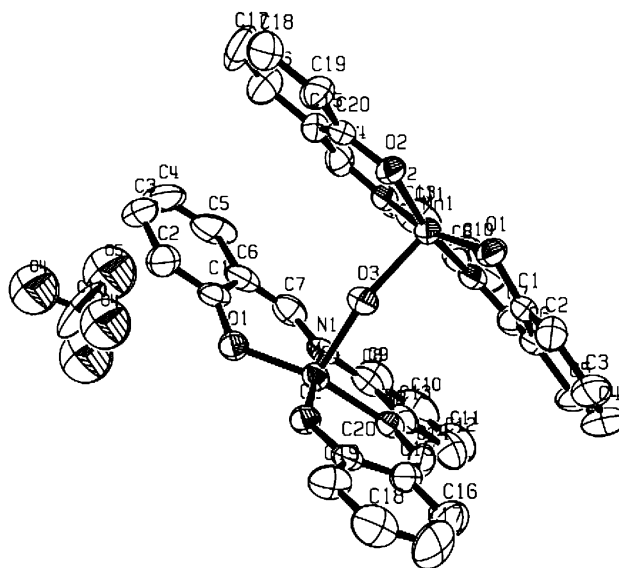


Fig. 2. ORTEP diagram for complex (5) [Mn₂(L)₂(μ-OH)(ClO₄)] showing the atom labeling scheme and 50% probability ellipsoid for the non-hydrogen atom. The H atom is excluded for clarity.

the remaining axial positions are occupied by O donors, one from MeOH and the other from the 2-(2-hydroxyphenyl)benzimidazole unit [35a]. The two phenolic oxygen atoms and two imine nitrogen atoms are located in the *cis* position. The equatorial Mn–O (av.1.88 Å) and Mn–N (av.1.98 Å) bond distances are all within the normal range observed for structurally characterized manganese(III) salen type complexes [17, 34]. However, the elongated axial bonds Mn(1)–O(3) = 2.1091(17) Å and Mn(1)–O(4) = 2.3528(19) Å arise due to Jahn-Teller distortion which is consistent with a similar type

Table 6. Selected bond distances (Å) and bond angles (°) for (5) and (7)

(5)		(7)	
Bond distances		Bond distances	
Mn(1)–O(1)	1.874(8)	Mn(1)–O(1)	1.8792(17)
Mn(1)–O(2)	1.867(8)	Mn(1)–O(2)	1.8901(17)
Mn(1)–O(3)	2.038(3)	Mn(1)–N(2)	1.9859(19)
Mn(1)–N(1)	1.97(1)	Mn(1)–N(1)	1.989(2)
Mn(1)–N(2)	1.96(1)	Mn(1)–O(3)	2.1091(17)
Mn(1) ... Mn(2)	3.918	Mn(1)–O(4)	2.3528(19)
Bond angles		Bond angles	
O(1)–Mn(1)–O(2)	91.7(4)	O(1)–Mn(1)–O(2)	90.26(7)
O(1)–Mn(1)–O(3)	99.6(3)	O(1)–Mn(1)–N(2)	173.81(8)
O(1)–Mn(1)–N(1)	90.3(4)	O(2)–Mn(1)–N(2)	93.23(8)
O(1)–Mn(1)–N(2)	163.3(4)	O(1)–Mn(1)–N(2)	93.55(8)
O(2)–Mn(1)–O(3)	94.9(4)	O(2)–Mn(1)–N(1)	173.65(8)
O(2)–Mn(1)–N(1)	168.0(4)	N(2)–Mn(1)–N(1)	82.54(8)
O(2)–Mn(1)–N(2)	92.8(4)	O(1)–Mn(1)–O(3)	92.87(7)
O(3)–Mn(1)–N(1)	96.4(4)	O(2)–Mn(1)–O(3)	95.32(7)
O(3)–Mn(1)–N(2)	96.0(3)	N(2)–Mn(1)–O(3)	91.90(7)
N(1)–Mn(1)–N(2)	82.1(5)	N(1)–Mn(1)–O(3)	89.57(7)
		O(1)–Mn(1)–O(4)	86.73(7)
		O(2)–Mn(1)–O(4)	91.10(7)
		N(2)–Mn(1)–O(4)	88.08(7)
		N(1)–Mn(1)–O(4)	84.06(8)
		O(3)–Mn(1)–O(4)	173.57(7)

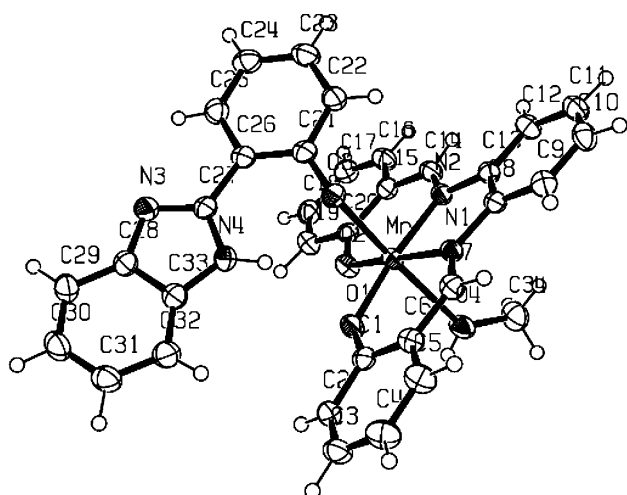


Fig. 3. ORTEP diagram for complex (7) $[Mn(L)(L')(MeOH)_2]$ showing the atom labeling scheme and 50% probability ellipsoid for the non-hydrogen atom. One MeOH moiety is excluded for clarity. $[HL' = 2-(2\text{-hydroxyphenyl})\text{benzimidazole}]$

manganese(III)(d^4) ion [37]. A similar type of elongated Mn–O bond distances has been found in the related di-aqua-(N,N')-3,5-dichlorobis-(salicylidene)-1,2-diaminoethane)-Mn(III) perchlorate complex containing coordinated water at both the axial positions with Mn–O distances 2.220(5) and 2.272(5) Å [32b]. With weakly coordinating axial ligands very long Mn–O distances can occur: 2.489(4) Å to one triflate oxygen atom in $[(3,3'-17\text{-crown-6-}o\text{-phsal})Mn(III)](CH_3COO)\text{-Ba}(\text{SO}_3\text{CF}_3)_2 \cdot 2\text{H}_2\text{O}$ [32e]. The basal angles are all nearly 90° , except for N(2)–Mn(1)–N(1) which is 82.54° . One MeOH moiety is free to form the crystal.

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Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data, CCDC no. 255192(5) and 255191(7). A copy of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK

(Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or from authors upon request.

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