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Preparation and characterization of novel cyclic tetranuclear manganese(III) complexes: $Mn^{III}_4(X\text{-salmphen})_6$ ($X\text{-salmphenH}_2 = N,N'$-di-substituted-salicylidene-1,3-diaminobenzene ($X = H$, 5-Br))

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Abstract—Novel cyclic tetranuclear manganese(III) complexes with Schiff base ligands, *N,N'*-substituted-salicylidene-1,3-diaminobenzene ($X = H$, 5-Br), X-salmphenH_2, Mn^{III}_4(X-salmphen)$_6$ have been prepared and characterized by spectroscopies, magnetic susceptibility, electrochemical measurements and X-ray crystallography. Two manganese ions of the tetranuclear complexes are bridged by two X-salmphen ligands and consist of a dimer unit, $[Mn_2(X\text{-salmphen})_2]^{2+}$. The residual two X-salmphen ligands bridge these dimer units. The resulting tetranuclear complexes constitute a dimer of the two dimeric structures that contains a intramolecular and intermolecular π–π stacking, between phenylene rings of X-salmphen ligands. The physicochemical properties of the tetranuclear complexes having a N_3O_3 donor set are found to be analogous to those observed for tris(*N*-dodecyl-salicylidenaminato)manganese(III) complexes, Mn^{III}(*N*-Dod-sal)$_3$. The structure of this complex is also determined by X-ray crystallography. The magnetic properties of the tetranuclear complexes indicate that there is little or no interaction among these central manganese ions. © 1997 Elsevier Science Ltd

Keywords: manganese(III) complex; tetranuclear complex; tetradentate Schiff base ligand; crystal structure.

Manganese plays an important role in biological redox systems, which is exemplified by the oxygen-evolving center of photosystem II (OEC of PSII) in green plants. The possibility is that a tetranuclear cluster forms the active site in OEC of PSII [1–3], although their precise arrangement and oxidation levels have not been determined unambiguously. In order to elucidate and mimic the functions of OEC many manganese complexes have been prepared in the past decade, which contain mono-, di-, tri- and tetranuclear structures [4–10] of various oxidation states, Mn^{II}, Mn^{III} and Mn^{IV}. From the point of view, we have investigated on the properties of high-valent manganese complexes with Schiff base ligands [11–15].

Recently, we have reported on the properties and molecular structures of di-μ-oxo di-manganese(IV) complexes, $[Mn^{IV}(\text{salophen})(\mu\text{-O})]_2$ (salophenH_2 = *N*, *N'*-disalicylidene-1,2-diaminobenzene), $[Mn^{IV}(\text{salbn})(\mu\text{-O})]_2$ (salbnH_2 = *N,N'*-disalicylidene-1,4-diaminobutane) and $[Mn^{IV}(N\text{-R-X-sal})_2(\mu\text{-O})]_2$ (*N*-R-X-salH = *N*-alkyl-substituted-salicylideneamine) obtained by the reaction of $KMnO_4$ with these ligands in MeCN [16,17]. In this paper, we describe the preparation and characterization of novel cyclic tetranuclear manganese(III) complexes with Schiff base ligands, *N,N'*-di-substituted-salicylidene-1,3-diaminobenzene ($X = H$, 5-Br), X-salmphenH_2, Mn^{III}_4(X-salmphen)$_6$ obtained by the reaction of $KMnO_4$ or manganese(III) acetate dihydrate with these ligands. In contrast to the salophenH_2 ligand, the tetradentate Schiff bases, X-salmphenH_2, did not yield a di-μ-oxo core even if the same synthetic method affording

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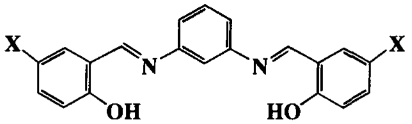

$[Mn^{IV}(salophen)(\mu\text{-}O)]_2$ was conducted. The X-ray structure analyses revealed that the cyclic tetranuclear manganese(III) complexes consist of each manganese ion surrounded by a N_3O_3 donor set. In order to compare the properties of these complexes, a mononuclear manganese(III) complex having a N_3O_3 ligation sphere, tris(*N*-dodecyl-salicylidenaminato) manganese(III) complex, $Mn^{III}(N\text{-Dod-sal})_3$ has been prepared and characterized.

EXPERIMENTAL

Preparation of $Mn^{III}{}_4(salmphen)_6$ (**1**)

The Schiff base ligand, *N,N'*-disalicylidene-1,3-diaminobenzene, $salmphenH_2$, was obtained from salicylaldehyde and *m*-phenylenediamine in ethanol. The tetranuclear manganese(III) complex, **1**, was prepared by the reaction of $salmphenH_2$ (316 mg, 1.00 mmol) and $KMnO_4$ (106 mg, 0.67 mmol) in dry MeCN (100 ml) with stirring at room temperature. The solution color changed from purple to brown and the solution was allowed to stand in the dark place at room temperature. A month later the resulting dark-brown crystals were collected on a glass filter (35% yields). In addition, **1** was found to be obtainable by the reaction of the Schiff base (474 mg, 1.5 mmol) and manganese(III) acetate dihydrate (268 mg, 1.0 mmol) in ethanol (100 ml) and then recrystallized from a mixed solvent of dichloromethane and MeCN (1 : 4) (75% yields). Single crystals of **1**·4MeCN prepared by the reaction of $salmphenH_2$ and $KMnO_4$ have been used for X-ray crystallographic characterization. Anal. Calcd for $Mn_4C_{128}N_{16}O_{12}$ ($[Mn_4(salmphen)_6]\cdot 4MeCN$): C, 67.73; H, 4.26; N, 9.87; Mn, 9.68%. Found: C, 67.12; H, 4.26; N, 9.75; Mn, 9.61%. IR spectrum on KBr pellets (cm^{-1}): 3480(w), 3425(w), 1606(vs), 1592(s), 1539(s), 1460(m), 1440(s), 1376(w), 1285(m), 1190(w), 1144(m), 1117(w), 950(w), 815(w), 751(s), 694(w), 528(w), 448(w).

Preparation of $Mn^{III}{}_4(5\text{-Br-salmphen})_6$ (**2**)

The tetradentate Schiff base ligand, *N,N'*-di-5-bromo-salicylidene-1,3-diaminobenzene, 5-Br-salmphenH_2, was obtained from 5-bromo-salicylaldehyde and *m*-phenylenediamine in ethanol. The complex **2** was prepared by the reaction of the Schiff base (474 mg, 1.00 mmol) in chloroform (30 ml) and manganese(III) acetate dihydrate (179 mg, 0.67 mmol) in ethanol (70 ml) and then recrystallized from a mixed solvent of chloroform and MeCN (1 : 2) (70% yields). Anal. Calcd for $Mn_4C_{122}H_{75}N_{13}O_{12}Br_{12}$ ($[Mn_4(5\text{-Br-salmphen})_6]\cdot MeCN\cdot 2H_2O$): C, 46.82; H, 2.54; N, 5.82; Mn, 7.02%. Found: C, 46.49; H, 2.60; N, 5.85; Mn, 7.08%. IR spectrum on KBr pellets (cm^{-1}): 3445(w), 1604(s), 1584(s), 1521(s), 1447(s), 1401(w), 1365(m), 1289(s), 1180(m), 1165(m), 1129(m), 1072(w), 953(w), 866(w), 820(m), 780(w), 704(w), 649(w), 533(w).

Preparation of $Mn^{III}(N\text{-Dod-sal})_3$ (**3**)

The bidentate Schiff base ligand, *N*-dodecyl-salicylideneamine, *N*-Dod-salH (Dod = $n\text{-}C_{12}H_{25}$) was prepared according to the method described in the literature [14]. The acetatobis(*N*-dodecyl-salicylidenaminato)manganese(III) complex, $Mn^{III}(N\text{-Dod-sal})_2(OAc)$ was prepared by the reaction of *N*-Dod-salH and a half molar amount of $Mn(OAc)_3\cdot 2H_2O$ in methanol at 60°C, and recrystallized from MeCN. The tris(*N*-dodecyl-salicylidenaminato)manganese(III) complex, $Mn^{III}(N\text{-Dod-sal})_3$, **3**, was prepared by the reaction of $Mn^{III}(N\text{-Dod-sal})_2OAc$ (691 mg, 1.00 mmol) with salophenH_2 (158 mg, 0.50 mmol) in MeCN at 60°C. After filtration of the resulting brown precipitates, which were identified as $Mn^{III}(salophen)OAc$, the filtrate was cooled to 0°C overnight to afford $Mn^{III}(N\text{-Dod-sal})_3$, **3**, as green plate crystals (55% yields). Single crystals of **3** have been used for X-ray crystallographic characterization. Anal. Calcd for $MnC_{57}H_{90}N_3O_3$ $\{Mn(N\text{-dod-sal})_3\}$: C, 74.39; H, 9.86; N, 4.57; Mn, 5.97%. Found: C, 74.52; H, 9.81; N, 4.42; Mn, 5.95%. IR spectrum on KBr pellets (cm^{-1}): 2910(s), 2825(m), 1628(s), 1615(s), 1600(m), 1542(m), 1464(m), 1444(s), 1385(w), 1332(w), 1304(s), 1291(s), 1196(w), 1145(w), 1116(w), 1026(w), 970(w), 907(w), 848(w), 803(w), 790(w), 759(m), 738(w), 633(w), 592(m).

Physical measurements

Elemental analyses were made on Yanaco Model CHN-CORDER MT-5. UV-visible and IR spectra were recorded on a Shimadzu Model UV-3100 spectrophotometer and Shimadzu Model IR-470 infrared spectrophotometer, respectively. Electrochemical studies were performed under argon, using a BAS Model CV-27 voltammograph equipped with a Graphtec Model WX 2400 XY recorder and a standard three-electrode assembly (glassy carbon working, Pt wire auxilliary, and Ag/AgCl MeCN 0.1 M $n\text{-}Bu_4NClO_4$, TBAP, reference electrode) with 0.1 M TBAP ($n\text{-}Bu_4NClO_4$) as the supporting electrolyte. All the redox potentials were corrected to the saturated calomel electrode (SCE). Magnetic susceptibility measurements were carried out by the Gouy method at room temperature. The temperature dependency of the magnetic susceptibilities was obtained by the Faraday method from 77 to 290 K.

X-ray crystallography

Single crystals of $[\mathrm{Mn^{III}}_4(\mathrm{salmphen})_6]\cdot 4\mathrm{MeCN}$ (**1**·4MeCN) were obtained by one-step reaction of the Schiff base and $KMnO_4$. A crystal was mounted in a glass capillary and coated with silicone oil. Data were collected on a Rigaku AFC7R four circle automated diffractometer with graphite monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å) at room temperature. Unit-cell parameters were obtained from least square fit of 25 reflections, $6.7 < 2\theta < 12.7°$. Three standard reflections were measured every 150 reflections; they showed no systematic decay throughout data collection. The data were corrected for Lorentz and polarization effects. All the calculations were carried out using the TEXSAN [18] crystallographic software package. The structure of **1**·4MeCN was solved using a combination of direct method (SHELX86) [19] and Fourier methods and refined by the full-matrix least-squares technique with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions but not refined.

Single crystals of mononuclear complex, $\mathrm{Mn^{III}}(N\text{-Dod-sal})_3$, **3**, were obtained by recrystallization from MeCN. A crystal was mounted in a glass capillary. Data were collected on a Rigaku AFC7R four circle automated diffractometer with graphite monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å) at room temperature. Unit-cell parameters were obtained from least square fit of 25 reflections, $6.7 < 2\theta < 12.2°$. Three standard reflections were measured every 150 reflections; they showed no systematic decay throughout data collection. The data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ scans) was also applied (transmission factors range from 0.573 to 1.000). All the calculations were carried out using the TEXSAN crystallographic software package. The structure of **3** was solved using a combination of direct method (SHELX86) and Fourier methods and refined by the full-matrix least-squares technique with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions but not refined. Unfortunately, reflections of the lamellar crystals were weak so that the number of observations was limited. Consequently, the structure is relatively imprecise (final values of agreement factors are $R = 0.087$, $R_w = 0.076$), but the general features of the structure are clear. Crystallographic data for the complexes **1** and **3** are summarized in Table 1.

RESULTS AND DISCUSSION

Electronic spectra

The electronic spectra of **1**, **2**, and **3** in dichloromethane (CH_2Cl_2) are shown in Fig. 1. The absorption bands appearing in the energy region higher than 25,000 cm^{-1} are thought to be associated mainly with the ligand transition. In the visible and near-IR region, the spectra of **1** and **2** exhibit two absorption bands

Table 1. Crystallographic parameters for **1** and **3**

Compound	**1**	**3**
Chemical formula	$Mn_4O_{12}N_{16}C_{128}H_{96}$	$Mn_1O_3N_3C_{57}H_{90}$
Formula weight	2270.01	920.29
Crystal color, habit	dark brown, prism	green, laminar
Crystal size (mm)	0.30 × 0.45 × 0.38	0.30 × 0.15 × 0.04
a (Å)	14.428(7)	19.47(2)
b (Å)	15.506(4)	38.874(10)
c (Å)	14.211(3)	15.228(7)
α (°)	105.61(2)	—
β (°)	91.92(3)	—
γ (°)	65.25(2)	—
V (Å^3)	2769(1)	11522(13)
Z	1	8
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pbca*
D_{calc}, g/cm^3	1.361	1.061
$2\theta_{\max}$, deg	55.0	50.0
Total data collected	12805	8482
Unique data	12294	8482
Obsd data ($I > 3\sigma(I)$)	3499	1331
R^a	0.055	0.087
Rw^b	0.040	0.076

[a] $R = \Sigma||F_o|-F_c||/\Sigma|F_o|$.

[b] $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o^2)$

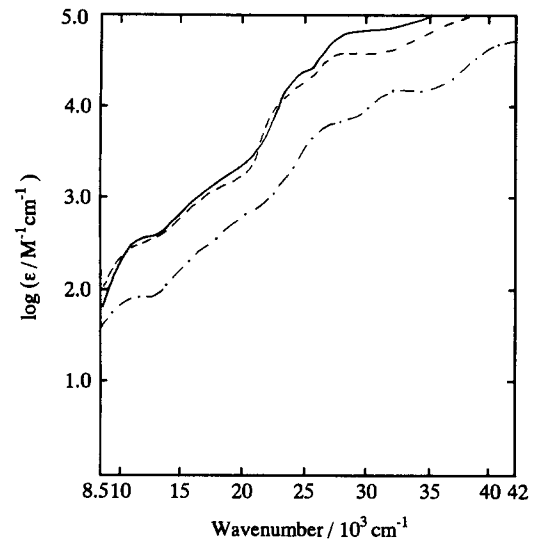

Fig. 1. Electronic spectra of **1**, **2** and **3** in dichloromethane; $Mn^{III}_4(salmphen)_6$, **1** (——), Mn^{III}_4(5-Br-salmphen)$_6$, **2**(– – –), and Mn^{III}(N-Dod-sal)$_3$, **3** (-·-·-).

around 17,900 (sh) ($\log\varepsilon = 3.19$) and 11,600 cm^{-1} ($\log\varepsilon = 2.55$) for **1** and 18,200 (sh) ($\log\varepsilon = 3.12$) and 11,500 cm^{-1} ($\log\varepsilon = 2.49$) for **2**. Based on the intensities and positions, the bands around 18,000 and 11,500 cm^{-1} can be assigned to the *d–d* transitions. The spectrum of Mn(*N*-Dod-sal)$_3$, **3**, also exhibits the absorption bands around 20,000 (sh) ($\log\varepsilon = 2.81$) and 11,800 cm^{-1} ($\log\varepsilon = 1.95$). These *d–d* transition bands around 10,000 cm^{-1} are observed characteristically in the spectra of tris(bidentate ligand) manganese(III) complexes, $Mn^{III}(L)_3$, having an octahedral configuration such as tris(α-picolinato) manganese(III), $Mn^{III}(PA)_3$, at 9800 cm^{-1} ($\log\varepsilon = 1.93$) and tris(acetylacetonato)manganese (III), $Mn^{III}(acac)_3$, at 8500 cm^{-1} ($\log\varepsilon = 1.99$) [20].

Electrochemistry

Cyclic voltammograms of the tetranuclear complexes **1** and **2** were measured in CH_2Cl_2 over the potential range from +1.20 to −1.30 V (*vs* SCE). Quasi reversible redox waves were observed at −0.37 and +0.81 V for **1** and −0.25 and +0.85 V for **2** (Fig. 2). By the introduction of an electron-withdrawing substituent, 5-Br group, the redox potentials of **2** are shifted to more positive values than those of **1**. These shifts can be explained in terms of a decrease in the electron density on the central manganese ion in the complexes. Chronoamperometric reduction and oxidation of **1** was performed at −1.00 and +1.10 V, respectively. Both of the reduction and oxidation at these potentials are found to be two electron process. This means that the reduction and oxidation processes of these tetranuclear complexes may undergo by two electron transfer processes, from $(Mn^{III})_4$ to $[(Mn^{II})_2(Mn^{III})_2]$ and $[(Mn^{III})_2(Mn^{IV})_2]$, respectively. The multiscannings from +0.30 to −0.70 V for both complexes **1** and **2** indicate that the redox couples of $(Mn^{III})_4 \leftrightarrow [(Mn^{II})_2(Mn^{III}{}_2)]$ are reversible. On the other hand, the peak heights of oxidation waves of **1** and **2** were gradually decreased by the multiscannings. These results indicate that the oxidized products of these Mn^{III} complexes, $[(Mn^{III})_2(Mn^{IV})_2]$ are not so stable and decompose. The cyclic voltammogram of the mononuclear complex **3** was measured in CH_2Cl_2 over the potential range from +1.20 to −1.30 V. The quasi reversible redox waves were observed at −0.56 and +0.50 V (Fig. 2), which can be assigned to the redox couples of $Mn^{III} \leftrightarrow Mn^{II}$ and $Mn^{III} \leftrightarrow Mn^{IV}$, respectively.

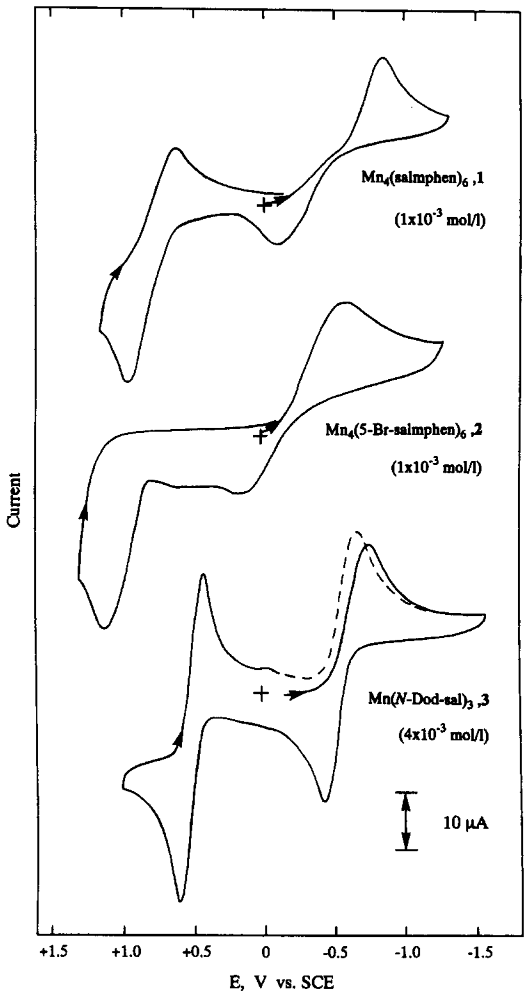

Fig. 2. Cyclic voltammograms of the tetranuclear complexes **1**, **2** and mononuclear complex **3** in dichloromethane.

Magnetic properties

The magnetic moments per one manganese ion of the complexes measured at room temperature are 4.77 μ_B for **1**, 4.85 μ_B for **2** and 4.78 μ_B for **3**. These values are close to the spin only value of 4.9 μ_B expected for a magnetically diluted high spin d^4 manganese(III) ion. From the magnetic susceptibility measurements on powdered samples of **1** and **2** in the temperature range 77–290 K, temperature-dependent magnetic moments of 4.73 μ_B at 77 K and 4.77 μ_B at 290 K for **1** and 4.84 μ_B at 77 K and 4.85 μ_B at 290 K for **2** per one quarter unit of tetranuclear complex were calculated. These results indicate that there is little or no intramolecular antiferromagnetic coupling between the metal centers of **1** and **2**. The four manganese ions are thus separated by the *m*-phenylene backbone of salmphen ligand making them essentially magnetically isolated (*vide infra*).

Molecular structures

The ORTEP plot of Mn^{III}_4(salmphen)$_6$, **1**, is shown in Fig. 3 and its selected bond distances and angles are listed in Table 2. This tetranuclear complex **1** crystallizes in the triclinic space group $P\bar{1}$ and has a center of symmetry, and thus only two manganese atoms are crystallographically independent. Two manganese ions, Mn(1) and Mn(2*) [or Mn(2) and Mn(1*)], are bridged by two salmphen ligands and consist of a dimer unit, $[Mn_2(salmphen)_2]^{2+}$. The residual two salmphen ligands bridge these dimer units. The resulting tetranuclear complex constitutes a dimer of the two dimer structure. Each of the manganese ions is surrounded by an octahedral N_3O_3 donor set. The distances of Mn(1)–Mn(2) and Mn(1)–Mn(2*) are 7.27 and 7.52 Å, respectively. On the other hand, the distances Mn(1)–Mn(1*) and Mn(2)–Mn(2*) are 10.26 and 10.65 Å, respectively. The bond distances of Mn(1)–N(1), Mn(1)–N(3), Mn(2)–N(2), and Mn(2)–N(4) (2.295 (6), 2.339 (7), 2.277 (7), and 2.336 (7) Å, respectively) are longer than those of Mn(1)–N(5) and Mn(2)–N(6) (2.088 (6) and 2.090 (7) Å, respectively). On the other hand, the differences among the bond distances of Mn(1)–O(1), Mn(1)–O(3), Mn(1)–O(5), Mn(2)–O(2), Mn(2)–O(4), and Mn(2)–O(6) (1.881 (5), 1.909 (5), 1.883 (6), 1.882 (6), 1.890 (6), and 1.893 (6) Å, respectively) are not so large as the differences in the distances of Mn—N bonds. Thus, it can be seen that the Jahn–Teller effect on each manganese(III) ion occurs along the axis containing trans imine nitrogen atoms (N(1)–Mn(1)–N(3) and N(2)–Mn(2)–N(4)).

As can be seen from Fig. 3, one of the most interesting features of **1** has intramolecular close π–π stacking, between N(6)–N(5*) and N(5)–N(6*) phenylene rings of *m*-phenylenediamine groups of salmphen

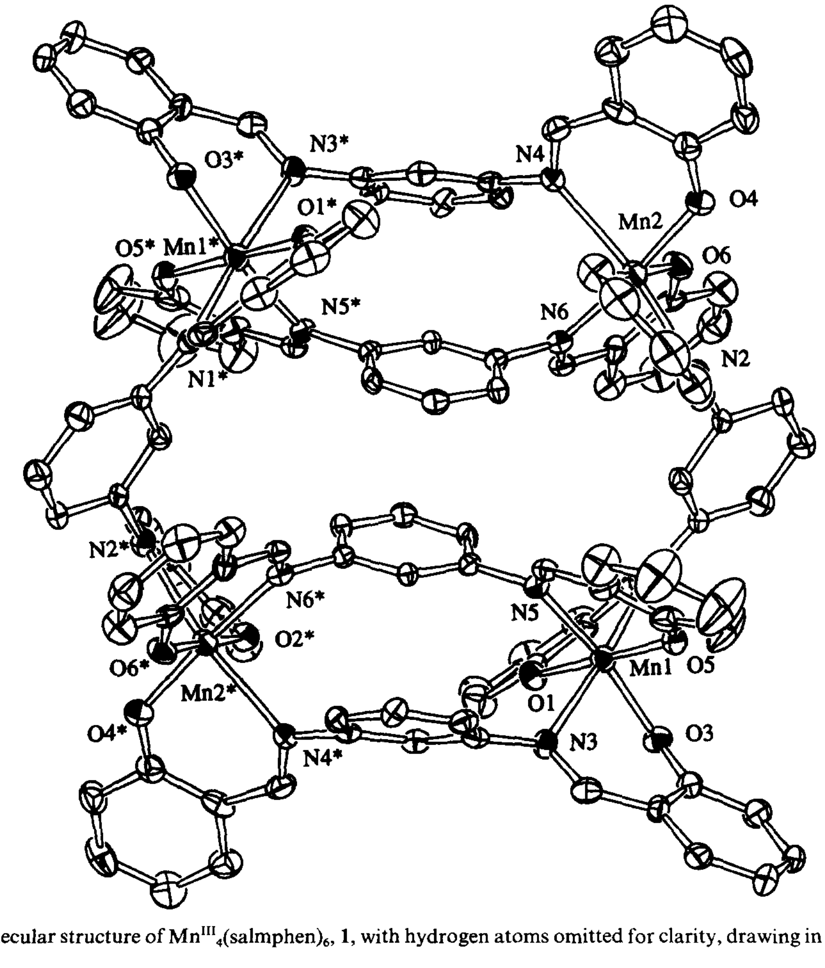

Fig. 3. The molecular structure of Mn^{III}_4(salmphen)$_6$, **1**, with hydrogen atoms omitted for clarity, drawing in 30% probability.

Table 2. selected interatomic distances (Å) and angles (°) for $Mn^{III}_4(salmphen)_6 \cdot 4MeCN$, **1**·4MeCN

Mn(1)—O(1)	1.881(5)	Mn(1)—O(3)	1.909(5)
Mn(1)—O(5)	1.883(6)	Mn(1)—N(1)	2.295(6)
Mn(1)—N(3)	2.339(7)	Mn(1)—N(5)	2.088(6)
Mn(2)—O(2)	1.882(6)	Mn(2)—O(4)	1.890(6)
Mn(2)—O(6)	1.893(6)	Mn(2)—N(2)	2.277(7)
Mn(2)—N(4)	2.336(7)	Mn(2)—N(6)	2.090(7)

O(1)—Mn(1)—O(3)	91.6(2)	O(1)—Mn(1)—O(5)	178.9(3)
O(1)—Mn(1)—N(1)	86.8(2)	O(1)—Mn(1)—N(3)	87.5(2)
O(1)—Mn(1)—N(5)	90.8(2)	O(3)—Mn(1)—O(5)	88.4(2)
O(3)—Mn(1)—N(1)	98.7(2)	O(3)—Mn(1)—N(3)	83.0(2)
O(3)—Mn(1)—N(5)	167.8(2)	O(5)—Mn(1)—N(1)	92.1(3)
O(5)—Mn(1)—N(3)	93.6(2)	O(5)—Mn(1)—N(5)	89.4(3)
N(1)—Mn(1)—N(3)	174.1(3)	N(1)—Mn(1)—N(5)	93.4(2)
N(3)—Mn(1)—N(5)	85.1(2)	O(2)—Mn(2)—O(4)	90.7(2)
O(2)—Mn(2)—O(6)	177.8(3)	O(2)—Mn(2)—N(2)	85.2(2)
O(2)—Mn(2)—N(4)	82.8(2)	O(2)—Mn(2)—N(6)	93.8(3)
O(4)—Mn(2)—O(6)	87.2(3)	O(4)—Mn(2)—N(2)	100.4(2)
O(4)—Mn(2)—N(4)	85.5(2)	O(4)—Mn(2)—N(6)	172.7(3)
O(6)—Mn(2)—N(2)	94.9(2)	O(6)—Mn(2)—N(4)	97.2(2)
O(6)—Mn(2)—N(6)	88.4(3)	N(2)—Mn(2)—N(4)	166.7(2)
N(2)—Mn(2)—N(6)	85.7(2)	N(4)—Mn(2)—N(6)	89.3(2)

ligands, which are coplanar and separated by only 3.67 Å on average of the distance between the corresponding carbon atoms of two phenylene rings. In addition, the packing diagram of **1** (Fig. 4) shows intermolecular stacking between N(3)–N(4*) and N(3*)–N(4*) phenylene rings of *m*-phenylenediamine groups of salmphen ligands, which are coplanar and separated by 3.77 Å on average. Such structures of metal complexes having π–π interactions have been reported for the silver complex with 1,4-bis(2-pyridoxy)benzene [21] and the copper complex with tetrakis(2-imidazolinyl)benzene [22], which have par-

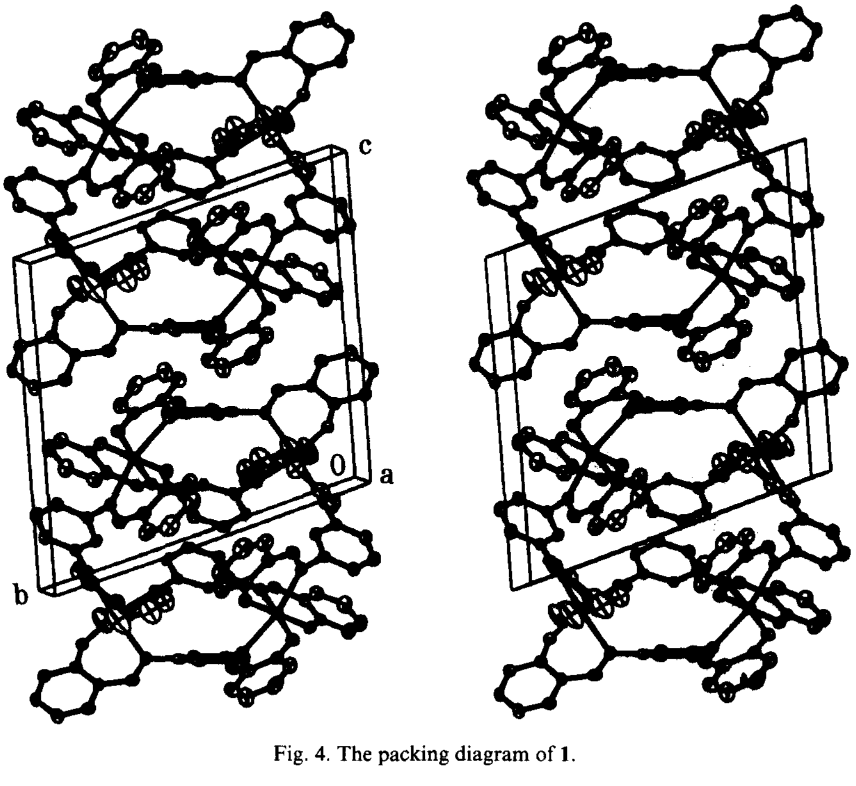

Fig. 4. The packing diagram of **1**.

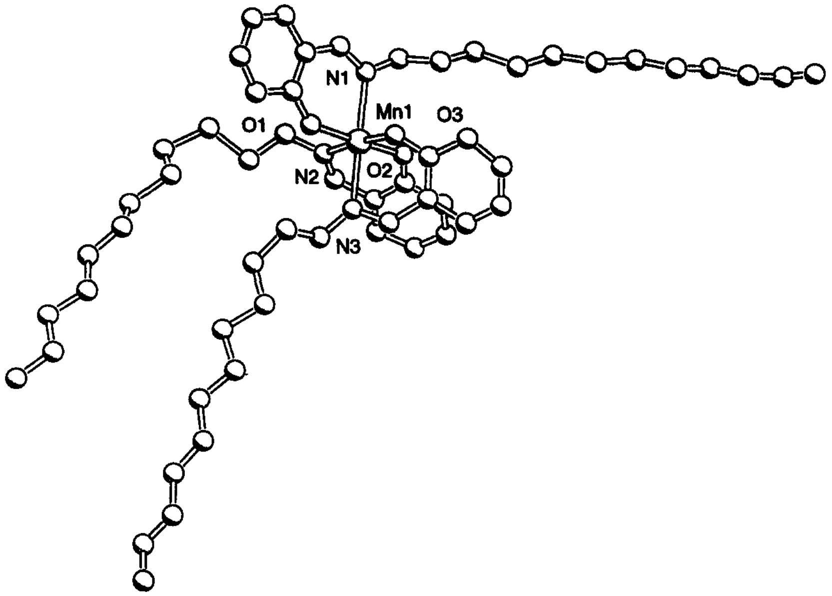

Fig. 5. The molecular structure of Mn^{III}(*N*-Dod-sal)$_3$, **3**, with hydrogen atoms omitted for clarity.

Table 3. Selected interatomic distances (Å) and angles (deg) for Mn^{III}(*N*-Dod-sal)$_3$, **3**

Mn(1)—O(1)	1.95(2)	Mn(1)—O(2)	1.82(2)
Mn(1)—O(3)	1.97(2)	Mn(1)—N(1)	2.31(3)
Mn(1)—N(2)	2.05(3)	Mn(1)—N(3)	2.33(2)
O(1)—Mn(1)—O(2)	176(1)	O(1)—Mn(1)—O(3)	92.3(9)
O(1)—Mn(1)—N(1)	84(1)	O(1)—Mn(1)—N(2)	90(1)
O(1)—Mn(1)—N(3)	92.3(10)	O(2)—Mn(1)—O(3)	89(1)
O(2)—Mn(1)—N(1)	92(1)	O(2)—Mn(2)—N(2)	87(1)
O(2)—Mn(2)—N(3)	90(1)	O(3)—Mn(2)—N(1)	90.0(9)
O(3)—Mn(1)—N(2)	175(1)	O(3)—Mn(1)—N(3)	86.0(10)
N(1)—Mn(1)—N(2)	94(1)	N(1)—Mn(2)—N(3)	174(1)
N(2)—Mn(2)—N(3)	90(1)		

allel benzene rings separated by 3.33 and 3.93 Å, respectively. The intermolecular π–π interactions are considered to exist in the present complex **1**, compared with these complexes.

The molecular structure of Mn^{III}(*N*-Dod-sal)$_3$, **3**, is shown in Fig. 5 and its selected bond distances and angles are listed in Table 3. This complex **3** crystallizes in the orthorhombic space group *Pbca*. By the long alkyl chain of the ligand *N*-Dod-sal, the complex is completely isolated and there is no metal–metal interaction with neighboring complexes. The metal center of the complex **3** is surrounded octahedrally by a N_3O_3 donor set similar to the metal center of the cyclic tetranuclear manganese(III) complex **1**. The bond distances of Mn(1)–N(1) and Mn(1)–N(3) (2.31 (3) and 2.33 (2) Å, respectively) are longer than those of Mn(1)–N(2) (2.05 (3) Å). On the other hand, the differences among the bond distances of Mn(1)–O(1), Mn(1)–O(2), and Mn(1)–O(3) (1.95 (2), 1.83 (2), and 1.97 (2) Å, respectively) are not so large as the differences in the distances of Mn—N bonds. Thus, the Jahn–Teller effect on manganese(III) ion may occur along the axis containing trans imine nitrogen atoms (N(1)–Mn(1)–N(3)). Previously, there has been reported only one X-ray determination undertaken on the manganese(III) complex with bidentate Schiff base ligand, Mn(*N*-Bz-sal)$_3$, where *N*-Bz-salH denotes *N*-benzyl-salicylideneamine [23]. Its structure has been shown that the three ligands arrange around a pseudo-tetragonally distorted manganese atom; such distortion has been ascribed to the Jahn–Teller effect.

In the previous paper [15], we have reported that the reaction of $KMnO_4$ with various tetradentate Schiff base ligands in MeCN afforded different two types of di-μ-oxo dimanganese(IV) complexes; one of them has a structure in which a dianion of salpnH_2 [24–26] or salbnH_2 is coordinated to each manganese ion as a tetradentate ligand, whereas the other has a structure in which that of salenH_2 or salophenH_2 is coordinated to two manganese ions as a bridging ligand. In these ligands a di-μ-oxo structure is maintained. However, the present X-salmphenH_2 afforded a cyclic tetranuclear octahedral manganese(III) complex. This may be attributed to the difference in the Schiff base ligands themselves; the X-salmphenH_2 ligands possess a relatively rigid structure and much longer distance between two imine nitrogen atoms compared those for the Schiff base ligands mentioned above. Therefore, a further reduced manganese(III) complex is formed as stable crystals in the course of reaction of $KMnO_4$ with X-salmphenH_2.

Each of the manganese ions of the cyclic tetranuclear manganese(III) complex **1** has an N_3O_3 ligation sphere and their configurations (bond lengths and angles) and electrochemical, spectral and magnetic properties are very similar to the mononuclear manganese(III) complex, **3**.

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