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Synthesis, Characterization and Catalytic Properties of Manganese(III) Schiff Base Complexes

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Abstract

The syntheses and spectral and electrochemical characterization of five manganese(III) complexes with Schiff base ligands are described. The crystal structure of the complex [Mn(SALENCY)(H_2O)(CH_3CH_2OH)]ClO_4 where SALENCY, $C_{20}H_{20}N_2O_2^{2-}$, is the dianion of the product formed from the condensation of two moles of salicylaldehyde with one mole of 1,2-diaminocyclohexane, has been established by X-ray diffraction techniques. The complex crystallizes in the space group $P2_1/n$ of the monoclinic system with four molecules in a cell of dimensions $a = 11.678(3)$, $b = 15.654(3)$, $c = 13.356(2)$ Å, and $\beta = 93.00(2)°$. The structure was solved by direct methods and refined by least-squares techniques to a final value of the weighted R factor of 0.0437 based on 1484 independent observed reflections. The complex is roughly octahedral, the Schiff base ligand occupying four basal sites while the axial sites are occupied by one water molecule and one ethanol molecule. The complex [Mn(TETRAMESALEN)Cl], where TETRAMESALEN, $C_{20}H_{22}N_2O_2^{2-}$, is the dianion of the product formed from the condensation of two moles of 2′-hydroxy-5′-methylacetophenone with one mole of 1,2-diaminoethane, crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a cell of dimensions $a = 11.009(4)$, $b = 12.459(3)$, $c = 13.967(4)$ Å, $\beta = 97.25(3)°$. The structure was solved by direct methods and refined to a final R factor of 0.0535 based on 2342 observed independent intensities. The complex is tetragonal pyramidal, the Schiff base ligand occupying the basal sites while the chloride is axial. The complex [Mn(MEPHSALEN)(C_2H_5OH)$_2$]ClO_4, where MEPHSALEN, $C_{30}H_{26}N_2O_2^{2-}$, is the dianion of the product formed from the condensation of two moles of 2′-hydroxy-5′-methylbenzophenone with one mole of 1,2-diaminoethane, crystallizes in the triclinic space group $P\bar{1}$ with four molecules in a cell of dimensions $a = 9.492(3)$, $b = 17.404(6)$, $c = 21.265(9)$ Å, $\alpha = 86.60(3)$, $\beta = 88.57(3)$, $\gamma = 86.34(3)°$. The data for this complex are of lower quality than those obtained for the other two complexes, but the structure has been refined to a final value of 0.090 based on 1263 independent intensities. There are two crystallographically independent molecules in the cell, but the geometry of each is substantially similar. In each case, the manganese atom is six-coordinate, the base of the pseudo-octahedron being occupied by the Schiff base ligand while the axial sites are occupied by ethanol ligands. The two six-coordinate complexes (SALENCY and MEPHSALEN) are very effective at catalyzing the epoxidation of cyclohexene by iodosobenzene, while the five-coordinate complex yields both epoxide and cyclohexenol.

Introduction

There has been intense recent interest in the study of manganese(III) complexes with ligands derived from the condensation of salicylaldehyde with diamines [1–4]. The oxidation products of manganese(II) complexes of these ligands have been variously formulated as monomers [3], dimers [1, 3] and polymers [2], but no truly definitive structural study has appeared. High oxidation state manganese complexes are of great importance in biological systems [5, 6] and in catalytic oxidative processes [7, 8]; the use of monomeric manganese(III) complexes of porphyrin and Schiff base ligands as metal catalysts for the epoxidation (and other oxidation) of alkenes has attracted considerable recent attention [9–13]. In the case of the Schiff base ligands, the modulation of the catalytic activity by substituents on the ligands [10] and by clay supports [9] has been studied. Consequently, we have undertaken a comprehensive synthetic and structural study of the manganese(III) complexes derived from Schiff base ligands formed by the condensation of aldehydes related to salicylaldehyde with a variety of diamines. The ligands studied are the dianions derived from TETRAMESALEN (1), SALENCY (2), MESALEN (3), MEPHSALEN (4) and SALTOLEN (5).

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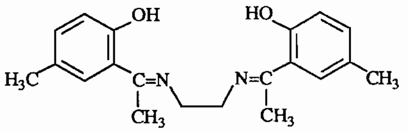

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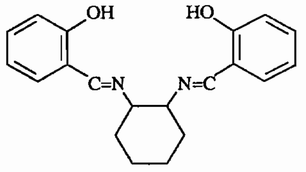

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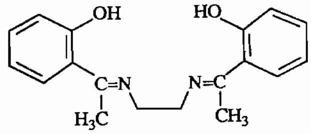

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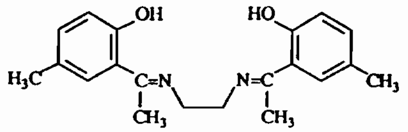

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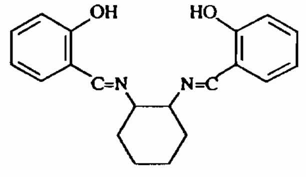

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Experimental

Syntheses

The following reagents were purchased from Aldrich Chemical Company and were used without further purification: salicylaldehyde, 2′-hydroxy-5′-methylacetophenone, 2′-hydroxy-5′-methylbenzophenone, 2′-hydroxyacetophenone, 1,2-diaminoethane, 1,2-diaminocyclohexane and 2,3-diaminotoluene. The ligands were prepared by the condensation of the appropriate diamine (0.01 mol) with the ketone or aldehyde (0.02 mol) in ethanol at 60 °C for 2 h, followed by slow cooling to room temperature or (in some cases) by evaporation of the solvent under reduced pressure. IR spectroscopy showed complete disappearance of the carbonyl stretching vibration and the appearance of the –C=N vibration in the region 1600–1625 cm^{-1}.

The manganese complexes were prepared by mixing equimolar ratios of manganese(II) salt (chloride, nitrate, or perchlorate) with the ligand in ethanol and stirring at room temperature for 10 min. An equimolar amount of sodium hydroxide was then added, and the resultant mixture was stirred for 2 h. The solution was filtered, and the filtrate was allowed to evaporate slowly at room temperature for several days; the complexes formed as dark red or brown needles. The complexes formed are listed in Table 1 along with their elemental analyses. In the complexes, the –C=N stretching vibration is shifted by roughly 15 cm^{-1}, to 1585–1603 cm^{-1}.

Spectroscopy

Electronic absorption spectra were recorded on a Hitachi SPEC 100-80 spectrometer, while infrared spectra were recorded on a Mattson Cygnus 100 FT-IR spectrometer.

TABLE 1. Physical and analytical properties of Mn(III) complexes[a]

Complex	Color	C	H	N	Cl
[Mn(TETRAMESALEN)Cl] (6)	dark red	58.33 (58.25)	5.38 (5.34)	6.68 (6.79)	8.43 (8.49)
[Mn(SALENCY)(OH$_2$)$_2$] (7)	brown	47.21 (47.03)	4.79 (4.74)	5.40 (5.48)	7.85 (6.95)
[Mn(MESALEN)Cl] (8)	dark brown	55.43 (56.26)	4.67 (4.68)	7.19 (7.29)	9.05 (9.11)
[Mn(MEPHSALEN)(OH$_2$)(EtOH)]ClO$_4$ (9)	red	56.48 (56.30)	5.62 (5.27)	3.84 (4.10)	5.04 (5.13)
[Mn(SALTOLEN)(OH$_2$)(CH$_3$CN)]NO$_3$·H$_2$O (10)	brown	52.45 (52.77)	4.25 (4.50)	11.00 (10.71)	

[a] Analyses were performed by Atlantic Microlab, Norcross, GA. Values in parentheses are observed values.

X-ray Crystallography

[Mn(SALENCY)(OH_2)(C_2H_5OH)]ClO_4 (7a)

A powdered sample of **7** was recrystallized from ethanol; as the structure analysis reveals, one water molecule is replaced by an ethanol molecule in this process, forming red–brown needles of **7a**. A crystal was mounted on a glass fiber and placed on a Nicolet R3m/V diffractometer. Experimental details and cell constant information are collected in Table 2. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were located in a difference Fourier synthesis, but hydrogen atoms on carbon atoms were placed in calculated positions (C–H = 0.96 Å) and were not refined. Hydrogen atoms bound to the oxygen atoms of water and ethanol were refined isotropically, and all other atoms were refined anisotropically. Final values of the agreement factors are $R_1 = 0.0544$, $R_w = 0.0437$. The positional parameters of the non-hydrogen atoms are presented in Table 3; see also 'Supplementary Material'.

[Mn(TETRAMESALEN)Cl] (6)

The complex crystallizes as dark red needles. Data were collected as above, and experimental details are presented in Table 2. The structure was solved as above, with no hydrogen parameter refined. Final agreement factors are $R_1 = 0.0535$, $R_w = 0.0543$. The positional parameters of the non-hydrogen atoms are presented in Table 4; see also 'Supplementary Material'.

[Mn(MEPHSALEN)(C_2H_5OH)$_2$]ClO_4 (9a)

A powdered sample of **9** was recrystallized from ethanol; as the structure analysis reveals, the water molecule is replaced by a second ethanol molecule in this process, forming red–brown needles of **9a**. Data were collected as above, and experimental details are presented in Table 2. The structure was solved as above, with no hydrogen parameter refined. Since we had very few observable data, only the manganese and the perchlorate atoms could be refined anisotropically, all other non-hydrogen atoms being refined isotropically. Final agreement factors are $R_1 = 0.0905$, $R_w = 0.0995$. The metrical parameters associated with this structure are obviously of very limited precision, but the present experiment does allow us to demonstrate the essential features of the structure for comparison with the other two structures; see 'Supplementary Material'.

All programs used in the three structure analyses were from the SHELXTL system as supplied by Nicolet.

Electrochemistry

Cyclic voltammetry was performed on a BAS-100A electrochemical analyzer using platinum or glassy carbon working electrodes. Voltages are reported relative to Ag/AgCl. Solutions were 10^{-3} M in manganese(III) complex in acetonitrile, with 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Catalytic Oxidation of Cyclohexene

Oxidation of cyclohexene was carried out using iodosobenzene as primary oxidant. This oxidant was prepared from iodobenzene [14]. The oxidation was performed in acetonitrile and the products were quantified by GC analysis using a Hewlett-Packard 5890 GC employing a thermal conductivity detector.

TABLE 2. Crystallographic data for **7a**, **6** and **9a**

Compound	7a	6	9a
Formula	$C_{22}H_{28}N_2O_8ClMn$	$C_{20}H_{22}N_2O_2ClMn$	$C_{34}H_{38}N_2O_8ClMn$
a (Å)	11.678(3)	11.009(4)	9.492(3)
b (Å)	15.654(3)	12.459(3)	17.404(6)
c (Å)	13.356(2)	13.967(4)	21.265(9)
α (°)	90	90	86.60(3)
β (°)	93.00(2)	97.25(3)	88.57(3)
γ (°)	90	90	86.34(3)
V (Å^3)	2438.2(9)	1901(1)	3499(2)
Z	4	4	4
Formula weight	538.9	412.8	693.1
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
T (°C)	22	22	22
(Å^3)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.68	0.82	0.49
NO	3209	4400	9199
NO [$>3\sigma(I)$]	1484	2342	1263
R	0.0544	0.0535	0.0905
R_w	0.0437	0.0543	0.0995

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 7a

	x	y	z	U_{eq}[a]
Mn(1)	8576(1)	−1177(1)	88(1)	39(1)
Cl	6972(3)	974(3)	2877(3)	80(2)
O(11)	7432(8)	1048(13)	1970(7)	222(9)
O(12)	7191(24)	158(12)	3106(25)	272(16)
O(13)	5843(11)	1285(21)	2875(10)	151(12)
O(14)	7580(13)	1476(10)	3598(10)	113(8)
O(22)	6841(60)	1690(35)	2994(47)	138(25)
O(23)	5887(41)	550(30)	2698(28)	97(16)
O(24)	7497(26)	489(27)	3655(24)	69(15)
O(1)	9276(5)	−1064(5)	−1123(4)	47(2)
O(2)	9991(4)	−1126(4)	821(4)	46(2)
C(1A)	8799(8)	−980(6)	−2029(6)	40(4)
C(2A)	9515(9)	−830(6)	−2814(7)	53(4)
C(3A)	9089(10)	−727(7)	−3769(7)	74(5)
C(4A)	7926(11)	−761(8)	−3991(7)	87(6)
C(5A)	7192(9)	−902(8)	−3250(7)	73(5)
C(6A)	7610(8)	−1028(7)	−2255(6)	44(4)
C(7A)	6803(7)	−1203(7)	−1530(7)	52(4)
C(1B)	10212(8)	−1258(7)	1792(7)	43(4)
C(2B)	11351(8)	−1292(7)	2135(6)	55(4)
C(3B)	11624(9)	−1392(7)	3144(8)	67(5)
C(4B)	10791(10)	−1454(7)	3828(8)	70(5)
C(5B)	9664(9)	−1445(6)	3504(7)	56(5)
C(6B)	9346(8)	−1357(6)	2487(7)	39(4)
C(7B)	8159(8)	−1352(6)	2206(7)	48(4)
C(8)	6453(7)	−1235(9)	1089(7)	79(5)
C(9)	5699(8)	−1558(7)	1906(7)	68(5)
C(10)	4463(9)	−1450(11)	1551(9)	123(8)
C(11)	4167(9)	−1743(11)	575(9)	126(8)
C(12)	4921(8)	−1441(8)	−225(7)	80(5)
C(13)	6180(8)	−1542(9)	127(7)	79(6)
N(1)	7037(6)	−1277(6)	−581(5)	47(3)
N(2)	7713(6)	−1306(5)	1304(5)	45(3)
O(1E)	8765(6)	−2640(4)	−3(5)	57(3)
C(1E)	9853(16)	−2961(8)	−288(11)	136(10)
C(2E)	9805(10)	−3826(11)	−437(8)	141(9)
O(1W)	8322(8)	254(6)	201(8)	58(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Structures of the Complexes

[Mn(SALENCY)(H$_2$O)(EtOH)]ClO$_4$ (7a)

The structure consists of [Mn(SALENCY)(H_2O)(EtOH)]$^+$ cations and perchlorate anions which are well separated from each other. The structure of the cation is depicted in Fig. 1, and the principal bond lengths and angles are presented in Tables 5 and 6, respectively.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 6

	x	y	z	U_{eq}[a]
Mn	9235(1)	2173(1)	346(1)	32(1)
Cl	10333(2)	3640(1)	1149(1)	50(1)
O(2)	7744(3)	2120(3)	856(3)	48(1)
N(1)	10442(4)	1815(3)	−573(3)	34(1)
O(1)	9835(3)	1061(3)	1151(2)	39(1)
C(1A)	10954(5)	640(4)	1245(3)	36(1)
N(2)	8478(4)	3088(3)	−732(3)	36(1)
C(8B)	7407(5)	3545(4)	−861(3)	38(2)
C(1B)	6661(5)	2530(4)	514(4)	37(1)
C(7B)	6449(5)	3245(4)	−272(4)	38(2)
C(7A)	11706(5)	628(4)	498(3)	37(2)
C(10)	9425(5)	3366(5)	−1354(4)	43(2)
C(4B)	4257(5)	3329(5)	−67(4)	46(2)
C(3B)	4500(5)	2628(5)	718(5)	49(2)
C(11)	10127(5)	2364(4)	−1517(3)	40(2)
C(8A)	11347(5)	1135(4)	−447(3)	37(2)
C(4A)	13288(5)	−368(5)	1536(4)	47(2)
C(2B)	5654(5)	2254(5)	998(5)	51(2)
C(2A)	11369(6)	117(4)	2115(4)	46(2)
C(5B)	2988(5)	3755(6)	−408(5)	60(2)
C(6B)	5229(5)	3630(5)	−530(4)	44(2)
C(9B)	7150(5)	4408(6)	−1615(5)	59(2)
C(5A)	14525(6)	−879(6)	1695(5)	64(2)
C(3A)	12518(6)	−374(5)	2257(4)	48(2)
C(9A)	12046(6)	854(5)	−1266(4)	50(2)
C(6A)	12861(5)	125(5)	674(4)	45(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

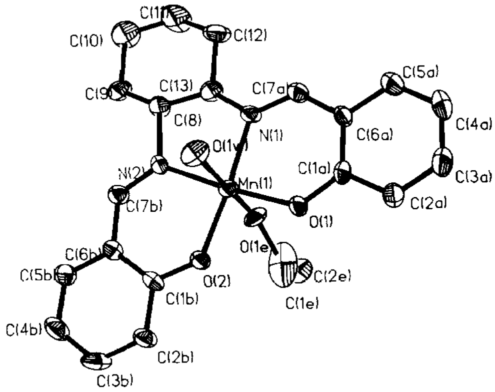

Fig. 1. View of the cation [Mn(SALENCY)(H_2O)(EtOH)]$^+$ in the structure of 7a.

The geometry of the cation is roughly octahedral, the base plane being occupied by the two nitrogen and two oxygen atoms of the SALENCY ligand while the axial sites are occupied by the oxygen atoms of the water and ethanol molecules. As is expected for a d^4 ion, the complex exhibits a Jahn–Teller distorted axial elongation, the Mn–O bond lengths to the water and ethanol oxygen atoms of 2.265(9) and 2.304(7) Å being much longer than the in-plane Mn–O and Mn–N distances of 1.859(5), 1.878(5) and 1.971(7), 1.966(7) Å, respectively. Presumably,

TABLE 5. Bond lengths (Å) in 7a

Mn(1)–O(1)	1.859 (5)	Mn(1)–O(2)	1.878 (5)
Mn(1)–N(1)	1.971 (7)	Mn(1)–N(2)	1.966 (7)
Mn(1)–O(1E)	2.304 (7)	Mn(1)–O(1W)	2.265 (9)
Cl–O(11)	1.356 (10)	Cl–O(12)	1.336 (20)
Cl–O(13)	1.405 (17)	Cl–O(14)	1.407 (15)
Cl–O(22)	1.142 (56)	Cl–O(23)	1.440 (47)
Cl–O(24)	1.402 (35)	O(1)–C(1A)	1.311 (10)
O(2)–C(1B)	1.325 (10)	C(1A)–C(2A)	1.395 (13)
C(1A)–C(6A)	1.407 (13)	C(2A)–C(3A)	1.354 (13)
C(3A)–C(4A)	1.376 (17)	C(4A)–C(5A)	1.360 (15)
C(5A)–C(6A)	1.405 (12)	C(6A)–C(7A)	1.413 (12)
C(7A)–N(1)	1.288 (11)	C(1B)–C(2B)	1.385 (12)
C(1B)–C(6B)	1.416 (13)	C(2B)–C(3B)	1.377 (14)
C(3B)–C(4B)	1.372 (16)	C(4B)–C(5B)	1.364 (15)
C(5B)–C(6B)	1.396 (12)	C(6B)–C(7B)	1.416 (13)
C(7B)–N(2)	1.290 (11)	C(8)–C(9)	1.524 (14)
C(8)–C(13)	1.393 (14)	C(8)–N(2)	1.489 (11)
C(9)–C(10)	1.505 (14)	C(10)–C(11)	1.408 (17)
C(11)–C(12)	1.497 (16)	C(12)–C(13)	1.528 (13)
C(13)–N(1)	1.471 (12)	O(1E)–C(1E)	1.436 (19)
C(1E)–C(2E)	1.369 (21)		

it is this weak axial coordination that leads to the facile replacement of water by ethanol in the conversion of 7 to **7a** (*vide supra*). Similar axial elongation at six-coordinate d^4 Mn(III) centers has recently been reported in a variety of mixed-valent Mn(III)/Mn(IV) complexes [15–21], in binuclear Mn(III) complexes [22–24], and in related monomeric and polymeric Mn(III) species [4, 25–27].

With the exception of the N(1)–Mn–N(2) angle, the bond angles at manganese are very regular, with *cis* angles falling in the narrow range of 88.3(4) to 92.8(3)° and *trans* angles in the range 175.1(2) to 177.8(3)°. As is commonly observed in complexes of salicylideneimine derivatives [26], the constraints of the five-membered ring cause the N(1)–Mn–N(2) angle of 82.6(3)° to be considerably smaller than the other *cis* angles in the structure.

The four basal atoms N(1), N(2), O(1), O(2) are roughly coplanar [maximum deviation 0.012 Å], and the manganese atom lies in this plane. The axial bonds to the water and ethanol ligands are perpendicular to this plane, the dihedral angles being 177.9

TABLE 6. Bond angles (°) in 7a

O(1)–Mn(1)–O(2)	92.0(2)	O(1)–Mn(1)–N(1)	92.6(3)
O(2)–Mn(1)–N(1)	175.1(3)	O(1)–Mn(1)–N(2)	175.2(3)
O(2)–Mn(1)–N(2)	92.8(3)	N(1)–Mn(1)–N(2)	82.6(3)
O(1)–Mn(1)–O(1E)	90.0(3)	O(2)–Mn(1)–O(1E)	89.2(3)
N(1)–Mn(1)–O(1E)	89.2(3)	N(2)–Mn(1)–O(1E)	89.8(3)
O(1)–Mn(1)–O(1W)	91.7(3)	O(2)–Mn(1)–O(1W)	92.2(3)
N(1)–Mn(1)–O(1W)	89.4(3)	N(2)–Mn(1)–O(1W)	88.3(4)
O(1E)–Mn(1)–O(1W)	177.8(3)	O(11)–Cl–O(12)	101.9(16)
O(11)–Cl–O(13)	112.7(8)	O(12)–Cl–O(13)	120.0(17)
O(11)–Cl–O(14)	110.8(9)	O(12)–Cl–O(14)	107.1(14)
O(13)–Cl–O(14)	104.3(12)	O(11)–Cl–O(22)	95.8(34)
O(11)–Cl–O(23)	106.1(16)	O(22)–Cl–O(23)	110.6(39)
O(11)–Cl–O(24)	122.0(15)	O(22)–Cl–O(24)	119.1(35)
O(23)–Cl–O(24)	102.7(22)	Mn(1)–O(1)–C(1A)	128.9(5)
Mn(1)–O(2)–C(1B)	128.7(5)	O(1)–C(1A)–C(2A)	117.9(8)
O(1)–C(1A)–C(6A)	124.0(8)	C(2A)–C(1A)–C(6A)	118.1(8)
C(1A)–C(2A)–C(3A)	121.5(9)	C(2A)–C(3A)–C(4A)	120.6(10)
C(3A)–C(4A)–C(5A)	120.1(9)	C(4A)–C(5A)–C(6A)	120.6(9)
C(1A)–C(6A)–C(5A)	119.1(8)	C(1A)–C(6A)–C(7A)	123.3(8)
C(5A)–C(6A)–C(7A)	117.7(8)	C(6A)–C(7A)–N(1)	125.3(8)
O(2)–C(1B)–C(2B)	117.7(8)	O(2)–C(1B)–C(6B)	123.3(8)
C(2B)–C(1B)–C(6B)	119.0(8)	C(1B)–C(2B)–C(3B)	119.8(9)
C(2B)–C(3B)–C(4B)	121.6(9)	C(3B)–C(4B)–C(5B)	119.6(9)
C(4B)–C(5B)–C(6B)	120.9(9)	C(1B)–C(6B)–C(5B)	119.0(8)
C(1B)–C(6B)–C(7B)	123.2(8)	C(5B)–C(6B)–C(7B)	117.7(9)
C(6B)–C(7B)–N(2)	126.1(9)	C(9)–C(8)–C(13)	115.7(9)
C(9)–C(8)–N(2)	116.1(8)	C(13)–C(8)–N(2)	109.1(8)
C(8)–C(9)–C(10)	108.5(8)	C(9)–C(10)–C(11)	116.1(10)
C(10)–C(11)–C(12)	115.6(11)	C(11)–C(12)–C(13)	109.9(8)
C(8)–C(13)–C(12)	114.7(9)	C(8)–C(13)–N(1)	111.4(9)
C(12)–C(13)–N(1)	116.6(8)	Mn(1)–N(1)–C(7A)	125.4(6)
Mn(1)–N(1)–C(13)	111.5(5)	C(7A)–N(1)–C(13)	122.8(7)
Mn(1)–N(2)–C(7B)	125.3(6)	Mn(1)–N(2)–C(8)	112.2(5)
C(7B)–N(2)–C(8)	122.1(7)	Mn(1)–O(1E)–C(1E)	116.8(6)
O(1E)–C(1E)–C(2E)	110.8(13)		

and 177.8°, respectively. The five-membered ring formed by Mn, N(1), N(2), C(8), C(13) shown in Fig. 1 is in the λ conformation, but in this centrosymmetric space group there are an equal number of molecules in the δ conformation.

The perchlorate anions in the crystal are disordered around a pseudo-threefold axis [the Cl–O(11) bond]. Thus, the two sets of positions O(12), O(13), O(14) and O(22), O(23), O(24) are rotated from each other by approximately 60°, with the former set being 73 ± 3% and the latter 27 ± 3% occupied. This form of disorder has been observed in other perchlorate structures [28].

[Mn(TETRAMESALEN)Cl] (6)

The complex is five-coordinate, the geometry at the Mn(III) center being approximately tetragonal pyramidal. A view of the complex is given in Fig. 2, and the principal bond lengths and angles are listed in Tables 7 and 8, respectively. The base of the tetragonal pyramid is occupied by the two O and two N atoms of the Schiff base, the axial site being occupied by a chloride ligand. The bond lengths in the manganese sphere are normal, the Mn–O distances of 1.852(4) and 1.871(4) Å, being comparable to those reported above while the Mn–N distances of 2.010(4) and 1.989(4) Å are slightly longer than in the six-coordinate complex.

The coordination at manganese is slightly distorted from idealized tetragonal pyramidal geometry, the four atoms in the base exhibiting a slight tetrahedral distortion and thereby deviating significantly from

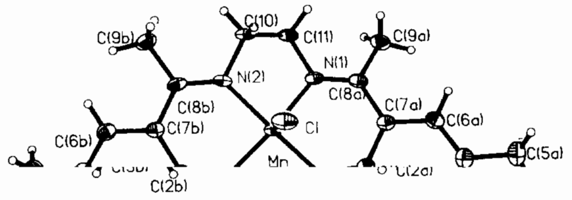

Fig. 2. View of the complex [Mn(TETRAMESALEN)Cl] (6).

TABLE 7. Bond lengths (Å) in 6

Mn–Cl	2.391 (2)	Mn–O(2)	1.871 (4)
Mn–N(1)	2.010 (4)	Mn–O(1)	1.852 (4)
Mn–N(2)	1.986 (4)	O(2)–C(1B)	1.330 (6)
N(1)–C(11)	1.487 (6)	N(1)–C(8A)	1.304 (7)
O(1)–C(1A)	1.331 (6)	C(1A)–C(7A)	1.411 (7)
C(1A)–C(2A)	1.403 (7)	N(2)–C(8B)	1.302 (7)
N(2)–C(10)	1.480 (7)	C(8B)–C(7B)	1.465 (8)
C(8B)–C(9B)	1.507 (8)	C(1B)–C(7B)	1.410 (7)
C(1B)–C(2B)	1.412 (8)	C(7B)–C(6B)	1.429 (7)
C(7A)–C(8A)	1.471 (7)	C(7A)–C(6A)	1.412 (8)
C(10)–C(11)	1.501 (8)	C(4B)–C(3B)	1.402 (9)
C(4A)–C(5A)	1.494 (9)	C(4A)–C(3A)	1.396 (9)
C(4A)–C(6A)	1.380 (8)	C(2A)–C(3A)	1.398 (9)

TABLE 8. Bond angles (°) in 6

Cl–Mn–O(2)	105.3(1)	Cl–Mn–N(1)	97.6(1)
O(2)–Mn–N(1)	156.6(2)	Cl–Mn–O(1)	99.6(1)
O(2)–Mn–O(1)	90.3(2)	N(1)–Mn–O(1)	90.5(2)
Cl–Mn–N(2)	93.2(1)	O(2)–Mn–N(2)	90.3(2)
N(1)–Mn–N(2)	83.8(2)	O(1)–Mn–N(2)	166.6(2)
Mn–O(2)–C(1B)	129.7(4)	Mn–N(1)–C(11)	111.4(3)
Mn–N(1)–C(8A)	127.9(3)	C(11)–N(1)–C(8A)	120.5(4)
Mn–O(1)–C(1A)	127.6(3)	O(1)–C(1A)–C(7A)	123.5(4)
O(1)–C(1A)–C(2A)	117.7(5)	C(7A)–C(1A)–C(2A)	118.6(5)
Mn–N(2)–C(8B)	130.0(4)	Mn–N(2)–C(10)	108.7(3)
C(8B)–N(2)–C(10)	120.6(4)	N(2)–C(8B)–C(7B)	120.9(5)
N(2)–C(8B)–C(9B)	119.7(5)	C(7B)–C(8B)–C(9B)	119.3(5)
O(2)–C(1B)–C(7B)	125.2(5)	O(2)–C(1B)–C(2B)	117.2(5)
C(7B)–C(1B)–C(2B)	117.6(5)	C(8B)–C(7B)–C(1B)	122.5(5)
C(8B)–C(7B)–C(6B)	119.6(5)	C(1B)–C(7B)–C(6B)	117.8(5)
C(1A)–C(7A)–C(8A)	122.9(5)	C(1A)–C(7A)–C(6A)	118.4(5)
C(8A)–C(7A)–C(6A)	118.7(5)	N(2)–C(10)–C(11)	107.9(4)
C(3B)–C(4B)–C(5B)	122.9(6)	C(3B)–C(4B)–C(6B)	117.1(5)
C(5B)–C(4B)–C(6B)	120.0(5)	C(4B)–C(3B)–C(2B)	121.1(6)
N(1)–C(11)–C(10)	108.4(4)	N(1)–C(8A)–C(7A)	120.9(5)
N(1)–C(8A)–C(9A)	120.4(4)	C(7A)–C(8A)–C(9A)	118.7(5)
C(5A)–C(4A)–C(3A)	120.9(6)	C(5A)–C(4A)–C(6A)	121.6(6)
C(3A)–C(4A)–C(6A)	117.5(5)	C(1B)–C(2B)–C(3B)	122.6(6)
C(1A)–C(2A)–C(3A)	121.1(6)	C(7B)–C(6B)–C(4B)	123.7(5)
C(4A)–C(3A)–C(2A)	121.1(5)	C(7A)–C(6A)–C(4A)	123.4(5)

planarity. The average deviation from the best plane through these four atoms is 0.084 Å, with O(1) and N(2) sitting above the plane while O(2) and N(1) lie below it. As is expected for a tetragonal pyramidal complex [29], the manganese lies well above the base plane on the side of the axial ligand, the distance from the plane being 0.305 Å in this case. The Mn–Cl vector is approximately perpendicular to the base plane, the dihedral angle being 175.6°. In the molecule depicted in Fig. 2, the conformation of the five-membered ring Mn, N(1), N(2), C(10), C(11) is λ, but in this centrosymmetric space group there are an equal number of δ conformers.

It is of value to compare the structure of **6** with those of two analogous five-coordinated Schiff base complexes of manganese(III), [Mn(ACEN)Cl] [30] and [Mn(SALEN)Cl] [31]. All three complexes have similar structures, but in [Mn(SALEN)Cl] the Mn atom is only 0.19 Å above the N_2O_2 plane, while in **6** and the ACEN complex the corresponding distances are 0.305 and 0.344 Å, respectively. This distinction is reflected in the Mn–Cl bond lengths, the values of 2.391(2) and 2.381(1) Å in **6** and the ACEN complex, respectively, being considerably shorter than that of 2.461(1) Å in the SALEN complex. Hence, the present result tends to confirm the suggestion of Pecoraro and Butler [31] that the chloride ion is forced to lie approximately 2.7 Å from the N_2O_2 plane because of contacts with the ligand atoms. In this view, the *sum* of the Mn–Cl bond length and the out-of-plane distance should be constant; the values of this parameter for the three complexes are 2.66 (SALEN), 2.725 (ACEN) and 2.696 (**6**).

The packing of the complexes is also different. The SALEN complex is a face-to-face 'dimer', with a Mn–Mn separation of only 3.458 Å [31]. In **6**, however, the closest Mn···Mn approach is 5.788 Å. Thus, the solid structure of **6** is more like that of the thiophenolate complex [Mn(SALEN)SR], which is also monomeric in the solid state [32].

[Mn(MEPHSALEN)(C_2H_5OH)$_2$]ClO_4 (9a)

There are two crystallographically independent cations and anions in the unit cell. The structures of the two cations are substantially similar, and that of one of them is shown in Fig. 3; see also 'Supplementary Material'. As was noted above, because of the paucity of data and the large number of variables in this structure, the metrical parameters here are less precisely determined than in the two previous structures, but the essential features of the structure are well characterized.

The principal difference between the two independent cations lies in the orientation of the coordinated ethanol moieties, i.e. in the rotation of the ethanol molecules around the Mn–O bonds. Both cations are distorted octahedral with *trans* axial ethanol molecules. The axial Mn–O bond lengths of 2.38(4), 2.27(4), 2.25(4), and 2.36(4) Å are much longer than the in-plane Mn–O distances of 1.82(4) to 1.89(4) Å, as expected for a Jahn–Teller elongated d^4 ion, and are comparable to the value of 2.304(7) Å reported above for **7a**. Presumably, as was the case for **7**, the relative weakness of the axial Mn–O bonds permits the easy conversion of **9** to **9a** upon recrystallization from ethanol. Other distances in the cations are normal and are comparable to their equivalent bonds in **7a** and in other related structures. The perchlorate anions in the structure appear to be ordered, but the parameters derived suggest that they must (at least) be undergoing severe thermal motion.

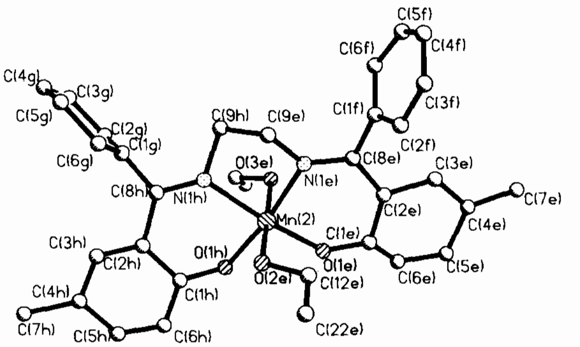

Fig. 3. View of the cation $[Mn(MEPHSALEN)(EtOH)_2]^+$ in the crystals of **9a**. The structure of only one of the two independent cations is shown here, but the other cation is substantially similar to this one.

Electrochemical Properties

Compound **6** does not appear to show any reversible electrochemistry, but complexes **7** and **9** both exhibit a single reversible couple in the cyclic voltammograms. For **7**, this couple has $E_{1/2}$ of −150 mV (versus Ag/AgCl) in acetonitrile, while for **9** the corresponding value is −186 mV. Presumably, this redox process represents the Mn(III) $\leftrightarrow$ Mn(II) couple.

Epoxidation of Cyclohexene

Comparative data for the epoxidation activities of **6**, **7** and **9** are presented in Table 9. The yields of epoxide found here are generally higher than those that have been reported before using copper, cobalt and manganese catalysts with Schiff base and macrocyclic ligands [9, 10, 33, 34]; similar yields to those reported here have been obtained with metal complexes of porphyrins and heteropolyanions [11–13]. Examination of the data in Table 9 would suggest that the six-coordinate complexes are more effective than the five-coordinate complex in catalyzing the epoxidation of cyclohexene. This result is consistent with the observation above that **6** does not show reversible electrochemical redox processes in aceto-

TABLE 9. Catalyzed oxidation[a] of cyclohexene by iodosobenzene

Catalyst	Epoxide (mmol)	Cyclohexenol (mmol)	Yield epoxide[b] (%)
6	0.0175	0.014	17.5
7a	0.075	0.013	75
9a	0.056	trace	56

[a] Conditions: 0.01 mmol catalyst, 0.1 mmol iodosobenzene, 0.97 mmol cyclohexene, and chlorobenzene (0.2 mmol) as internal standard. Solutions made up to 5 ml with acetonitrile at room temperature, 2–3 h reaction time. [b] Based on amount of iodosobenzene added.

nitrile, and is also consistent with the structural results which suggest much weaker axial coordination for **7a** and **9a** than for **6**. It has been suggested [9, 34] that the mechanism for this oxidation involves the transfer of an oxygen atom from iodosobenzene (or other oxygen donor) to the catalyst, forming a Mn(V) oxo complex, $LMn{=}O^+$, which then acts as a two electron oxidant to the substrate (cyclohexene) to form the epoxide. Presumably, therefore, it is essential that the axial coordination at the Mn(III) complex be weak in order to allow the formation of the intermediate Mn(V) oxo complex. It is well established [30] that in the six-coordinate complexes the axial ligands are readily replaced by polar solvent molecules, which in turn could be replaced by the oxo ligand. The five-coordinate complex **6** is clearly more robust than this in acetonitrile solution. The electronic spectrum of **6** in acetonitrile contains bands at 286, 418 and 488 nm. The spectrum in dichloromethane is apparently identical to this, which may suggest that the chloride remains bound in acetonitrile. Further confirmation for this hypothesis comes from experiments designed to precipitate the chloride. Addition of an excess of an acetonitrile solution of silver perchlorate to an acetonitrile solution of **6** gives no detectable precipitate of AgCl. The use of silver nitrate solution in acetonitrile does slowly produce turbidity, and eventually (after more than 10 min) a detectable white precipitate of silver chloride. The electronic spectrum of the filtrate from this reaction is different from that above, the band at 488 nm having disappeared. This result suggests that the chloride ion can be slowly removed in acetonitrile by silver ion, but that the five-coordinate complex remains intact in this solvent in the absence of silver ion. While no structural results are available, our spectroscopic and analytical data (Table 1) suggest that **8** is a five-coordinate monomer analogous to **6** but that **10** is a six-coordinate complex with the weak axial ligands water and acetonitrile. Consequently, we anticipate that **10** is a more suitable candidate than **8** for further investigation.

Supplementary Material

Tables of hydrogen atom coordinates, anisotropic librational parameters (U_{ij}), observed and calculated structure amplitudes for the three structures, and of positional parameters, bond lengths and angles for complex **9a** are available from the authors on request.

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