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Structure of *N,N'*-Ethylenebis(salicylideneiminato)manganese(III) Chloride Acetonitrile Solvate

BY VINCENT L. PECORARO* AND WILLIAM M. BUTLER

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, *USA*

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Abstract. $Mn[C_{16}H_{14}N_2O_2]Cl.CH_3CN$, $M_r = 397·7$, monoclinic, $P2_1/n$, $a = 10·415\,(7)$, $b = 12·671\,(8)$, $c = 13·184\,(8)$ Å, $\beta = 96·56\,(5)°$, $V = 1728\,(1)$ Å^3, $Z = 4$, $D_x = 1·529$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 9·05$ cm^{-1}, $F(000) = 816$, $T = 300$ K, $R = 0·033$, $wR = 0·033$ for 1791 unique reflections with $(I) > 3\sigma(I)$. The title Mn^{III}(salen)Cl complex displays a square-pyramidal geometry similar to that of Fe^{III}(salen)Cl. The bond lengths for atoms in the manganese coordination sphere are Mn(1)—O(1), 1·878; Mn(1)—O(2), 1·906; Mn(1)—N(1), 1·981; Mn(1)—N(2), 1·993; Mn(1)—Cl(1), 2·461 Å. Important angles described by the five atoms bound to Mn(1) are O(1)—Mn(1)—Cl(1), 98·7; O(2)—Mn(1)—Cl(1), 97·2; N(1)—Mn(1)—Cl(1), 94·8; O(1)—Mn(1)—N(1), 92·2; O(1)—Mn(1)—N(2), 168·6; N(2)—Mn(1)—Cl(1), 91·4; O(1)—Mn(1)—O(2), 94·8; O(2)—Mn(1)—N(1), 165·1; O(2)—Mn(1)—N(2), 89·1; N(1)—Mn(1)—N(2), 81·6°. The Mn ion lies 0·19 Å above an equatorial plane consisting of two phenolate O and two imine N atoms. This manganese out-of-plane displacement is unusually short for five-coordinate Schiff-base or porphyrin complexes. A detailed structural comparison of the Mn(salen)Cl molecule with Mn(acen)Cl [acen = *N,N'*-ethylenebis(acetylacetone imine)], *M*(tpp)Cl (M=Mn^{3+}, Fe^{3+}; tpp = tetraphenylporphyrin), Fe(salenCl and Mn(salen)acetate proves useful toward understanding the apparently disparate chemistry between Mn^{3+} and Fe^{3+} salen complexes. The Mn ions of adjacent Mn(salen)Cl molecules are within 3·5 Å, but do not interact.

Introduction. Study of the coordination chemistry of manganese has undergone a renaissance over the past five years due in part to the increased recognition of this element's role in biological systems. There does not appear to be a single structural type for the manganese center(s) in manganoenzymes. Indeed, the known variations already range from the mononuclear sites in a superoxide dismutase (Weisiger & Fridovich, 1973) and a sweet potato acid phosphatase (Sugiura, Kawabe, Tanaka, Fujimoto & Ohara, 1981) to the proposed multinuclear center of the thylakoid-membrane-associated oxygen-evolving complex of photosystem II (Dismukes & Siderer, 1981). Unfortunately, the chemistry of manganese in the catalytically relevant 3+ and 4+ oxidation states is less well developed than for the Mn^{2+} ion, with structural data available for only a handful of Mn^{III} compounds.

Mn^{III} Schiff-base complexes are among the simplest models for the active sites of manganoenzymes. Metal complexes of the Schiff-base ligand *N,N'*-bis(salicylideneiminato)ethylene (salen) have been extensively studied (Hobday & Smith, 1972/1973) and have been shown to adopt three main structural types. These are mononuclear (Gerloch & Mabbs, 1967*a*) *M*(salen)*X* (where X = halide), binuclear (Gerloch & Mabbs, 1967*b*) $M(\text{salen})_2$ and bridged binuclear (Lewis, Mabbs & Richards, 1967) $M(\text{salen})_2O$. The complexes of Mn^{III}(salen)*X* (X = I,Br,Cl) have been prepared and are soluble in aqueous and methanolic solutions. In contrast, Fe(salen)*X* has low solubility in water or methanol (Gerloch, Lewis, Mabbs & Richards, 1968). Furthermore, while Fe(salen)*X* reacts rapidly with base

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* To whom correspondence should be addressed.

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to form an oxy-bridged dimer, Mn(salen)X is essentially inert. We report here the structure of Mn^{III}(salen)Cl and compare it to the previously described structure Fe(salen)Cl (Gerloch & Mabbs, 1967*a*). In addition, we have compiled bond length and angle data for other Mn^{3+} and Fe^{3+} complexes to facilitate the discussion of these salen complexes.

Experimental. The title complex was prepared *via* an $MnCl_2$ (0·01 mol) assisted Schiff-base condensation of 2 equivalents of salicylaldehyde (0·02 mol) with ethylenediamine (0·01 mol) in methanol at room temperature. Schiff-base formation and aerial oxidation of the manganese yielded a dark-brown solid which gave crystals of Mn(salen)Cl when recrystallized by slow evaporation from acetonitrile. Dark-brown block (0·166 × 0·186 × 0·172 mm); Syntex $P2_1$ diffractometer; least-squares refinement of 15 reflections in the range $15 < 2\theta < 22°$ for cell constant determination; systematic absences: $0k0$, $k = 2n$; $h0l$, $h+l = 2n$; $2\theta_{max} = 40°$; h: 0 to 11, k: 0 to 13, l: −14 to 14; no absorption correction; less than 5% random variation in three standard reflections (204, 023, 014) measured every 50 reflections; no significant crystal decay; scan speed variable based on intensity, 2·5–12° min^{-1}; 2430 data collected; θ–2θ scans; 1791 unique reflections with $(I) > 3\sigma(I)$; background time ratio 0·8; data reduced using *SHELX* (Sheldrick, 1976); structure by direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refined with anisotropic thermal parameters for all non-H atoms. H-atom positions were calculated and included in F_c, but not refined, with fixed U values of 0·05; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F) + 0{\cdot}0001F^2]$; final $R = 0{\cdot}033$, $wR = 0{\cdot}033$. Maximum shift/e.s.d. was $< 0{\cdot}4$. Final difference Fourier map contained no peaks $< -0{\cdot}40$ or $> 0{\cdot}32$ e $Å^{-3}$. Error of an observation of unit weight 1·12. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The Mn(salen)Cl complex is illustrated in Fig. 1 and a packing diagram is given in Fig. 2. Important bond lengths and angles have been summarized in Table 1.* The coordination polyhedron can be described as a square pyramid with the Mn^{III} ion being displaced from the O(1), N(1), N(2), O(2) plane by 0·19 Å toward an axially coordinated chloride ligand. As seen from Table 3, and as discussed below, this is the shortest out-of-plane displacement for a square pyramidal Mn^{III} complex yet determined. The Mn—N and Mn—O bond lengths are unexceptional for a high-spin Mn^{III} ion bound to imine or phenoxide ligands. The Mn—Cl bond, however, is relatively long at 2·461 Å. As will be discussed below, this is probably due to the short manganese out-of-plane displacement. The N—Mn—N and O—Mn—N bond angles are typical of metal complexes with salen as a ligand. In contrast, the Cl—Mn—R (R=N, O) angles reported in Table 2 are smaller than observed in other five-coordinate Mn^{III} and Fe^{III} complexes [*e.g.* the average Cl—Mn—R angle for Fe(salen)Cl is 106·5°].

The packing diagram illustrates the relative orientation of the Mn(salen)Cl molecules. The crystal consists of four discrete Mn(salen)Cl and four acetonitrile molecules per unit cell. The closest Mn—Mn contacts appear at the center of the cell where two Mn(salen)Cl molecules are oriented with the base of each square pyramid facing the other. The manganese ions of these adjacent molecules are separated by 3·458 Å; however, the ions do not exhibit appreciable magnetic interaction [$\mu_{eff} = 4{\cdot}84$ BM ($1 \text{ BM} = 9{\cdot}27 \times 10^{-24}$ J T^{-1}) compared to the spin-only 4·9 BM (Boucher, 1974)].

The subtle differences in the structures of Mn(salen)Cl and Fe(salen)Cl can be explained using ligand-field theory. The highest energy d orbital for a high-spin, square-pyramidal Mn^{III} or Fe^{III} ion is the $d_{x^2-y^2}$. In the d^4 case, Mn^{III}, this orbital will be unoccupied, while the d^5 Fe^{III} ion will have this orbital partially filled. As a metal ion moves into the salen plane, the $d_{x^2-y^2}$ orbital increases in energy while the d_{xz} and d_{yz} orbitals are stabilized. Thus, for the Mn^{III} ion, with an empty $d_{x^2-y^2}$ orbital, the lowest energy d orbital configuration occurs when the Mn^{III} ion is within the

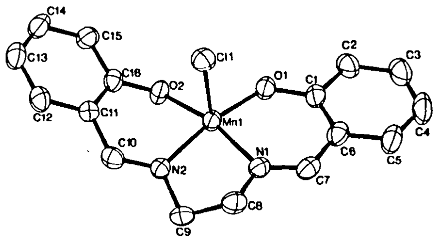

Fig. 1. *ORTEP* diagram (Johnson, 1965) of the molecule Mn(salen)Cl with thermal ellipsoids at 50% probability.

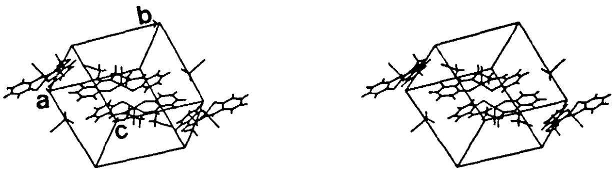

Fig. 2. Stereoview of the unit cell showing packing of Mn(salen)Cl and solvent. The a, b and c axes are oriented as shown.

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* Lists of structure factors, anisotropic thermal parameters, additional bond lengths and angles, H-atom coordinates and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42993 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

basal plane. In contrast, Fe^{III}, with a half-filled *d* shell, need not exhibit this preference. Both Mn^{III}(salen) and Fe^{III}(salen) must have axially coordinated ligands to achieve electrical neutrality. Axial chloride ligation causes a displacement of the metal ion from the basal plane toward the ligand. A large displacement, associated with the formation of a strong Fe—Cl bond, can occur without a net loss in ligand-field stabilization energy (LFSE). In contrast, as the Mn ion is displaced from the basal plane to form a bond to the chloride, it substantially loses LFSE.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2)

U_{eq} is defined as one third of the trace of the U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Mn(1)	0·4383 (1)	0·5254 (1)	0·3751 (1)	0·0306
Cl(1)	0·3834 (1)	0·4437 (1)	0·2064 (1)	0·0415
O(1)	0·5888 (2)	0·5974 (2)	0·3491 (2)	0·0354
C(1)	0·6035 (4)	0·6962 (3)	0·3185 (3)	0·0362
C(2)	0·7280 (4)	0·7298 (3)	0·3029 (3)	0·0448
C(3)	0·7481 (5)	0·8314 (4)	0·2700 (4)	0·0569
C(4)	0·6461 (6)	0·9026 (3)	0·2513 (4)	0·0607
C(5)	0·5247 (5)	0·8715 (3)	0·2679 (3)	0·0499
C(6)	0·4991 (4)	0·7683 (3)	0·3006 (3)	0·0373
C(7)	0·3684 (4)	0·7427 (3)	0·3155 (3)	0·0374
N(1)	0·3293 (3)	0·6520 (2)	0·3437 (2)	0·0330
C(8)	0·1913 (4)	0·6343 (3)	0·3509 (3)	0·0406
C(9)	0·1820 (4)	0·5550 (3)	0·4364 (3)	0·0405
N(2)	0·2757 (3)	0·4718 (2)	0·4229 (2)	0·0316
C(10)	0·2522 (4)	0·3743 (3)	0·4387 (3)	0·0357
C(11)	0·3445 (4)	0·2902 (3)	0·4306 (3)	0·0319
C(12)	0·2998 (4)	0·1861 (3)	0·4276 (3)	0·0393
C(13)	0·3838 (4)	0·1031 (3)	0·4214 (3)	0·0438
C(14)	0·5135 (4)	0·1230 (3)	0·4209 (3)	0·0427
C(15)	0·5612 (4)	0·2253 (3)	0·4258 (3)	0·0370
C(16)	0·4782 (4)	0·3100 (3)	0·4308 (3)	0·0307
O(2)	0·5281 (2)	0·4079 (2)	0·4395 (2)	0·0320
N(3)	0·4753 (4)	0·2553 (4)	0·9793 (4)	0·0795
C(17)	0·4291 (5)	0·3336 (5)	0·9546 (4)	0·0571
C(18)	0·3699 (5)	0·4331 (4)	0·9222 (4)	0·0625

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

Mn(1)—Cl(1)	2·461 (1)	Mn(1)—N(2)	1·993 (3)
Mn(1)—O(1)	1·878 (2)	Mn(1)—O(2)	1·906 (2)
Mn(1)—N(1)	1·981 (3)		
Cl(1)—Mn(1)—O(1)	98·7 (1)	N(1)—Mn(1)—N(2)	81·6 (1)
Cl(1)—Mn(1)—N(1)	94·8 (1)	Cl(1)—Mn(1)—O(2)	97·2 (1)
O(1)—Mn(1)—N(1)	92·2 (1)	O(1)—Mn(1)—O(2)	94·8 (1)
Cl(1)—Mn(1)—N(2)	91·4 (1)	N(1)—Mn(1)—O(2)	165·1 (1)
O(1)—Mn(1)—N(2)	168·6 (1)	N(2)—Mn(1)—O(2)	89·1 (1)

Table 3. *Out-of-plane and metal–chloro bond lengths* (Å) *for* Mn^{III} *and* Fe^{III} *Schiff-base and porphyrin complexes*

Complex	*M*—plane*	*M*—Cl†	Reference
Mn(salen)Cl	0·19	2·461	This work
Mn(acen)Cl‡	0·344	2·381	Boucher & Day (1977)
Mn(tpp)Cl‡	0·27	2·363	Tulinsky & Chen (1977)
Mn(salen)O_2CCH_3§	0·0	2·201¶	Davies, Gatehouse & Murray (1973)
$MnCl_5$	–	2·53, 2·34‖	Bellitto, Tomlinson & Furlani (1971)
Fe(salen)Cl	0·46	2·238	Gerloch & Mabbs (1967*a*)
Fe(tpp)Cl‡	0·383	2·192	Hoard, Cohen & Glick (1967)

* Distance of metal from center of best least-squares plane of basal coordinating atoms.

† Metal to axial chloride distance unless otherwise noted.

‡ Abbreviations used: acen, *N,N'*-ethylenebis(acetylacetone imine); tpp, tetraphenylporphyrin.

§ Six-coordinate, infinite chain structure with bridging acetates.

¶ Mn—O bond length.

‖ Basal Mn—Cl bond length.

An Mn^{III}—Cl bond is approximately 2·32–2·34 Å in Schiff-base and porphyrin complexes. The Mn^{III}—Cl bond in Mn(salen)Cl (2·461 Å) is significantly longer than normal. The origin of this elongation may be understood by considering the distance from the Cl atom to the center of the basal plane (the sum of columns 1 and 2 in Table 3). For the porphyrin complexes (four nitrogen donors) this distance is 2·59—2·63 Å, while salen and acen (two nitrogen and two oxygen donors) range between 2·65 and 2·72 Å. It appears that the chloride ion maintains a nearly constant distance from the center of the plane *regardless of the metal atom* (presumably owing to contacts with N or O atoms). If the chloride ion is required to be 2·7 Å from the basal plane due to van der Waals contacts, the normal Fe^{III}—Cl bond length (2·2 Å) and bond strength can be preserved when the Fe^{III} atom lies well out of this plane (Table 3). A large out-of-plane displacement occurs since the stabilization afforded through covalent interaction with the phenol π system and from LFSE is less than that obtained by the strong FeCl bond. In Fe(salen)Cl, the Fe^{III}—Cl bond is so strong that donor solvents do not displace the chloride ion. For this reason, Fe(salen)Cl acts as a molecular species and is insoluble in aqueous or alcoholic solutions. This is not true for Mn^{III} complexes in general, especially Mn(salen)Cl. In this system, optimal stabilization occurs when Mn^{III} is in the basal plane. Thus, with a 0·19 Å displacement, the Mn^{III}—Cl bond length in Mn(salen)Cl must exceed 2·4 Å so that the chloride just contacts the imine N atoms [*e.g.*, the N(2)—Cl distance is 3·205 Å which compares with the sum of the van der Waals radii for N—Cl which is 3·20 Å (Pauling, 1960)]. This elongation (from 2·32 to 2·461 Å) represents a weakening in the Mn—Cl bond strength and underlies the observation that when dissolved in donor solvents the chloride ion dissociates from Mn(salen)Cl resulting in a 1:1 electrolyte (Van Den Bergen, Murray, O'Connor & West, 1969). We would expect that in solution Mn(salen)$^+$ is probably a discrete tetragonally distorted octahedral species with solvent molecules in axial sites as has been proposed based on spectral data (Boucher & Day, 1977). In this sense it would resemble an individual octahedral unit seen for the polymeric Mn(salen)acetate. The same factors should affect the Mn(acen)Cl complex. The acen has a stronger ligand field than salen (Boucher & Day, 1977) so that the Mn^{III} can keep an equivalent ligand-field stabilization energy while extending farther from the basal plane. This results in a shorter (*i.e.*, stronger) Mn—Cl bond. However, in solution Mn(acen)Cl behaves similarly to Mn(salen)Cl giving a solvated cationic complex (Boucher & Day, 1977). Again, a tetragonally distorted structure is preferred.

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Structures of μ-Oxo-bis[(benzenesulfonato)triphenylantimony(V)] and μ-Oxo-bis[(trifluoromethylsulfonato)triphenylantimony(V)]

By Hans Preut, Robert Rüther and Friedo Huber

Fachbereich Chemie, Universität Dortmund, Postfach 500 500, *D*-4600 *Dortmund* 50, *Federal Republic of Germany*

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Abstract. (I) $[(C_6H_5)_3SbO_3SC_6H_5]_2O$, $M_r = 1036{\cdot}5$, monoclinic, $P2_1/c$, $a = 16{\cdot}142\,(6)$, $b = 17{\cdot}733\,(6)$, $c = 16{\cdot}141\,(6)$ Å, $\beta = 108{\cdot}28\,(5)°$, $V = 4387$ Å^3, $Z = 4$, $D_x = 1{\cdot}569$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}39$ mm^{-1}, $F(000) = 2072$, $T = 292\,(1)$ K, $R = 0{\cdot}044$ for 3712 observed reflexions $[I > 3\sigma(I)]$. (II) $[(C_6H_5)_3SbO_3SCF_3]_2O$, $M_r = 1020{\cdot}3$, monoclinic, $P2_1/c$, $a = 20{\cdot}596\,(8)$, $b = 10{\cdot}296\,(5)$, $c = 19{\cdot}546\,(9)$ Å, $\beta = 108{\cdot}24\,(5)°$, $V = 3937$ Å^3, $Z = 4$, $D_x = 1{\cdot}721$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}57$ mm^{-1}, $F(000) = 2008$, $T = 292\,(1)$ K, $R = 0{\cdot}055$ for 2652 observed reflexions $[I > 3\sigma(I)]$. Two $(\mu\text{-O})$—$SbPh_3$—O—$S(O_2)R$ [$R = C_6H_5$ (I), CF_3 (II)] units with slightly distorted trigonal-bipyramidal surroundings at the Sb atoms – O atoms in apical and C(phenyl) atoms in equatorial positions – are linked *via* a bent Sb—O—Sb bridge in the molecules (I) [139·8 (3)°] and (II) [136·5 (5)°]. The $(\mu\text{-O})$—Sb bond lengths are in the range 1·937 (10) to 1·980 (8) Å. The Sb—O bonds to the unidentately coordinated sulfonate groups are in the range 2·247 (5) to 2·37 (1) Å and appear to have appreciably high ionic character.

Introduction. Only rather few structures of distiboxans are known, and the question why the Sb—O—Sb bridge in such compounds is bent in some examples [$(Ph_3SbN_3)_2O$ (Ferguson & Ridley, 1973); $(Me_3SbX)_2O$, $X = ClO_4$, Cl and N_3 (Ferguson, March & Ridley, 1975)] or linear in others [$(Ph_3SbOO$—*tert*-$C_4H_9)_2O$ (Starikova, Shchegoleva, Trunov & Pokrovskaya, 1978)] still waits to be answered. We recently reported as a first structure of $(R_3SbO_3SR')_2O$ compounds (R, R' = organic groups) that of $(Ph_3SbO_3SCH_2CH_2OH)_2O$, in which we found a linear bridge (Preut, Rüther & Huber, 1985). We now describe the structures of two other compounds of the same formula type, which however have a bent Sb—O—Sb bridge.