

Some New Manganese(III) Complexes of the Tetradentate Schiff Base Ligand 1,3-N,N'-propylenebis(salicylideneaminato), [Mn(ligand)X]

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Abstract

Some new complexes of type [Mn(saltm)X] (saltm = 1,3-N,N'-propylenebis(salicylideneaminato); X = F, Cl, Br, I, NCS, CN, CH₃CO₂) have been isolated and characterised by a number of spectroscopic and magnetic techniques. The complexes (except for X = CH₃CO₂) are assigned a pentaco-ordinate monomeric structure, and [Mn(saltm)(CH₃CO₂)₂] is assigned a hexaco-ordinate dimeric structure. Unlike complexes of type [Mn(saltm)(H₂O)]₂²⁺, none of the complexes described here exhibit photolysis behaviour in aqueous solution.

Introduction

The tetradentate O₂N₂ Schiff base ligand salen {salen = N,N'-ethylenebis(salicylideneaminato)} forms a number of manganese(III) complexes of type [Mn(salen)X] (X = Cl, Br, I, CH₃CO₂) and the Busalen {Busalen = 4-sec-butyl-N,N'-ethylenebis(salicylideneaminato)} ligand forms similar complexes [1–7]. There are relatively few such complexes formed by the Schiff base saltm [8] {saltm = 1,3-N,N'-propylenebis(salicylideneaminato)}, examples being some oxidation products of [Mn(saltm)] [9] and a manganese(III) complex of the 4-sec-butyl-substituted ligand [Mn(Busaltm)(H₂O)]ClO₄ [10].

As part of a wide study [11, 12] of the metal complexes of tetradentate Schiff base ligands we report here some manganese(III) complexes of saltm, [Mn(saltm)X] (X = F, Cl, Br, I, NCS, CN, CH₃CO₂), and some [Mn(salen)X] complexes are included for comparison.

Our interest in complexes of this type derives, in the most part, from their ability to serve as model compounds for the manganese-dependent dioxygen evolution system, photosystem II, PPSII, in green plant photosynthesis [10, 13–17]. Recently we

have prepared and characterised a number of [Mn(SB)(H₂O)]ClO₄ (SB = dianion of a tetradentate Schiff base ligand) complexes, and successfully demonstrated the ability of some of these complexes, e.g. [Mn(saltm)(H₂O)]ClO₄·2H₂O, to liberate dioxygen from the coordinated water under visible light radiation [12, 18, 19].

The nature of the ligand is crucial to the photolysis activity, a small change in the ligand backbone, from the trimethylene-containing saltm to the dimethylene-containing salen causes a dramatic decrease in photolysis behaviour. The subtle effect of backbone change has also been demonstrated by us in the isolation of the unusual [Mn(salen)(CO)]₂(ClO₄)₂ complex [11]; no such complex could be isolated with the saltm ligand.

The complexes reported here were found to be inactive in water photolysis, suggesting that the coordinated anion in [Mn(SB)X] does not undergo solvolysis to form [Mn(SB)(H₂O)]₂X₂ in water. Nonetheless, these studies serve to emphasise that subtle changes in coordination geometry can have dramatic effects on the properties of the complexes.

Experimental

The ligands were prepared by standard methods.

Complex Preparation

[Mn(salen)(CH₃CO₂)]

Manganese(II) acetate tetrahydrate (24.5 g; 0.1 mol) dissolved in ethanol (150 cm³) was mixed with a solution of the ligand, salenH₂, (26.8 g; 0.1 mol) dissolved in ethanol (50 cm³). The mixture turned immediately dark green and a small amount of precipitate was formed. The mixture was refluxed in air for 2 h, during which time the solid dissolved. The solution was filtered and evaporated to 25 cm³. Upon cooling dark green crystals formed and these were collected by filtration, washed with cold ethanol (3 × 25 cm³), then with anhydrous

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TABLE I. The Manganese Complexes and their Physical and Spectroscopic Data.

Complex	%C ^a	%H ^a	%N ^a	%Mn ^a	%X ^a	μ_{eff}^b	Δ^c	$\nu(\text{OH})^d$	$\nu(\text{CN})^d$	$\nu(\text{CO})^d$	$\nu(\text{Mn-O})^d$	$\nu(\text{Mn-N})^d$	$\nu(\text{Mn-X})^d$	Electronic Spectral Bands ^e		
[Mn(salen)(OAc)]·H ₂ O	54.7(54.7)	4.5(4.7)	6.7(7.0)	13.9(13.8)		4.7	96	3000	1618	1295	460	300	217(32600)	237(37500)	280(17100)	397(4750)
[Mn(salen)F]·H ₂ O	51.5(53.5)	4.8(4.6)	7.0(7.8)			4.9	121	3200	1618	1310	452	385	215(20800)	234(15800)	285(10600)	390(3400)
[Mn(salen)(NCS)]·H ₂ O ^f	49.9(51.3)	3.6(4.0)	9.6(10.5)	13.8(13.8)	8.0(8.0)	4.8	117	3220	1610	1295	450	380	215(31800)	236(34050)	280(15250)	396(4350)
[Mn(salen)(CN)]·H ₂ O	56.1(55.9)	4.0(4.3)	12.4(11.7)	14.7(15.0)		4.8	121	3200	1615	1310	450	385	219(32000)	235(35200)	277(16600)	382(4630)
[Mn(saltm)(OAc)]·2H ₂ O	52.0(52.9)	5.0(5.3)	6.2(6.5)	13.7(13.1)		4.7	101	3300	1610	1305	460	390	213(27400)	231(26630)	278(17080)	368(6250)
[Mn(saltm)F]·2H ₂ O	50.3(52.1)	5.3(5.1)	6.9(7.1)		5.8(5.2)	4.9	130	3300	1610	1300	455	385	215(21500)	234(31040)	285(12700)	390(4280)
[Mn(saltm)Cl]·H ₂ O	53.4(52.6)	5.0(4.7)	6.7(7.2)	14.4(14.2)		4.8	133	3200	1610	1305	450	380	213(32200)	232(30300)	278(18700)	374(6850)
[Mn(saltm)Br]·H ₂ O	47.1(47.3)	4.2(4.1)	6.5(6.5)	12.0(12.7)		4.7	136	3200	1615	1305	450	380	213(23800)	231(23400)	277(4650)	368(5350)
[Mn(saltm)I]·H ₂ O	41.3(43.0)	4.0(3.8)	5.4(5.9)		24.1(25.5)	4.7	134	3300	1615	1300	455	380	220(20500)	240(19930)	280(11210)	395(3720)
[Mn(saltm)(NCS)]·H ₂ O ^g	51.3(52.5)	4.5(4.4)	11.0(10.3)	12.8(13.3)		4.8	125	3250	1610	1300	450	380	213(32600)	230(29300)	278(17740)	373(6550)
[Mn(saltm)(CN)]·H ₂ O	56.5(56.9)	4.8(4.6)	11.0(11.1)			4.8	129	3300	1610	1310	450	380				

^aFound (Calc). ^b μ_B . ^c $\text{Ohrm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in H₂O ($10^{-3} \text{mol dm}^{-3}$). ^d cm^{-1} . ^enm; ϵ_{max} in parentheses ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). ^f $\nu(\text{CN})$, 2050 cm^{-1} . ^g $\nu(\text{CN})$, 2052 cm^{-1} .

diethyl ether ($3 \times 25 \text{cm}^3$), and dried *in vacuo*. The [Mn(saltm)(CH₃CO₂)] complex was prepared in a similar manner using saltmH₂.

Other complex preparations

All other complexes were prepared as follows: The [Mn(ligand)(CH₃CO₂)] (0.01 mol) (ligand = salen, saltm) complex dissolved in ethanol (150cm^3) was mixed with NaX (0.01 mol) in ethanol (50cm^3), causing an immediate colour change. The mixture was refluxed for 2 h, reduced in volume to 50cm^3 and, upon cooling in an ice-bath, a solid precipitated. This was collected, washed with cold ethanol ($3 \times 25 \text{cm}^3$), anhydrous diethylether ($3 \times 25 \text{cm}^3$), and dried *in vacuo*.

Yields of all complexes were almost quantitative.

Physical Measurements

Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer, electronic spectra on a Cary 210 instrument. Magnetic moments were obtained at room temperature by the Gouy method, and conductivity measurements were made in aqueous solution employing a Cambridge Instruments conductivity bridge. Mass spectra were obtained on the FAB instrument of the Chemistry Department and elemental analyses by the UMIST Micro-analytical Service.

Results and Discussion

The formation of the [Mn(ligand)X] complexes is quite facile, and air oxidation of the original manganese(II) to manganese(III) occurs rapidly. The complexes isolated are listed in Table I, together with their microanalytical data and some physical and spectroscopic properties.

All of the complexes are obtained as hydrates, but it appears that the water molecules are not co-ordinated. On heating the complexes to *ca.* 100 °C for 2 h the water can be removed, but this does not lead to a change in the infrared spectral bands other than those associated with O-H vibrations. Thus, the ease with which water molecules are removed, coupled with an otherwise constant vibrational spectrum, leads us to conclude that the water molecules are not co-ordinated, and thus the complexes listed in the Table are best formulated [Mn(ligand)X]·nH₂O ($n = 1, 2$).

There are, therefore, two obvious structures for the complexes in the solid state, *viz.* five-co-ordinate monomeric [Mn(ligand)X], or a hexa-co-ordinate anion-bridged dimeric [Mn(ligand)X]₂. There are two pieces of evidence which point strongly to the former case: (i) The complexes are quite soluble in methanol, ethanol, acetone and, to a lesser degree, in water. (ii) Although little information is avail-

able in the literature on the energy of $\nu(\text{Mn}-\text{X})$ vibrations, our own previous experience with the infrared spectra of $[\text{MnCl}_2]^{2-}$ [20] and $[\text{Mn}(\text{OEPH}_3)\text{X}_3]$ ($\text{E} = \text{P, As}; \text{X} = \text{Cl, Br}$) [21] strongly suggests that the $\nu(\text{Mn}-\text{X})$ vibrations listed in the Table occur at energies to be expected for terminal rather than bridging $\text{Mn}-\text{X}$ moieties. It should also be mentioned here that we were able to clearly identify $\nu(\text{Mn}-\text{O})$ and $\nu(\text{Mn}-\text{N})$ vibrations (see Table I) associated with the co-ordinated ligand. Thus, it can be concluded that these complexes are monomeric and penta-co-ordinate. This is further substantiated in the case of the $[\text{Mn}(\text{ligand})(\text{NCS})]$ complexes, for which the $\nu(\text{CN})$ vibration [22] of the pseudohalide clearly indicates a $\text{Mn}-\text{NCS}$ linkage and not a $\text{Mn}-\text{NCS}-\text{Mn}$ linkage. Moreover, the room-temperature magnetic moments (see Table I) of the complexes are almost exactly those expected for magnetically dilute manganese(III) systems; no lowering of the magnetic moment due to spin-pairing via a $\text{Mn}-\text{X}-\text{Mn}$ system is observed. Additionally, we point out that the fast atom bombardment mass spectrum of the $[\text{Mn}(\text{saltm})\text{X}]$ ($\text{X} = \text{Cl, Br}$) complexes exhibit an intense peak at 335 e.m.u., assigned to $[\text{Mn}(\text{saltm})]^+$.

The acetate complexes, $[\text{Mn}(\text{ligand})(\text{OAc})]$ (ligand = salen, saltm), appear to be different, however. They exhibit a somewhat reduced magnetic moment (this reduction in the spin-only value is slight, but the acetate bridge is not expected to lead to strong anti-ferromagnetic interactions) and are much less soluble than the halide or pseudohalide complexes. Indeed, a single crystal X-ray diffraction study of the salen derivative shows it to have a polymeric acetate bridged structure [3]. We similarly assign a polymeric structure to $[\text{Mn}(\text{saltm})(\text{OAc})]$.

We were particularly interested in any photolysis behaviour of these complexes in aqueous solution. None was observed. It is thus useful to compare this behaviour with that of the aqua-dimers $[\text{Mn}(\text{saltm})(\text{H}_2\text{O})_2]^{2+}$ [12, 19]. The latter complexes (as the perchlorate and, to a certain extent, the nitrate derivatives) exhibit water photolysis activity: aqueous solutions evolve dioxygen and, at the same time reduce *p*-benzoquinone to hydroquinone, when irradiated with visible light (NB the salen derivatives are much less active). There is evidence for the existence of a dimeric $[\text{Mn}(\text{saltm})(\text{H}_2\text{O})_2]^{2+}$ structure in the solid state which, to a large extent persists in solution for the perchlorate species and, to a lesser extent for the nitrate, the latter anion being a better co-ordinator than the former [12]. The complexes studied here are, however, different. They are monomeric in the solid state. Moreover, they are almost 1:1 electrolytes in aqueous solution, Table I, but it is interesting to note that this presumably does not lead to the formation of the aquo-bridged dimers $[\text{Mn}(\text{ligand})(\text{H}_2\text{O})_2]^{2+}$ necessary for photolytic prod-

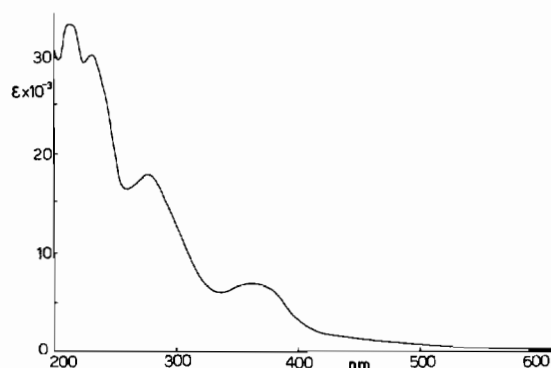


Fig. 1. The electronic spectrum of $[\text{Mn}(\text{saltm})(\text{NCS})]$ in aqueous solution.

uction of dioxygen. Moreover, we have previously pointed out that those complexes which are photoactive exhibit an absorption at 590 nm in their electronic spectra. None of the complexes studied here exhibit such a band (see Table I and Fig. 1).

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