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High-valent Manganese Complexes of Tetradentate Schiff Base Ligands. ESR-active and ESR-silent Dimeric Species

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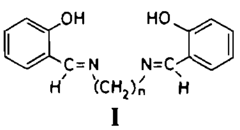
Abstract

Two new complexes of type $[Mn(SB)(Me_2CO)]Y$ (SB is a dianion of a tetradentate Schiff base ligand, $Y = NO_3$ or ClO_4) have been synthesised and characterised. The complexes are probably dimeric via bridging acetone ligands. Base hydrolysis of these complexes in chloroform yielded new dimeric species tentatively assigned as $[Mn_2(SB)_2(O)(OH)]\cdot H_2O$ and $[Mn(SB)(O)]_2\cdot H_2O$. Elemental analyses, infrared, electronic and ESR spectra, as well as conductivity and room temperature magnetic susceptibility measurements are reported.

Introduction

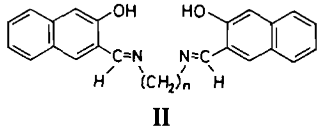
The chemistry of manganese is of considerable current interest following the realisation that the active site in photosystem II in green plant photosynthesis involves a dinuclear unit with two manganese atoms in high oxidation states.

Our own interest is in the chemistry of manganese with Schiff's base ligands of the type **I** and **II** which are well known to stabilise the metal in the +2, +3 and +4 oxidation states [2–5]. We have shown that the coordinated water molecule in $[Mn(saltm)(H_2O)]ClO_4$ (saltm – **I** with $n = 3$) is susceptible to photolysis by visible light with release of molecular oxygen, and that such behaviour is very dependent of the nature of the Schiff-base, since complexes of **I** ($n = 2$ or 4) are much less active [6]. A similar sensitivity to the detailed structure of the ligand is shown in interactions with small molecules: we have isolated the first carbonyl complex of a metal in the +3 oxidation state $[Mn(salen)(CO)]_2(ClO_4)_2$, but could not obtain the corresponding saltm complex [7].



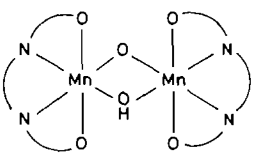
I

H_2salen n = 2
H_2saltm n = 3

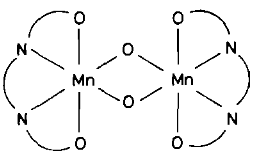


II

$H_2naphen$
$H_2naphtm$



III



IV

We now report new manganese(III) complexes of the ligands **I** ($n = 2$) and **II** ($n = 3$) and the characterisation of oxidised complexes containing these ligands. In addition, oxidised products of complexes of ligands **I** ($n = 3$) and **II** ($n = 2$) have been isolated.

Results and Discussion

The complexes isolated are listed in Table I together with magnetic moments, conductivities, ESR, IR vibrational and electronic spectral data, Table II.

The manganese(III) complexes, $[Mn(SB)(Me_2CO)]^+$ (SB = salen, maphtm) were prepared using a modification of the method of Boucher and Coe [4] for the preparation of $[Mn(SB)(H_2O)]^+$ (see 'Experimental'). The acetone molecule is coordinated to the manganese as evidenced by the $\nu(C{=}O)$ band in the infrared spectrum of the complex, 1610 cm^{-1}, shifted considerably to lower energy from that of free acetone, 1710 cm^{-1}. Applying a static vacuum over a long period did not result in loss of the coordi-

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TABLE I. Analytical and Magnetic Data for the Complexes

Compound	Colour	%C[a]	%H[a]	%N[a]	%M[a]	μ_{eff}[b]	g[c]	Λ_o[d]
$[Mn(salen)(Me_2CO)]NO_3$	Brown	51.3(51.7)	4.7(4.5)	9.8(9.5)	12.3(12.6)	4.9		67.6
$[Mn_2(salen)_2(O)(OH)]\cdot H_2O$	Red–brown	55.1(55.3)	4.2(4.5)	7.9(8.1)	15.6(16.0)	2.9	2.2278	
$[Mn(salen)O]_2\cdot H_2O$	Red–brown	55.3(55.4)	4.2(4.3)	8.0(8.1)	15.7(16.0)	2.1		
$[Mn_2(saltm)_2(O)(OH)]\cdot H_2O$	Red–brown	54.6(54.8)	5.0(5.3)	7.6(7.7)	14.8(15.2)	2.8	2.2184	
$[Mn(saltm)O]_2\cdot H_2O$	Red–brown	54.8(54.4)	4.9(5.2)	7.4(7.7)	14.9(15.2)	2.0		
$[Mn_2(naphen)_2(O)(OH)]\cdot H_2O$	Brown	66.5(66.8)	4.3(4.5)	6.5(6.2)	12.5(12.9)	2.8	2.2148	
$[Mn(naphen)O]_2\cdot H_2O$	Dark brown	66.7(66.9)	4.2(4.4)	6.4(6.5)	12.4(12.9)	2.0		
$[Mn(naphtm)(Me_2CO)]ClO_4\cdot H_2O$	Green	62.1(62.1)	5.9(5.6)	5.2(5.2)	9.8(10.2)	4.6		82.6
$[Mn_2(naphtm)_2(O)(OH)]H_2O$	Red–brown	64.3(64.7)	5.0(5.3)	5.8(6.0)	11.7(11.9)	2.7	2.2112	
$[Mn(naphtm)O]_2\cdot 2H_2O$	Red–brown	64.4(64.7)	5.1(5.2)	5.9(6.0)	11.7(12.0)	1.9		

[a] % Found (% Calculated). [b] μ_B. [c] ESR g-value in chloroform solution at 93 K (10^{-3} M). [d] ohm^{-1} cm^2 mol^{-1}, 10^{-3} M solutions in DMF.

TABLE II. Infrared and Visible Spectra of the Complexes

Complex	Infrared (cm^{-1})				Visible Reflectance (nm)	
	ν(OH)	ν(CN)	ν(MO)	ν(MN)	Maximum	Shoulders
$[Mn(salen)(Me_2CO)]NO_3$[a]		1625	470	380	440	580, 615
$[Mn_2(salen)_2(O)(OH)]\cdot H_2O$	3500br	1615	460	375	490	
$[Mn(salen)O]_2\cdot H_2O$	3500br	1615	460	375	465	
$[Mn_2(saltm)_2(O)(OH)]\cdot H_2O$	3400br	1625	465	370	495	
$[Mn(saltm)O]_2\cdot H_2O$	3400br	1625	465	370	465	
$[Mn_2(naphen)_2(O)(OH)]\cdot H_2O$	3400br	1615	460	380	495	
$[Mn(naphen)O]_2\cdot H_2O$	3400br	1615	460	380	465	
$[Mn(naphtm)(Me_2CO)]ClO_4\cdot H_2O$[b]	3480br	1620	465	385	430	560, 580, 615
$[Mn_2(naphtm)_2(O)(OH)]\cdot H_2O$	3500br	1620	465	380	495	
$[Mn(naphtm)O]_2\cdot H_2O$	3400br	1620	465	385	465	

[a] $\nu(NO_3)$ 1365 cm^{-1}, ν(C=O) 1610 cm^{-1}. [b] $\nu(ClO_4)$ 1095 cm^{-1}, ν(C=O) 1610 cm^{-1}.

nated acetone. Infrared spectra exhibit strong unsplit absorptions at 1365 cm^{-1}, $[Mn(salen)(Me_2CO)]NO_3$, and 1095 cm^{-1}, $[Mn(naphtm)(Me_2CO)]ClO_4$, assignable to uncoordinated anions. Moreover the conductivity measurements in dimethylformamide, Table I, fall within the range expected for 1:1 electrolytes [5]. The reflectance spectra of the two manganese-(III) complexes are similar, Table II (see also Fig. 1), and are different from the other higher oxidation state complexes reported here. The room temperature magnetic moments, 4.6–4.9 μ_B, are significantly lower than that expected for spin-only $3d^4$ complexes. This suggests considerable spin-pairing and in the solid state these complexes may be assigned a dimeric structure with bridging acetone ligands. This would be consistent with substantial shift in ν(C=O) on coordination of acetone in these complexes. Although Boucher and Coe [4] assign pentacoordinate structures to the $[Mn(SB)(H_2O)]^+$ complexes, strong evidence was gained from fast atom bombardment mass spectral data that these aquo complexes are aquo-bridged hexacoordinate dimers [2], in the solid state, although it is not possible to make such a definite assignment for the acetone complexes prepared here. It is probable that most complexes

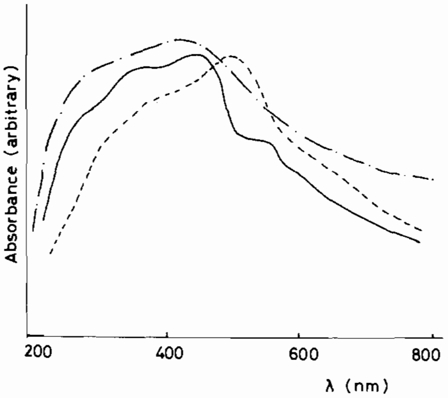

Fig. 1. Reflectance spectra of the high-valent manganese Schiff base complexes: ——— $[Mn(naphtm)(Me_2CO)]ClO_4\cdot H_2O$, ------ $[Mn_2(napthm)_2)(O)(OH)]\cdot H_2O$, –·–·– $[Mn(naphtm)(O)]_2\cdot H_2O$.

of type [Mn(SB)(solvent)]$^+$ are hexacoordinate dimers in the solid state.

We were particularly interested in seeing if the postulated [4, 5] mixed-valence dimers Mn^{III}/Mn^{IV} and the Mn^{IV}/Mn^{IV} dimers could be differentiated, since their methods of preparation are not too disimilar and colours and elemental analysis are similar.

Both sets of complexes are non-conducting in dimethylformamide. Their mull infrared spectra are almost similar, and differ from those of the [Mn(SB)(H_2O)]$^+$ complexes in that the intensity of the ν(Mn–O) band increases but that of ν(Mn–N) decreases in the higher-valent complexes. It is interesting to note, however, that the energies of the significant infrared bands, Table II, are remarkably close in all complexes, despite relative band intensity differences.

The electronic spectra do show a distinct difference between the Mn^{III}/Mn^{IV} and Mn^{IV}/Mn^{IV} dimers, the former having a band maximum of the broad absorption peak at 490 nm, whereas the latter absorb at 460 nm, Fig. 1. The mixed-valence manganese(III, IV), $S = (2, 3/2)$ and manganese(IV, IV) $S = (3/2, 3/2)$ Schiff base complexes exhibit magnetic moments at room temperature in the ranges 2.9–2.7 and 2.1–1.9 μ_B/Mn atom, respectively, in agreement with the values found for other such compounds [4, 7–15].

However, the most important evidence which illustrates the essential difference between mixed valence dimers, structure **III**, and the Mn(IV, IV) dimers, structure **IV**, is that the former give a broad ESR signal, g close to 2.2, Table I, both in the solid state and in chloroform at 93 K, whereas Mn(IV, IV) dimers are ESR-silent. A comparison might be made between these Schiff base complexes and the bipyridyl system of Calvin and co-workers [15] where a similar ESR distinction exists.

Experimental

Materials

The aldehydes and diamine were obtained from Aldrich Chemical Company. The ligands were prepared by the method of Diehl and Hach [16]. All other materials were Reagent Grade and used without further purification.

Complex Preparation

[Mn(SB)(Me$_2$CO)] Y (Y = NO$_3$, ClO$_4$)

The ligand (0.01 mol) was dissolved in a 3:1 mixture of acetone and ethanol (100 cm^3) and to this solution was added the manganese(II) hexahydrate salt (0.02 mol) in ethanol (25 cm^3). A dense yellow precipitate of the manganese(II) complex formed, and the mixture was stirred for 10 min. On the addition of sodium hydroxide solution (0.018 mol) the reaction mixture darkened rapidly and the stirring was continued for 5d with no attempt to exclude air or light. The dark solid which resulted was filtered, washed with dry ethanol (2 X 25 cm^3) and dried over $CaCl_2$ *in vacuo.*

[Mn$_2$(SB)$_2$(O)(OH)]·H$_2$O

The [Mn(SB)(H_2O)]ClO_4 complex [4] (0.001 mol) was dissolved in chloroform (500 cm^3) in a modified three-neck flask with a stopcock at the bottom. A pressure-equalising dropping funnel was charged with NaOH (0.001 mol in 20 cm^3) and hydrogen peroxide (0.45 cm^3 of 30 vol.% H_2O_2). Both solutions were saturated with dinitrogen and then the aqueous phase was added over a 20 min period. After the addition the flask was shaken vigorously and the chloroform phase became red–brown. This was separated and concentrated (25 cm^3). Addition of petroleum ether (300 cm^3, 40–60 °C) caused precipitation of the crude complex. After filtration this was recrystallised from chloroform/petroleum ether and dried *in vacuo.*

[Mn(SB)O]$_2$·H$_2$O

A solution [6] of [Mn(SB)(H_2O)]ClO_4 (0.004 mol) in chloroform (500 cm^3) was shaken with ten separate washes of aqueous NaOH (0.015 mol total) in air. The resulting red–brown chloroform solution was separated and dried over $CaCl_2$. After volume reduction (50 cm^3) the solid was precipitated by the addition of petroleum ether and dried *in vacuo.*

Physical Measurements

These are the same as previously described [6].

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