Manganese(III) Complexes with $Mn^{III}N_3O_3$ (S = 2) Co-ordination by Sexidentate Schiff-base Ligands: Synthesis, Spectra and Electrochemistry

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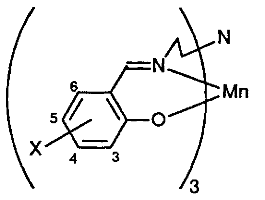
Complexes of high-spin manganese(III) (μ_{eff} = 4.79–5.30 at 298 K) with a closely related group of sexidentate Schiff-base ligands have been prepared and their solution properties thoroughly investigated. The brown to green crystalline complexes display ligand-to-metal charge-transfer transitions in the range 330–400 nm in addition to a crystal-field transition in the range 560–600 nm. The solution stereochemistry has been determined by paramagnetically shifted ^1H NMR spectroscopy. Unlike the C_3 symmetry in the solid-state structure, in solution the $Mn^{III}N_3O_3$ co-ordination sphere is severely distorted ($\approx C_1$ symmetry). Cyclic voltammetric studies in dimethylformamide solution reveal an irreversible Mn^{III}–Mn^{II} couple [E_{pc} in the range −0.62 to −0.05 V *vs.* saturated calomel electrode (SCE)] and a quasi-reversible Mn^{IV}–Mn^{III} couple (E_f in the range +0.42 to +0.86 V *vs.* SCE).

There has been intense recent interest in the chemistry of the higher oxidation states of manganese, because of their great importance in biological systems[1] and in catalytic oxidative processes.[2] As part of our investigations of complexes of manganese[3] we have undertaken a programme to reveal the properties of manganese complexes in the +3 oxidation state with sexidentate Schiff-base ligands formed by the condensation of tris(2-aminoethyl)amine with salicylaldehydes. As the substituents on these ligands can be varied prior to complexation we thus have an opportunity to modify or tune the properties and reactivity of these complexes while still retaining the same metal ion in a given oxidation state and in the same co-ordination environment. It is interesting that the three-dimensional X-ray structure of {tris[2-(5′-chloro-2′-hydroxybenzylidene)ethyl]aminato)(3 −)} manganese(III) has been reported[4] and it provides an unique example of a manganese(III) compound with C_3 symmetry. Our endeavour in this system is set in this background. We report here the solution structure, as revealed by paramagnetically shifted ligand-proton resonances, and electrochemical studies to reveal the accessibility of the +4 oxidation state of manganese using Schiff-base ligands H_3L^1–H_3L^6.

Experimental

Chemicals and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Ethanol was distilled from magnesium ethoxide, acetonitrile from calcium hydride. Chloroform was dried over fused calcium chloride before a final reflux and distillation. Diethyl ether was dried first with fused calcium chloride and then refluxed with and stored over sodium. Dimethylformamide (dmf) was purified as described previously.[3] Tetrabutylammonium perchlorate was prepared as before.[3] Substituted salicylaldehydes were obtained from the appropriate phenols by the Duff reaction.[5] The salt $[NBu_4][MnO_4]$ was prepared as described.[6]

Ligand Syntheses.—Tris[2-(2′-hydroxybenzylidene)ethyl]amine (H_3L^1) and its substituted derivatives H_3L^2–H_3L^6 were prepared by published procedures,[7] whereby tris(2-aminoethyl)amine was treated with the stoichiometric amount of salicylaldehyde or the appropriately substituted derivative, in hot ethanol. The crude solids were recrystallized from chloroform to afford yellow crystalline products shown to be pure by their ^1H NMR spectra.



X	Complex
H	$[MnL^1]$
3-Me	$[MnL^2]$
4-Me	$[MnL^3]$
5-Me	$[MnL^4]$
3,4-Me_2	$[MnL^5]$
3,5-Cl_2	$[MnL^6]$

Syntheses of Complexes.—The complexes were prepared by two general procedures. Details are therefore given for two representative complexes.

$[MnL^3]$. To a solution of H_3L^3 (110 mg, 0.22 mmol) in hot ethanol (20 cm^3) was added solid $Mn(O_2CMe)_2 \cdot 4H_2O$ (54 mg, 0.22 mmol). The mixture was stirred at 330 K for 15 min. Then $[NBu_4][MnO_4]$ (27 mg, 0.075 mmol) was added portionwise to oxidize the yellow manganese(II) compound thus formed to green-brown manganese(III). The mixture was stirred for 30 min, followed by solvent evaporation. The brown mass thus obtained was dissolved in hot acetonitrile (5 cm^3) and filtered through a G-4 frit. The filtrate was treated with diethyl ether (*ca.* 5 cm^3) and kept in a refrigerator. The precipitated brown microcrystalline complex was filtered off, washed with a small amount of acetonitrile–diethyl ether (1:3 v/v) and dried *in vacuo* (0.096 g, 78%). In the case of $[MnL^1]$ the brown mass was dissolved in chloroform instead of acetonitrile and a similar method was followed. The complexes $[MnL^2]$ and $[MnL^4]$ were synthesised by using similar procedures.

$[MnL^6]$. A hot ethanolic (20 cm^3) solution of H_3L^6 (146.3 mg, 0.22 mmol) was treated with $Mn(O_2CMe)_2 \cdot 4H_2O$ (54 mg, 0.22 mmol) and the solution was stirred at 330 K for 15 min. To that $[NBu_4][MnO_4]$ (27 mg, 0.075 mmol) was added portionwise to give a deep green solution. The stirring was

Table 1 Microanalytical, molar conductance and magnetic moment data for the manganese(III) complexes

Complex	Analysis[a] (%) C	H	N	$\Lambda_M{}^b/\Omega^{-1}$ cm^2 mol^{-1}	$\mu_{eff}{}^c$
[MnL^1]	63.10	5.70	11.20	6	4.79
	(63.55)	(5.30)	(11.00)		
[MnL^2]	65.00	6.15	10.50	7	5.30
	(65.20)	(5.95)	(10.15)		
[MnL^3]	64.90	6.10	10.45	7	4.87
	(65.20)	(5.95)	(10.15)		
[MnL^4]	65.10	6.25	10.30	7	5.13
	(65.20)	(5.97)	(10.15)		
[MnL^5]	66.15	6.85	10.15	6	5.23
	(66.65)	(6.55)	(9.40)		
[MnL^6]	44.80	3.05	8.35	7	4.79
	(45.20)	(2.90)	(7.80)		

[a] Calculated values in parentheses. [b] In dimethylformamide. [c] Measured in dmf solution using the Evans method.[8]

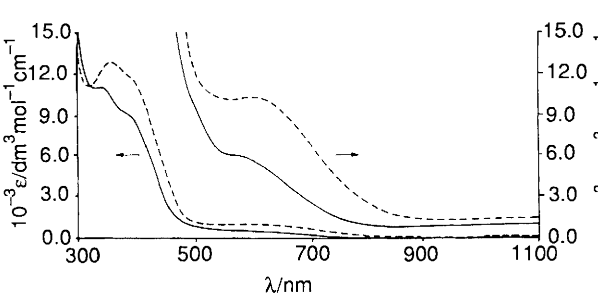


Fig. 1 Absorption spectra of [MnL^3] (——) and [MnL^6] (- - -) in dimethylformamide

continued for 30 min and the solvent reduced in volume *in vacuo*. The resulting greenish brown solid was dissolved in dimethylformamide (5 cm^3) and was filtered through a G-4 frit. The filtrate was set aside to evaporate slowly at room temperature. The highly crystalline green solid which formed was filtered off and dried in the air. Recrystallization from dimethylformamide afforded the complex in good yield and purity (0.114 g, 72%). The complex [MnL^5] was prepared similarly.

Measurements.—A Perkin-Elmer Lambda-2 spectrophotometer was used to obtain the electronic spectral data. The ^{1}H NMR spectra were obtained on either a PMX-60 JEOL (60 MHz) or a Brüker WM-400 (400 MHz) spectrometer using CDCl$_3$ solutions. The 400 MHz NMR spectra were obtained by Analytical Facilities, Regional Sophisticated Instrumentation Centre, Lucknow, India. Chemical shifts are reported as positive values downfield from SiMe$_4$ as internal standard. Conductivity measurements were made on dmf solutions with an Elico type CM-82 T conductivity bridge (Hyderabad, India) with solute concentrations of *ca*. 10^{-3} mol dm^{-3}. The electrochemical data were obtained by using a PAR model 370-4 electrochemistry system: 174A polarographic analyser, 175 universal programmer and RE 0074 *x-y* recorder. Potentials are reported at 298 K referenced to a saturated calomel electrode (SCE) and are uncorrected for junction potentials. All experiments were done under a dinitrogen atmosphere. The solutions were *ca*. 1.00 × 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in supporting electrolyte, [NBu$_4$][ClO$_4$]. A PAR G0021 glassy carbon electrode was used as the working electrode in cyclic voltammetric experiments. The system was calibrated as before.[3] With the same electrode assembly in dmf solution and at a scan rate of 50 mV s^{-1} the values of the formal potentials (E_f) and the peak-to-peak separation (ΔE_p) for ferrocene, [Fe(η-C$_5$H$_5$)$_2$], were 0.50 V and 80 mV respectively. The magnetic susceptibility measurements were made by the NMR method;[8] the susceptibility of dmf[9a] and diamagnetic corrections[9b] were taken from the literature.

Results and Discussion

Syntheses and Absorption Spectra.—The manganese(III) complexes characterized in this work are set out in Table 1. The complexes [MnL^1] and [MnL^4] were synthesised[10] previously following air oxidation of manganese(II) complexes. We also tried air oxidation of the reaction mixtures and also used manganese(III) as starting reagent in the preparation of the manganese(III) complexes with all the ligands H$_3$L^1–H$_3$L^6. However, we could not isolate any analytically pure crystalline complex following the reported procedure.[10] For obvious reasons we looked for a clean oxidizing agent. The versatility of [NBu$_4$][MnO$_4$] has been reported[11] and hence in this work it has been used as the oxidizing agent. The complexes were prepared readily as highly crystalline brown to green solids and are soluble in reasonable concentrations only in dmf and dissolve moderately in chloroform and dimethyl sulphoxide. The solution studies were performed in chloroform and dmf. Conductivity measurements (in dmf solution) show the compounds to be non-conducting. The magnetic moments (in dmf solution) determined by the NMR method[8] give values of μ_{eff} in the range 4.79–5.30 (Table 1) consistent with the presence of monomeric high-spin d^4 (S = 2) manganese(III) systems and in excellent agreement with the reported solution-state value (5.05) for the tris[2-(5′-chloro-2′-hydroxybenzylidene)ethyl]amine derivative.[10]

The absorption spectral results (300–1100 nm) for the complexes in dmf solution are in Table 2 and Fig. 1. Two allowed bands occur in the 330–400 nm region. These are assigned as L→Mn charge-transfer transitions as in the case of other manganese(III)–salicylaldimine complexes.[12] The absorptions in the visible region at 560–600 nm are observed as shoulders and are assigned as ^{5}E ⟶ ^{5}T$_2$ transitions[13] (octahedral notation or its components in lower symmetry group). The tail of a broad feature as seen in the near-infrared region at *ca*. 1100 nm (Fig. 1) as well as in the work of Cook *et al.*[10] is also observed for other manganese(III) six-co-ordinate complexes.[13] Our results on complexes [MnL^1] and [MnL^4] are in excellent agreement with that already reported.[10] The spectral behaviour of the complexes in chloroform solution was very similar to that in dmf.

In view of the high-spin d^4 configuration in these complexes, the absorption spectra are expected to experience strong Jahn–Teller distortions.[14] The low symmetry in chloroform solution of these complexes (see below) could cause distortions beyond those due to Jahn–Teller effects and is expected to increase the multiplicity of bands. This has not been revealed in the absorption spectra.

Solution Stereochemistry.—As we did not succeed in throwing light on the symmetry of these complexes from absorption spectral studies, ^{1}H NMR spectroscopy was utilized for a better understanding of the chelate-ring dispositions around the metal centre.

The high-spin d^4 configuration is predicted to give observable NMR signals,[15] and indeed such signals are seen in the ^{1}H NMR spectra of the present complexes. A representative spectrum is shown in Fig. 2. As expected, the spectra are relatively broad and are shifted considerably from the usual diamagnetic region.[16]

The signal assignments for the complexes are provided (Table 2) by a combination of the expected behaviour for paramagnetically shifted resonances and integrated area ratios. The results reveal that, except for occasional degeneracies in shifts and instances where excessive signal broadening prohibits complete resolution, three signals of equal intensity for each substituent are observed. The present investigation demon-

Table 2 Spectroscopic data for manganese(III) complexes

Complex	Electronic spectral data[a] λ/nm (ε/dm^3 mol^{-1} cm^{-1})			^{1}H NMR shift[b] (δ)			
				H^3	H^4	H^5	H^6
[MnL^1]	568 (sh)	368 (sh)	343	+2.80	+1.67[c]	−11.54	+6.95
	(595)	(9 900)	(10 600)	+3.47	+7.47	+1.33	+9.86
				+3.75[d]	+9.06	+1.67[c]	+11.00
[MnL^2]	582 (sh)	385 (sh)	330	+1.00	+0.39	−23.24	+3.31
	(1 060)	(9 200)	(10 900)	+1.60	+6.08	−14.55	+9.92
				+2.30	+9.31	−4.79	+11.31
[MnL^3]	569 (sh)	381 (sh)	336	+3.48	+9.66[e]	−11.66	+6.82
	(600)	(9 100)	(11 000)	+4.00		−1.55	+8.99
				+4.38		+2.33	+13.33
[MnL^4]	598 (sh)	391 (sh)	350	+3.40[f]	+1.55	+1.00	+6.92
	(720)	(9 200)	(11 000)		+7.35	+1.23	+9.89
					. . .[g]	+2.32	+10.88
[MnL^5]	587 (sh)	387 (sh)	331 (sh)	+2.00	+14.78(2)[h]	−22.40	+6.76
	(778)	(7 950)	(11 000)	+2.23	+20.07	−11.39	+9.80
					. . .[g]	−6.00[i]	+11.31
[MnL^6]	599	386 (sh)	356	—	—	—	—
	(1025)	(11 800)	(12 800)				

[a] Solvent is dimethylformamide. [b] Solvent is $CDCl_3$. NCH_2CH_2 resonances: [MnL^1], δ −3.75, +13.50, +22.37 (vbr); [MnL^2], +13.50, +16.25; [MnL^3], +1.88, +18.76, +20.89; [MnL^4], −3.50; [MnL^5], −6.00. Azomethine proton: [MnL^1], δ +45.12; [MnL^2], +62.50; [MnL^3], +46.00; [MnL^4], could not be located; [MnL^5], +51.00. [c] Overlaps. [d] Appears as a shoulder. [e] Only one signal is observed. [f] A broad feature. [g] All three signals could not be located. [h] Signals occur with 2:1 intensity ratio. [i] Overlaps with NCH_2CH_2 resonance.

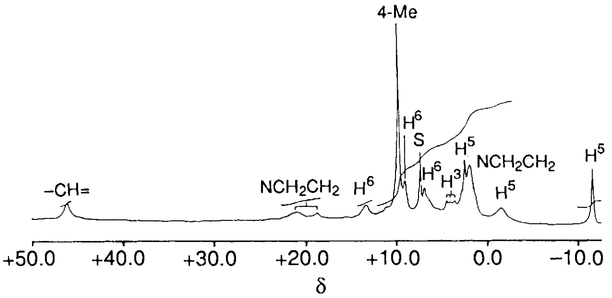


Fig. 2 Proton NMR spectrum (400 MHz) of [MnL^3] in $CDCl_3$ at *ca.* 298 K (solvent peak is marked by S)

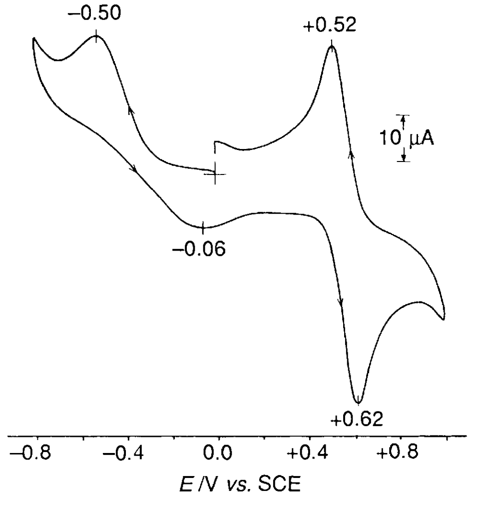


Fig. 3 Cyclic voltammogram of [MnL^1] (1.0×10^{-3} mol dm^{-3}) in dimethylformamide (0.2 mol dm^{-3} [NBu_4][ClO_4]) at a glassy carbon electrode; scan rate 50 mV s^{-1}

Table 3 Cyclic voltammetric data[a] at 298 K

Complex	Mn^{III}–Mn^{II} couple	Mn^{IV}–Mn^{III} couple	
	E_{pc}/V	E_f/V	ΔE_p/mV
[MnL^1]	−0.50	0.57	100
[MnL^2]	−0.52	0.48	80
[MnL^3]	−0.51	0.51	100
[MnL^4]	−0.52	0.52	70
[MnL^5]	−0.62	0.42	90
[MnL^6]	−0.05 (110)[b]	0.86	80

[a] Glassy carbon electrode; the supporting electrolyte is [NBu_4][ClO_4]; all potentials are referenced to the SCE. $E_f = 0.5\ (E_{pc} + E_{pa})$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively; $v = 50$ mV s^{-1}. [b] The couple is quasi-reversible.

strates conclusively that in solution the symmetry of the complexes is very low ($\approx C_1$). Besides distortions caused by Jahn–Teller forces expected for a d^4 high-spin grossly octahedral situation, those due to spatial dispositions of ligand chelate rings (stereochemical distortions) are also possible. In the present complexes both are expected to be operative. It is worth mentioning here that in the solid-state structure[4] of the tris[2-(5′-chloro-2′-hydroxybenzylidene)ethyl]amine derivative an octahedral arrangement of the ligand (N_3O_3) atoms about the metal was observed and there was no indication of heptadentate behaviour. The overall molecular symmetry was C_3. Additionally, it is to be noted that the diamagnetic, water-soluble complex {tris[2-(2′-hydroxy-5′-sulphonatobenzylidene)ethyl]amine}indate(3−) is rigid on the NMR time-scale at ambient temperature.[17] However, the situation is very different for paramagnetic systems like the present one and the vanadium(III) complexes[18] of these ligands.

Electrochemistry.—In order to understand the role of manganese in biological electron-transfer reactions, studies on synthetic manganese complexes with various organic ligands affording various donor atom types would be of paramount importance. From this standpoint the redox chemistry of [Mn^{III}L] complexes in dmf has been studied by cyclic voltammetry.

Manganese(III)–*manganese*(II) *couple.* A typical cyclic voltammogram is shown in Fig. 3. An initial cathodic scan of each complex exhibits a one-electron reduction wave corresponding to the reduction of manganese(III) to manganese(II). This redox couple is irreversible due to the lability of the reduced manganese(II) form. The cathodic peak potentials (E_{pc}) are summarized in Table 3. The voltammograms are generally similar in all cases (Fig. 3, Table 3). The manganese(III)–manganese(II) reduction potentials (V *vs.* SCE) are known for four other groups of mononuclear $Mn^{III}N_3O_3$ complexes. They include tris(pyridino-2-carboxylato)manganese(III) (+0.36 V),[19] tris(quinolin-8-olato)manganese(III) (−0.30 V),[19] [Mn(tcta)] (tcta = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate) (+0.56 V),[20] and a hexadentate ligand system tacn [1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane] (−0.82 V).[21] Barring the case of [MnL^6], the potentials observed here are fairly negative suggesting a better stabilization of the manganese(III) state by the present hexadentate ligand system. We note further that the pendant phenol arm tacn derivative[21] exhibits the most negative formal potential.

Within the present group of complexes, the E_{pc} values of the Mn^{III}–Mn^{II} couple are sensitive to X. The values decrease with increasing electron-releasing power of the substituents (Table 3).

Manganese(IV)–*manganese*(III) *couple.* Interestingly, an anodic scan exhibits a quasi-reversible oxidative response (Fig. 3, Table 3). Here also the voltammograms are generally similar in all cases. The formal potentials were calculated from the average of the peak potentials for the oxidation and reduction waves and are recorded in Table 3. The oxidative responses observed are assignable as manganese(III) ⟶ manganese(IV) oxidation. This seems quite reasonable since the accessibility of the +4 oxidation state of manganese is well documented for other Schiff-base systems.[22] We observe that, unlike the reduction case, the oxidative response is quasi-reversible in nature. On the cyclic voltammetric time-scale, as the metal is oxidized to the +4 state the electron distribution becomes such that the three d electrons are now in the d_{xy}, d_{xz} and d_{yz} orbitals. This would render the complex kinetically inert and hence the observed effect.

The Mn^{IV}–Mn^{III} formal potentials (V *vs.* SCE) for other systems having MnN_3O_3 co-ordination spheres are: tris(pyridine-2-carboxylato)manganese(III) (1.35),[19] tris(quinolin-8-olato)manganese(III) (0.73)[19] and 1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (−0.29).[21] Barring the case for the hexadentate ligand system [MnL^6], the complexes are easily oxidizable.

Here also the E_f values of the Mn^{IV}–Mn^{III} couple depend on X. The values increase with increasing electron-withdrawing power of the substituents.

Conclusion

Our goal of exploring the solution properties of the complexes has been achieved. Unlike the C_3 symmetry present in the solid-state structure of the tris[2-(5′-chloro-2′-hydroxybenzylideneene)ethyl]amine derivative, in solution the molecular symmetry is very low for the present group of complexes, $\approx C_1$. Obviously, the metal co-ordination environment is very much distorted from a perfect octahedral situation. This is revealed by the paramagnetically shifted ^1H NMR resonances. The complexes display an irreversible Mn^{III}–Mn^{II} couple in dmf solution. The accessibility of an additional reversible Mn^{IV}–Mn^{III} couple reveals that the cage-like structure of these hexadentate ligands is ideally suited for stabilizing manganese in a higher oxidation state. Both the redox couples display a systematic shift in formal potential under the influence of substituent X. Interestingly, the formal potentials for the above redox couples can be modulated by *ca.* 400 mV. We have also been able to develop a rich vanadium chemistry using these ligands and this will be reported elsewhere.

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