MANGANESE (III) COMPLEXES OF 1, 8-BIS (SALICY-LIDENEAMINO)-3,6-DIIMINOCTANE

B. C. SHARMA AND C. C. PATEL

(Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012)

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ABSTRACT

Manganese (III) complexes of bivalent hexadentate Schiff base, triethylene-tetramine-bissalicylaldehyde, trien-sal, having the composition [Mn (trien-sal)] X, (where X = ClO_4^-, NO_3^-, NCS^-, Br^- or I^-) have been prepared and their physico-chemical properties studied. The molar conductances of the complexes show that they are 1:1 electrolytes in acetone, indicating the non-coordinated nature of the anions. Their normal magnetic moments of about 4·85 B.M. show them to be spin-free type with four unpaired electrons. Their infrared spectra show that the secondary amino groups of the ligand also coordinate to the metal ion, making the ligand hexacoordinating. It is suggested that the complexes have tetragonally distorted octahedral structure. The electronic spectra of the complexes agree with this assignment.

Key words: Manganese (III), Hexadentate Schiff base, Triethylenetetramine-bissalicyl-aldehyde, trien-sal, octahedral structure.

The Schiff base, 1, 8-bis (salicylideneamino)-3, 6-diiminoctane [triethylenetetramine-bissalicylaldehyde, trien-sal, (I)] formed by the condensation of one molecule of triethylenetetramine with two molecules of salicylaldehyde is expected to behave as a bivalent hexadentate ligand. Thus it should be possible to prepare complexes with bivalent and trivalent metal ions, where a single ligand can occupy all the six positions in the coordination sphere.
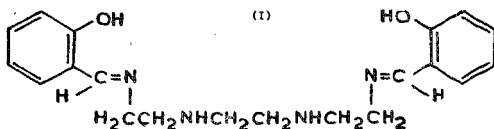
(I)

Calvin *et al.* [1] have found that for a series of salicylaldimine complexes, increase in the number of chelate rings results in greater stability for the complex. Complexes with the present ligand will have five chelate rings and thus these are expected to be of very high stability, useful especially for the stabilization of comparatively unstable oxidation states like Mn (III). In continuation of our work [2–4] on manganese (III) complexes of bidentate and tetradentate schiff bases, we report here the preparation and physicochemical studies on the complexes of a hexadentate schiff base of the type [Mn (trien-sal)] X (X = ClO_4^-, NCS$^-$, NO_3^-, Br$^-$ or I$^-$). Bailar *et al.* [5] have reported the preparation of [Mn(trien-sal)]I·H_2O.

MATERIALS AND METHODS

Triethylenetetramine, salicylaldehyde, lithium carbonate, potassium iodide and potassium thiocyanate were B.D.H. reagents of A. R. grade and were used as such. Triethylenetetramine-trissalicylaldehyde was prepared by the method of Sarma *et al.* [6]. Manganese (III) acetate dihydrate was prepared by the method of Christensen [7]. Lithium perchlorate, bromide and nitrate were prepared by dissolving lithium carbonate in perchloric, hydrobromic and nitric acids respectively and crystallising the salts from their aqueous solutions.

Preparation of the complexes

All the complexes were prepared by the same general method. Manganese (III) acetate dihydrate ($\sim 0·01$ mole) and triethylenetetramine-trissalicylaldehyde ($\sim 0·01$ mole) were refluxed in 50 ml methyl alcohol for 10 minutes on a water-bath, 0·01 mole of lithium salt, LiX (X = ClO_4^-, NO_3^-, or Br$^-$), was added and the contents were further refluxed for 3 hours. In the case of the iodide and the thiocyanate complexes, calculated amounts ($\sim 0·01$ mole) of potassium iodide and potassium thiocyanate respectively, were added instead of the lithium salt. The solution was filtered and allowed to stand overnight when a crystalline product was obtained. The mother liquor was decanted off and the crystals were washed first with benzene followed by a 1:1 mixture of acetone and water. The complexes were recrystallised from methyl alcohol and dried in vacuum over concentrated H_2SO_4. Attempts to prepare the corresponding chloride complex were not successful.

Analyses

Manganese in the complexes was estimated iodometrically by dissolving the complexes in water and proceeding as described earlier [2–4], Per-

chlorate was analysed by Kurz's method [8] by reducing it to chloride and determining the latter by Volhard's method. Halides and thiocyanate were estimated by Volhard's method. Nitrogen was estimated by Kjeldahl's semimicro method. In the case of the nitrate complex, carbon, hydrogen and nitrogen were estimated by microanalytical methods. The analytical data are given in Table I.

Physicochemical studies

Molar conductance studies of the complexes in acetone were carried out using a Siemen's conductivity bridge with platinized platinum electrodes. The magnetic susceptibility measurements were carried out at room temperature with a Gouy apparatus using mercury (II) tetrathiocyanatocobaltate (II) as the calibrant. The electronic spectra of the complexes were recorded in methanol on a Unicam recording spectrophotometer model—SP 700 A. The infrared spectra of the complexes were recorded on a Carl-Zeiss UR–10 double beam spectrophotometer provided with LiF, NaCl and KBr prisms.

RESULTS AND DISCUSSION

Condensation of salicylaldehyde with triethylenetetramine does not give triethylenetetramine-bissalicylaldehyde (I), the ligand under study, but instead an additional salicylaldehyde molecule reacts with the two hydrogens on the secondary amino groups to give triethylenetetramine-trissalicylaldehyde (II)[6]. This is similar to the behaviour of ammonia [9] which on reaction with salicylaldehyde does not give the product, salicylaldimine. Instead, the reaction proceeds further and hydrosalicylamide is obtained by the condensation of an additional molecule of salicylaldehyde with two hydrogens on two different salicylaldimine molecules.

However, when manganese (III) acetate dihydrate and triethylenetetramine-trissalicylaldehyde are reacted in equimolar ratio, the additional salicylaldehyde molecule splits off leaving triethylenetetramine-bissalicylaldehyde, (I), coordinated to manganese (III). Examination of the models by Sarma *et al.* [6] has shown that when secondary nitrogens coordinate to a metal ion salicylaldehyde across them splits off.

The molar conductances of the complexes in acetone (Table I) are in the range 105–135 ohm^{-1} cm^2 mole^{-1}. The molar conductance[10] values for 1:1 and 1:2 electrolytes in acetone are expected in the range 120–140 and 180–240 ohm^{-1} cm^2 mole^{-1} respectively. Thus the present complexes behave as 1:1 electrolytes, showing that the anions are not coordinated to

TABLE I

Analytical data, magnetic moments and conductance values of the manganese (III) complexes

Temp. for measurements = $300 \pm 4°$ K

| Complex	Analytical data						Molar conductance (Ohm^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
	Mn (%)		Anion (%)		N (%)			
	Calcd.	Found	Calcd.	Found	Calcd.	Found		
[Mn (trien-sal)] ClO$_4$	10·84	10·99	19·62	19·20	11·04	11·28	131·7	4·86
[Mn (trien-sal)] NCS	11·82	12·01	12·47	12·19	15·05	14·96	128·0	4·88
[Mn (trien-sal)] NO$_3$*	11·68	11·64	..	..	14·92	15·48	135·2	4·87
[Mn (trien-sal)] Br	11·25	11·14	16·43	16·20	11·50	11·67	105·1	4·88
[Mn (trien-sal)] I	10·24	10·53	23·60	24·15	10·48	10·76	127·6	4·83

* Satisfactory C, H analyses were also obtained.

TABLE II

Some infrared spectral bands (in mull) of manganese (III) complexes with their probable assignments

Complex	$\gamma_{C=N}$	$\gamma_{C=C}$	$\gamma_{C=O}$	$\gamma_{C=N}$	γ_{NH}
[Mn (trien-sal)] ClO$_4$	1620	1545	1312	1208	3255, 3320
[Mn (trien-sal)] NCS	1630	1545	1312	1210	3115, 3295
[Mn (trien-sal)] NO$_3$	1625	1545	1315	1208	3160, 3220 3470, 3550
[Mn (trien-sal)] Br	1625	1545	1310	1208	3105, 3288 3420, 3495
[Mn (trien-sal)] I	1625	1545	1310	1208	3320, 3430 3480, 3585

the metal ion. From the analytical and conductance data, the present complexes can be represented as [Mn (trien-sal)] X.

(I)

(II)
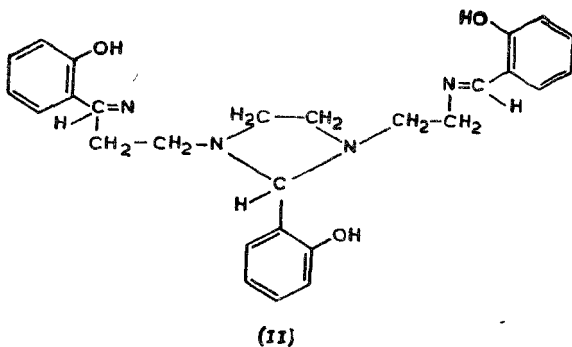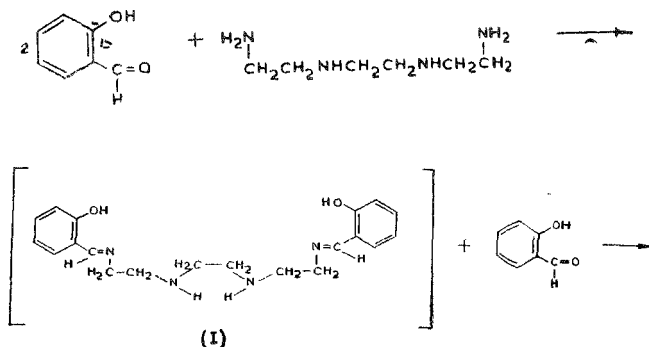
The magnetic moment values of the complexes (Table I) are very close to the value expected for a high-spin complex with four unpaired electrons. These normal values also indicate the absence of any intermolecular interactions.
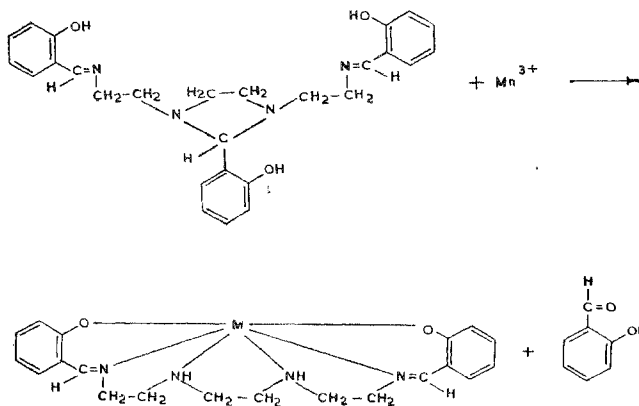
Infrared spectra

While triethylenetetramine-trissalicylaldehyde (II) shows no bands in the region 3100–3600 cm⁻¹, all the complexes show multiple peaks in this region (Table II). These peaks which are comparatively sharp can be assigned to NH in the absence of any water molecule as shown by the analytical data. The appearance of NH shows that one salicylaldehyde molecule has split off from (II) on complex formation leaving (I) coordinated to manganese (III). The explanation of the multiple peaks may be that the coordination of secondary nitrogen atoms to the metal drains off electrons from these atoms and some effect similar to the formation of amine salts is responsible for the appearance of these peaks. Amine salts are known to give a number of sharp peaks in the NH stretching region [11] where the extra peaks have been assigned to combination bands [11–12] whose intenstities have been increased due to the anharmonicity of N–H vibration in structures like $N^+—H\cdots X^-$.

Strong bands appearin garound 1625, 1545 and 1310 cm⁻¹ may be assigned to $\gamma_{C=N}$, $\gamma_{C=C}$ and γ_{C-C} respectively. A set of bands occurring in the region 1100–1200 cm⁻¹ may be due to $\gamma_{C\ N}$. These assignments are in agreement with those of previous workers [5, 6].

As shown by the conductivity data, none of the anions is coordinated to the metal ion. This is further confirmed by the IR spectra of the complexes. In the perchlorate complex, a strong band (γ_3) occurs at 1080–1130 cm^{-1} and another (γ_4) at 622 cm^{-1}. The positions and non-splitting nature of these bands show that perchlorate in the complex retains its Td symmetry and consequently its ionic nautre [13, 14].

In the non-coordinated nitrate ion, the γ_2, γ_3 and γ_4 modes are expected around 830, 1390 and 720 cm^{-1} respectively [15]. Coordination is expected to split the γ_3 and γ_4 modes. In the [Mn (trien-sal)] NO$_3$ complex, two unsplit bands occurring at 1360 and 830 cm^{-1} can be assigned to γ_3 and γ_2 modes respectively, suggesting non-coordinated nature of the nitrate ion in the complex. In the thiocyanate complex, a strong band at 2065 cm^{-1} due to $\gamma_{C\equiv N}$ and a band at 765 cm^{-1} due to γ_{C-S} suggest that thiocyanate [14] is not coordinated to the metal ion.

Electronic spectra and structure of the complexes

The electronic spectral bands of the complexes along with their values and assignments are given in Table III. A very strong band occurs in all the complexes at 25,000 cm^{-1} ($\epsilon \approx 5 \cdot 5 \times 10^3$ mole litre^{-1} cm^{-1}). This band appears to be of charge-transfer origin from ligand to the metal $(\pi \rightarrow t_2)^{16}$ because of its high intensity. For an octahedral manganese (III) complex, only one d-d band ($5_{Eg} \rightarrow 5_{T2g}$) should be expected. However, in the present complexes, three different bands are observed around 20000, 17500 and 9000 cm^{-1} respectively. The bands around 20,000 and 17500 cm^{-1} are broad shoulders, the first occurring on the side of the steeply rising charge transfer band. The third band around 9000 cm^{-1} is also very broad. The observance of multiple bands and their broad nature indicates that the symmetry of the complexes has been lowered from octahedral to tetragonal which can explain the appearance of these three bands. In the case of axially elongated tetragonal distortion these bands can be assgined to $5_{B1} \rightarrow 5_E$, $5_{B1} \rightarrow 5_{B2}$ and $5_{B1} \rightarrow 5_{A1}$ transitions respectively in terms of the energy level diagram given on p. 222.

The expected octahedral geometry of the complexes of manganese (III) with d^4 electronic configuration is susceptible to tetragonal distortion due to Jahn-Teller effect. But because of the chelating nature of the hexadentate ligand and the donor atom inequivalence, the Jahn-Teller effect alone need not be invoked to explain the tetragonal splitting. The large splitting observed (of the order of 10,000 cm^{-1}) cannot be explained
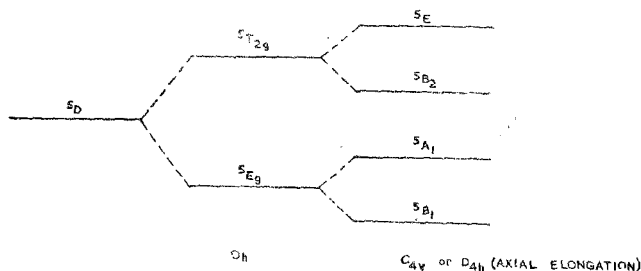
TABLE III

Electronic spectral data (cm^{-1}) of manganese (III) complexes with probable assignments

Complex	Charge transfer	d-d transitions		
	$\pi \to t_2$	$5_{B1} \to 5_E$	$5_{E1} \to 5_{B2}$	$5_{B1} \to 5_{A1}$
[Mn (trien-sal)] ClO$_4$	25,640 ($4 \cdot 69 \times 10^3$)*	20,400 (sh) ($\sim 6 \cdot 8 \times 10^2$)	17,850 (sh) ($\sim 1 \cdot 9 \times 10^2$)	9,090 (b) ($1 \cdot 09 \times 10^2$)
[Mn (trien-sal)] NCS	25,640 ($5 \cdot 16 \times 10^3$)	19,600 (sh) ($\sim 5 \cdot 6 \times 10^2$)	17,540 (sh) ($\sim 1 \cdot 8 \times 10^2$)	9,090 (b) ($1 \cdot 25 \times 10^2$)
[Mn (trien-sal)] NO$_3$	25,640 ($5 \cdot 55 \times 10^3$)	19,600 (sh) ($6 \cdot 2 \times 10^2$)	17,540 (sh) ($\sim 2 \cdot 5 \times 10^2$)	9,090 (b) ($1 \cdot 20 \times 10^2$)
[Mn (trien-sal)] Br	25,640 ($4 \cdot 52 \times 10^3$)	20,400 (sh) ($\sim 7 \cdot 3 \times 10^2$)	17,540 (sh) ($\sim 1 \cdot 8 \times 10^2$)	9,090 (b) ($1 \cdot 26 \times 10^2$)
[Mn (trien-sal)] I	25,640 ($5 \cdot 76 \times 10^3$)	19,600 (sh) ($\sim 6 \cdot 6 \times 10^2$)	17,540 (sh) ($\sim 2 \cdot 5 \times 10^2$)	9,090 (b) ($1 \cdot 17 \times 10^2$)

* ε values in the parentheses.

by other phenomena such as the solvent interaction or spin-orbit coupling. An electronic level splitting of the order obtained can occur, only if sizable effective distortion of the nuclear geometry from a regular octahedron around

central metal ion occurs. Recently, Davis *et al.* [17] have explained the electronic spectra of many manganese (III) complexes involving chelating ligands, especially the nature of low energy band, on the basis of Jahn-Teller distrotion. In general, the electronic spectra of the present complexes are similar to those observed by Davis *et al.* for manganese (III) complexes involving chelating ligands. The D_q value of about 1750–1800 cm^{-1} in the present complexes are quite comparable to the values of 1790 and 1587 cm^{-1} for Mn (acac)$_3$ and Mn (tropolone)$_3$ respectively [17]j The distortion in the hexadentate ligand complexes of manganese (III) may be due to the cumulative effect of the inequivalent donor atoms of the ligand, its chelate, bonding and the Jahn Teller distortion due to the electronic distribution in manganese (III) *d*-orbitals.

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