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Acetato-N, N'-Ethylenebis (5-bromosalicylideneiminato)-manganese(III)

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RECENTLY some Schiff bases with more than one coordinating centres have been used to stabilize Mn(III) ion as the metal chelates.¹⁻¹² We have isolated a Mn(III) complex of the dibasic quadridentate Schiff base derived from 5-bromo-salicylaldehyde and ethylene-diamine (BRSALEN-H₂), the preparation and properties of which are described here.

Experimental

Manganese (III) acetate dihydrate was prepared as described previously.⁽¹⁰⁾ The Schiff base, BRSALEN-H₂, was prepared by warming 5-bromo-salicylaldehyde and ethylenediamine in methanol on water bath. The yellow coloured Schiff base recrystallised from methanol melted at 189°-192° (lit.¹³ m.p. 192-194°). All other solvents and chemicals were purified as described previously.¹⁰ The molar conductance, electronic spectra, infrared spectra, and magnetic susceptibility were measured and elemental analyses were performed as described previously.¹⁴

Preparation of the Mn (III)-Schiff base complex : An equimolar mixture of the Schiff base (4.26 g, 0.01 mole) and manganese (III) acetate dihydrate (2.68 g, 0.01 mole) in methanol (~ 200 ml) was refluxed (1 hr). The resulting solution was filtered and concentrated by passing air through it whereby the dark brown separated out. The complex was filtered off, washed with cold benzene and dried in avacuum desiccator over P₂O₅. (Found : Mn, 10.29 ; N, 5.20% ; calc. for [Mn(BRSALEN)(CH₃COO)] : Mn, 10.21 ; N, 5.21%). $\Lambda_M = 2.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ (conc. $6.58 \times 10^{-4} M$ in acetonitrile), $\mu_{\text{eff}} = 4.92 \text{ B.M.}$ (31°C) ; ν_{max} at 24, 150 cm⁻¹ (log $\epsilon \approx 3.5$) and at 20, 490 cm⁻¹ (log $\epsilon \approx 3.0$) (in acetonitrile) ; I. R. spectral data are discussed in results and discussion.

Results and Discussion

Elemental analyses of the compound correspond to the formula [Mn(BRSALEN)(CH₃COO)] (where, BRSALEN-H₂ = a molecule of the dibasic quadridentate Schiff base) and its paramagnetic moment of 4.92 B. M. is close to the spin-only value for high spin d⁴ system. It is moderately soluble in methanol and acetonitrile and is practically nonconducting in acetonitrile. The molar conductance value supports the coordination of acetate ion, which is further substantiated by infrared spectral data. The medium intensity bands observed at 1600 and 1351 cm⁻¹ are due to the asymmetric and symmetric COO⁻ stretching frequency respectively in the complex. The difference of 249 cm⁻¹ between the two bands and their positions indicate monodentate nature of the acetate group.¹⁵ The C=N and phenolic C-O stretching frequencies in the free ligand are observed at 1647 and 1284 cm⁻¹ respectively. These two bands in the Mn(III) complex have been shifted to 1639 and 1304 cm⁻¹ respectively. The lowering of the C=N stretching frequency is an indication of the coordination of imine nitrogen atom.¹⁶ The shift of phenolic C-O frequency in the complex in the complex is due to the change of hydrogen bonded structure to covalent mental bonded structure.¹⁶

The electronic spectra of the Mn(III) complex in acetonitrile show two bands, one at 24, 150 cm⁻¹ (log $\epsilon \approx 3.5$) and the other broad band at 20,490 cm⁻¹ (log $\epsilon \approx 3.0$). Usually the high-spin Mn (III) complexes¹⁷ with octahedral geometry give one charge transfer band around 25,000 cm⁻¹ (log $\epsilon \approx 3.5$) and a spin-allowed d-d transition band, ⁵E_g → ⁵T_{2g} around 20,000 cm⁻¹ (log $\epsilon \approx 2.5$). The high energy band observed in this compound may be considered as a charge transfer band, while the band at 20,490 cm⁻¹ may be assigned to d-d transition. This broad band occurring at lower frequency with increased intensity, suggests the lowering of the octahedral symmetry.

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Zinc(II) Complexes with some Substituted Thiourea

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NARDELLI and co-workers¹ have made an extensive study of complexes of urea, methyl urea, thioacetamide, thiourea with a number of metal ions and indicated² that the tendency of the metal to coordinate to the organic molecule decreases on passing from $SC(MH_2)_2$ to $SC(NMe_2)_2$ and more heavily substituted thiourea molecules. It was, therefore, thought worthwhile to study the complex formation with N-phenyl and Di-phenyl thiourea and this communication describes six compounds of the composition $[ZnL_2X_2]$ where L is N-Phenyl or N, N'-Diphenyl thiourea and X is Cl^- , Br^- or NCS^- .

0.001M acetone solution using Toshniwal's Conductivity Bridge. Infra-red spectra were recorded on Nujol mulls with a Unicam SP-200 Spectrophotometer. Relevant analytical, conductance and I. R. data are recorded in Table 1.

The six zinc complexes reported in the present investigation correspond to the composition $[ZnL_2X_2]$ from their analysis. These are white crystalline solids, have low melting points and are fairly soluble in acetone in which medium they are found to be non-electrolytes. Infrared spectra provide evidence for the bonding of the ligand to the metal since most of the ligand absorption bands are modified in the complexes. The assignment of absorption bands observed for the metal substituted thiourea complexes are as done by Olliff². From the infrared study in the range of 2-15 μ of methyl thiourea complexes of zinc, Quagliano and coworkers³ have noted that the metal is bonded through sulfur atom. Flint and Goodgame reported⁴ the I. R. spectra of thiourea complexes of zinc and cadmium halides and showed complexes having the composition ML_2X_2 to be tetrahedral. In the case of the two thiocyanate complexes of zinc (II) in addition to the modified ligand absorption bands very sharp bands were observed at 2100 or 2080 cm^{-1} and $\sim 800 cm^{-1}$ region attributable to $\nu(C-N)$ and $\nu(C-S)$ respectively indicative of a N-bonded terminal thiocyanate. Hence the halide and thiocyanate complexes are four coordinated presumably having a tetrahedral environment around the metal ion. The sharp bands observed in the region $\sim 3200 cm^{-1}$ are undoubtedly assigned to the N-H stretching vibration and that at $\sim 1500 cm^{-1}$ correspond to the N-C-N stretching of the (B_1) type. The bands observed near about $\sim 730 cm^{-1}$ are assigned to the C-S stretching frequency. Bands around $\sim 1080 cm^{-1}$ are attributed to N-C-N bending vibrations.

TABLE I—ANALYSIS, MELTING POINT, CONDUCTANCE AND I. R. SPECTRAL DATA OF ZINC COMPLEXES

Compound	M.P. (°C.)	Conductance (mhos/cm ₂)	%Zinc		%Halogen or thiocyanate		I.R. Spectra (Cm. ⁻¹)			
			Found	Reqd.	Found	Reqd.	$\nu(C-S)$	N-C-N Bend	N-C-N Strength (B_1)	$\nu(N-H)$
ZnCl ₂ (N-Ph.tu) ₂	150	10.8	14.57	15.78	15.75	16.05	730s	1085s	1495br	3200s
ZnBr ₂ (N-Ph.tu) ₂	175	6.8	12.06	12.30	30.58	30.08	735s	1080s	1490br	3180s
Zn(NCS) ₂ (N-Ph.tu) ₂	147	9.6	13.23	13.42	23.63	23.80	740s	1085s	1495s	3200s
ZnCl ₂ (Diph.tu) ₂	185	8.1	10.75	10.96	11.65	11.91	725s	1080s	1500br	3250s
ZnBr ₂ (Diph.tu) ₂	159	9.4	9.95	9.83	23.92	24.03	730s	1075s	1500br	3200s
Zn(NCS) ₂ (Diph.tu) ₂	135	9.9	10.04	10.19	17.84	18.08	725s	1080s	1505s	3250s

Ph.tr—Phenyl thiourea

Ethanol solution of zinc chloride, bromide and thiocyanate (20 ml) were treated with ethanolic solution of substituted thiourea in 1:2 ratio separately and the solution refluxed for one hour. Then 10 ml CCl_4 was added to each of the reaction mixtures and refluxing continued for three hours. The resulting clear solution was kept for two to three days after addition of 5 ml more of CCl_4 . White crystalline compounds separated out. The compounds were suction filtered, washed with ethanol, followed by ether and dried *in vacuo*. Metal and halogen or thiocyanate were estimated by standard methods after alkali fusion (for anions only). Conductance was measured in

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