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Manganese(III) Complexes of Schiff Bases

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RECENTLY we have used various Schiff bases of salicylaldehyde, substituted salicylaldehydes and acetylacetone with different diamines to synthesise metal chelates of iron(III)¹, cobalt(III)^{2,3,4}, chromium(III)², and manganese(III)^{2,5}. We have now isolated some manganese(III) complexes of the dibasic tetradentate Schiff base derived from orthohydroxyacetophenone and ethylenediamine (abbreviated as HAEN-H₂), the preparation and properties of which are described in this note.

Experimental

Manganese(III) acetate dihydrate was prepared by a previously published method⁶. All the solvents and chemicals were purified and dried by standard methods, the molar conductance, electronic spectra and magnetic susceptibilities were measured and elemental analyses were performed as described previously². Infrared spectra (KBr) were obtained through the commercial service from Central Drug Research Institute, Lucknow.

Preparation of the Mn(III)-Schiff base complexes :

Mn(HAEN)(CH₃COO)(H₂O) : An ethanolic solution (20 ml.) of the Schiff base, HAEN-H₂ (0.02 mole) was added to manganese(III) acetate dihydrate (0.02 mole) dissolved in hot ethanol (20 ml), and the mixture was refluxed on water-bath for about an hour. The volume of the mixture was then reduced to half and cooled when dark brown crystals separated out. The crystals were filtered off, washed thoroughly with a mixture of benzene-petroleum ether (1 : 1, v/v) and dried in a vacuum desiccator. (Found : Mn, 14.00; N, 7.04%; calc. for Mn(HAEN)(CH₃COO)(H₂O) : Mn, 13.85; N, 6.60%; $\mu_{eff} = 4.87$ B.M. (24°); $\Lambda_M = 10.02$ ohm⁻¹ cm² mole⁻¹ (Conc. 1.1×10^{-3} M in acetonitrile); ν_{max} at 25,000 cm⁻¹ (log $\epsilon = 3.56$) and at 20,850 cm⁻¹ (log $\epsilon = 2.89$) (in methanol); ν_{as} COO at 1540 cm⁻¹ and ν_{sym} COO at 1420 cm⁻¹; $\nu_{C=N}$ at 1595 cm⁻¹; ν_{C-O} (phenolic) at 1310 cm⁻¹ and $\nu_{C=N}$ at 1605 cm⁻¹ and ν_{C-O} (phenolic) at 1285 cm⁻¹ for free Schiff base HAEN-H₂).

Mn(HAEN)X (where, X = Cl, Br, I) : The compounds were prepared by the addition of the appropriate lithium halides to a refluxing (1-2 hr) mixture of manganese(III) acetate dihydrate and the Schiff base (all in equimolar quantities). The coloured complexes separated out on slow cooling, were washed and dried as before.

Mn(HAEN)Cl : Brown (Found : Mn, 14.62; N, 7.39; Cl, 9.00%; calc. for Mn(HAEN)Cl : Mn, 14.29; N, 7.28; Cl, 9.20%; $\mu_{eff} = 4.88$ B.M. (at 24°); $\Lambda_M = 12.5$ ohm⁻¹ cm² mole⁻¹ (Conc. 1.5×10^{-3} M in acetonitrile); ν_{max} at 24,890 cm⁻¹ (log $\epsilon = 3.59$) and at 20,958 cm⁻¹ (log $\epsilon = 2.99$ (in methanol).

Mn(HAEN)Br : Brown (Found : Mn, 13.21; N, 6.40; Br, 18.90%; calc. for Mn(HAEN)Br : Mn, 12.81; N, 6.53; Br, 18.65%; $\mu_{eff} = 4.7$ B.M. (at 23°); $\Lambda_M = 9.8$ ohm⁻¹ cm² mole⁻¹ (Conc. 1.0×10^{-3} M in acetonitrile); ν_{max} at 24,900 cm⁻¹ (log $\epsilon = 3.60$) and at 20,000 (log $\epsilon = 3.00$) (in methanol).

Mn(HAEN)I : Reddish-brown (Found : Mn, 11.67; N, 6.02; I, 27.01%; calc. for Mn(HAEN)I : Mn, 11.54; N, 5.88; I, 26.68%; $\mu_{eff} = 4.90$ B.M. (at 24); $\Lambda_M = 15.8$ ohm⁻¹ cm² mole⁻¹ (Conc. 1.1×10^{-3} M in acetonitrile); ν_{max} at 24,780 cm⁻¹ (log $\epsilon = 3.52$) and at 20,900 cm⁻¹ (log $\epsilon = 2.88$) (in methanol).

Results and Discussion

The complexes are all coloured and quite stable when dried. The elemental analyses correspond to the formulae shown for the complexes under investigation and are all paramagnetic with effective magnetic moments in the range 4.70-4.90 B.M., which is fairly close to the spin-only value for high-spin d⁴ system. They are moderately soluble in methanol, acetonitrile and nitromethane and are practically non-conducting in acetonitrile. The molar conductance values support the coordination of the anions (i.e., CH₃COO, Cl, Br, and I). The IR spectrum of Mn(HAEN)(CH₃COO)(H₂O) has been measured in KBr phase, and ν_{as} COO and ν_{sym} COO bands are observed at 1540 cm⁻¹ and 1420 cm⁻¹ respectively, and the difference between these two bands is 120 cm⁻¹ indicating (possibly) the unidentate nature of acetate ion⁷. The ν_{as} COO band has been shifted to lower frequency compared with other unidentate acetate ion⁷. This is considered to be a consequence of hydrogen bonding by the acetate ion, the structure having strong intramolecular hydrogen-bonding between the non-coordinated carboxy-oxygen atoms and a water molecule as well as intermolecular hydrogen-bonding between each of the carboxy-oxygen atoms and water molecules coordinated to other Mn(III) ion. The $\nu_{C=N}$ and ν_{C-O} (phenolic) are observed at 1605 cm⁻¹ and 1285 cm⁻¹ respectively in the free ligand, which have been shifted to 1595 cm⁻¹ and 1310 cm⁻¹ respectively in the complex. The lowering of the C = N stretching frequency is an indication of the coordination of imine-nitrogen atom and thus indicating the less double bond character in the C = N bond⁸. The shift of phenolic C-O to higher frequency in the complex is possibly due to the change of hydrogen bonded structure to covalent metal bonded structure⁹.

The electronic spectra of the complexes Mn(HAEN)(CH₃COO)(H₂O) and Mn(HAEN)X in methanol, measured in the region 16,000–25,000 cm⁻¹, consists of an intense band in the range 24,780–25,000 cm⁻¹ (log ϵ = 3.52–3.60) and a broad band in the range 20,000–20,958 cm⁻¹ (log ϵ = 2.88–3.00). Usually the high-spin Mn(III) complexes with octahedral geometry give one charge transfer band around 25,000 cm⁻¹ (log ϵ = 3.5) and a spin-allowed *d-d* transition band, ⁶E_g → ⁶T_{2g} around 20,000 cm⁻¹ (log ϵ = 2.5)⁹. In the present complexes, the high energy bands may be considered as charge transfer in origin, while the low-energy bands may be assigned to the *d-d* transition. The broadness of the bands in the visible region with increased intensity is most likely due to lowering of the symmetry of the chelates from the regular octahedral geometry. The Mn(HAEN)

X complexes (where X = Cl, Br, or I) may even attain a square pyramidal geometry with the anion occupying the axial position.

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