Manganese (III) complexes with Schiff bases derived from heterocyclic β-diketones and some diamines

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Manganese(III) Schiff base complexes of the type [Mn(SB)OAc].H2O (where SB is derived from 4-benzoyl and 4-acetyl substituted 1-phenyl-3-methyl-2-pyrazolin-5-one and various diamines, viz., ethylenediamine (en), propylenediamine (pn), butylenediamine (bn) and hexylenediamine (hexn) have been prepared and their physicochemical properties studied. They are non-electrolytes in nature and their magnetic moments are close to 4.9 BM indicating spin-free type nature of the complexes and absence of any kind of exchange interaction. From IR, NMR, and TGA data, presence of a water molecule of crystallization is indicated. Electronic spectra show one charge transfer band and more than one d-d transitions. On the basis of analytical and physical data, the complexes are suggested to have five coordinated structures with square-pyramidal configuration.

There is currently a resurgence of interest in the biochemistry as well as the coordination chemistry of trivalent manganese due to its biological importance. Several enzymes, viz., manganese superoxide dismutase, azide insensitive catalase, manganese oxidase, and photosynthetic oxygen evolving complex probably involve Mn(III) in the catalytic cycle. Binding of manganese in these enzymes is by O and N donor groups of the amino acid side chains like, tyrosine phenoxide, histidine imidazole, carboxylate from aspartic or glutamic acid, etc. Several Schiff base complexes have been synthesised as models for some of these metalloproteins. Schiff base complexes have gained additional importance due to their possible application as superoxide dismutase mimics and their catalytic role in the epoxidation of olefins.

Mn(III) complexes have been studied comparatively less due to their low stability as the oxidation potential of the Mn²⁺-Mn³⁺ couple is very small, i.e., ca. 1.51 eV. Electrochemical studies have revealed that diatomic ligands are effective in the stabilization of higher oxidation states of manganese. This is the case with N and mixed O-N donor ligands. The work we have reported herein is such an effort. We have studied the Schiff base complexes derived from acyl and aryl substituted heterocyclic β-diketones and various linear diamines.

Materials and Methods

1,4-Dioxane was LR grade reagent and was used after distillation. 1-Phenyl-3-methyl-2-pyrazolin-5-one and hexylenediamine were purchased from E. Merck. Ethylenediamine (LR), propylenediamine (BDH) and butylenediamine (SISCO) were used without further purification. Mn(OAc)₂.2H₂O was prepared by the oxidation of Mn(OAc)₂.4H₂O using Christensen’s method. Carbon, hydrogen and nitrogen analyses were obtained from CDRI, Lucknow. Manganese was determined by EDTA after decomposing the complex with a mixture of 10 ml HNO₃, 5 ml conc. H₂SO₄ and 3 ml of HClO₄. The proton NMR spectra were recorded in DMSO at IIT Mumbai. IR spectra in KBr were obtained in the range of 4000-400 cm⁻¹ using Perkin-Elmer IR spectrophotometer. The molar conductances of the complexes were recorded in 10⁻³ M methanol solution on an ELICO conductivity bridge, type CM 82T. The electronic spectra were recorded on a Shimadzu 160A UV-Vis spectrophotometer using methanol as the solvent blank. Magnetic measurements were carried out by the Gouy method. Thermal studies were carried out with a Mettler M-3 thermobalance equipped with a TA-3000 microprocessor.
Synthesis of 1-phenyl-3-methyl-4-benzoyl (and 4-acetyl) 2-pyrazolin-5-one

The ligands 1-phenyl-3-methyl-4-benzoyl-2-pyrazoline-5-one (Hpmbzp) and its 4-acetyl derivative (Hpmacp) were prepared from 1-phenyl-3-methyl-2-pyrazolin-5-one and benzoylchloride or acetyl chloride in dioxane medium as reported earlier.

Synthesis of the Schiff base complexes

The complexes were prepared by two methods: (i) by reacting the stoichiometric amounts of the Schiff bases and the metal salt and (ii) by carrying out in situ reaction of diamines, heterocyclic β-diketone derivative and the metal salt. However, in both the cases complexes of the same stoichiometry were isolated (similar colour, infrared spectra and metal contents were observed). But we have adopted the in situ reaction in the present investigation as exemplified below:

The ligand Hpmbzp (5.6 g; 0.02 mol) or Hpmacp (4.4 g; 0.02 mol) was dissolved in methanol (80 ml). To this, ethylenediamine (0.7 ml; 0.01 mol), propylenediamine (0.9 ml; 0.01 mol), butylenediamine (1.0 ml; 0.01 mol) or hexylenediamine (0.6 g; 0.01 mol) was added. The solution was allowed to stand for 10 min at room temperature. Methanolic solution of manganese(III) acetate dihydrate (0.01 mol, 2.68 g) was added at once and the reaction mixture was refluxed for 2 hr on a water bath. The dark brown solution thus obtained was filtered and the solution was reduced to 1/3rd its volume and allowed to stand overnight at room temperature whereupon a brown coloured solid mass separated. Addition of ether helped the crystallization. The mother liquor was decanted off and the complex was dried over CaCl₂.

Results and Discussion

The Schiff base ligands were prepared by general condensation method and characterized by elemental analyses as well as IR and ¹H NMR studies. The ligands under present study can exist in the tautomeric forms (I) and (II).

The infrared spectra of all the Schiff base ligands showed a broad band in the region 3400-3430 cm⁻¹ which may be due to νOH. The free νOH is generally observed between 3500 and 3600 cm⁻¹. The observed low value of this band is due to intermolecular or intramolecular hydrogen bonding. This suggests the presence of structure [II], at least in the solid state. The same is true for solution state which is substantiated by the presence of an NMR signal at about δ 11.3 ppm due to enolic proton. The alkyl groups, CH₃, CH₂ show characteristic stretching absorption bands in the range 2990-2880 cm⁻¹, deformation bands at 1470 and 1390 cm⁻¹ and the rocking modes at 700 and 690 cm⁻¹. The phenyl groups shows C-H stretching at 3060 cm⁻¹ and C=C stretching at 1540 cm⁻¹. A band observed at ~1500 cm⁻¹ is assigned to pyrazoline ring C=C stretch. The bands at 1630, 1590 and 1350 cm⁻¹ can be very safely assigned to νC=NO (azomethine), νC=N (pyrazoline ring) and νC=O respectively. These assignments are in good agreement with our previous findings.

The proton NMR spectra of the ligands show the phenyl multiplet at δ 7.07 - 8.07 ppm. The sharp singlet observed at about δ 2.5 ppm is assigned to methyl protons of the pyrazoline ring.
Table 1 — Physical, analytical and $^1$H NMR spectral data of the Schiff bases

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>Molec. Formula</th>
<th>M.P./Decomp. temp., °C</th>
<th>Calc.(Found), %</th>
<th>$^1$H NMR spectral data, δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-1</td>
<td>C$_2$H$_2$N$_2$O$_2$</td>
<td>319</td>
<td>78.26</td>
<td>7.78</td>
</tr>
<tr>
<td>SB-2</td>
<td>C$_2$H$_2$N$_2$O$_2$</td>
<td>290</td>
<td>78.44</td>
<td>6.00</td>
</tr>
<tr>
<td>SB-3</td>
<td>C$_3$H$_3$N$_2$O$_2$</td>
<td>&gt;290</td>
<td>78.62</td>
<td>6.20</td>
</tr>
<tr>
<td>SB-4</td>
<td>C$_4$H$_4$N$_2$O$_2$</td>
<td>310</td>
<td>77.66</td>
<td>6.47</td>
</tr>
<tr>
<td>SB-5</td>
<td>C$_5$H$_3$N$_2$O$_2$</td>
<td>&gt;275</td>
<td>83.26</td>
<td>8.58</td>
</tr>
<tr>
<td>SB-6</td>
<td>C$_6$H$_3$N$_2$O$_2$</td>
<td>&gt;280</td>
<td>83.19</td>
<td>6.12</td>
</tr>
<tr>
<td>SB-7</td>
<td>C$_7$H$_3$N$_2$O$_2$</td>
<td>300</td>
<td>83.33</td>
<td>6.34</td>
</tr>
<tr>
<td>SB-8</td>
<td>C$_8$H$_3$N$_2$O$_2$</td>
<td>&gt;280</td>
<td>83.45</td>
<td>6.76</td>
</tr>
</tbody>
</table>

*Limiting frequencies of the multiplet; † Intermediate frequencies of the signal

Table 2 — Magnetic moments, and electronic absorption bands of the Schiff base complexes with their probable assignments

<table>
<thead>
<tr>
<th>Complex</th>
<th>M.L.</th>
<th>Charge-transfer</th>
<th>$d-d$ transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-SB1</td>
<td>4.88</td>
<td>27000(3.97)*</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB2</td>
<td>4.90</td>
<td>27250(3.91)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB3</td>
<td>4.92</td>
<td>27027(3.80)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB4</td>
<td>4.89</td>
<td>27000(3.87)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB5</td>
<td>4.86</td>
<td>27173(3.89)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB6</td>
<td>4.92</td>
<td>27548(3.89)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB7</td>
<td>4.87</td>
<td>26890(3.92)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
<tr>
<td>Mn-SB8</td>
<td>4.83</td>
<td>27322(3.90)</td>
<td>$\pi \rightarrow \pi^*$ (LMCT)</td>
</tr>
</tbody>
</table>

* Values in parentheses are log $\varepsilon$ values

The signal due to enolic proton is observed at about $\delta$ 11.3 ppm as described earlier. Methylene signals are listed in Table 1.

The Schiff base complexes are brown in colour, insoluble in water and are stable in air for extended periods of time. When treated with potassium iodide, iodine is liberated. This is an indication of manganese in $+3$ oxidation state which is also supported by the solid state magnetic measurements. The magnetic moment values (Table 2) of the complexes are very close to the values expected for a high-spin complex with four unpaired electrons. These values also confirm the absence of any exchange or super-exchange interactions in the complexes.

The infrared spectra of the complexes show lowering of azomethine $C=\pi$ stretching frequency by 5-20 cm$^{-1}$, indicating coordination through azomethine nitrogen. The $C=\pi$ (cyclic) band of the ligands remains unchanged in their complexes. This rules out the possibility of coordination via ring nitrogen. The $\nu C=\pi$ is raised by 10 cm$^{-1}$ in the spectra of complexes compared to the position in Schiff bases. This implies the deprotonation of enolic group on complexation. In all the complexes, a weak band is obtained at about 1580 cm$^{-1}$. This may be due to asymmetric COO stretching of the acetate group. The symmetric COO stretching band of the acetate group has been obscured due to a number of macrocyclic ligand vibrations. A broad and medium intensity band around 3400 cm$^{-1}$ is due to $\nu OH$ of lattice held water molecule. This is in accordance with TGA data which reveal the loss of one water molecule in the temperature range 95-115°C.

The molar conductances (Table 2) of the complexes for freshly prepared $10^{-3}$ M methanol solutions are in the range 5.8 to 18.02 ohm$^{-1}$ cm$^2$ mol$^{-1}$.

The $^1$H NMR spectra of the complexes are representative only in the case of en and pn complexes (Mn-SB-1,2,6 and 7). The important features of these spectra are: (a) change in the relative peak positions of the methylene bridge...
protons with respect to the corresponding Schiff bases and (b) the broadening of the spectra. The broadening of the spectra may be due to the contact mechanisms of both the types — through the bonds and through the space. In complexes, the unpaired spins are delocalized onto the methylene protons through the bonds and hence methylene signals are broadened and their positions are changed. Though, the delocalization does not extend up to 1-phenyl and 3-methyl protons as indicated by their unchanged peak positions, the broadening of these signals may be, due to through-space contact mechanism. However, common to the spectra of all the complexes is the presence of a broad signal at δ 11.0 ppm attributable to H2O protons and a peak at about δ 1.8 ppm assignable to -CH3COO group. The -C-CH3 protons are observed at δ 2.41-2.44 ppm, whereas -C-C6H5 protons are merged with 1-phenyl multiplets making them intense. The spectra of baza and hexa complexes could not be interpreted because of complexity.

Lever has shown that for a given metal-ligand distance, only the total charge along each of the cartesian axis is relevant. Hence, square planar MX4, 6-coordinated MX2Y2 and MX3Y complexes may all be treated in a similar fashion while considering the tetragonal distortion of the complexes. If we extend the same arguments to MX2Y2Z type tetragonally distorted systems, the energy-level diagram shown in Fig. 1 can be used to explain the electronic spectra of a [d^6] system.

The absorption spectra of the present complexes show an intense charge transfer band around 27000 cm^-1 and two d-d transitions around 19,000 cm^-1 and 13000 cm^-1. Since, Mn^3+ ion is easily reducible, charge-transfer will be from ligand to metal (LMCT) corresponding to \( \pi \rightarrow \tau \) transition. Keeping in view the dianionic, quadridentate nature of the Schiff base ligands and monovalent, coordinating behaviour (vide infra and IR spectra) of the acetate group, a square-pyramidal structure seems to be the most probable one. It is further evidenced by the presence of a ligand field band around 19000 cm^-1 diagnostic of \( C_{4v} \) symmetry. Considering \( C_{4v} \) as the effective symmetry and that the basal ligand atoms are equivalent, the observed bands may be assigned as \( 5B_1 \rightarrow 5B_2 \) (13000 cm^-1) and \( 5B_1 \rightarrow 5E \) (19000 cm^-1). A band \( 5B_1 \rightarrow 5A_1 \) should occur (Fig. 1). But many workers have reported that this low energy band is many times not observed.

Thus, taking into account, the analytical data and physical properties of the complexes, 5 coordinated square-pyramidal structure (III) in which O2N2 moiety forms the basal plane and the acetate group coordinated at axial position may be suggested for all the complexes.

References


Chistensen O T, Z anorg Chem, 27(1901)325.


