Complexes of Copper(II), Nickel(II), Cobalt(II), Iron(III), Manganese(II) & Zinc(II) with Schiff Base Derived from 2-Hydrazinobenzoxazole & Salicylaldehyde

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Copper(II), Nickel(II), Cobalt(II), Iron(III), Manganese(II) and Zinc(II) complexes of the Schiff base derived from 2-hydrazinobenzoxazole and salicylaldehyde have been synthesized and characterized on the basis of elemental analyses, conductance, magnetic moment, TGA, infrared, electronic and ESR spectral data. These chelates have been screened for fungicidal activity and found to be more active than the ligand.

In continuation of our earlier work on some transition metal complexes derived from active organic molecules, we now report here the synthesis and characterization of a few more transition metal complexes of the Schiff base derived from 2-hydrazinobenzoxazole and salicylaldehyde (2-HBO, Sal). The fungicidal activities of the complexes against three fungi, viz. Curcularia sp., Fusarium sp. and Alternaria sp. have been measured. The Schiff base (2-HBO, Sal) has been reported to be fungicidal and insecticidal, but no attempt has been made to synthesize metal chelates of this active organic molecule and study their nature.

All the metal chlorides used were of AR grade. o-Aminophenol (Wilson lab.), carbon disulphide (Wilson lab.), hydrazine hydrate (98%, Ranbaxy) and salicylaldehyde (E. Merck) were used for the preparation of the ligand. The ligand 2-HBO, Sal was prepared by reported procedure and its purity checked by TLC and melting point determination (lit. 251°C).

**Table 1—IR and Electronic Spectral Data**

<table>
<thead>
<tr>
<th>Ligand/complex*</th>
<th>IR frequencies (cm⁻¹)</th>
<th>Electronic spectral bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₄N₂O₂H₁₁</td>
<td>vN—H 3250-1640</td>
<td>vC=N (free ring)</td>
</tr>
<tr>
<td></td>
<td>vC=N 1610</td>
<td>22620, 30300</td>
</tr>
<tr>
<td></td>
<td>vC=O 3400</td>
<td></td>
</tr>
<tr>
<td>Cu(C₁₄N₂O₂H₁₀)₂</td>
<td>vN—H 3260</td>
<td></td>
</tr>
<tr>
<td>NiC₁₄N₂O₂H₁₀Cl</td>
<td>vN—H 3300</td>
<td></td>
</tr>
<tr>
<td>CoC₁₄N₂O₂H₁₀Cl</td>
<td>vN—H 3350</td>
<td></td>
</tr>
<tr>
<td>Fe₂(C₁₄N₂O₂H₁₀Cl₂)</td>
<td>vN—H 3350</td>
<td></td>
</tr>
<tr>
<td>MnC₁₄N₂O₂H₁₀Cl</td>
<td>vN—H 3400</td>
<td></td>
</tr>
<tr>
<td>ZnC₁₄N₂O₂H₁₀Cl</td>
<td>vN—H 3400</td>
<td></td>
</tr>
</tbody>
</table>

- Satisfactory elemental analyses were also obtained

Synthesis of metal chelates—The complexes were prepared by refluxing the methanolic solutions of metal chlorides (0.001 M) and the ligand (0.002 M) for 3-4 hr. The Cu(II) complex separated out immediately as a green crystalline compound. The chelates of other metal ions separated on raising the pH to ~8 by the addition of ammonia solution (1:1). The separated products were filtered, washed with hot methanol followed by pet. ether (60-80°) and dried in vacuo.

Elemental analyses, magnetic susceptibility measurements and thermogravimetric analyses were carried out by the methods described earlier. IR spectra were also recorded as reported earlier. Electronic spectra and ESR spectra were recorded in nujol mull at room temperature on UV-visible spectrophotometer DMR-21 and EPR-E_4 spectrometer respectively.

The analytical results indicate 1:1 (M:L) stoichiometry for all the complexes except the Cu(II) complex, where 1:2 stoichiometry is found. The complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of 1 x 10⁻³ M solution of the complexes in DMF (2-20 mho cm⁻¹ mol⁻¹) show them to be non-electrolytes.

Important infrared and electronic spectral bands of the complexes are given in Table 1. The infrared spectrum of the ligand shows a broad peak around 3250-2750 cm⁻¹, which has been attributed to a combination of vO—H (phenolic), vN—H and vC—H modes. The appearance of vOH and vNH modes at such a low region may be due to strong intramolecular hydrogen bonding. In the IR spectrum of the ligand two sharp peaks at 1640 and 1610 cm⁻¹ are assigned to vC = N (free azomethine) and vC = N (ring) respectively. The sharp bands observed at 1260 and 1025 cm⁻¹ are attributable to vC—O (phenolic) and ring C—O—C stretch respectively. The absence of a broad peak in the region 3250-2750 cm⁻¹ and appearance of a new peak around 3400-3300 cm⁻¹, assignable to vN—H in all the complexes, indicate the cleavage of intramolecular hydrogen bond and deprotonation of phenolic OH and its participation in coordination. The shift in phenolic vC—O (+10-50 cm⁻¹) in all the complexes further confirms the involvement of oxygen.
of phenolic group in coordination\(^6\). The shift in \(\nu_C = N\) (both free and ring), towards lower wave numbers indicates the coordination of nitrogens of both the azomethine groups. Further, no change is observed in \(C - O - C\) stretching frequency in complexes suggesting non-involvement of the oxygen of the ring in chelate formation. Hence it is concluded that 2-HBO.Sal is behaving as a monobasic tridentate ligand with ONN donor system. In the spectrum of Mn(II) complex, a broad band around 3450-3200 cm\(^{-1}\) is observed which may be due to the overlapping of \(\nu N - H\) and coordinated water bands. The presence of coordinated water is further confirmed by appearance of a new peak at 795 cm\(^{-1}\) (ref. 8) and thermogravimetric analysis. Thermogravimetric analysis of the chelates shows that only Mn(II) complex contains coordinated water. TGA reveals weight loss equivalent to two water molecules per mole of Mn(II) complex at about 150\(^\circ\)C. The peaks in the region 600-250 cm\(^{-1}\) are assigned to \(\nu M - O\), \(\nu M - N\) and \(\nu M - Cl\) vibrations\(^9,10\).

(Cu(II), Mn(II) and Fe(III) complexes are found to be paramagnetic. The \(\mu_{eff}\) value (5.6 B.M.) for Mn(II) complex is low when compared to reported values for other high-spin Mn(II) complexes. The low value may be due to the presence of Mn(II) species and spin-exchange in solids\(^11\). The low \(\mu_{eff}\) value for Fe(III) complex (4.7 B.M.) when compared to values for other high-spin Fe(III) complexes may be attributed to metal-metal interactions\(^12\). The electronic spectral data of the complexes are presented in Table 1. The band at 15151 cm\(^{-1}\) in Cu(II) complex is assigned to \(2E_g \rightarrow 2T_{2g}\) transition\(^13\). The other two bands at 27780 and 32260 cm\(^{-1}\) are due to charge-transfer. On the basis of the magnetic moment and electronic spectral data, octahedral geometry is proposed for the Cu(II) complex. The electronic spectra of Mn(II) and Fe(III) complexes show very weak bands and hence are not of much help in deciding the band transitions. For Mn(II) and Fe(III) complexes, octahedral and binuclear octahedral structures are proposed respectively.

Ni(II) complex is found to be diamagnetic. The band at 20000 cm\(^{-1}\) is due to \(1A_{1g} \rightarrow 1A_{2g}\) transition and that at 27780 cm\(^{-1}\) is due to charge-transfer. Magnetic moment and electronic spectrum of Ni(II) complex are very similar to those of reported Ni(II) square-planar complexes\(^16\). The observed magnetic moment for Co(II) complex is 2.1 B.M. which agrees well with reported values for low-spin Co(II) complexes with one unpaired electron. The square-planar geometry for Co(II) complex is characterized by a narrow band near 8500 cm\(^{-1}\) and a broad strong band around 20000 cm\(^{-1}\). The electronic spectrum of Co(II) complex shows a strong broad band at 16390 cm\(^{-1}\) which is assigned to \(2A_{1g} \rightarrow 2B_{1g}\) transition\(^17\). The magnetic moment value and the electronic spectral band suggest a square-planar disposition for Co(II) complex\(^20\). Zn(II) complex is found to diamagnetic.

Fungicidal activity—The ligand 2-HBO.Sal and its metal chelates were screened for the antifungal activity against three fungi, viz., Curvularia sp., Fusarium sp. and Alternaria sp. by spore germination method\(^21\) at room temperature at three different concentrations, i.e., at 1000 ppm, 500 ppm and 200 ppm. The time taken for the germination of these spores at room temperature is generally 4-5 hr. It was found that the inhibition by the metal chelates is more than that by the ligand. In general the order of inhibition is: Cu(II) > Zn(II) > Fe(III) ~ Ni(II) > Co(II) > Mn(II).

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