Preparation and characterization of a series of new Ni(II) and Co(II) complexes of the type [ML2], where 
L = tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine and salicylaldehyde, substituted salicyl-
aldehyde (X-Salaep), o-hydroxyacetophenone (Hapaep), o-hydroxybutyrophenone (Hppaep) or o-hydroxybutyrophenone (Hbpaep) have been described. Chromium(III) complexes with tridentate Schiff bases have been observed by Rastogi and Sutton (1973, 1974, 1975) with Cr(III) complexes with 2-(2'-aminoethyl) pyridine and their complexes of 2-(2'-aminoethyl)pyridine and their complexes of 2-(2'-aminoethyl)pyridine and other 2-substituted pyridine ligands and Cr(III) complexes; it may be assigned to the region 8850-9850, 17000-18000 cm⁻¹ [v₁, 3A₂(F)→3T₂(F)], 16785-14000 cm⁻¹ [v₂, 3A₂(F)→3T₁(F)] and (27515-25050 cm⁻¹ [v₃, 3A₂(F)→3T₁(F)] indicating O₆ geometry for these complexes. In the case of Co(II) complexes three bands observed in the region 8850-9850, 17000-19800 and 20850-215000 cm⁻¹ may be assigned to

**Terdentate Ligands: Part II — Octahedral Ni(II), Co(II) and Cr(III) Complexes of Schiff Bases Derived from 2-(2'-Aminoethyl)pyridine**

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Received 18 December 1975; revised 22 February 1977

Preparation and characterization of a series of new Ni(II) and Co(II) complexes of the type [ML2], where L = tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine and salicylaldehyde, substituted salicylaldehyde (X-Salaep), o-hydroxyacetophenone (Hapaep), o-hydroxybutyrophenone (Hppaep) or o-hydroxybutyrophenone (Hbpaep) have been described. Chromium(III) complexes of the composition [CrL2]Cl are also reported. Analytical, conductance, magnetic, electronic and IR spectral data show that all the complexes have octahedral geometry.

Earlier we have reported the preparation and characterization of several transition metal complexes of 2-(2'-aminoethyl)pyridine (1,2). Now we report here the preparation of Ni(II), Co(II) and Cr(III) complexes with tridentate Schiff bases (I) derived from 2-(2'-aminoethyl)pyridine and their characterization on the basis of analytical, conductance, magnetic, electronic and IR spectral studies.

**Complexes with X-Salaep** — Salicylaldehyde and substituted salicylaldehyde (0-025 mole) and 2-(2'-aminoethyl)pyridine (0-025 mole) in ethanol were mixed and stirred on a magnetic stirrer for 15 min at 60-70°. After the addition of metal chloride (0-01 mole) and the contents refluxed for about 3 hr. The solution was evaporated in vacuo and on refrigeration for several days solid complexes were obtained. These were recrystallized from ethanol; yield 45-48%.

**Analytical, magnetic moment, melting point and conductivity data of the complexes are listed in Table 1.**

The magnetic moments observed for Ni(II) (2.96-3.42 BM), Co(II) (4.85-5.12 BM) and Cr(III) (3.70-3.82 BM) complexes are consistent with octahedral symmetry for these complexes. The increase in the magnetic moment from that of spin-only value in the case of Ni(II) complexes may be due to some “mixing in” of upper states via spin-orbit coupling. Higher orbital contribution for octahedral Co(II) complexes of 2-(2'-aminoethyl) pyridine and other 2-substituted pyridine ligands has been observed by Rastogi and Sutton et al. The value for Cr(III) complexes is slightly less than that expected for three unpaired spins in O₆ environment.

Judging from the greater value of magnetic moment for X-Salaep (where X = H, 5-Cl, 5-NO₂ and 5,6-benzo) complexes of Ni(II) (3.31-3.42 BM), Co(II) (5.02-5.12 BM), Cr(III) (3.80-3.82 BM) as compared with the value of Hapaep [Ni(II), 2.26; Co(II), 4.95; Cr(III) 3.77 BM], Hppaep [Ni(II), 2.26; Co(II), 4.92; Cr(III) 3.75 BM] and Hbpaep [Ni(II), 2.96; Co(II), 4.85; Cr(III) 3.70 BM] complexes; it may be concluded that the geometry of the latter compounds is distorted from the regular octahedron.

Three bands have been observed in the electronic spectra of Ni(II) complexes in the region (10400-8980 cm⁻¹) [v₁, 3A₂(F)→3T₂(F)], 16785-14000 cm⁻¹ [v₂, 3A₂(F)→3T₁(F)] and (27515-25050 cm⁻¹ [v₃, 3A₂(F)→3T₁(F)] indicating O₆ geometry for these complexes. In the case of Co(II) complexes three bands observed in the region 8850-9850, 17000-19800 and 20850-215000 cm⁻¹ may be assigned to
Table 1 — Analytical, Magnetic, Thermal and Conductivity Data of Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% M</th>
<th>m.p. (°C)</th>
<th>Am in nitromethane</th>
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<tr>
<td>Ni(Salaep)₆</td>
<td>65.84</td>
<td>5.22</td>
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<tr>
<td>Ni(Hapaep)₆</td>
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<td>5.66</td>
<td>10.48</td>
<td>10.87</td>
<td>200</td>
<td>38</td>
</tr>
<tr>
<td>Ni(5,6-Benzo-Salaep)₆</td>
<td>72.92</td>
<td>4.68</td>
<td>5.80</td>
<td>8.97</td>
<td>200</td>
<td>38</td>
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<td>Ni(Hapaep)₆</td>
<td>66.85</td>
<td>5.66</td>
<td>10.48</td>
<td>10.87</td>
<td>200</td>
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<tr>
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<td>4.08</td>
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<tr>
<td>Ni(Hapaep)₂</td>
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<td>5.68</td>
<td>9.82</td>
<td>10.90</td>
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<tr>
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<td>6.08</td>
<td>9.82</td>
<td>10.90</td>
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<tr>
<td>Cr(5,6-Benzo-Salaep)₂</td>
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<td>4.92</td>
<td>9.60</td>
<td>8.97</td>
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<td>4.92</td>
<td>9.60</td>
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<tr>
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<td>90</td>
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<td>Cr(Hppaep)₂Cl</td>
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</table>

a, decomposes, and b, colour changes to brown at 170° ± 5°.

The transition $[^{1}T_{1g}(F) \rightarrow ^{2}T_{2g}(F)]$, $[^{1}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)]$ and $[^{4}T_{2g}(F) \rightarrow ^{2}A_{1g}(F)]$ respectively.

Three bands have been observed in the electronic spectra of Cr(III) complexes which are specifically due to spin-allowed transitions $[^{3}A_{2g} \rightarrow ^{3}T_{1g}(F)]$ (16080-18400 cm⁻¹); $[^{3}A_{2g} \rightarrow ^{3}T_{2g}(F)]$ (22580-25050 cm⁻¹) and $[^{3}A_{2g} \rightarrow ^{3}T_{1g}(F)]$ (34360-39550 cm⁻¹). Using the relations suggested by Figgis, the splitting energy 10Dq can directly be derived from the first spin-allowed band ($v_1$).

Examination of splitting energy values indicates that the steric effect in these compounds increases on changing the substituent Y (structure I) from H to CH₃, C₂H₅, C₆H₅ and this weakens the M-N bond of the azomethine linkage (see discussion of IR data also) which in turn may result in the distortion of the $O_{h}$ geometry for these compounds in the sequence: Hapaep < Hppaep < Hpaep. Further, it can also be argued that the higher values of splitting energy for [5-NO₂-Salaep] complexes [Ni(II), 10400 cm⁻¹]; Co(II), 10511 cm⁻¹; Cr(III), 18400 cm⁻¹] as compared to the other X-Salaep complexes of metal ions (where X-H, 5-Cl, 5,6-Benzo) cannot be explained on the basis of steric factor and may be interpreted in terms of difference in the inductive effects of various X-substituents. This indicates that the effect of NO₂ is stronger than that of Cl⁻ or 5,6-benzo group.

The IR spectral studies have been made empirically by comparing the spectra of the free ligands and the complexes with those of 2-(Z'-aminoethoxy) pyridine and its Ni(II), Co(II) and Cr(III) complexes and by reference to the literature on the spectra of similar compounds.

Coordination through imine nitrogen is expected to lower $v_C = N$. In the present complexes, the lowering is not as large as expected because of the presence of conjugation in the free ligands, which is expected to somewhat lower the $v_C = N$ frequency. Further, as compared with other complexes the extent of lowering in $v_C = N$ is minimum in Hpaep complexes [Cr(III) (27 cm⁻¹); Ni(II) (20 cm⁻¹); Co(II) (16 cm⁻¹)] indicating that the steric hindrance in these complexes is comparatively more.

The double bond character of antisymmetric and symmetric C=C and C=N vibrations is increased in complexes due to the donation of electrons by the nitrogen atom of pyridine ring. The positions of the new bands in the complexes are almost unchanged from those of pyridine ion, and the increase in their position from that of free ligand is an indication of coordination of pyridine to the metal atom.

Lever and others have observed that the increase in the frequency of ring breathing modes upon complexation is a clear indication of pyridine coordination. In the present studies, the increase in the frequency of this band follows the sequence: Cr(III) (24-20 cm⁻¹) > Ni(II) (17-15 cm⁻¹) > Co(II) (15-12 cm⁻¹).

The authors are thankful to the UGC, New Delhi and the State CSIR, Lucknow, for the financial support.

References
Cu(II) & Ni(II) Complexes with Schiff Bases Derived from 2-Hydroxypropioophenone

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A series of mixed ligand complexes of the types ML₂ and MLL' [M = Cu(II) or Ni(II); L = Schiff bases derived from 2-hydroxypropioophenone and L' = Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde] have been prepared and characterized on the basis of analytical, magnetic moment and electronic and IR spectral data. Complexes have been assigned square-planar structures. Aminexchange reactions have been carried out in some cases.

In continuation of our work on the reactions of coordinated Schiff bases, we report here the preparation and reactions of binary and ternary complexes, containing Schiff bases derived from 2-hydroxypropioophenone.

The binary and mixed Schiff base complexes of the type ML₂ and MLL' [M = Cu(II) or Ni(II); L = Schiff bases obtained from 2-hydroxypropioophenone and L' = Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde] were prepared as described earlier. The amine-exchange reactions with alkyl amines (mono and di) were also carried out. Reaction with 2-hydroxyalkylamines were also carried out in the case of Cu(II) complexes by adding monoethanol amine or isopropanol amine (1 ml) to Cu(II) Schiff base complex (1 g) in 25 ml EtOH and refluxing the mixture for 2 hr on a water-bath with occasional stirring. The resulting blue solid was filtered, washed with ethanol, dried and finally analysed. All the complexes gave satisfactory metal and nitrogen analysis. The parent complexes were analysed for carbon content also.

The parent Schiff base complex of the type ML₂, bis[N-1-(2'-hydroxyphenyl)propylideneiminio] M(II), [II], R=H], was prepared by the reaction of 2-hydroxypropioophenone with the metal ammine compound.

The parent mixed Schiff base complexes MLL' have the structure (IIA) and (IIB) (R=H). In the case of bis[N-1-(2-hydroxyphenyl)propylideneiminio]M(II), the exchange of ammonia by alkyl amines was incomplete as shown by analysis, only exception being the complex (I) with R = CH₃ and M = Ni(II) (complex No. 9 in Table I). This may be because the ethyl group in (I) causes the steric hindrance to the entry of alkyl amines.

Parent complexes (I), (IIA) and (IIB) (all with R = H), on reaction with concentrated ethylene diamine (en) or propylene diamine (pn), undergo amine-exchange reaction giving corresponding cis diamine Schiff base complexes (III), (IIIA) and (IIIB) respectively.

Finally, when Cu(II) complexes of the type (I), (IIA) or (IIB) (all with R = H) were treated with monoethanol amine or isopropanol amine, interesting complexes of the type (IV) were obtained.

Similar observation is also made in the case of mixed Schiff base complex of 2-hydroxypropioophenone and 2-hydroxy-1-naphthaldehyde (IIB, R = H), one of the ligands forms a tridentate Schiff base complex (IV) and another ligand is knocked out. It is seen that in the case of mixed Schiff base complexes, hydroxyalkylamine brings about amine-exchange on salicyaldimine or naphthaldimine forming a tridentate ligand and Z-hydroxypropionimine is removed. Thus, a monomeric complex of Cu(II) involving the tridentate Schiff base and a water molecule at the fourth coordination position is formed. 2-Hydroxy-1-naphthaldehyde...