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

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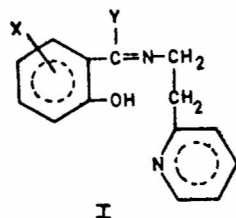
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Preparation and characterization of a series of new Ni(II) and Co(II) complexes of the type $[ML_2]$, where L = tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine and salicylaldehyde, substituted salicylaldehyde (X-Sal, X = 5-Cl, 5-NO₂, 5,6-Benzo) (X-Salaep), *o*-hydroxyacetophenone (Hapaep), *o*-hydroxypropiofenone (Hppaep) or *o*-hydroxybutyrofenone (Hbpaep) have been described. Chromium(III) complexes of the composition $[CrL_2]Cl$ are also reported. Analytical, conductance, magnetic, electronic and IR spectral data show that all the complexes have octahedral geometry.

EARLIER we have reported the preparations and characterization of several transition metal complexes of 2-(2'-aminoethyl)pyridine¹⁻³. 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, conductivity, 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) in ethanol and an aqueous solution of sodium acetate (0.02 mole) the reaction mixture was stirred for 1 hr and then refluxed for 3-5 hr. The contents were kept in a silica dish for slow crys-



- X-Saldep; Y=H, X=H, 5-Cl, 5-NO₂ or 5, 6-Benzo
 Hapaep; X=H, Y=CH₃
 Hppaep; X=H, Y=C₂H₅
 Hbpaep; X=H, Y=C₃H₇

tallization and recrystallized from ethanol; yield 80-85%.

Complexes with Hapaep — A mixture of 2-(2'-aminoethyl)pyridine (0.025 mole) and *o*-hydroxyacetophenone (0.025 mole) in absolute ethanol was stirred and refluxed at 70° for about 3-4 hr. To this was added an ethanolic solution of metal chloride (0.01 mole) and the contents refluxed for about an hour. A solution of sodium ethoxide was added dropwise and the reaction mixture further refluxed for 8 hr with constant stirring. The contents were allowed to stand overnight when crystals of the crude complex were obtained which were recrystallized from ethanol; yield ~75%.

Complexes with Hppaep — They were prepared by a procedure similar to that used for Hapaep complexes using *o*-hydroxypropiofenone (0.025 mole) and reaction mixture was refluxed for 12 hr at about 70° and then concentrated *in vacuo*. It was refrigerated for two days when the crystals of the crude product were obtained. The compound was recrystallized twice from ethanol; yield 55-60%.

Complexes with Hbpaep — These were prepared as above employing *o*-hydroxybutyrofenone (0.025 mole) and the reaction mixture was refluxed at 70° for 18 hr. Concentration of reaction mixture and subsequent refrigeration did not produce crystals. 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 coupling⁴. Higher orbital contribution for octahedral Co(II) complexes of 2-(2'-aminoethyl)pyridine and other 2-substituted pyridine ligands has been observed by Rastogi¹ and Sutton *et al.*⁵. The value for Cr(III) complexes is slightly less⁶ than that expected for three unpaired spins in *O_h* 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), 3.01; 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) [ν_1 , ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$], (16785-14000 cm⁻¹) [ν_2 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$] and (27515-25050 cm⁻¹) [ν_3 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$] indicating *O_h* geometry for these complexes. In the case of Co(II) complexes three bands observed in the region 8850-9850, 17000-19800 and 20850-21500 cm⁻¹ may be assigned to

TABLE 1 — ANALYTICAL, MAGNETIC, THERMAL AND CONDUCTIVITY DATA OF COMPLEXES

Compound	Found				m.p. (°C)	ΔM in nitro- methane
	% C	% H	% N	% M		
Ni(Salaep) ₂	65.84	5.22	10.96	11.46	202 ^a	32
Ni(5-Cl-Salaep) ₂	58.27	4.22	9.58	10.12	195 ^b	45
Ni(5-NO ₂ -Salaep) ₂	56.02	4.08	13.96	9.75	215	37
Ni(5,6-Benzo-Salaep) ₂	72.92	4.64	8.50	8.87	195-210 ^a	40
Ni(Hapaep) ₂	66.85	5.66	10.48	10.87	200	38
Ni(Hppaep) ₂	67.88	6.08	9.82	10.23	210	30
Ni(Hbpaep) ₂	68.80	6.52	9.42	9.77	200-205 ^a	—
Co(Salaep) ₂	65.67	5.20	10.95	11.48	220	15
Co(5-Cl-Salaep) ₂	58.04	4.22	9.66	10.12	280	32
Co(5-NO ₂ -Salaep) ₂	56.00	4.08	13.85	9.78	300	27
Co(5,6-Benzo-Salaep) ₂	72.92	4.64	8.48	8.92	230	20
Co(Hapaep) ₂	66.88	5.68	10.35	10.90	210 ^b	14
Co(Hppaep) ₂	67.80	6.08	9.85	10.35	200 ^b	18
Co(Hbpaep) ₂	68.77	6.52	9.47	9.94	196 ^b	—
Cr(Salaep) ₂ Cl	62.42	4.80	10.32	9.64	230 ^a	78
Cr(5-Cl-Salaep) ₂ Cl	55.40	3.95	9.21	8.48	300	96
Cr(5-NO ₂ -Salaep) ₂ Cl	53.40	3.90	13.32	8.22	300	94
Cr(5,6-Benzo-Salaep) ₂	65.08	4.92	9.60	8.80	270	77
Cr(Hapaep) ₂ Cl	63.42	5.28	9.80	9.12	210	75
Cr(Hppaep) ₂ Cl	64.38	5.69	9.35	8.68	205	90
Cr(Hbpaep) ₂ Cl	65.39	6.20	9.12	8.12	190-200	88

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

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

Three bands have been observed in the electronic spectra of Cr(III) complexes which are specifically due to spin-allowed transitions [ν_1 , ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$] (16080-18400 cm⁻¹); [ν_2 , ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$] (22580-25050 cm⁻¹) and [ν_3 , ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$] (34360-39550 cm⁻¹). Using the relations suggested by Figgis, the splitting energy 10Dq can directly be derived from the first spin-allowed band (ν_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, C₃H₇ 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 < Hbpaep. 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 these 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 group⁷.

The IR spectral studies have been made empirically by comparing the spectra of the free ligands and the complexes with those of 2-(2'-aminoethyl)pyridine³ and its Ni(II), Co(II) and Cr(III) complexes and by reference to the literature⁸⁻¹³ on the spectra of similar compounds.

Coordination through imine nitrogen is expected to lower $\nu C=N$. 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 $\nu C=N$ frequency^{14,15}. Further, as compared with other

complexes the extent of lowering in $\nu C=N$ is minimum in Hbpaep 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 ion¹⁶, and the increase in their position from that of free ligand is an indication of coordination of pyridine to the metal atom¹⁷.

Lever¹⁸, Sinha¹⁹ 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).

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

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A series of mixed ligand complexes of the types ML_2 and MLL' [$M = Cu(II)$ or $Ni(II)$; $L =$ Schiff bases derived from 2-hydroxypropiophenone 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. Amine-exchange reactions have been carried out in some cases.

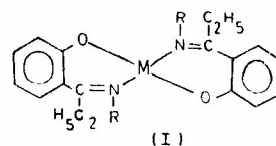
IN continuation of our work on the reactions of coordinated Schiff bases¹⁻⁵, we report here the preparation and reactions of binary and ternary complexes, containing Schiff bases derived from 2-hydroxypropiophenone.

The binary and mixed Schiff base complexes of the type ML_2 and MLL' [$M = Cu(II)$ or $Ni(II)$, $L =$ Schiff bases obtained from 2-hydroxypropiophenone and $L' =$ Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde] were prepared as described earlier¹⁻⁵. The amine-exchange reactions with alkyl amines (mono and di) were also carried out. Reaction with 2-hydroxyalkyl amines 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 ML_2 , bis[N-1-(2'-hydroxyphenyl)propylideneimino] $M(II)$, [(I), $R=H$], was prepared by the reaction of 2-hydroxypropiophenone with the metal ammine compound.

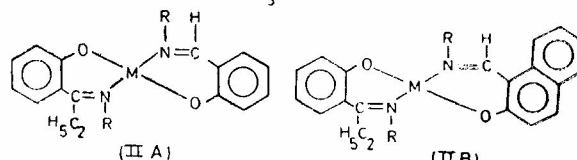
The parent mixed Schiff base complexes MLL' have the structure (IIA) and (IIB) ($R=H$).

In the case of bis[N-1-(2-hydroxyphenyl)propylideneimine] $M(II)$, the exchange of ammonia by alkyl



(I)

$M = Cu(II)$ OR $Ni(II)$
 $R = H$ OR CH_3



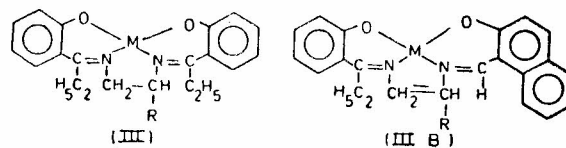
(II A)

(II B)

$M = Cu(II)$ OR $Ni(II)$
 $R = H, CH_3$ OR C_2H_5

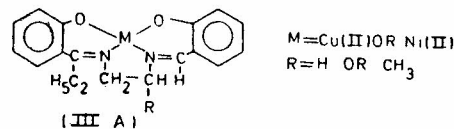
amines was incomplete as shown by analysis, only exception being the complex (I) with $R = CH_3$ and $M = Ni(II)$ (complex No. 9 in Table 1). This may be because the ethyl group in (I) causes the steric hindrance to the entry of alkyl amines.

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.



(III A)

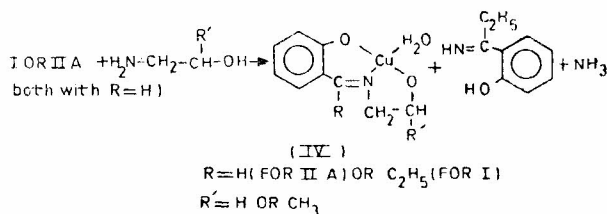
(III B)



(III A)

$M = Cu(II)$ OR $Ni(II)$
 $R = H$ OR CH_3

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.



(IV)

$R = H$ (FOR II A) OR C_2H_5 (FOR I)
 $R' = H$ OR CH_3

Similar observation is also made in the case of mixed Schiff base complex of 2-hydroxypropiophenone 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 salicylaldehyde or naphthaldehyde forming a tridentate ligand and 2-hydroxypropiophenoneimine 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