

## MIXED-LIGAND COMPLEXES OF IRON-, COBALT- AND NICKLE (II) WITH 2-AMINO-3-HYDROXYPYRIDINE AND SOME NITROGEN DONORS.

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2-Amino-3-hydroxypyridine (AHP), a potential complexation reagent for spectrophotometric, polarographic and titrimetric determinations of different metal ions<sup>1</sup>, has been used in the synthesis of analgesics<sup>2</sup>. Its mixed-ligand metal complexes with a nitrogen donor as the co-ligand can be considered as potential species for effecting its biological activity. The present paper describes the syntheses of Fe<sup>II</sup>, Co<sup>II</sup> and Ni<sup>II</sup> mixed-ligand complexes of AHP with ammonia, methylamine, ethylamine and pyridine.

### RESULTS AND DISCUSSION

The compositions of the complexes are given in Table 1. Molar conductance values (Table 1) indicate that the complexes are non-ionic in nature.

In spectra of AHP reveal bands at 3425 (OH.....N), 3375 (NH asym) and 3125 cm<sup>-1</sup> (NH sym). In the metal complexes, the V<sub>OH</sub> band of AHP (3425 cm<sup>-1</sup>) disappears, which can be attributed to simultaneous deprotonation and formation of M-O bond at 3-position of AHP. The M-O bonding is further confirmed<sup>3</sup> due to the presence of a band at 400-440 cm<sup>-1</sup>. The V<sub>NH</sub> sym ligand band (3125 cm<sup>-1</sup>) is shifted to lower side by 40-30 cm<sup>-1</sup> in the complexes indicating

coordination of N of the amino group at 2-position to the metal ion. A band at 380-360 cm<sup>-1</sup> found in the complexes is assigned to V<sub>M-N</sub> band<sup>3</sup>. Appearance of a band at 3225 cm<sup>-1</sup> (NH) in the complexes indicates coordination of NH<sub>3</sub> /MeNH<sub>2</sub> /EtNH<sub>2</sub>. In case of the mixed-ligand complexes of pyridine, a change in band of characteristic ring vibration (1460 cm<sup>-1</sup>) of pyridine to higher frequencies suggests that nitrogen of pyridine is bonded with the metal atom<sup>4</sup>.

The electronic spectral band at 11220-11290 cm<sup>-1</sup> observed in the spectrum of the Fe<sup>II</sup> complexes may be attributed to <sup>5</sup>T<sub>2g</sub> -- <sup>5</sup>E<sub>g</sub> transition, which supports octahedral geometry around metal ion. In mixed-ligand complexes of Co<sup>II</sup>, the bands observed at 8560-8600, 16260-17000 and 20020-20090 cm<sup>-1</sup> can be assigned to <sup>4</sup>T<sub>1g</sub> (F) -- <sup>4</sup>T<sub>2g</sub> (F), <sup>4</sup>T<sub>1g</sub> (F) -- <sup>4</sup>A<sub>2g</sub> (F) and <sup>4</sup>T<sub>1g</sub> (F) -- <sup>4</sup>T<sub>1g</sub> (P) transitions respectively. These bands suggest octahedral geometry for the Co<sup>II</sup> complexes<sup>5,6</sup>. The Ni<sup>II</sup> complexes showing three bands assigned to <sup>3</sup>A<sub>2g</sub> (F) - <sup>3</sup>T<sub>2g</sub> (F), <sup>3</sup>A<sub>2g</sub> (F) -- <sup>3</sup>T<sub>1g</sub> (F) and <sup>3</sup>A<sub>2g</sub> (F) -- <sup>3</sup>T<sub>2g</sub> (P) transitions respectively, which are typical of octahedral geometry<sup>6</sup>.

TG, DTA and DSC results follow a similar pattern for all the complexes. TG results show weight-loss in two steps.

TABLE 1- ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compound.**/ (Colour)	Metal % found/ (Calcd.)	Mol. Cond. $\text{o}^{-1} \text{cm}^{-1} \text{mol}^{-1}$	$\mu_{\text{eff}}$ B.M.
Fe(L <sub>1</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (Black)	18.2 (18.1)	2.3	5.6
Co(L <sub>1</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (Black)	18.0 (18.9)	3.2	4.9
Ni(L <sub>1</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> (Brown)	18.9 (18.9)	4.0	3.1
Fe(L <sub>1</sub> ) <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (Voilet)	16.6 (16.5)	3.3	5.5
Co(L <sub>1</sub> ) <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (Black)	17.4 (17.3)	5.1	4.9
Ni(L <sub>1</sub> ) <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (Brown)	17.4 (17.3)	5.2	3.1
Fe(L <sub>1</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> (Voilet)	15.3 (15.3)	2.1	5.5
Co(L <sub>1</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> (Black)	16.0 (16.0)	2.0	5.0
Ni(L <sub>1</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> (Green)	16.0 (16.0)	4.3	3.0
Co(L <sub>1</sub> ) <sub>2</sub> (Py) <sub>2</sub> (Black)	13.4	3.3	4.9
Fe(L <sub>1</sub> ) <sub>2</sub> (Py) <sub>2</sub> (Voilet)	12.9 (13.0)	4.5	5.5
Ni(L <sub>1</sub> ) <sub>2</sub> (Py) <sub>2</sub> (Green)	13.6 (13.5)	4.1	3.0

\* All compounds gave satisfactory C, H and N analyses. \*\* HL<sub>1</sub> = AHP.

The first-step decomposition starts in each case at 182-195<sup>o</sup> and continues without break upto 407-419<sup>o</sup>. The observed weight-loss corresponds to the loss of two molecules of N-donor ligand, i.e. NH<sub>3</sub>, CH<sub>3</sub> NH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> or C<sub>5</sub>H<sub>5</sub>N. The second-step decomposition corresponds to the loss of 2-amino-3-hydroxypyridine leading to the formation of metal oxide at 640-649<sup>o</sup>. In case of the Fe<sup>II</sup> and Co<sup>II</sup> complexes, the weight of residue corresponds to the formation of Fe<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> and in case of the Ni<sup>II</sup> complex to NiO.

The TG data are supplemented by DTA and DSC studies. Each complex shows two thermal effects in the DTA curves. The first one, an endothermic peak with  $t_{\text{max}} 293 \pm 18^{\circ}$  is attributed to the liberation of two molecules of NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> or py, and the second being an exothermic peak assigned to simultaneous decomposition and redox processes of the complex. The  $t_{\text{max}}$  of exothermic peaks lies in the range  $572 \pm 37^{\circ}$ .

## EXPERIMENTAL

All reagents were of AnalaR grade. Solutions were prepared in double-distilled water. AHP was procured from Aldrich. Solutions of the metal salt (50 mmol), AHP (100 mmol) and a N-donor ligand (100 mmol) were mixed to give a total volume of 50 ml. The mixture was refluxed for 1-1.5 h, then concentrated, cooled and the resulting complex washed and dried under reduced pressure over P<sub>2</sub>O<sub>5</sub>.

Metal contents were estimated following standard methods<sup>7</sup>. C, H and N analyses were performed at C.D.R.I., Lucknow. Molar conductances in MeNO<sub>2</sub> solution (10<sup>-3</sup> M) was measured using a Toshniwal instrument. Electronic spectra (nujol) were recorded on a Beckman DU-64 spectrophotometer and ir spectra (KBr) on a Perkin-Elmer 601 spectrophotometer. TG, DTA and DSC measurements were carried out with 9900 Du Point TA, Leeds and Northrup DTA unit and 910 DSC module. In TG and DTA nitrogen atmosphere and in DSC oxygen atmosphere were maintained with a flow rate of 60-70 ml min<sup>-1</sup>.

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