

**IR spectra**—A comparison of i.r. spectra of HAANAA and HAANAP with those of their complexes shows the formation of complexes through nitrogen and oxygen atoms of active groups. In the i.r. spectra of ligands the bands appearing at  $1600\text{ cm}^{-1}$  due to azomethine groups have been shifted in complexes to  $1540\text{--}1575\text{ cm}^{-1}$  because of the formation of metal-nitrogen (M-N) bonds which is further confirmed by the appearance of bands at  $540\text{--}565\text{ cm}^{-1}$ . Formation of (M-O) bonds due to the deprotonation of carboxylic and hydroxyl groups of HAANAA and HAANAP is evidenced by the appearance of bands at  $425\text{--}440\text{ cm}^{-1}$  and  $440\text{--}465\text{ cm}^{-1}$  respectively. However, a band at  $1700\text{ cm}^{-1}$  due to ketonic group in HAANAP is shifted to  $1685\text{--}1725\text{ cm}^{-1}$  because of chelation through this group. The acidic complex of Sm(III) gives no white ppt with alcoholic silver nitrate solution but the appearance of a weak band at  $360\text{ cm}^{-1}$  may suggest the formation of M-Cl bond.

Department of Chemistry,  
S.S.V. College, Hapur,  
February 6, 1978.

P. SINGH.\*  
R. L. GOEL.  
V. SINGH.

\* To whom all correspondence should be made.

1. Singh, P., Singh, V. and Goel, R. L., *Curr. Sci.*, 1976, 45, 137.
2. —, —, Singh, B. P. and Mahesh, R. P., *Ind J. Chem.*, 1975, 13, 734.
3. —, —, Goel, R. L. and Singh, B. P., *J. Ind. Chem. Soc.*, 1975, 52, 958.
4. Gill, N. S. and Nyholm, R. S., *J. Chem. Soc.*, 1959, p. 3997.
5. Donoghue, J. T. and Drago, R. S., *Inorg. Chem.*, 1963, 2, 1158.
6. Jorgensen, C. K., Pappalarado, R. and Rittershaus, E. Z., *Naturf.*, 1964, 19 a, 424.
7. Rastogi, D. K., *Aust. J. Chem.*, 1972, 25, 729.
8. Jorgensen, C. K. and Judd, B. R., *Molec. Phys.*, 1964, 8, 281.

### SCHIFF BASE COMPLEXES OF Cu(II) AND Ni(II) WITH 2, 4-DIHYDROXYACETOPHENONE ETHYLENEDIAMINE

THE complexes of Cu(II) and Ni(II) with 2,4-dihydroxyacetophenone ethylenediamine (DHAED) have been prepared and characterised by analytical, spectral, magnetic susceptibility and thermogravimetric data. The ligand functions as a dibasic and tetradentate one and the complexes are of 1:1 (metal-ligand) stoichiometry, each being associated with two molecules of water. The complexes are coloured and insoluble in common organic solvents and decompose above  $300^\circ\text{C}$ .

### Experimental

**Preparation of the ligand.**—To 10 g of 2,4-dihydroxyacetophenone in 100 ml of 95% alcohol, 2.2 ml of ethylenediamine were added and refluxed (with a low flame) for about half an hour. The yellow precipitate (DHAED) obtained was filtered and washed thoroughly with water and next with alcohol. It was dried in vacuum over fused  $\text{CaCl}_2$  (decomposition temperature  $285^\circ\text{C}$ ).

**Preparation of Cu(II) complex.**—To 0.998 g of copper acetate monohydrate (analar) in 50 ml of 95% alcohol, 1.64 g of DHAED was added and refluxed for about one hour. The dark brown precipitate obtained was cooled, filtered and washed with water followed by 50 ml of alcohol. The complex was further purified by refluxing it with 50 ml of alcohol for one hour and finally vacuum dried over fused  $\text{CaCl}_2$ .

**Preparation of Ni(II) complex.**—To 1.24 g of nickel acetate tetrahydrate (BDH) in 50 ml of 95% alcohol, 1.64 g of DHAED was added and refluxed for 3 hours. The red complex obtained was purified as in the case of Cu(II) complex.

The magnetic susceptibility measurements were made at room temperature by Guoy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant. The infrared spectra ( $4000\text{--}625\text{ cm}^{-1}$ ) in KBr pellet and the far infrared spectra ( $700\text{--}100\text{ cm}^{-1}$ ) of the reagent as well as of the complexes were recorded using IR (Perkin Elmer-257) and Fourier Far IR spectrophotometers respectively. The ultraviolet and visible spectra in DMF and in nujol respectively were recorded on DMR-21 spectrophotometer. The thermograms of the complexes were recorded using a Stanton recording thermobalance. The conductance measurements were carried out in dimethylformamide using Toshniwal Type CL 01/02 A conductivity bridge.

### Results and Discussion

The analytical data presented in Table I indicate that Cu(II) and Ni(II) complexes of DHAED can be represented as  $\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$  respectively. The complexes are insoluble in water, dilute mineral acids and common organic solvents such as benzene, chloroform, nitrobenzene, etc. They are slightly soluble in dimethylformamide and 1,4-dioxan.

The Cu(II) complex is found to be paramagnetic with an effective magnetic moment of 1.88 B.M. and Ni(II) complex diamagnetic.

The conductivity measurements reveal that both the complexes are non-electrolytes in DMF at the concentration  $10^{-3}\text{ M}$ .

The electronic spectrum of Cu(II) complex shows a broad peak at 520 nm whereas that of Ni(II) complex at 540 nm. The peaks at 345 nm and

TABLE I  
Elemental analysis of metal complexes of DHAED

Complex	Metal %	Carbon %	Hydrogen %
Cu (C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ) · 2H <sub>2</sub> O	14.79 (14.91)	50.84 (50.76)	5.73 (5.45)
Ni (C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ) · 2H <sub>2</sub> O	13.68 (13.94)	51.54 (51.35)	5.56 (5.51)

Values in parenthesis are the calculated ones.

285 nm in Cu(II) complex and at 305 nm and 265 nm in Ni(II) complex may be charge-transfer bands.

The weak infrared absorption bands at 2896 cm<sup>-1</sup> and at 2840 cm<sup>-1</sup> in the reagent are assumed to be due to intermolecularly and intramolecularly hydrogen bonded OH groups respectively. The Cu(II) and Ni(II) complexes have somewhat broad bands at 3452 cm<sup>-1</sup> and at 3320 cm<sup>-1</sup> respectively and these are attributed to the ν OH frequencies of water molecules. The bands in the region 3160–3020 cm<sup>-1</sup> in Cu(II) complex and at 2950 cm<sup>-1</sup> in Ni(II) complex may be due to intermolecular hydrogen bonding persisting in the complexes. The C=N stretching frequency which appears as a shoulder at 1625 cm<sup>-1</sup> in the reagent is shifted to 1595 cm<sup>-1</sup> in both the complexes indicating coordination through nitrogens of the azomethine groups. The ν C–O band that appears at 1160 cm<sup>-1</sup> in the reagent is shifted to higher frequencies as 1185 cm<sup>-1</sup> and 1175 cm<sup>-1</sup> in Cu(II) and Ni(II) complexes. This gives evidence that the coordination is also through oxygens of O-hydroxy groups. In the reagent and the complexes two more bands at 1230 cm<sup>-1</sup> and around 995 cm<sup>-1</sup> due to C–N and C–C stretchings have also been observed<sup>1</sup>. The bands at 500 cm<sup>-1</sup> and at 470 cm<sup>-1</sup> in the complexes represent M–N and M–O vibrations respectively<sup>2</sup>.

The thermograms of Cu(II) and Ni(II) complexes show initial weight loss curves in the temperature range 200°–260° C and 200°–240° C respectively. These curves, in each case, correspond to the weight loss of two water molecules. The loss of water molecules at these high temperatures indicates that they are coordinated. Since the Ni(II) complex has been found to be diamagnetic, it may be described as a tetragonal diamagnetic one<sup>3,4</sup> with the water molecules in the axial position. The sharp decomposition associated with the loss of ligand starts at

310° C in both the complexes. The final products of decomposition of the complexes above 500° C correspond, in each case, to metallic oxide.

The authors are thankful to Prof. G. Aravamudan, I.I.T., Madras, for magnetic and thermogravimetric data and to Prof. C. C. Patel, I.I.Sc., Bangalore, for C, H analysis. One of the authors (SSH) is grateful to University Grants Commission for the award of a Junior Research Fellowship.

Department of Chemistry, S. SRIHARI,  
Sri Venkateswara University, N. APPALA RAJU,  
Tirupati 517 502,  
April 18, 1978.

1. Hazzard, B. J., *Organicum*, 1st Edition, Pergamon Press, 1973, p. 102.
2. Patel, M. N. and Patel, R. P., *J. Indian Chem. Soc.*, 1975, 52, 1046.
3. Nyholm, R. S., *J. Chem. Soc.*, 1950, p.2061.
4. Burstall, F. H. and Nyholm, R. S., *Ibid.*, 1952, p. 3570.

#### COMPARATIVE STUDY OF RELATIVE ORDER OF LIGAND FIELD STRENGTH IN ISOMERIC SUBSTITUTED COBALTIC COMPLEXES

MAGNETIC susceptibility and temperature independent paramagnetism (T.I.P.) " $\chi_p$ " of the cobaltic complexes of the type [Co en<sub>2</sub> (R) Cl] Cl<sub>2</sub> where 'R' is an amine have been reported<sup>1</sup>, " $\chi_p$ " values have been theoretically calculated using Griffith and Orgels<sup>2,3</sup> formula. Assuming " $\chi_p$ " as a measure of ligand field strength<sup>2</sup>, a comparative study<sup>4</sup> has been made. In the present investigation a similar study is undertaken for cobaltic complexes with different substituted amines.

#### Results and Discussion

Griffith and Orgels<sup>2</sup> theory suggests that " $\chi_p$ " term should decrease as the ligand field strength increases. Hence aniline should have the highest ligand field strength and the substitution at different positions of aniline should result in a decrease in the ligand field strength. It would be interesting to compare " $\chi_p$ " values of isomeric substituted amines.

The order of " $\chi_p$ " values for toluidines is ortho > meta > para and for chloroanilines also it is ortho > meta. The order for the calculated " $\chi_p$ " with respect to toluidines and chloroanilines also follows the same trend as can be seen from the last column of Table I. Hence the agreement is good for toluidines and chloroanilines.

This order is different in anisidines where meta > para > ortho and in phenetidines when meta > ortho > para. Since the substituents used in this investigation are all ortho-para oriented, it could be expected that for ortho-para isomeric compounds the electronegativity of nitrogen should be greater than that in