

Synthesis and Characterization of Metal Complexes of Copper(II), Nickel(II) and Cobalt(II) with Bis-(1,2-Diphenyl-1-Hydroxyimino-2-Ethylidene) 1,3-Diamino Benzene

K. SAHU*, SHIV CHANDRA YADAV and KAILASH MAHTO
P.G. Department of Chemistry, B.R.B. College, Samastipur, India

The ligand bis-(1,2-diphenyl-1-hydroxyimino-2-ethylidene)-1,3-diamino benzene reacts with metal acetates to give inner complex of the type M_2L_2 , where $M = Cu(II)$ and $M_2L_2 \cdot 4H_2O$ where $M = Ni(II)$ and $Co(II)$. The neutral complexes of $Cu(II)$ are devoid of water molecules while $Ni(II)$ and $Co(II)$ complexes are found to contain four molecules of water. Besides the neutral complexes, complexes of other two different series such as $M_2(LH_2)X_4$ where $M = Cu(II)$ and $X = Cl^-$, Br^- , I^- , NO_3^- and $M_2(LH_2)_2X_4$, where $M = Co(II)$ and $Ni(II)$; $X = Cl^-$, Br^- , I^- , NO_3^- , have been prepared where the ligand co-ordinates with the metal ion in its uncharged form. IR electronic spectra and magnetic moment measurements have been used to characterize the compounds.

INTRODUCTION

Metal complexes with ligands capable of coordinating to two or more metal ions have evoked great interest in recent years¹⁻⁵. In the present paper we report the synthesis followed by characterization of a series of metal complexes with the ligand derived from the condensation of 1,2-diphenyl-1-hydroxyimino-2-ethylidene and 1,3-diamino benzene.

EXPERIMENTAL

Preparation of bis-(1,2-diphenyl-1-hydroxyimino-2-ethylidene) 1,3-diamino benzene.

1,2-Diphenyl-1-hydroxyimino-2-one (0.01 mol) and 1,3-diamino benzene (0.005 mol) were mixed with the help of agate and mortar. They went into an intimate mixture which subsequently turned into a homogeneous liquid after triturating them together about 1 h. The product was kept *in vacuo* for four or five days when it turned into a solid mass. The compound having light yellow colour was powdered, recrystallised from a little ethyl alcohol and analysed.

Preparation of di-[bis-(1,2-diphenyl-1-hydroxyimino-2-ethylidene) 1,3-diamino benzene] dicopper(II) Cu_2L_2

1,2-Diphenyl-1-hydroxyimino ethane-2-one (0.01 mol) was dissolved in 15 mL absolute alcohol. The solution was warmed to boiling. To this solution an alcoholic solution of cupric acetate monohydrate (0.005 mol) was added dropwise with constant shaking when the colour of solution became grey. An alcoholic solution of 1,3-diamino benzene (0.005 mol) was added and the whole solution was refluxed on a hot water bath for 30 min when a deep green

precipitate was formed. The solid product was filtered, washed with alcohol and ether and dried at room temperature. The dried product was analysed for its constituents.

Similar procedures were adopted for the preparation of other neutral complexes.

Preparation of (tetrachloro) di-[bis-(1,2-diphenyl-1-hydroxyimino-2-ethylidene) 1,3-diamino benzene] dinickel(II), Ni₂(LH₂)₂Cl₄

1,2-Diphenyl-1-hydroxyimino ethane-2-one (0.01 mol) was dissolved in minimum volume of absolute alcohol on warming. It was added to an alcoholic solution of nickel(II) chloride hexahydrate (0.005 mol) with constant shaking. The solution acquired pinkish colour. An ethanolic solution of 1,3-diamino benzene (0.005 mol) was added to this and the whole solution was refluxed on a hot water bath for 1/2 h when a reddish brown precipitate was formed. After cooling, it was filtered, washed with alcohol and finally with ether. It was analysed after drying. Other halo complexes of Ni(II) and Co(II) were prepared by adopting similar procedures. Halo complexes of Cu(II) were prepared in the same way using metal salts and the ligand in the molar ratio 2 : 1.

RESULTS AND DISCUSSIONS

Analytical data of the complexes are recorded in Table-1. The infrared spectra of the inner complexes of Ni(II) and Co(II) show a strong band in each case around 3300 cm⁻¹. The band is well distinct from the hydrogen bonded N—O—H stretching mode and the band broadening reflects the overlap between symmetric and asymmetric modes of coordinated water. The spectra of halo complexes of Ni(II) and Co(II) show a band around 3285 cm⁻¹ indicating the presence of hydrogen bonded structure of N—O—H groups of the uncharged ligand. Cu(II) complex of the type Cu₂(LH₂)Cl₄ favours the presence of free N—O—H groups also.

The spectra of the ligand and the metal complexes which fall within the vicinity of 1600 cm⁻¹ are attributed to $\nu(\text{C}=\text{N})$ stretching mode. the $\nu(\text{C}=\text{N})$ suffers a shift on the low frequency side in the metal complexes lying around 1590 cm⁻¹ and is more perturbed by the overlapping of the phenyl ring vibrations supporting the coordination of the nitrogen atoms with the metal ion in all cases. Two distinct bands appearing in the region 1100–900 cm⁻¹ for the ligand and complexes of two different types have been assigned to $\nu(\text{N}-\text{O})$ of N—O—H; however, the band positions are considerably shifted towards high frequency region on complexation. Halo complexes having formula M₂LH₂X₄ reveal strong and sharp absorptions near 1120 cm⁻¹ and 1010 cm⁻¹ showing a high frequency shift.

Besides these, two or three more bands appear in the region 1580–1450 cm⁻¹ which may be due to phenyl ring vibration. A sharp band of medium intensity appears at 1250 cm⁻¹ in the ligand due to C=N mode and the band position is shifted towards lower frequency region in the complex which occurred here at 1230 cm⁻¹.

Infrared data indicate symmetric bidentate bonding between the metal ions and the ligand in case of M₂L₂·nH₂O. The halo complexes of cobalt(II) and nickel(II)

TABLE-1
 ANALYTICAL DATA OF THE COMPLEXES

Compounds	Colour	% Found (Calculated)				Magnetic moment (B.M.)
		M	N	C	Halogen	
Cu ₂ L ₂	Deep green	10.76 (11.10)	9.40 (9.94)	69.80 (70.15)	–	1.24
Cu ₂ (LH ₂)Cl ₄	Light green	15.56 (15.73)	7.09 (7.86)	51.54 (51.83)	17.87 (18.29)	1.29
Cu ₂ (LH ₂)Br ₄	Brown	16.37 (16.59)	6.85 (7.19)	50.22 (50.94)	19.05 (19.39)	1.26
Cu ₂ (LH ₂)(NO ₃) ₄	Yellowish green	14.02 (14.32)	12.25 (12.45)	45.47 (45.82)	–	1.34
Ni ₂ L ₂ ·4H ₂ O	Reddish brown	9.35 (10.15)	9.13 (9.83)	66.55 (67.05)	–	2.95
Ni ₂ (LH ₂) ₂ Cl ₄	Reddish brown	8.90 (9.48)	8.50 (9.11)	62.57 (63.10)	10.90 (11.58)	2.80
Ni ₂ (LH ₂) ₂ Br ₄	Light brown	7.87 (8.31)	7.67 (8.04)	55.03 (55.43)	21.50 (22.21)	2.94
Ni ₂ (LH ₂) ₂ I ₄	Yellowish brown	7.02 (8.00)	6.61 (7.18)	48.82 (49.24)	30.33 (31.12)	3.10
Ni ₂ (LH ₂) ₂ (NO ₃) ₄	Light yellow	8.14 (8.53)	11.83 (12.18)	57.85 (58.25)	–	3.05
CoL ₂ ·4H ₂ O	Chocolate brown	9.49 (10.22)	9.10 (9.79)	66.24 (66.86)	–	2.41
Co ₂ (LH ₂) ₂ Cl ₄	Yellowish green	9.39 (9.83)	8.49 (9.02)	62.47 (62.73)	10.79 (11.32)	2.12
Co ₂ (LH ₂) ₂ Br ₄	Light brown	7.86 (8.34)	7.46 (8.10)	55.02 (55.34)	21.39 (22.14)	1.92
Co ₂ (LH ₂) ₂ I ₄	Reddish brown	7.02 (7.94)	6.30 (7.15)	48.76 (49.15)	30.31 (30.96)	2.26
Co ₂ (LH ₂) ₂ (NO ₃) ₄	Reddish brown	8.27 (8.72)	11.81 (11.97)	57.77 (57.92)	–	1.86

are believed to possess a structure where the two ligand molecules form hydrogen bonded macrocyclic complexes with disposition of the halide ions in *trans* manner⁶. The infrared spectra provide further support in favour of binuclear structure for bromo and chloro complexes of Cu(II) (Fig. 1).

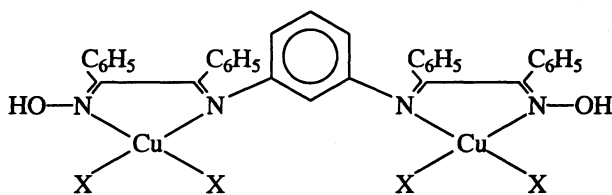


Fig. 1

The magnetic moment values are found to vary from 1.22–1.33 B.M. for Cu(II) complexes indicating subnormal magnetic behaviour with a possibility of metal-metal bonding. The spectra shows a broad band near $16,500\text{ cm}^{-1}$ apart from a dominating charge transfer band beyond $30,000\text{ cm}^{-1}$. The ligand field represents two or three superimposed absorptions which is comparable both in band position and band width with the Cu(II) complexes with similar structures and this may be on account of loss of symmetry giving low ligand field D_{2h} and C_{2v} in these cases⁷.

In Ni(II) complexes the figure shows magnetic moment between 2.80–3.10 B.M. at room temperature which favours octahedral arrangement of ligand atoms around metal ions with small amount of tetragonal distortion⁸. The electronic spectra consist of four characteristic spin allowed transitions. The figure shows a small variation in the band position from inner aquo-complex to halo complexes. The first band at $11,000\text{ cm}^{-1}$ is assigned to ${}^3B_{1g} \longrightarrow {}^3T_{2g}$ transition. The next two bands which appear at $16,000$ and $19,000\text{ cm}^{-1}$ are assigned to ${}^3B_{1g} \longrightarrow {}^3A_{2g}$ and ${}^3B_{1g} \longrightarrow {}^3E_g$ transitions respectively. The last band of greater intensity observed between $28,000$ – $26,000\text{ cm}^{-1}$ is assigned to ${}^3B_{1g} \longrightarrow {}^3T_{1g}(P)$ transition.

The magnetic moment values for halo complexes of cobalt(II) have been found in the region 1.8–2.1 B.M. while the neutral complex gives its value 2.4 B.M. The low magnetic moment values suggest that the cobalt(II) complexes are of low spin type⁹ having one unpaired electron. The slightly high value may be due to spin-orbit interaction of ${}^1A_{1g}$ state with ${}^2A_{2g}$ and other higher levels.

The electronic spectra of Co(II) complexes of two different types show a pair of bands at $16,000\text{ cm}^{-1}$ and $20,000\text{ cm}^{-1}$. The broad band lying in the vicinity of $20,000\text{ cm}^{-1}$ manifests some amount of tetragonal distortion in octahedral structure.

The low frequency band at $16,000\text{ cm}^{-1}$ is assigned to ${}^2A_{1g} \longrightarrow {}^2A_{2g}$ transition. The second band of greater intensity at $20,000\text{ cm}^{-1}$ is assigned to transition ${}^2A_{1g} \longrightarrow {}^2E_g$. A highly intense band beyond $25,000\text{ cm}^{-1}$ may be due to metal to ligand charge transfer M-L (π_g).

REFERENCES

1. W.J. Stratton and P.J. Ogren, *Inorg. Chem.*, **9**, 2588 (1970).
2. S. Satpathy and B. Sahoo, *J. Inorg. Nucl. Chem.*, **32**, 2223 (1970).
3. B.F. Hoskins and D.G. Vince, *Aust. J. Chem.*, **25**, 2039 (1972).
4. B. Beckett and B.F. Hoskins, *J. Chem. Soc. Dalton Trans.*, 291 (1972).
5. M.S. Ma and R. Angelici, *J. Inorg. Chem.*, **19**, 363, 924 (1980).
6. J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).
7. J. Chakrabarti and B. Sahoo, *Indian J. Chem.*, **20A**, 431 (1981).
8. A.B.P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
9. Y. Nishida and S. Kida, *Bull. Chem. Soc. (Japan)*, **45**, 461 (1972).