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Complexes of Copper(II), Nickel(II) and Cobalt(II) with *Bis*(2-hydroxyimino-1-phenylpropylidene)-1,2-diaminobenzene

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A number of metal complexes of the types ML [M = Co(II), Ni(II), Cu(II)], M(H_2L)X_2 [M = Co(II), Ni(II); X = Cl^-, Br^-, I^-] and Cu_2LX_2 (X = Cl^-, Br^-), where H_2L = *bis*(2-hydoxyimino -1-phenylpropylidene)-1,2-diaminobenzene have been synthesized and characterized.

Key Words: Copper(II), Nickel(II) and Cobalt(II) complexes, *Bis*(2-hydroxyimino-1-phenylpropylidene)-1,2-diaminobenzene

INTRODUCTION

Metal complexes with acetylacetone dioxime (aado) and diacetylazine dioxime (daado) have received special attention[1-4] as the *bis*-complexes such as M$(aado)_2$ and $M_2(daado)_2$ simulate as exo-bidentate and exo-quardridentate ligands, respectively leading to the formation of binuclear, trinuclear and tetranuclear metal clusters[5-7].

In present paper, the synthesis and structural elucidation of metal complexes with the ligand *bis*(2-hydroxyimino-1-phenylpropylidene)-1,2-diaminobenzene have been reported.

EXPERIMENTAL

Preparation of complexes

CuL: 1-Phenyl-1,2-propandione-2-oxime (0.01 mol) was taken in absolute alcohol and the solution gently warmed. To this solution, cupric acetate monohydrate (0.01 mol) was added when colour of the solution turned grey. An ethanolic solution of 1,2-diamino benzenc (0.005 mol) was added to it with constant shaking and the mixture was heated on water bath. A green precipitate was obtained. It was filtered, washed with alcohol and ether.

Cu_2LX_2 (X = Cl^-, Br^-): To an ethanolic solution of *bis*(2-hydroxyimino-1-phenylpropylidene)-1,2-diaminobenzene Cu(II) (CuL) (0.005 mol) was added slowly hot ethanolic solution of cupric chloride dihydrate (0.005 mol) with shaking. A heavy green precipitate so obtained was filtered, washed with a small quantity of ethanol and ether and dried under vaccum.

M(H_2L)X_2 [(X = Cl^-, Br^-, I^-, M = Co(II), Ni(II)]: To an alcoholic solution of the metal salt (0.01 mol), a hot ethanolic solution of 1-phenyl-1,2-propandione-2-oxime (0.01 mol), was added followed by the addition of an ethanolic solution of

1,2-diamino benzene (0.005 mol) with vigorous shaking. The orange, red or dark red crystals separated out on standing were filtered, washed with alcohol and ether and dried under vaccum.

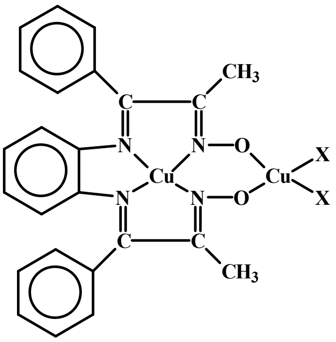

Fig. 1

RESULTS AND DISCUSSION

The complexes of the type, $M(H_2L)X_2$ show a strong band centered at 3390 cm^{-1} assigned to ν(O–H) mode of the N-O-H groups intramolecularly hydrogen bonded[7,8] indicating neutral form of the ligand in these complexes. A medium intensity band at 1695 cm^{-1} was observed for $M(H_2L)X_2$ complexes, while for ML and Cu_2LX_2 complexes it disappeared indicating this band probably being due to N-O-H deformation[1-4]. The azomethane and oxime C=N group stretching vibrations at 1630 and 1445 cm^{-1} of free ligand were most perturbed by complexation. The IR bands due to phenyl ring systems of the ligand found at 1585, 1565, 1495 and 1440 cm^{-1} were almost unaffected in the metal complexes. For ML complexes, the high frequencies C-N band, shifted to a lower frequency region and the low frequency C-N band suffered a blue shift. For Cu_2LX_2 ($X = Cl^-, Br^-$) complexes, one band was observed in the low frequency region 450-200 cm^{-1} which could be assigned to terminal $\nu_{\text{Cu-halogen}}$ modes.

Three distinct IR bands appeared in the region 1095-895 cm^{-1} for the ligand and the complexes, the middle one of which is assigned to ν(N–O). The ligand band at 1005 cm^{-1} was shifted to the region 1115-1085 cm^{-1} in the $M(H_2L)X_2$ complexes. For the Cu_2LX_2 complex, there was a lowering of frequency of this band to the region 1035-995 cm^{-1} which probably arise[5] due to the formation of new links between the Cu(II) inner complex (CuL) and Cu(II) salts (CuX_2) as shown in structure (I).

Magnetic moment and electronic shectra: The binuclear Cu_2LX_2 complexes showed μ_{eff} of 1.69 to 1.89 BM per copper atom. The electronic spectra of the complexes have been studied in the ligand filed region 10100-25100 cm^{-1} (Table-1). The spectra of Cu(II) complexes composed of two broad bands at 12100-12800 and 17100-17900 cm^{-1}. It would be reasonable to say that the high frequency band arises for the chromophore, CuN_4 in D_{4h} symmetry, and the low frequency band

TABLE-1
ELECTRONIC SPECTRAL BAND (cm^{-1}) AND MAGNETIC MOMENT VALUES (BM) OF Co(II), Ni(II) AND Cu(II) COMPLEXES

$Ni(H_2L)X_2$	$^3B_{1g} \rightarrow {}^3A_{2g}$	$^3B_{1g} \rightarrow {}^3A_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	μ_{eff} (BM)
$Ni(H_2L)Cl_2$	13100	18800	24800	2.89
$Ni(H_2L)Br_2$	13900	18600	24900	2.81
$Ni(H_2L)I_2$	14000	19100	24700	2.82
$Co(H_2L)X_2$	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	CT Band		
$Co(H_2L)Cl_2$	16100	24100		5.02
$Co(H_2L)Br_2$	16200	23600		5.05
$Co(H_2L)I_2$	15300	23600		5.12
ML	Assignment			
CuL	14100	CuN_4 ligand field band		1.70
NiL	20800	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{2g}$ $^1A_{1g} \rightarrow {}^1E_g$		Diamg.
CoL	21000	$^2A_{1g} \rightarrow {}^2B_{1g}$		2.09
Cu_2LX_2	Chormophore			
	CuO_2X_2	CuN_4		
Cu_2LCl_2	12300	17600		1.72
Cu_2LBr_2	12800	17100		1.69

originates from the chromophore, CuO_2X_2 under a lower symmetry such as C_2. A single broad band centred at 14100 cm^{-1} was observed for the complex CuL having the CuN_4 geometry. The broad band, which shows considerable structure represents two or three superposed absorptions. The band is comparable both in position and width with the earlier reported planar Cu(II) complexes and lead us to believe that all the inner complex salts of Cu(II) are essentially square planar.

The nickel(II) complexes of the type, $M(H_2L)X_2$ with uncharged ligand, showed μ_{eff} of 2.69-3.0 BM at room temperature suggesting an octahedral arrangement of the ligand atoms around the central Ni(II) ion. The electronic spectra consist of three bands at 13100-14100, 20100 and 24100 cm^{-1}. The positions, intensities and widths correspond to octahedral Ni(II) with certain amount of tetragonal distortion. The Ni(II) inner complex are diamagnetic in nature. The electronic spectra consist of a broad band at 20100-22100 cm^{-1}. The width of the spectra manifests that the band represents a group of two to three transitions under a square planar environment possessing[9,10] the chromophore NiN_4.

$Co(H_2L)X_2$ complexes have μ_{eff} of 4.89-5.1 BM and show a multiplet band structure in the region 16100-19100 cm^{-1}, the band width spreading over 3100 cm^{-1} suggesting an octahedral environment around Co(II) ion in these complexes. The Co(II) inner complex salt is of low spin type possessing magnetic moment of 2.0 BM. The spectra showed a broad band at 20100-22100 cm^{-1}, which manifests, that Co(II) ion is placed in a square planar ligand field. However, the high intensity of these bands arise probably due to charge transfer transition.

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