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Complexes of Cobalt(II), Nickel(II) and Copper(II) with an Ambivalent Schiff Base Ligand

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Condensation of 1-phenyl-1,2-propandione-2-oxime with 1,2-diaminobenzene in an ethanolic medium yields a Schiff base ligand, bis-(1-phenyl-2-hydroxyimino-1-propylidene) 1,2-diaminobenzene, H_2L. A number of 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^-, ClO_4^-, NO_3^-] and $[Cu_2LX_2]$ [X = Cl^-, Br^-, I^-, ClO_4^-, NO_3^-] have been synthesized and characterized on the basis of their elemental analyses, magnetic moment, infrared and electronic spectral data as well as conductivity measurements where the ligand behaves as a tetradentate ligand in the first two series and in a hexadentate manner in the third one.

INTRODUCTION

In continuation of our recent earlier works[1–10] on the isolation and characterization of transition metal complexes with Schiff base ligands derived by the condensation of monoximes of diketones and amines, seventeen complexes (three of the type ML, ten of the type $M(H_2L)X_2$ and four of the type Cu_2LX_2) have been prepared and characterized in the present investigation.

EXPERIMENTAL

All the chemicals used were of AR grade. The complexes were prepared by following the procedure as reported earlier.[1] A representative procedure for each category is described.

[*CuL*]: 1-Phenyl-1,2-propanedione-2-oxime (1.63 g, 0.01 mol) was taken in absolute ethanol and gently warmed. To this solution, cupric acetate monohydrate (1.00 g, 0.005 mol) was added when the colour of the solution turned grey. An ethanolic solution of 1,2-diaminobenzene (0.54 g, 0.005 mol) was added to it with constant stirring and the mixture was heated on a water bath. A greyish green precipitate formed slowly on standing. It was filtered washed with ethanol and ether.

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[*Ni*(H_2L)Cl_2]: To an ethanolic solution of nickel(II) chloride hexahydrate (2.38 g, 0.01 mol), a hot ethanolic solution of 1-phenyl-1,2-propanedione-2-oxime (3.26 g, 0.02 mol) was added followed by the addition of an ethanolic solution of 1,2-diaminobenzene (1.08 g, 0.01 mol) with vigorous shaking. The reddish brown crystals which separated on standing were filtered, washed with ethanol and ether and dried *in vacuo.*

[Cu_2LCl_2]: N,N′-*ortho*-phenylene-bis-(1-phenyl-1,2-propanedione-2-oximato) copper(II) (2.3 g, 0.005 mol) was dissolved in a minimum amount of ethanol and to it an ethanolic solution of cupric chloride dihydrate (0.85 g, 0.005 mol) was added with constant stirring. A green solid compound was immediately obtained which was filtered, washed with a small quantity of alcohol followed by ether, and dried *in vacuo.*

The compounds were analysed by the standard procedure.[11] Magnetic moments were determined by Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were made by Pascal's constant. The conductance measurements were carried out in *ca.* 10^{-3} M solution of methanol with Systronics 303 direct reading conductivity meter. Electronic spectra (MeOH) were obtained on a Perkin-Elmer spectrophotometer and IR spectra (KBr) on an Acculab-10 spectrophotometer at CDRI, Lucknow. The analytical data, colour, conductivity values and magnetic moment data are recorded in Table-1. Relevant bands in electronic spectra are recorded in Table-2.

RESULTS AND DISCUSSION

Analytical data are in good agreement with the proposed formulation of the complexes. All the complexes are crystalline, coloured and stable having high melting points above 200°C. The molar conductance values of 10^{-3} M solution in methanol medium (10–20 $ohm^{-1}\ cm^2\ mol^{-1}$) show that the compounds are non electrolytic in nature indicating thereby that the anions are coordinated to the metal ions.

The complexes of the type [$M(H_2L)X_2$] show a strong and broad IR band centered at 3385 cm^{-1} which is assignable to O—H stretching mode of N—O—H group. The position and width indicate presence of intramolecular hydrogen bonding. The free ligand also exhibits presence of this band and it can be inferred that the ligand is present in its neutral form in the complexes. A medium intensity band is present in the spectra of the complexes of the type [$M(H_2L)X_2$] as well as in the spectra of the ligand H_2L in the vicinity of 1700 cm^{-1} and can be assigned to the deformation vibration of N—O—H group. This band is significantly absent from the spectra of the complexes of the type [ML] and [Cu_2LX_2] and indicate the ligand to be present in its anionic form L^{2-} in the latter series of complexes due to deprotonation of the ligand. The azomethine and oxime >C=N groups stretching vibrations appearing at 1640 and 1460 cm^{-1} in the spectrum of the ligand are most perturbed on complexation ($\Delta\nu$ = 30–40 cm^{-1}). The IR bands at 1590, 1570, 1500 and 1440 cm^{-1} are almost unaffected in all the metal complexes.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complexes	Colour	Analysis %, found (calcd.)			Λ_M (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
		Metal	Nitrogen	Halogen		
[CuL]	Green	15.42 (15.44)	13.58 (13.60)	—	10	1.30
[NiL]	Orange red	14.40 (14.49)	13.62 (13.75)	—	10	2.10
[CoL]	Dark brown	14.50 (14.49)	13.78 (13.75)	—	10	1.80
[Cu_2LCl_2]	Green red	23.18 (23.27)	10.31 (10.25)	13.02 (13.00)	12	1.85
[Cu_2LBr_2]	Greenish black	20.52 (20.01)	8.78 (8.81)	25.20 (25.19)	11	1.90
[$Cu_2L(NO_3)_2$]	Green	21.00 (21.21)	13.98 (14.02)	—	13	1.85
[$Cu_2L(ClO_4)_2$]	Deep green	18.16 (18.88)	8.28 (8.30)	10.48 (10.53)	10	3.10
[$Ni(H_2L)Cl_2$]	Yellowish red	12.15 (12.29)	11.52 (11.66)	14.75 (14.79)	13	3.05
[$Ni(H_2L)Br_2$]	Dark red	10.32 (10.37)	9.80 (9.84)	31.60 (31.63)	12	2.80
[$Ni(H_2L)I_2$]	Dark red	8.88 (8.90)	8.40 (8.44)	38.56 (38.31)	10	2.85
[$Ni(H_2L)(NO_3)_2$]	Orange	11.08 (11.07)	10.36 (10.50)	—	10	2.95
[$Ni(H_2L)(ClO_4)_2$]	Red	9.56 (9.70)	9.18 (9.21)	11.56 (11.67)	13	2.90
[$Co(H_2L)Cl_2$]	Light red	12.10 (12.29)	11.60 (11.66)	14.18 (14.79)	15	4.95
[$Co(H_2L)Br_2$]	Red	10.50 (10.37)	9.56 (9.84)	31.52 (31.63)	13	5.00
[$Co(H_2L)I_2$]	Brown red	8.36 (8.90)	8.40 (8.44)	38.00 (38.31)	12	5.10
[$Co(H_2L)(NO_3)_2$]	Orange red	11.00 (11.07)	10.36 (10.50)	—	13	5.15
[$Co(H_2L)(ClO_4)_2$]	Dark red	9.68 (9.70)	9.00 (9.21)	11.62 (11.67)	12	5.20

TABLE-2
ELECTRONIC SPECTRAL BANDS (cm^{-1}) OF
Ni (II), Co (II) AND Cu (II) COMPLEXES

$[Ni(H_2L)X_2]$	$^3A_{2g} \leftarrow {}^3B_{1g}$	$^3E_g \leftarrow {}^3B_{1g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$[Ni(H_2L)Cl_2]$	13500	19700	24700
$[Ni(H_2L)Br_2]$	13800	19000	24600
$[Ni(H_2L)I_2]$	13600	19600	24000
$[Ni(H_2L)(NO_3)_2]$	13300	20000	25000
$[Ni(H_2L)(ClO_4)_2$	14000	19900	24800

$[Co(H_2L)X_2]$	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
$[Co(H_2L)Cl_2]$	17000
$[Co(H_2L)Br_2]$	17500
$[Co(H_2L)I_2]$	16800
$[Co(H_2L)(NO_3)_2]$	19000
$[Co(H_2L)(ClO_4)_2]$	18500

$[Cu_2LX_2]$	Chromophore	
	CuO_2X_2	CuN_4
$[Cu_2LCl_2]$	12200	17500
$[Cu_2LBr_2]$	12800	17000
$[Cu_2L(NO_3)_2]$	12300	17400
$[Cu_2L(ClO_4)_2]$	12700	17900

[ML]	Band position	Assignment
[CuL]	14000	CuN_4 ligand field band
[NiL]	21000	$^1A_{2g} \leftarrow {}^1A_{1g}$
		$^1B_{2g} \leftarrow {}^1A_{1g}$
		$^1E_g \leftarrow {}^1A_{1g}$
[CoL]	21000	$^2B_{1g} \leftarrow {}^1A_{1g}$

For complexes of the type, [ML], the high frequency azomethine ν(C—N) bands are shifted to lower frequency region and the low frequency oxime ν(C—N) bands suffer a blue-shift which can be attributed to the variation in electronic environment due to coordination with metal ions.

Three distinct infrared bands appear in the region 1110–900 cm^{-1} for the ligand and the complexes; the middle one of these is assigned to (N—O) stretching. In the spectrum of the ligand, this band appears at 1010 cm^{-1} and is shifted to the region 1110–1090 cm^{-1} in the complexes $[M(H_2L)X_2]$ and [ML]. For the complexes $[Cu_2LX_2]$, this band occurs at a lower frequency (1040–1030 cm^{-1}) in comparison to that in the spectrum of CuL. The lowering most probably arises due to the formation of new links between the copper(II) inner complex [CuL] and copper(II) salts CuX_2 as shown in Fig. 1.

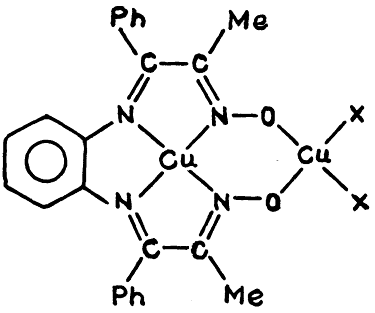

Fig. 1

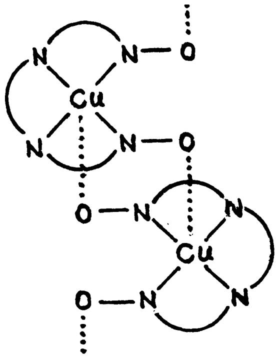

Fig. 2

In the low frequency region all the complexes of the types, [ML], $[M(H_2L)X_2]$ and $[Cu_2LX_2]$ show a sharp band of medium intensity in the region 470–450 cm^{-1} and is assigned to the metal-nitrogen stretching vibration. An additional band in the region 600–500 cm^{-1} in the spectra of $[M(H_2L)X_2]$, $[Cu_2LX_2]$ and [CuL] has been assigned to the metal-halogen or metal-oxygen stretching vibration. The ligand does not show any significant band in the low frequency region.

Magnetic and Electronic Spectral Data

The copper(II) complexes of the type $[Cu_2LX_2]$ exhibit two broad bands, one in the range 13,000–12000 cm^{-1} and another in the range 18,000–17,000 cm^{-1} with magnetic moments in the range 1.8 to 1.9 B.M. It would be reasonable to say that the high frequency band arises for the chromophore CuN_4 under D_{4h} symmetry whereas low frequency band originates from the chromophore CuO_2X_2 under a lower symmetry such as C_2. A single broad band centred at 14,000 cm^{-1} was observed for the complex CuL. The abnormally low value of magnetic moment of 1.3 B.M. is suggestive of some sort of interaction between adjacent Cu-atoms where planar units with CuN_4 chromophore are arranged in linearly stacked chains as in Fig. 2.

The nickel(II) complexes of the type $[Ni(H_2L)X_2]$ possess room temperature magnetic moment in the range 2.8–3.1 B.M. Electronic spectra consist of three bands at 13,000–14,000, 20,000 and 25,000 cm^{-1}. The positions, intensities and width correspond to octahedral nickel(II) with certain amount of tetragonal distortion. The nickel(II) inner complex NiL in diamagnetic and electronic spectrum shows a broad band at 20,000–22,000 cm^{-1}. The width of the spectrum manifests that the band represents a group of two to three transitions under a square-planar environment possessing the chromophore NiN_4.

$[Co(H_2L)X_2]$ complexes have μ_{eff} in the range 4.9–5.2 B.M. and exhibit a multiplet band structure in the region 16,000–19,000 cm^{-1} indicating octahedral environment around cobalt(II) ion in these complexes. The cobalt(II) inner complex, CoL is of low spin type possessing magnetic moment of 2.1 B.M. The electronic spectrum shows a broad band at 20,000–22,000 cm^{-1} with some amount of structure which manifests that cobalt(II) ion is placed in a square-planar ligand field. However, high value of molar extinction coefficient arises most presumably due to charge transfer transition.

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