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Copper(II) Complexes with Schiff Base Ligands 1,2-Diphenyl-2-Alkyliminoethan-1-one Oxime

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A number of complexes of the type $[CuL_2^{1-4}]$ and $[Cu_2L_2^{1-4}X_2]$ where $X = Cl^-$, Br^-, NO_3^- and ClO_4^-, HL^{1-4} = Schiff base ligands derived by the condensation of 1,2-diphenyl-1-hydroxyiminoethan-2-one with n-butylamine (HL^1), iso-butylamine (HL^2), n-propylamine (HL^3) and isopropylamine (HL^4) have been synthesized and characterised on the basis of elemental analyses, magnetic susceptibility, conductivity, infrared, ESR and electronic spectral data.

INTRODUCTION

Schiff base ligands having azomethine functional group > C═N— are produced by the union of an active carbonyl group and a primary amine. The metal complexes of Schiff bases have received great attention during recent years due to their paramount biological and industrial importance as evidenced by the literature.[1-3] This study has prompted us to prepare copper(II) complexes with Schiff bases derived from 1,2-diphenyl-1-hydroxyiminoethan-2-one and aliphatic amines. These ligands act first in a bidentate manner to produce a series of complexes of the type $[CuL_2^{1-4}]$ which further extend their denticity to 3 to produce another series of complexes $[Cu_2L_2^{1-4}X_2]$.

EXPERIMENTAL

All the chemicals used were E. Merck reagents except 1,2-diphenylethan-1,2-dione which was Loba quality. 1,2-Diphenyl-1-hydroxyiminoethan-2-one was prepared according to the literature method[6] (m.p. 145°C; Lit. 143°C). The ligands HL^{1-4} were synthesized by condensing equimolar quantities of 1,2-diphenyl-1-hydroxyiminoethan-2-one and aliphatic amines in an ethanolic medium. The solid products were separated by allowing the solution to stand overnight in a dish.

Preparation of the complexes

The complexes with all the four ligands HL^{1-4} were prepared by the method reported earlier.[7] The preparation of one typical complex in each series is described as:

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TABLE-1
ELEMENTAL ANALYSIS, ELECTRONIC SPECTRA AND MAGNETIC MOMENT DATA OF THE COMPOUNDS

Sl. No.	Compounds (colour)	Found (Caled.) %			λ_{max} (electronic) cm^{-1}	μ_{eff} (B.M.)
		M	N	Halogen		
1.	CuL_2^1 (Green)	10.32 (10.23)	8.92 (9.01)	—	14100(15)	1.15
2.	CuL_2^2 (Green)	10.19 (10.23)	8.89 (9.01)	—	14110(17)	1.17
3.	CuL_2^3 (Yellowish green)	10.87 (10.72)	9.32 (9.44)	—	14100(20)	1.15
4.	CuL_2^4 (Blackish green)	10.57 (10.72)	9.57 (9.44)	—	14115(18)	1.17
5.	$Cu_2L_2^1Cl_2$ (Dark green)	17.00 (16.83)	7.29 (7.40)	9.36 (9.25)	12600(5) 17200(8)	1.90
6.	$Cu_2L_2^2Cl_2$ (Greyish green)	17.00 (16.83)	7.32 (7.40)	9.12 (9.25)	12610(5) 17210(8)	1.92
7.	$Cu_2L_2^3Cl_2$ (Reddish green)	19.23 (19.17)	8.57 (8.44)	10.66 (10.55)	12600(8) 17200(9)	1.90
8.	$Cu_2L_2^4Cl_2$ (Yellowish green)	19.00 (19.17)	8.31 (8.44)	10.60 (10.55)	12610(7) 17210(5)	1.92
9.	$Cu_2L_2^1Br_2$ (Greyish brown)	15.00 (15.02)	6.73 (6.62)	19.01 (18.95)	12400(6) 17400(10)	1.95
10.	$Cu_2L_2^2Br_2$ (Deep brown)	14.94 (15.02)	6.53 (6.62)	18.85 (18.93)	12415(7) 17410(10)	1.96
11.	$Cu_2L_2^3Br_2$ (Blackish brown)	15.72 (15.54)	6.97 (6.85)	19.50 (19.58)	12410(8) 17410(9)	1.95
12.	$Cu_2L_2^4Br_2$ (Dark brown)	15.41 (15.54)	7.00 (6.85)	19.42 (19.58)	12420(5) 17420(5)	1.97
13.	$Cu_2L_2^1(NO_3)_2$ (Brown)	15.21 (15.35)	11.78 (11.84)	—	12800(8) 17300(9)	1.95
14.	$Cu_2L_2^2(NO_3)_2$ (Deep brown)	15.27 (15.35)	11.80 (11.84)	—	12800(7) 17310(10)	1.97
15.	$Cu_2L_2^3(NO_3)_2$ (Greyish brown)	15.99 (15.89)	11.80 (12.30)	—	12820(6) 17310(6)	1.96
16.	$Cu_2L_2^4(NO_3)_2$ (Yellowish brown)	16.00 (15.89)	12.33 (12.30)	—	12820(5) 17320(8)	1.96
17.	$Cu_2L_2^1(ClO_4)_2$ (Greyish red)	14.45 (14.38)	6.47 (6.34)	—	12500(7) 17530(9)	1.90
18.	$Cu_2L_2^2(ClO_4)_2$ (Dark red)	14.29 (14.38)	6.23 (6.34)	—	12520(6) 17510(10)	1.92
19.	$Cu_2L_2^3(ClO_4)_2$ (Yellowish red)	15.00 (14.85)	6.44 (6.08)	—	12510(6) 17520(10)	1.94
20.	$Cu_2L_2^4(ClO_4)_2$ (Bluish red)	15.00 (14.85)	6.44 (6.08)	—	12510(6) 17520(10)	1.93

TABLE-2
IMPORTANT IR BANDS (cm^{-1}) OF THE LIGANDS AND COPPER(II) COMPLEXES

Sl. No.	Compounds	ν(O—H)	ν(C—N) (Azomethine)	ν(C—N) (Oxime)	ν(N—O)
1.	HL^1	3420mb	1630s	1455s	1090s
2.	HL^2	3425mb	1635s	1450s	1095s
3.	HL^3	3415mb	1630s	1445s	1090s
4.	HL^4	3420mb	1635s	1450s	1085s
5.	CuL_2^1	—	1605s	1475s	1085s
6.	CuL_2^2	—	1605s	1470s	1090s
7.	CuL_2^3	—	1610s	1470s	1085s
8.	CuL_2^4	—	1610s	1485s	1080s
9.	$Cu_2L_2^1Cl_2$	—	1615s	1480s	1055s
10.	$Cu_2L_2^2Cl_2$	—	1605s	1480s	1060s
11.	$Cu_2L_2^3Cl_2$	—	1615s	1480s	1065s
12.	$Cu_2L_2^4Cl_2$	—	1610s	1475s	1060s
13.	$Cu_2L_2^1Br_2$	—	1620s	1470s	1055s
14.	$Cu_2L_2^2Br_2$	—	1610s	1485s	1055s
15.	$Cu_2L_2^3Br_2$	—	1605s	1470s	1060s
16.	$Cu_2L_2^4Br_2$	—	1615s	1470s	1055s
17.	$Cu_2L_2^1(NO_3)_2$	—	1615s	1475s	1060s
18.	$Cu_2L_2^2(NO_3)_2$	—	1615s	1470s	1060s
19.	$Cu_2L_2^3(NO_3)_2$	—	1620s	1485s	1055s
20.	$Cu_2L_2^4(NO_3)_2$	—	1615s	1470s	1055s
21.	$Cu_2L_2^1(ClO_4)_2$	—	1610s	1485s	1065s
22.	$Cu_2L_2^2(ClO_4)_2$	—	1620s	1475s	1055s
23.	$Cu_2L_2^3(ClO_4)_2$	—	1615s	1480s	1060s
24.	$Cu_2L_2^4(ClO_4)_2$	—	1620s	1480s	1065s

Bis-(1,2-diphenyl-2-isopropyliminoethan-1-hydroxyiminato) copper (II) [CuL_2^4]

An ethanolic solution of 1,2-diphenyl-2-isopropyl-iminoethan-1-one oxime (0.01 mol) was treated with an aqueous alcoholic (20 : 80) solution of cupric acetate monohydrate (0.005 mol). The mixture was heated under reflux over a water bath for 4 h when a blackish green precipitate was obtained. It was filtered, washed and dried *in vacuo.*

Dichlorobis-(1,2-diphenyl-2-isobutylimino-1-hydroxyiminato) dicopper (II) [$Cu_2L_2^2Cl_2$]

An ethanolic solution of bis-(1,2-diphenyl-2-isobutyliminoethan-1-hydroxy-iminato) copper(II) (0.005 mol.) was treated with an alcoholic solution of copper(II) chloride dihydrate (0.005 mol) at room temperature. A greyish green solid was obtained which was filtered, washed with ether and dried *in vacuo.*

The compounds were analysed using standard procedures[8] such as copper

iodimetrically, halogens as their respective silver halides and carbon, hydrogen and nitrogen by semimicro combustion methods.

The infrared spectra of the ligands and the complexes were recorded on a Beckmann IR-20 spectrophotometer. The conductivity measurements were made on a Systronic conductometer model 303 using dimethylsulfoxide as a solvent. Magnetic moments were measured by the Gouy method using $Hg[Co(CNS)_4]$ as the calibrant. The absorption spectra of dimethylsulfoxide solution of these complexes were recorded on Cary-2390 spectrophotometer using a pair of 1 cm quartz cuvetts. Analytical, electronic, spectral and magnetic moment data are recorded in Table-1. IR spectral data are recorded in Table-2.

RESULTS AND DISCUSSION

The molecular formulae of the complexes have been assigned on the basis of their analytical data (Table-1). The formula of first series has been found to be $[CuL_2^{1-4}]$, where second series possess formula $[Cu_2L_2^{1-4}X_2]$.

The vibrational spectra (Table-2) of the complexes have been recorded in the frequency region 4000–400 cm^{-1} and structurally important vibrational bands for O—H stretch, >C=N stretch (oxime and azomethine) and N—O stretch provide unequivocal evidences supporting the structure of the complexes.

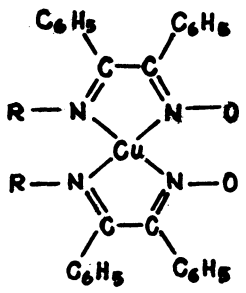
The infrared spectra of ligands HL^{1-4} show a broad and strong band in the region 3425–3415 cm^{-1} which is assigned to ν(O—H) of the N—OH groups. This band is significantly absent in the spectra of the complexes of both the type $[CuL_2^{1-4}]$ and $[Cu_2L_2^{1-4}X_2]$ indicating ligands to coordinate in their anionic form. Ligands also exhibit two sharp and strong bands in the regions 1635–1630 cm^{-1} and 1455–1445 cm^{-1} which have been attributed to >C=N stretching vibrations of azomethine and oxime groups respectively.

In the spectra of complexes azomethine band undergoes a red shift (1620–1605 cm^{-1}), whereas oxime band shows blue shift (1485–1470 cm^{-1}). These shifts can be attributed to the variation in electronic environment due to coordination of both the nitrogen atoms towards copper(II) ions.

The next group of bands in the spectra of the ligands appearing in the region 1095–1085 cm^{-1} has been assigned to the ν(N—O). This band has been found to remain practically unperturbed in $[CuL_2^{1-4}]$ but shows a marked red shift (1065–1055 cm^{-1}) in $[Cu_2L_2^{1-4}X_2]$ indicating coordination of O-atom also towards Cu(II) ion.

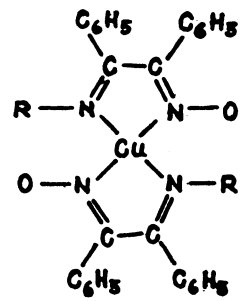
The appearance of few additional sharp and intense bands in the spectra of copper(II) complexes in comparison to ligands in far infrared region 600–400 cm^{-1} indicates the presence of metal-halogen and metal-oxygen bands. Besides these, one more band at 1485 cm^{-1} has been observed which is characteristic of the phenyl ring system. The other bands of phenyl groups might have been superimposed by the oxime and azomethine ν(C=N) bands.

On the basis of above discussions $[CuL_2^{1-4}]$ may be assigned structure I or II whereas $[Cu_2L_2^{1-4}X_2]$ may be presumed to have structure III.



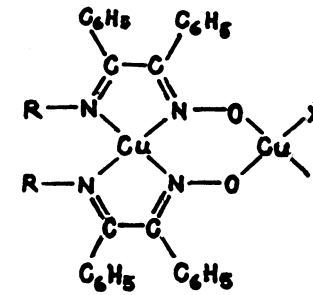
R = -n-C_4H_9 , -i-C_4H_9
-n-C_3H_7 , -i-C_3H_7

(I)



R as in (I)

(II)



R as in (I)

(III)

These structures are supported by magnetic moment, ESR and electronic spectral studies as discussed in the following paragraphs.

Magnetic Moment, Electronic Spectra, ESR and Conductivity data

The complexes of type $[CuL_2^{1-4}]$ possess magnetic moments in the range 1.15–1.17 B.M. The ESR spectrum of one of the complexes, CuL_2^1, shows one line and the anisotropy of the g-tensors is well resolved. The $g^{\parallel}$ and $g^{\perp}$ values are 2.248 and 2.036 respectively at room temperature. The electronic spectra of the complexes exhibit a broad band, the centre of gravity of which lies in the range 14100–14115 cm^{-1} (ε = 15–20). The band shows considerable structure representing at least two superimposed absorptions assignable to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ under square planar or strongly distorted octahedral geometry. The low moments are surely indicative of antiferromagnetic interactions with the structure of the complex having linear stacked chains involving direct copper-copper interactions.

The complexes of type $[Cu_2L_2^{1-4}X_2]$ have μ_{eff} values in the range 1.9–2.0 B.M. per copper atom. The electronic spectra of the complexes consist of two broad bands, the first one in the region 12400–12820 cm^{-1} (ε = 5–8) and a second band in the region 17200—17520 cm^{-1} (ε = 8–10). The high frequency band arises due to chromophore CuN_4 and the low frequency band originates due to the chromophore CuO_2X_2 both under C_2 symmetry.

Molar conductance values for both the series of complexes are found in the range 15–20 ohm^{-1} cm^2 mol^{-1} which support non-electrolytic nature of the complexes.

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