

Binuclear Copper (II) Complexes with Hydroxyimine Ligand

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ABSTRACT

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A series of binuclear copper (II) complexes of the type, $[Cu_2LX_2]$ ($X=Cl^-$, Br^- , NO_3^- , ClO_4^-) has been synthesized by reacting an ethanolic solution of inner complex of copper (II), $[Cu(L)]$ with ethanolic solution of copper (II) salts in equimolar quantities. H_2L is the Schiff base ligand, 2, 9-dihydroxyimino-4, 7-diaza-5, 6-methylbenzo-3,8-dimethyl-3, 7-diaza-3,7-deccadiene. Characterization has been done on the basis of spectral, conductivity and magnetic studies.

Keywords : Binuclear copper (II) complexes, Spectral study, Hydroximine ligands

I. INTRODUCTION

Extensive studies have been done on binuclear copper (II) complexes during recent years creating rejuvenated interest in the field¹⁻¹¹. Consequently, the synthesis and characterization of a series of binuclear copper (II) complexes of the type, $CuLCuX_2$ [$X=Cl^-$, Br^- , NO_3^- and ClO_4^-] being reported in the present communication.

II. Experimental

2.1 Preparation of H_2L

2,3-diaminotulene (6.2 g, 0.05 mol) was mixed with diacetymonoxime (10.1 g, 0.1 mol) with the help of agate and mortar when they went into homogenous liquid after triturating them together for fifteen minutes. The solution was transferred into a beaker and it was stirred vigorously with a glass rod for more than an hour. During the course of stirring, the

reaction mixture gradually became more and more viscous. It was slightly cooled by dipping the beaker in ice cold water when the viscous liquid immediately solidified and the compound was dried under vacuum. The compound, which possessed a yellow color, was recrystallised from ethanol and analysed. The melting point of the compound was found to be $182 \pm 2^\circ C$. The compound is susceptible to moisture.

2.2 Preparation of complexes

$[Cu L CuCl_2]$

An alcoholic solution of the metal chelates ligand (3.38 g, 0.01 mol) was treated with an ethanolic solution of cupric chloride hexahydrate (3.3 g, 0.01 mol) and the mixture was vigorously shaken. Green crystalline compound was obtained after allowing the solution to stand for some time. It was subsequently filtered, washed with alcohol followed by ether, dried under vacuum and analyzed.

[Cu L CuBr₂]

An alcoholic solution of the metal chelates ligand (3.38 g, 0.01 mol) was treated with an ethanolic solution of cupric bromide hexahydrate (2.3 g, 0.01 mol) and the mixture was vigorously shaken. Green crystalline compound was obtained after allowing the solution to stand for some time. It was subsequently filtered, washed with alcohol followed by ether, dried under vacuum and analyzed.

[Cu L Cu (NO₃)₂]

The alcoholic solution of the chelate ligand, 2,9-dihydroximinato-4, 7- diaza-3, 8-dimethyl-5,6:(methylbenzo) 3, 7-decadiene copper (II) (1.68 g, 0.005 mol) was allowed to react with an alcoholic solution of copper (II) nitrate (1.38 g, 0.005 mol) when a green solid product was obtained immediately. It was filtered, washed with alcohol followed by ether, dried and analyzed.

[Cu L Cu (ClO₄)₂]

The metal chelate ligand (1.68 g, 0.005 mol) was dissolved in 20ml. of absolute alcohol and the solution was treated with an alcoholic solution of cupric perchlorate (1.58 g, 0.005 mol) and the mixture was vigorously shaken. Deep green crystals were obtained which were filtered, washed first with small quantities of alcohol and then with ether. It was subsequently dried under vacuum and analyzed for its constituents.

Table I : The analytical results have been presented in

Compounds	% of elements Found (Calculated)				
	% C	% H	% N	% M	% X
H ₂ L	62.46 (62.50)	19.42 (19.44)	6.88 (6.94)	—	—
[Cu L Cu Cl ₂]	36.98 (37.42)	3.10 (3.12)	11.46 (11.64)	26.08 (26.40)	14.36 (14.76)

[Cu L Cu Br ₂]	31.07 (31.58)	2.60 (2.63)	9.80 (9.82)	22.02 (22.28)	27.88 (28.07)
[Cu L Cu (NO ₃) ₂]	33.06 (33.70)	2.79 (2.80)	10.32 (10.48)	23.48 (23.78)	23.00 (23.22)
[Cu L Cu (ClO ₄) ₂]	29.15 (29.55)	2.45 (2.46)	9.17 (9.19)	20.68 (20.85)	32.08 (32.67)

III. IR SPECTRA

Infrared spectra of the complexes of the type [Cu₂L X₂] have been recorded in the frequency region 4000 – 400 cm⁻¹ and vibrational bands of structural significance has been recorded in Table II. Of particular significance in the Vibrational spectra of the binuclear copper (II) complexes, is the shift of the N-O bands to a lower frequency region. This shift unequivocally suggests further coordination of the oxime groups of the inner complex salts to a neighboring copper (II) ion. Infrared spectra of nitrate and perchlorate salts show characteristic features indicating that nitrate and perchlorate ions are coordinated to the copper ion through one of their oxygen atoms in an unidentate manner.

TABLE –II: INFRARED SPECTRAL BANDS IN cm⁻¹

Compound s	VO-H	VC-N azomethi ne	VC-N Oxime	VC-H ^{ph}	VN-O
[H ₂ L]	336 0 302 0	1635	146 0	1580,15 65 1500,14 40	101 0
[Cu ₂ LCl ₂]	-	1610	150 0	1580,15 70 1480,14 40	104 0
[Cu ₂ LBr ₂]	-	1605	144 5	1585,15 70	104 0

				1490,14 45	
[Cu ₂ L(NO ₃) ₂]	-	1600	152 0	1585,15 70 1500,14 35	109 0
[Cu ₂ L(ClO ₄) ₂]	-	1595	151 5	1590,15 75 1485,14 40	112 5

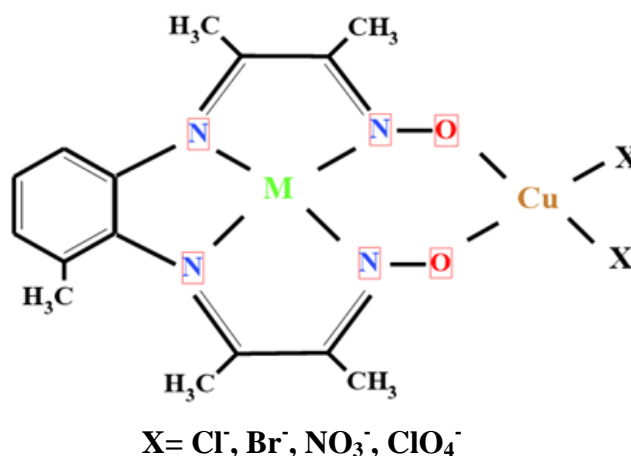
ELECTRONIC SPECTRA AND MAGNETIC MOMENT

During the course of the present investigation, it has been found that the binuclear complexes of copper (II) have magnetic moments in the region 1.7 to 1.9 B.M. per copper atom having the ground term 2D. The electronic spectra of the complexes have been studied in the ligand field region 10,000 – 25000 cm⁻¹. The band positions are recorded in table III. In all the cases, the spectra appear to consist of two broad ligand field bands, the first one in the region 10,500 – 13000 cm⁻¹ and a second band in the region 17,000 – 19,500 cm⁻¹. These spectral features resemble the features of the spectra reported for the bi and Trinuclear schiff base metal clusters and lead us to believe that the copper (II) ions are in similar ligand field environments respectively. Both of the bands arise due to two d-d transitions differing in their energies due to two different ligand fields. It would be reasonable to say that while the high frequency band arises for the chromophore, CuN₄ under D_{4h} symmetry, the low frequency band originates due to the chromophore, CuO₂X₂ under a lower symmetry C₂.

TABLE III : ELECTRONIC SPECTRAL BANDS (cm⁻¹) and MAGNETIC MOMENT

Complexes	Chromophore CuO ₂ X ₂	Chromophore CuN ₄	μ_{eff} in B.M
[Cu ₂ LCl ₂]	12,000	17,600	1.85
[Cu ₂ LBr ₂]	12,600	17,700	1.80
[Cu ₂ L(NO ₃) ₂]	12,500	17,800	1.75
[Cu ₂ L(ClO ₄) ₂]	12,900	18,000	1.90

On the basis of above discussions planar structure (fig. 1) has been proposed for the complexes.



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