Binuclear Complexes of Copper(II) with the ligand 1-hydroxyimino-2-(4'-iminophenol) benzene H_2L

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Abstract : A series of binuclear cluster complexes of the type $Cu_2(HL)_2X_2$ where X=Cl-, Br-, NO_3^-, ClO_4^- have been synthesised by treating ethanolic solution of copper(II) salts in the molar ratio(1:1). The constituents of each compounds have been estimated by established analytical method such as copper by iodometry, halide as their respective silver halides and nitrogen by standard Kjeldahl method. Their structure has been elucidated on the basis of analytical, infrared and electronic spectral data and magnetic susceptibility value. According to this observation $Cu_2(HL)_2X_2$ gives a low frequency band which is attributed to Cu-X bonding on the basis of observation the complex is square-plannar. The possibility of the complexes of the type $Cu_2(HL)_2Cl_2$ having elimeric $Cu_2(HL)_4Cl_4$ structure.

Keywords : Dimeric, imine nitrogen, Iodometry, Kjeldahl method, square-planar.

I. INTRODUCTION

A new area of research that has emerged during the past few year in the synthesis of binuclear transition metal cluster that have attained an important place in contemporary research activities. These clusters offer wide scope for studying the unsual electronic and physico chemical properties associated with the proximity of metal ion centre and their corporate functioning.

II. MATERIAL & METHODS

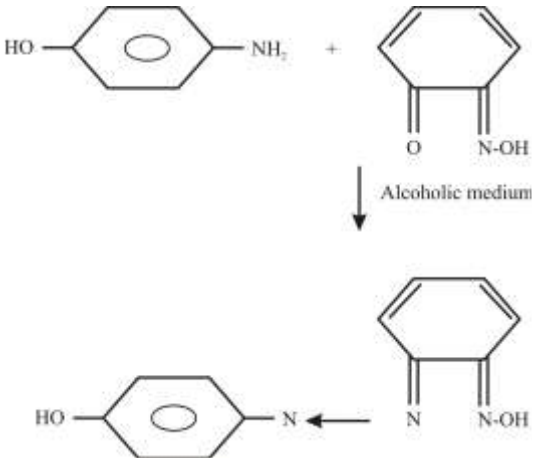
The constituents of compounds have been estimated by established analytical method.

On chemical analysis, stoichiometry of the complexes were found to be of the type $Cu(H_2L)_2X_2$, X=Cl^-, Br^-, I^-, No_3^-, ClO_4^-, H_2L = 1-hydroxyimino-2-4'-iminophenol) benzene. The copper(II) complexes were found to be of the type $Cu(HL)_2$, $Cu_2(HL)_2X_2$ and $Cu_3(HL)_2X_4$.

Orthobenzoquinonemonoxine was of Aldrich quality P-hydroxyaniline, A BDH reagent was redistiled before use. The copper salt were reagent grade chemicals from S. Merck.

Preparation of the ligand

An ethanolic solution of 4-hydroxyaniline (0.1 mol) was mixed with an ethanolic solution of orthobenzoquinone monoxime (0.1 mol) and mixture solution was refluxed on a hot water bath for an hour. It was allowed to cool down and kept in a petty dish. An yellow crystalline solid was obtained which was filtered, dried and recrystallized. The overall reaction can be represented as -



It was analysed as $C_{12}H_{10}N_2O_2$ to give the following results.

Elements	Found %	Calculated %
Carbon	67.30	67.28
Hydrogen	4.66	4.67
Nitrogen	13.11	13.08
Oxygen	14.97	14.95

II. Copper(II) bis-(1-hydroxyiminato-2-(4'-iminophenol), benzene dichloro copper(II), $Cu_2(HL)_2Cl_2$

Bis [1-hydroxyiminato-2-[4'-iminophenol benzene (0.005 mol) derived in a minimum volume of ethanol was treated with an alcoholic solution of copper (II) chloride dihydrate (0.005 mol). The reaction mixture was heated under reflux over a hot water bath for four hours when a green precipitate of copper(II) complex was obtained. The precipitate was filtered washed with cold water followed by ethanol and ether dried in vaccum.

It was analysed as $Cu_2(C_{12}H_9N_2O_2)Cl_2$

Elements	Found %	Calculated %
Carbon	46.10	46.00
Hydrogen	2.88	2.87
Nitrogen	8.92	8.94
Oxygen	10.21	10.22
Copper	20.30	20.28
Chloride	11.33	11.34

III. Copper(II) bis (1-hydroxyiminato-2-(4' iminophenol) benzene dibromo copper(II), $Cu_2(HL)_2Br_2$

Bis-[1-hydroxyiminato-2-(4'-iminophenol) benzene (0.005 mol.) dissolved in a minimum volume of ethanol was treated with an alcoholic solution of copper(II) bromide hexahydrate (0.005 mol.). The reaction mixture was heated under reflux over a hot water bath for four hours when greyish brown precipitate of copper(II) complex was obtained. The precipitate was filtered, washed with cold water followed by ethanol and ether and dry in vaccum. It was analysed as $(C1_2H_9N_2O_2)Br_2$

Elements	Found %	Calculated %
Carbon	40.30	40.29
Hydrogen	2.48	2.51
Nitrogen	7.85	7.83
Oxygen	8.94	8.95
Copper	17.75	17.76
Bromide	22.34	22.35

III. Results and Discussion

The complexes were analysed by standard procedure. The magnetic susceptibility measurement were carried out using Guoy method with Co(Hg(CN_5) as the calibrant. Spectral data are provided in Table (1) and Table (2).

Infrared spectra

In the complexes of the type $Cu_2(HL)_2X_2$ ($XzCl^-$, Br^-, I^-, ClO_4^-), one band is observed in the low frequency region (600-200 cm^-). In $Cu_2(HL)_2Cl_2$ it appears at 420 cm^- and 318 cm^- in $Cu_2(HL)_2Br_2$ which can be assigned to terminal metal halogen stretching vibration. In case of $Cu_2(HL)_2(NO_3)_2$ and $Cu_2(HL)_2(ClO_4)_2$ the band appear at 485 cm^- and 545 cm^- respectively.

In the complexes of the type $Cu_2(HL)_2X_2$ the most important band is due to ν_{N-O} as the bond would be more elucidative on the structure of complexes and bonding between inner complex of copper(II) cu(HL)2.

Table - 1 Infrared spectra of Copper(II) complexes.

Compounds	ν_{O-H} (R-OH)	ν_{O-H} (N-OH)	ν_{C-H} Azomethi	ν_{C-N} Oxime	ν_{N-O}
HL	3330 mb	3365 mb	1640s	1450s	1085s
$Cu(HL)_2$(A)	3320 mb	-	1620s	1430s	1075s
$Cu(HL)_2$(B)	-	3345 mb	1620s	1430s	1050s
$Cu_2(HL)_2Cl_2$(A)	3315 mb	-	1605s	1410s	1040s
$Cu_2(HL)_2Br_2$(A)	3320 mb	-	1610s	1415s	1045s
$Cu_2(HL)_2(NO_3)_2$(A)	3315 bm	-	1610s	1415s	1045s
$Cu_2(HL)_2(ClO_4)_2$(A)	3315 mb	-	1605s	1405s	1040s
$Cu_2(HL)_2Cl_2$(B)	-	3335 mb	1605s	1405s	1050s
$Cu_2(HL)_2Br_2$(B)	-	3340 mb	1610s	1410s	1045s
$Cu_2(HL)_2(NO_3)_2$(B)	-	3340 mb	1610s	1410s	1050s
$Cu_2(HL)_2(ClO_4)_2$(B)	-	3335 mb	1605s	1405s	1050s

m = medium, b = broad, s = strong

Based on analytical data and IR spectral evidence the mode of bonding in the complexes with ligand is believed to take place as shown i fig. (1)

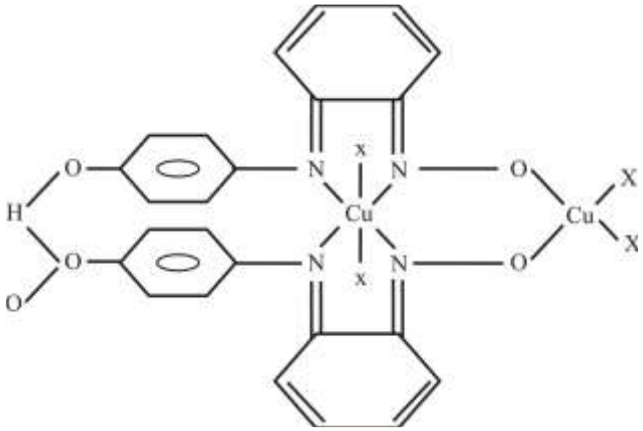


Fig. 1.

Electronic Spectra and Magnetic Properties

The copper(II) complex of the type $Cu(HL)_2$ gives a broad band. The centre of gravity which lies at 14100-14115 cm^{-1} have been attributed to the ligand field due to the chromophore CuN_4.

The broad band which shows considerable structure represents at least two superimposed absorptions assignable to the transition.

$^2A_1g \leftarrow {}^2B_1g$ for

$$a_1^2 g^{e4} g^{b2} 2gb_{1g}^1 \rightarrow a_1^2 g_g^4 b_g^1 b_1^2 g$$

and

$$2E_{1g} \leftarrow 2\ B_{1g}$$

$$a_1^2 g^{e4} g^{b2} 2gb_{1g}^1 \rightarrow a_{1g}^2 e_g^3 b_{2g}^2 b_{1g}^2$$

The ligand is comparable both in position and width with earlier reported planar copper(II) complexes and lead us to believe that the inner complex salt of Cu(II) is square planar.

Table - 2 Electronic spectra of the complex of the types $Cu(HL)_2$, $Cu_2(HL)_2X_2$, $Cu_3(HL)_2X_4$

Complexes	Chromophore CuN_4	Chromophore CuO_2X_2	Chromophore $Cu'O_2{}^1X_2{}^1$	μ_{eff} B.M.
$Cu(HL)_2$	14100	-	-	1.30
$Cu_2(HL)_2Cl_2$	17100	12600	-	1.85
$Cu_2(HL)_2Br_2$	17200	12400	-	1.90
$Cu_2(HL)_2(NO_3)_2$	17200	12800	-	1.90
$Cu_2(HL)_2(ClO_1)l_2$	17300	12500	-	1.85
$Cu_3(HL)_2Cl_4$	17100	12600	12550	1.80
$Cu_2(HL)_2Br_4$	17200	12400	12380	1.75
$Cu_2(HL)_2(NO_3)_4$	17200	12800	12770	1.85
$Cu_2(HL)_2(ClO_4)_4$	17300	12500	12480	1.80

The copper(II) complexes of the type $Cu_2(HL)_2X_2$ and $Cu_3(HL)_2X_4$ have magnetic moments in the region 1.75 to 1.95 B.M. per copper atom having the ground term ^2D. The electronic spectra of the complexes have been studied in the ligand field region 10,000-25,000 cm^{-1}. The spectra appear to consist of two broad bands the first one is the region 12000-18000 cm^{-1} and a second band in the region 17000-18000 cm^{-1} high frequency band arises for a chromophore and D_4h symmetry and low frequency band originates due to the chromophore $Cu_2O_2X_2$.

These spectral features resemble, the feature of the spectra reported for the bi and trinuclear cluster complexes and lead us to believe that the Cu2(HL)2X2 and Cu3(HL)2X4 are square planar with some amount of distortion.

IV. Acknowledgment

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