

Study of Cu (II) Complexes and Determination of Their Structure with The Schiff's Base Ligand

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ARTICLE INFO

Article History:

Accepted: 05 April 2023

Published: 28 April 2023

Publication Issue

Volume 10, Issue 2

March-April-2023

Page Number

971-977

ABSTRACT

The article proposes preparation of Cu (II) complexes with Schiff's base ligand were carried out in the presence of various bases like water, an oxygen donor molecule, ammonia, pyridine, phenyl isocyanide and different picolines, which are nitrogen donor molecule by a general procedure.

Keywords: Hydroxamic acids, Ligands, Schiff's base ligands

I. INTRODUCTION

Preparation of Cu (II) complexes with the Schiff's base ligand carried out in the presence of various bases like ammonia, pyridine, phenyl isocyanide and different picolines, which are nitrogen donor molecules by a general procedure given below:

0.173 gram (0.001 mole) of the ligand dissolved in the minimum volume of alcohol was added to 0.17 gram (0.001 mole) of Cu (II) chloride dehydrate (BDH) dissolved in ethanoic aqueous solution with regular shaking and stirring. The resulting solution was then refluxed and green crystals separated out by allowed the solution to stand for three days at room

temperature. The product was separated by filtration washed with a small amount of acetone and then dried over KOH in a dedicator.

The complexes of Cu(II) ion with Schiff's base ligand (LH₂) were prepared separately in each case with oxygen and nitrogen donor bases like, H₂O, ammonia, quinoline, pyridine, phenylisocyanide, α -picoline, β -picoline, γ -picoline. The metal ligand ratio was maintained as 1:1 in each case.

On the basis of elemental analysis, the complexes were found to possess the general molecular formula [Cu(L)(B)₃]. Where B = water, Ammonia, quinoline, phenyl isocyanide, α -picoline, β -picoline and γ -picoline.

Table 1 Elemental Analysis of the Cu(II) complexes with the ligand 2-(2-mercaptobenzylidene imino) benzohydroxamic acid LH₂.**Table 1**

Sl. No.	Compound ↓ Element →	Metal	Found % (Calculated%) Carbon	Hydrogen	Nitrogen	Sulphur
1.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (H ₂ O) ₃]	16.16	43.20	4.14	7.26	8.16
		(16.38)	(43.35)	(4.12)	(7.22)	(8.25)
2.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (NH ₃) ₃]	16.32	43.51	4.99	18.24	8.20
		(16.51)	(43.69)	(4.94)	(18.20)	(8.32)
3.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₉ H ₇ N) ₃]	8.56	68.02	4.33	9.79	4.30
	Quinoline	(8.81)	(68.28)	(4.30)	(9.71)	(4.44)
4.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₆ H ₅ NC) ₃]	9.70	65.10	4.85	10.85	4.83
	(Phenyl-isocynide)	(9.88)	(65.36)	(3.89)	(10.89)	(4.98)
5.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₅ N) ₃]	11.00	60.72	4.40	12.34	5.40
	(Pyridine)	(11.13)	(60.99)	(4.38)	(12.26)	(5.60)
6.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	10.12	62.52	5.10	11.44	5.10
	(α-Picoline)	(10.36)	(62.69)	(5.06)	(11.42)	(5.22)
7.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	10.22	62.46	5.12	11.48	5.12
	(β-Picoline)	(10.36)	(62.69)	(5.06)	(11.42)	(5.22)
8.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	10.80	62.40	5.14	11.54	5.18
	(γ-Picoline)	(10.36)	(62.69)	(5.06)	(11.42)	(5.22)

Table 2 Magnetic moments of the Cu (II) complexes with the ligand 2-(2-mercapto benzylidene imino) benzo hydroxamic acid LH₂.**Table 2**

Sl. No.	Compound	Colour	<i>M_{eff}</i> (B. M.)	Magnetic Properties
1.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (H ₂ O) ₃]	Green	1.90	Paramagnetic
2.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (NH ₃) ₃]	Parrot white	1.96	Paramagnetic
3.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₉ H ₇ N) ₃]	Parrot green	1.95	Paramagnetic
	Quinoline			
4.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₆ H ₅ NC) ₃]	Parrot green	1.97	Paramagnetic
	(Phenyl-isocynide)			
5.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₅ N) ₃]	Deep green	2.00	Paramagnetic
	(Pyridine)			
6.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	Deep green	1.98	Paramagnetic
	(α-Picoline)			
7.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	Deep green	1.96	Paramagnetic
	(β-Picoline)			
8.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	Parrot green	1.95	Paramagnetic
	(γ-Picoline)			

II. MAGNETIC PROPERTIES OF CU (II) COMPLEXES

The valence shell electronic configuration of copper is $3d^{10}4s^1$. Thus Cu (II) is a $3d^9$ system having one unpaired electron in 3d-orbital.

There is one and only one free ion 2D for d^9 . In weak octahedral field, the ground term for d^9 is 2E_g and in weak tetrahedral field, the ground term is 2T_2

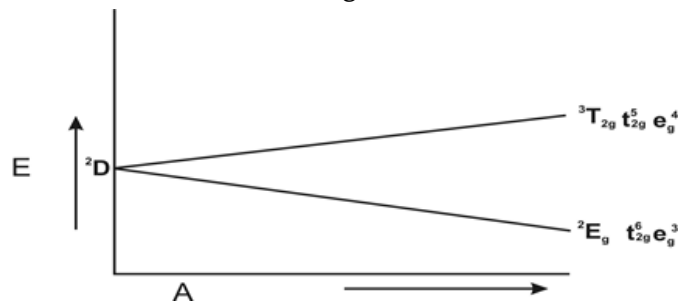


Figure. 1(Splitting in octahedral field)

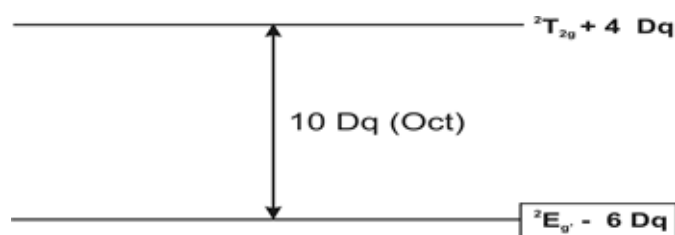


Figure. 2(Splitting in octahedral field)

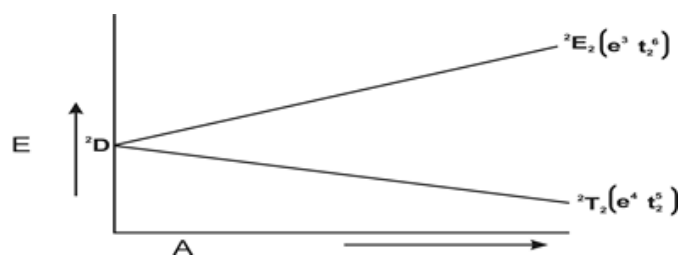


Figure. 3(Splitting in tetrahedral field)

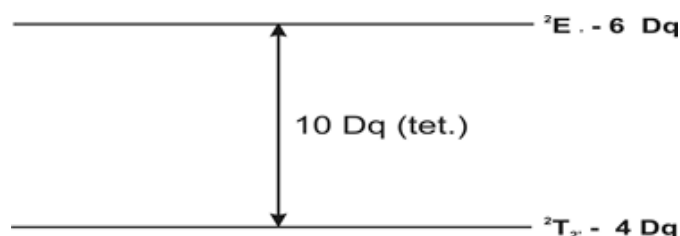


Figure. 4(Splitting in tetrahedral field)

In cases of distortion, either by tetragonal (non-equivalence of ligand) or by John-Teller distribution, 2T_2 splits as B_{2g} and E_g which further splits as A_{1g} and B_{1g} .

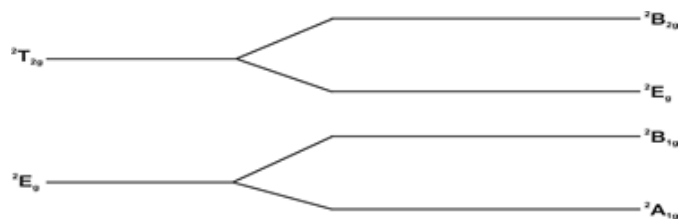


Figure. 5 (Octahedral Distribution)

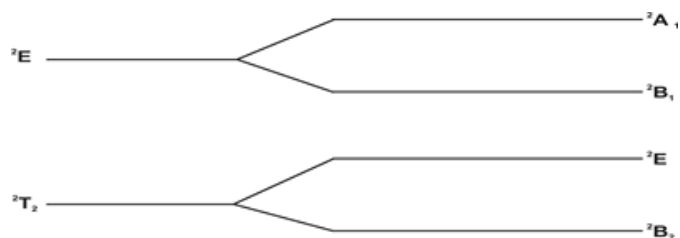


Figure. 6 (Tetrahedral Distortion)

Cu (II)- $3d^9$ has one unpaired electron, so Cu (II) may form outer orbital octahedral complex by sp^3d^2 hybridisation and tetrahedral complexes by sp^3 hybridisation on promotion of a 3d-electron to 5s orbital, one of the five 3d-orbitals may be made empty to take part in dsp^2 hybridisation for the formation of square planar complexes.

It is evident that all three classes of Cu (II) complexes contain one unpaired electron and so all are expected to exhibit paramagnetic character corresponding 1.73 B.M.

$$\mu_s = \sqrt{n(n+2)} = \sqrt{3} = 1.73 \text{ B. M.}$$

In weak octahedral field ground term is $2E_g$ and as there is no orbital contribution, there is contribution from first order Zeeman effect:

$$\mu_{eff} = \mu_s \left(1 - \frac{2\lambda}{10Dq} \right)$$

If for Cu (II), $\lambda = -830 \text{ cm}^{-1}$ and $10 Dq$ is 13000 cm^{-1} .

$$\begin{aligned} \mu_{eff} &= 1.73 \left(1 - \frac{2(-830)}{13000} \right) \\ &= 1.73 \left(1 + \frac{2 \times 830}{13000} \right) = 1.90 \text{ B.M.} \end{aligned}$$

Thus μ_{eff} for Cu(II) octahedral is expected to be greater than μ_s .

Ground term for Cu(II) complexes in tetrahedral field is $2T_2$. So there is orbital contribution due to T-ground term. Hence μ_{eff} for tetrahedral Cu(II)

complexes is expected to be greater than $\mu_S \cdot \mu_{eff}$ for tetrahedral Cu(II) complexes have been reported in the range of 2.15-3.0 B.M.[1-5].

Large orbital contribution to magnetic moment has been observed. Distorted octahedral ground terms is $2A_{1g}$ and so neither orbital contribution nor first order Zeeman effect contribution is expected and so μ_{eff} for distorted octahedral complexes is expected to be near μ_S value only.

However, a large number of Cu(II) complexes with subnormal values of magnetic moment at room temperature have been reported[228-230]. Such complexes have the values of magnetic moment in the range of 0 to 1.73 B.M.

The complexes which display magnetic moment value below 1.73 B.M. are referred to as magnetically subnormal complexes.

In case of subnormal complexes, the lowering of magnetic moment value is attributed to exchange interaction or metal-metal bonding leading to partial overlap of unpaired electron of bivalent Copper in its complexes.

Copper forms many complexes in which Cu-Cu distances are short enough to indicate significant M-M interactions but in no case actual Cu-Cu bonds are present [231]. Attempts to specify the detailed nature of this interaction have been plagued by controversy and there are still considerable difference of opinion about its precise nature. Melkin has interpreted antiferromagnetic exchange between coupled pairs of Cu-atoms.

In spite of several favorable observations in support of the above measurable difference between the magnetic moment value and geometry of the complex, the magnetic moment data cannot be used as the only criteria, for a number of other factors also affect the above data as it is quite evident from Cu (Acetylacetonato)₂ complex.

In the present investigation, the value of magnetic moment obtained for the Cu(II) complexes are in the

range of 1.90-2.00 B.M. suggesting the distorted octahedral nature of the complexes.

Table 3 Data of electrical conductance of the [Cu (L)(B)₃] complexes with the ligand 2-(2-mercapto benzylidene imino) benzohydroxamic acid.

Table 3

Sl. No.	Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvents
1.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(H ₂ O) ₃]	15	DMF
			DMF
2.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(NH ₃) ₃]	11	DMF
3.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₉ H ₇ N) ₃]	13	DMF
	Quinoline		
4.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₆ H ₅ NC) ₃]	11	DMF
	(Phenyl-isocynide)		
5.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₅ H ₅ N) ₃]	15	DMF
	(Pyridine)		
6.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₅ H ₄ NCH ₃) ₃]	12	DMF
	(α -Picoline)		
7.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₅ H ₄ NCH ₃) ₃]	17	DMF
	(β -Picoline)		
8.	[Cu(C ₆ H ₁₁ N ₃ O ₃)(C ₅ H ₄ NCH ₃) ₃]	11	DMF
	(γ -Picoline)		

These complexes are insoluble in common organic solvents viz., carbon tetrachloride, methanol, ethanol, dioxane, THF (tetrahydrofuran), pyridine, acetone but they are partially soluble in DMSO (dimethyl sulphoxide) and appreciably in DMF (dimethyl formamide). The molar conductance of the complexes of Cu(II) ions with 2-(2-mercapto benzylidene imino) benzohydroxamic acid as ligand (LH₂) have been

measured at 10^{-3} M DMF solution at room temperature.

III. ELECTRONIC SPECTRA OF BEHAVIORS OF CU(II) COMPLEXES

The electronic spectra of Cu(II) complexes have been explained on the basis of crystal field model [6-7].

Taking into consideration the John-Teller distortion, the d-d band in both cause is expected to be broad and unsymmetrical. In the distorted octahedral or tetrahedral field three d-d bands are expected.

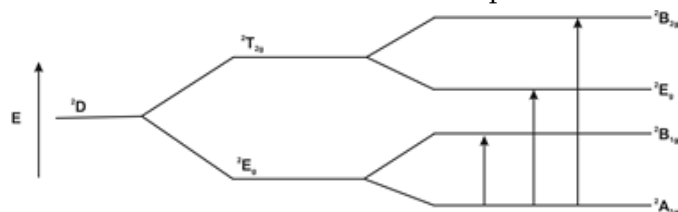


Figure. 7

Viz. ${}^2A_{1g} \rightarrow {}^2B_{1g}$, ${}^2A_{1g} \rightarrow {}^2E_g$, ${}^2A_{1g} \rightarrow {}^2B_{2g}$

Holmet et al [8], Goodgame and Cotton [9] reported three bands for octahedral Cu(II) complexes in the range of $10,000\text{ cm}^{-1}$.

The energy level diagram in case of square planar complexes of Cu(II) as suggested by Ballhausen [10] gives rise to three transitions in square planar or distorted octahedral field.

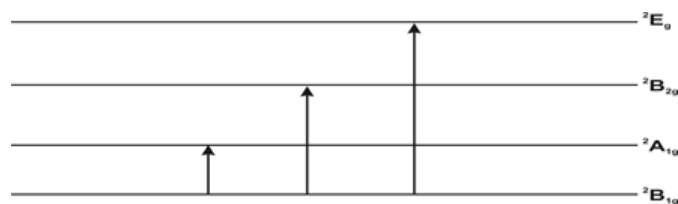


Figure. 8

i.e., ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$

In the visible spectra of square planar and tetrahedral Cu(II) complexes three bands have been reported.

Hathvay et al [11] have reported three bands (18000 cm^{-1} , 16000 cm^{-1}) of $[\text{Cu}(\text{en})_2]^{2+}$ complex with slight difference in band positions are tentatively assigned as the ${}^2E_g \leftarrow {}^2B_{1g}$, ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and ${}^2B_{2g} \leftarrow {}^2B_{1g}$ transitions respectively.

According to Figgis [12] the Cu(II) complex with acetylacetonone display two bands in the vicinity of

15000 cm^{-1} and $15,500\text{ cm}^{-1}$ and bands at higher energies due to charge transfer. He assigned the two bands due to transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$.

Some workers have reported a band around 15500 cm^{-1} for square planar Cu(II) complexes which may be assigned as ${}^2B_{1g} \rightarrow {}^2E_g$. For tetrahedral complexes transition occurs around 7500 cm^{-1} to 11000 cm^{-1} corresponding to ${}^2T_2 \rightarrow {}^2E$.

However Sacconi et al [13] studying the electronic spectra of salicylidineamino Cu(II) complexes, reported that flattening of the tetrahedral geometry results in the splitting of both ground and excited levels giving rise to four transitions. They however obtained only three peaks at 85000 , 13600 and 21000 cm^{-1} and assigned a pseudo tetrahedral geometry.

A. Ranchandraiah et al [14] have reported bands at 10500 cm^{-1} and 14000 cm^{-1} for pseudo-tetrahedral Cu(II) complexes. An extra low intensity band assigned to $dx^2 - y^2 \rightarrow dz^2$ transition was reported for certain Cu(II) Schiff base complexes, with a pseudo-tetrahedral geometry. Thus the presence of three bands instead of one for Cu(II) complexes can be attributed to perturbation of ground as well as excited term in tetragonal or distorted tetrahedral field. The electronic spectra of the Cu (II) complexes taken under study are given in the table.

Table 4

Data of Electronic Spectra of the Cu(II) complexes with the ligand 2-(2-mercapto benzyldine imino) benzo hydroxamic acid.

Sl. No.	Complexes	cm^{-1}	
1.	$[\text{Cu}(\text{C}_6\text{H}_{11}\text{N}_3\text{O}_3)(\text{H}_2\text{O})_3]$	15950(b)	13.40
2.	$[\text{Cu}(\text{C}_6\text{H}_{11}\text{N}_3\text{O}_3)(\text{NH}_3)_3]$	1600 (b)	13.50
3.	$[\text{Cu}(\text{C}_6\text{H}_{11}\text{N}_3\text{O}_3)(\text{C}_9\text{H}_7\text{N})_3]$	15750 (b)	13.80
	Quinoline		
4.	$[\text{Cu}(\text{C}_6\text{H}_{11}\text{N}_3\text{O}_3)(\text{C}_6\text{H}_5\text{NC})_3]$	15900 (b)	12.90

	(Phenyl-isocynide)		
5.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₅ N) ₃]	15400 (b)	12.90
	(Pyridine)		
6.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	16250 (b)	13.80
	(α-Picoline)		
7.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	15600 (b)	13.10
	(β-Picoline)		
8.	[Cu(C ₆ H ₁₁ N ₃ O ₃) (C ₅ H ₄ NCH ₃) ₃]	16000 (b)	13.10
	(γ-Picoline)		

b=broad.

In our present investigation the electronic spectra for Cu (II) complexes obtained are in the range of 15400-16200 cm⁻¹ indicating the distorted octahedral structure of the complexes.

IV.I.R. SPECTRA OF THE CU (II) COMPLEXES

The infrared spectra of the Schiff's base H₂L and its metal complexes of the type CuLB₃ have been recorded in the region 4000-200 cm⁻¹. Comparison of the spectra provides valuable information regarding mode of bonding. Above 3000 cm⁻¹, the spectrum of the ligands shows a strong band at 3250 cm⁻¹ and can be assigned to V_{O-H} of the NHOH group. The band at 2985 cm⁻¹ has been assigned to V_{N-H}. The 1st band remains unperturbed in the spectra of complexes where as 2nd band disappears indicating non-involvement of Oxygen of the oxime group and involvement of the oxime group and involvement of the Nitrogen in the coordination[15]. The appearance of a new band in the range 450-470 cm⁻¹ assigned to V_{M-N} also supports the fact of strong.

The azomethine band at 1650 cm⁻¹ in the ligand molecule is also shifted to lower frequency in almost all the complexes by 75 to 55 cm⁻¹. This shift of ν (C=N) band towards lower frequency in the complexes suggests the coordination of the azomethine nitrogen of the ligand in the formation of

the complexes. The strong and sharp band due to oxime group (C=N-OH) of the ligand located at 1470-1490 cm⁻¹ is also shifted to higher frequency by the complex formation.

In case of aqua-complexes, the appearance of one more band in the range of 750-830 cm⁻¹ due to the rocking and wagging mode of vibrations, suggest that H₂O is present in the coordination sphere. A separate band for water molecule is not obtained due to the overlapping of ν_(O-H) vibration.

In case of amine complexes, separate band for ν_(N-H) of coordinated ammonia molecule is not obtained due to overlapping of ν_(O-H) vibration.

The complexes containing pyridine and different picolines, however, display some extra bands in the finger print zone of infrared region.

The pyridine ring stretching mode of vibration located at 960-1000 cm⁻¹ in the complexes has been taken to be characteristic vibration of coordination pyridine and different picolines. From the I.R. spectral studies, it is found for three isocyanide ν (C=N) band is obtained at 2130 cm⁻¹ and for isocyanide in the complexes ν (C=N) band is obtained at 2240 cm⁻¹. The increase in ν (C=N) band of isocyanide in the complex indicates the coordination of isocyanide in the complex formation.

Thus on the basis of elemental analysis, measurement of electrical conductance and magnetic moment, I.R. and electronic spectral behavior, it may be suggested that Cu(II) ion forms octahedral complexes with the ligand Schiff's base (LH₂) in presence of various base like ammonia, pyridine, phenyl isocyanide and different picolines.

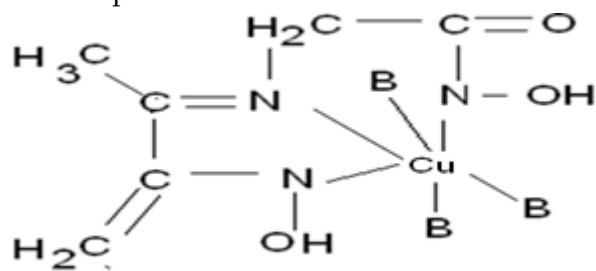


Figure 9

Where, B= Water, Amonia, Pyridine, Phenylisocyanide and α, β and γ Picolines.

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