Structural Studies of Divalent Transition Metal Copper-Complexes with Tetradentate Hydroxamic Acid

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ABSTRACT: -

A large number of complexes of Copper (II) metals have been prepared with the ligand 1,3-bis (2-imino benzohydroxamic acid)- p-bromo benzoyl acetone in presence of different bases. The ligand molecule behaves as bi-anionic tetra dentate ligand. The general molecular formulae of the complexes have been found to be $[Cu(L)(B)_2]$ where L=ligand and B=bases such as water, ammonia phenyl-isocyanide, quinoline and pyridine. On characterization by usual methods, such as elemental analysis, magnetic moment, electronic and I.R. spectra, all the complexes have been found to be mono-meric and non-electrolyte in nature. Due to presence of unpaired electrons in 3d-orbital, all copper complexes are paramagnetic in nature. On the basis of elemental analysis and different spectral studies, the geometry of copper complexes was proposed to be distorted octahedral.

Key words: - Copper salt, 2-amino-benzhydroxamic acid,4-bromo benzoyl acetone, Schiff base.

1. INTRODUCTION: -

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first synthesized by Hugo Schiff in 1864. These compounds containing a general formula $RCH = N - R^1$ where R and R^1 are alkyl, aryl, cycloalkyl or heterocyclic groups are also known as anils, imines or azomethines. Schiff bases are the condensation products of an amine and carbonyl compounds, and are important class of ligand that coordinates to metal ions via azomethine nitrogen (C=N). The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines, and these provided binding site for the metal ions through non-bonding electrons of the nitrogen. They also have many other hetero- elements like oxygen and sulphur which provided binding sites through non-bonding electrons. They are crystalline solids which are feebly basic, but at least some form insoluble salts with strong acids. They also offer a versatile and flexible Series of ligand capable of binding with various metal ions to gives complexes with suitable properties for theoretical or practical applications. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable in general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are less sterically hindered than that of ketones. The extra carbon of ketones donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands capable of forming very stable complexes with transition metals. A considerable number of complexes has been formed with tetra dentate Schiff base ligand in presence of different bases. Schiff bases containing nitrogen, oxygen & Sulphur atoms as their donor sites have been used at large scale to form the complexes with the transition metals. But at least work has been done to form the complexes with such Schiff base which contains hydroxamic acid group in its moiety. In this paper, we the report the formation of Copper (II) complexes with Schiff base ligand 1,3-bis (2-imino benzohydroxamic acid) p-bromo benzoyl acetone which contains hydroxamic acid group in its moiety.

2. MATERIALS AND METHODS:-

Chemicals and Reagents :- Ethyl acetate, p-bromo aceto phenone, methyl benzoate, hydroxylamine ethyl alcohol, ether KOH , DMF, Acetates / chlorides of Copper (II) metal, ammonia, quinoline, phenyl-isocyanide and pyridine. All the chemicals used were also taken from either from E. Merck extra pure or BDH (AR). They were used without further purification.

Physical Measurements: -

The estimation of metal and non-metals present in the complexes has been done by standard methods. Copper has been estimated by iodiometrically. Carbon, Hydrogen & Nitrogen were estimated by semi-macro-duma’s method. Bromide was estimated gravimetrically as silver Bromide method. The measurement of electrical conductivity of the solutions of the complexes was done by conductivity meter bridge manufactured by Wiss-Techen Wearch Stathen type-LBR-at room temperature. Pure DMF and conductivity water were used as solvent. Hitachi-320 spectrophotometer were used to record the electronic absorption spectra of the complexes. Perkin Elmer 577 spectrophotometer was used to record the infra-red spectra of the complexes and the ligand in nujol mull. For the measurement of the magnetic susceptibilities of the complexes was done by Gouy's method by using Mercury tetrathio cyanato-cobaltate (II), Hg [Co $(SCN)_4$] as calibrant.

Synthesis of Schiff base ligand (L): -

The Schiff base ligand 1,3-bis (2-imino benzohydroxamic acid)- p-bromo benzoyl acetone was prepared by adding 24.1 g (0.1 mol) of p-bromobenzyl acetone in 25 ml ethanol and 15.2 g (0.1 mol) of 2-amino-benzhydroxamic acid in 25 ml ethanol. The resulting solution was refluxed for 2-3 h. On cooling the reaction mixture, the yellow crystalline solid was formed. The precipitate is washed with distilled water and ethanol several times and is then recrystallized with ethanol to obtain the required Schiff base.

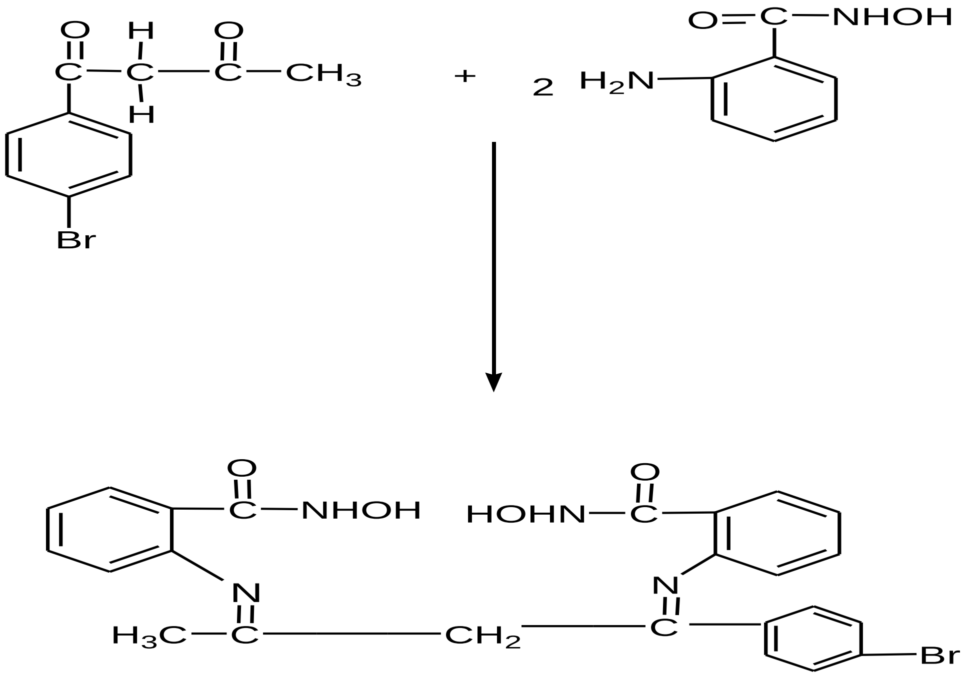

Fig.1. Schiff base ligand

Synthesis of the copper complexes:-

The copper complexes were prepared by refluxing 0.01 mol of the ligand-1,3-bis (2-imino benzohydroxamic acid) p-bromo benzoyl acetone was completely dissolved in ethyl alcohol. Similarly, 0.01 mole of Copper (II) salt was completely dissolved in minimum volume of aqueous-ethanolic solution. Both the solutions were mixed together gradually with regular shaking. The mixture solution was filtered and the filtrate was refluxed on water bath for one and half an hour at room temperature. During the course of reflux process, the colour of the solution was gradually changed and crystals of light green colour was separated out by allowing the solution to stand overnight. The product/solid was separated by filtration and the residue was washed with a small amount of cold ethyl alcohol and then dried over KOH pellets placed in a desiccator. The ratio of the metal and the ligand was always kept 1:1 respectively. The colour of the complexes formed with different bases were found to be slightly different with slight variation of time of reflux.

3. RESULTS AND DISCUSSION: -

All the metal complexes are coloured, solid, stable at room temperature and non- hygroscopic in nature. The complexes are insoluble in water but are soluble in some common organic solvents such as Dimethylsulphoxide (DMSO), Dimethylformamide (DMF), methanol, acetone, ethanol and chloroform. The observed molar conductance of the complexes in DMF at room temperature is consistent with the non-electrolytic nature of the complexes, due to the low conductivity values. The analytical data of the ligand and Its copper (II) complexes are presented in Table 1. All the metal chelates have 1:1 (metal: ligand) stoichiometry.

Table 1. Analytical data of ligand and its copper (II) complexes.

Compounds	Elemental analysis found (Calcd), %				
	M(Cu)	C	H	N	Br
[Cu ($C_{24}H_{19}N_4$ Br O_4) (H2O)$_2$]	10.16(1O.46)	47.10(47.48)	3.80(3.89)	9.25(9.13)	12.92(13.19)
[Cu ($C_{24}H_{19}N_4$ Br O_4) (NH_3)$_2$]	10.20(10.50)	47.30(47.48)	4.15(4.13)	13.94(13.89)	12.94(13.23)
[Cu ($C_{24}H_{19}N_4$ Br O_4) (C_9H_7N)$_2$]	7.30(7.66)	60.40(60.83)	4.00(3.95)	10.18(10.13)	9.32(9.65)
[Cu ($C_{24}H_{19}N_4$ Br O_4) (C_6H_5NC)$_2$]	7.90(8.17)	58.32(58.76)	3.75(3.71)	10.88(10.81)	10.12(10.30)
[Cu ($C_{24}H_{19}N_4$ Br O_4) (C_6H_5N)$_2$]	8.32(8.71)	55.60(55.87)	4.00(3.98)	11.60(11.53)	10.48(10.54)

The Copper (II) complexes, one broad and unsymmetrical band has been obtained in the range of 13250-13650 cm^{-1} indicating distorted octahedral geometry for all the complexes. The values of electrical conductance for Copper (II) complexes have been found to be in the range of 12-22 s cm^{-1} indicating non-electrolytic nature of the complexes. The values of magnetic moments for the Copper (II) complexes have been found to be 1.84-1.98 BM, which indicates distorted octahedral nature of the complexes. Comparison of I.R. Spectra of the ligand & the complexes: The Schiff base ligand, 1,3-bis (2 - imino benzo hydroxamic acid) P-bromo benzoyl acetone is highly sensitive in the enol form to form the complexes. This is expected that two hydrogen atoms of two Oxime group (-N=O-H) have been deprotonated producing negative charges on each of nitrogen atom. Two azomethine groups are capable to participate in bond formation with the metal cations. Thus, the ligand behaves as bi anionic tetra - dentate molecule. Thus, the two nitrogen atoms of oxime group and two nitrogen atoms of two azomethine groups are the bonding sites of the ligand molecule. In almost all the complexes, (OH) band, azomethine band (C=N), oxime band (C=N) and (N-O) band of the ligand molecule are appreciably affected after the complex formation. The strong and sharp bands due to the vibrations of (O-H) and (N-H) bonds of the ligand obtained at 3260 cm^{-1} disappears in all the complexes of the ligand and a new broad band appears in the complexes at about 3430-3480 cm^{-1} confirming the presence of at least one free (-OH) group even in the complexes. The disappearance of the strong band at 1240 cm^{-1} further suggests the deprotonation of the hydroxy group (-OH) group i.e., (N - OH) proton located at hydroxamic acid moiety. The azomethine band located at 1640 cm^{-1} in the ligand molecule is also shifted to lower frequency in almost all the complexes by about 45-60cm^{-1}. This shift of (>C=N) band towards lower frequency in the complexes suggests the coordination of azomethine nitrogen of the ligand in the formation of the complexes.

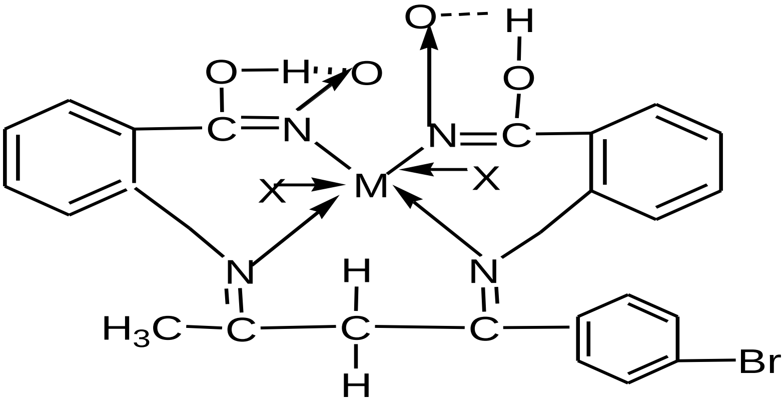

Fig 2. Structure of metal complexes. M = Cu (II).

4.CONCLUSION: -

A new Schiff base has been prepared by the condensation of p-bromobenzyl acetone with 2-amino-benzhydroxamic acid in an alcoholic medium. The ligand molecule behaves as bi-anionic tetra dentate ligand. The observed molar conductance of the complexes in DMF at room temperature is consistent with the non-electrolytic nature of the complexes, due to the low conductivity values. The values of magnetic moments for the Copper (II) complexes have been found to be 1.84-1.98 BM, which indicates distorted octahedral nature of the complexes. Comparison of I.R. Spectra of the ligand & the complexes: The Schiff base ligand, 1,3-bis (2 - imino benzo hydroxamic acid) P-bromo benzoyl acetone is highly sensitive in the enol form to form the complexes. On the basis of elemental analysis and different spectral studies, the geometry of copper complexes was proposed to be distorted octahedral.

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