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# Synthesis and Characterization of Co(II) and Cu(II) Complexes with Tetradentate Schiff base Ligand

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## Abstract

A noble series of Co (II) and Cu (II) complexes with tetradentate Schiff base ligand have been prepared from the condensation reaction of p-bromobenzoyl acetone and 2-amino-benzohydroxamic acid in ethanolic medium at room temperature. The synthesized Schiff base and its metal complexes were characterized by elemental analysis, molar conductivity measurements, magnetic moment measurements, IR and UV-Vis spectral data investigations. The metal (II) complexes are coloured and stable in air. The molar conductivity data of the complexes in DMF solution indicates they are non-electrolytic nature. All metal (II) complexes are paramagnetic in nature due to presence of unpaired electrons in d-orbital. The IR spectral data indicates Schiff base acts as tetradentate and coordinate through two oxyimino nitrogen atoms and two azomethine nitrogen atoms. Thus, on the basis of elemental analysis and spectral studies octahedral geometry For Co (II) complexes and distorted octahedral geometry for Cu (II) complexes were proposed.

**Keywords:** Metal salt, 2-amino-benzohydroxamic acid, 4-bromo benzoyl acetone, Schiff base.

## 1. Introduction

Schiff bases are the versatile class of organic compounds synthesized from the condensation of a primary amine 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 important class of ligand that coordinates to metal ions via azomethine nitrogen

(C=N). active carbonyl compounds [1-8]. 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[9-14]. 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. Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes due to effective conjugation. The presence of azomethine group, which is responsible for stability, reactivity and biological activity of Schiff bases and their metal complexes [15-21]. Schiff bases and their metal complexes are used in catalyst, antimicrobials, antioxidants, dyes optical materials and analytical chemistry. 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 tetradentate 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. The Schiff bases contain nitrogen and oxygen play an important role in coordination chemistry and bioinorganic compounds due to their flexibility and denticity. Symmetrical Schiff base ligands with nitrogen and oxygen donor atoms are well known to coordinate with various metal ions and this has attracted by many researchers due to their availability and catalytic and biological applications. I report in this paper synthesis and characterization of Co(II) and Cu(II) complexes with tetradentate Schiff base ligand

## 2. Experimental

**Chemical required:** -Ethyl acetate, p-bromo acetophenone, methyl benzoate, hydroxylamine ethyl alcohol, ether KOH, DMF, Acetates / chlorides of cobalt (II), copper (II), ammonia, 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.

The elemental analysis data was obtained using Perkin-Elmer elemental analyser. The molar

conductivity of the complexes were measured by using digital conductivity meter using DMF 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. The magnetic susceptibility of synthesized complexes were measured by Gouy method using Hg [Co (SCN)<sub>4</sub>] as a calibrant.

### Synthesis of Schiff base ligand(L): -

The Schiff base ligand 1,3- bis (2-imino benzohydroxamic acid)- p-bromo benzoyl acetone has been prepared by the condensation of 2-amino benzohydroxamic acid and p-bromo benzoyl acetone under suitable conditions. 0.1 mole of p-bromo benzoyl acetone was completely dissolved in 20 ml of ethyl alcohol and 0.1 mole of 2-amino benzohydroxamic acid was also completely dissolved in 20 ml of ethyl alcohol. Both the solutions were filtered separately and the filtrates of both the solution were mixed gradually with regular shaking. Then the resulting solution was refluxed under condenser fitted with a water tap for about three hours. Then the solution was cooled under ice bath while a dirty yellowish solid was obtained. The solid was separated by filtration and washed with cold water followed by a small amount of cold ethyl alcohol. The compound was found to be easily soluble in acetone, less soluble in cold methyl alcohol but more soluble in hot ethyl alcohol. The compound was recrystallised with ether and dried. The melting point of the compound was recorded and found to be 162<sup>0</sup>C. The compound was further analysed and found to contain. C =56.52%, H =4.10, N =11.10% Br =15.20% which corresponds to the molecular formula (C<sub>24</sub> H<sub>21</sub> N<sub>4</sub> Br O<sub>4</sub>).

### Synthesis of the cobalt complexes: -

The undertaken Co (II) complexes were obtained by refluxing ethanolic solution of symmetrical Schiff base ligand 1,3-bis (2-imino benzohydroxamic acid) p-bromo benzoyl acetone and Cobalt (II) chloride hexahydrate in a molar

ratio (ligand: metal) 1:1. The mixture solution was filtered and the filtrate was refluxed on water bath for one and half an hour at room temperature. During reflux process, the colour of the solution was gradually changed and crystals of light pink 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 anhydrous  $\text{CaCl}_2$  in a desiccator. The colour of the complexes formed with different bases were found to be slightly different with slight variation of time of reflux.

#### Synthesis of the copper complexes: -

The undertaken copper (II) 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 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 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 anhydrous  $\text{CaCl}_2$  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

The microanalytical data of the Schiff base and its cobalt (II) and copper (II) complexes are listed in Table 1. All the metal complexes are coloured, solid, stable at room temperature and non-hygroscopic in nature. The metal complexes are soluble in some common organic solvents such as Dimethylsulphoxide (DMSO), Dimethylformamide (DMF), methanol, acetone, ethanol, and chloroform. The molar conductivity data of metal complexes are listed in Table 2. The values of electrical conductance for Cobalt (II) complexes have been found to be in the range of 10 -18 and copper (II) complexes have been found to be 16-20  $\text{cm}^2 \text{mol}^{-1}$ . The lower molar conductance values of investigated metal complexes in DMF at room temperature revealed their non- electrolytic nature. All the metal chelates have 1:1 (metal: ligand) stoichiometry.

**Table 1. Microanalytical data of the Schiff base and its metal complexes**

Coordination compounds	Colour	% Found (Calculated)			
		C	H	N	M
$\text{C}_{24} \text{H}_{21} \text{N}_4 \text{Br O}_4$	Yellow	56.52 (56.59)	4.10 (4.16)	11.10 (11.05)	-
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{Br O}_4) (\text{H}_2\text{O})_2]$	Light pink	47.36 (47.48)	3.84 (3.89)	9.35 (9.30)	9.72 (9.78)
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{Br O}_4) (\text{NH}_3)_2]$	Pink	53.16 (53.24)	4.58 (4.65)	15.44 (15.50)	11.76 (11.80)
$[\text{Co}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	Light brown	57.10 (57.77)	3.98 (3.90)	11.16 (11.23)	7.76 (7.87)
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{Br O}_4) (\text{H}_2\text{O})_2]$	Light green	47.18 (47.48)	3.80 (3.89)	9.28 (9.23)	10.32 (10.46)
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{Br O}_4) (\text{NH}_3)_2]$	Blue	47.60 (47.65)	4.15 (4.17)	13.94 (13.89)	10.40 (10.50)
$[\text{Cu}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	Light black	55.50 (55.41)	4.00 (3.88)	11.20 (11.16)	8.32 (8.43)

**Table 2. Molar conductivity data of metal complexes**

Compounds	Solvent	$m \text{ (}^{-1} \text{ cm}^2\text{mol}^{-1}\text{)}$
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	DMF	18
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	DMF	16
$[\text{Co}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	DMF	10
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	DMF	20
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	DMF	24
$[\text{Cu}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	DMF	16

**Table 3. Electronic spectral data of metal (II) complexes**

Compounds	$\lambda_1(\text{cm}^{-1})$	$\lambda_2(\text{cm}^{-1})$	C.T( $\text{cm}^{-1}$ )
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	15250	22850	33350
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	15350	22800	34000
$[\text{Co}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	15100	22500	33400
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	13250	-	25500
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	13250	-	25250
$[\text{Cu}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	13400	-	25450

**Table 4. Magnetic moment data of metal (II) complexes**

Compounds	$\mu_{\text{eff}}$	Magnetic behaviour
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	4.98	Paramagnetic
$[\text{Co} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	4.94	Paramagnetic
$[\text{Co}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	4.86	Paramagnetic
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{H}_2\text{O})_2]$	2.06	Paramagnetic
$[\text{Cu} (\text{C}_{24}\text{H}_{19}\text{N}_4 \text{ Br O}_4) (\text{NH}_3)_2]$	1.94	Paramagnetic
$[\text{Cu}(\text{C}_{24}\text{H}_{19}\text{N}_4\text{BrO}_4) (\text{C}_6\text{H}_5\text{N})_2]$	1.96	Paramagnetic

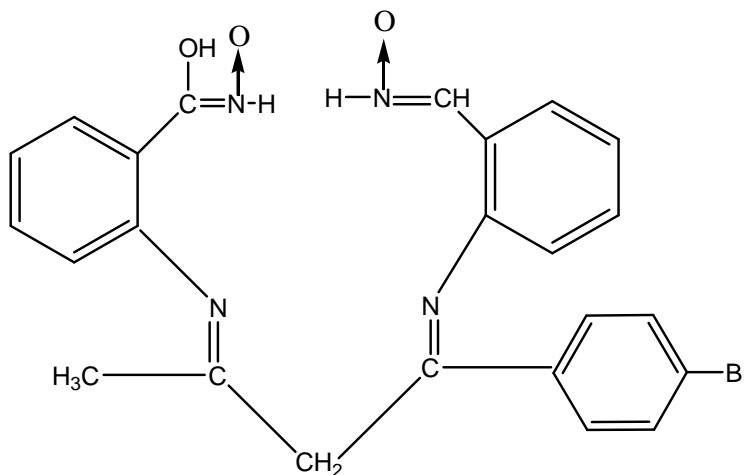


Figure 1. Proposed structure of Schiff base ligand.

### Electronic absorption spectra and magnetic behaviour: -

The electronic spectral data of metal complexes are listed in Table 3. Co (II) complexes show two absorption bands, due to J.T distortion the band obtained in the range of 15100-15350  $\text{cm}^{-1}$  is broad and unsymmetrical. The first transition takes place between  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( ${}^4\text{E}_g + {}^4\text{B}_{2g}$ ). The second band obtained in the range of 22500-22850  $\text{cm}^{-1}$  is sharp; and symmetrical due to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  which is spin as well as symmetry allowed transition, indicating Octahedral geometry for all the complexes. The values of magnetic moments for the Cobalt (II) complexes have been found to be 4.86-4.98 BM, suggested octahedral nature of the complexes. Electronic spectra of Cu (II) complexes have been explained by C.F model. Cu (II) complexes is expected to give one d-d band i.e.,  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{E}_g \rightarrow {}^2\text{T}_2$  respectively. The d-d band in both cases is expected to be broad and unsymmetrical due to J.T distortion. All copper (II) complexes show one broad and unsymmetrical band in the range of 13250-13400  $\text{cm}^{-1}$  indicating distorted octahedral geometry for all the complexes. The magnetic moment of Cu (II) complexes has been found to be in the range of 1.94-2.06 B.M, suggested distorted octahedral geometry of Cu (II) complexes.

### Infrared spectra: -

The Schiff base ligand, 1,3-bis (2 - imino benzo hydroxamic acid) P-bromo benzoyl acetone is highly sensitive into 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  $\text{cm}^{-1}$  disappears in all the complexes of the ligand and a new broad band appears in the complexes at about 3430-3480  $\text{cm}^{-1}$  confirming the presence of at least one free (-OH) group even in the complexes. The disappearance of the strong band at 1240  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  in the ligand molecule is also shifted to lower frequency in almost all the complexes by about 45-60 $\text{cm}^{-1}$ . 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.

The appearance of one more band in the range of 740 - 860  $\text{cm}^{-1}$  due to rocking and wagging mode of vibration suggests that  $\text{H}_2\text{O}$  is present in the coordination sphere. The pyridine ring breathing mode of vibration located at 990  $\text{cm}^{-1}$  in the complexes has been taken to be characteristic vibrations of coordinated pyridine. The appearance of (M - N) band obtained between 420-460  $\text{cm}^{-1}$  in all the complexes, suggested the coordination through nitrogen atoms of azomethine, oximinio and bases such as ammonia and pyridine of the ligand.

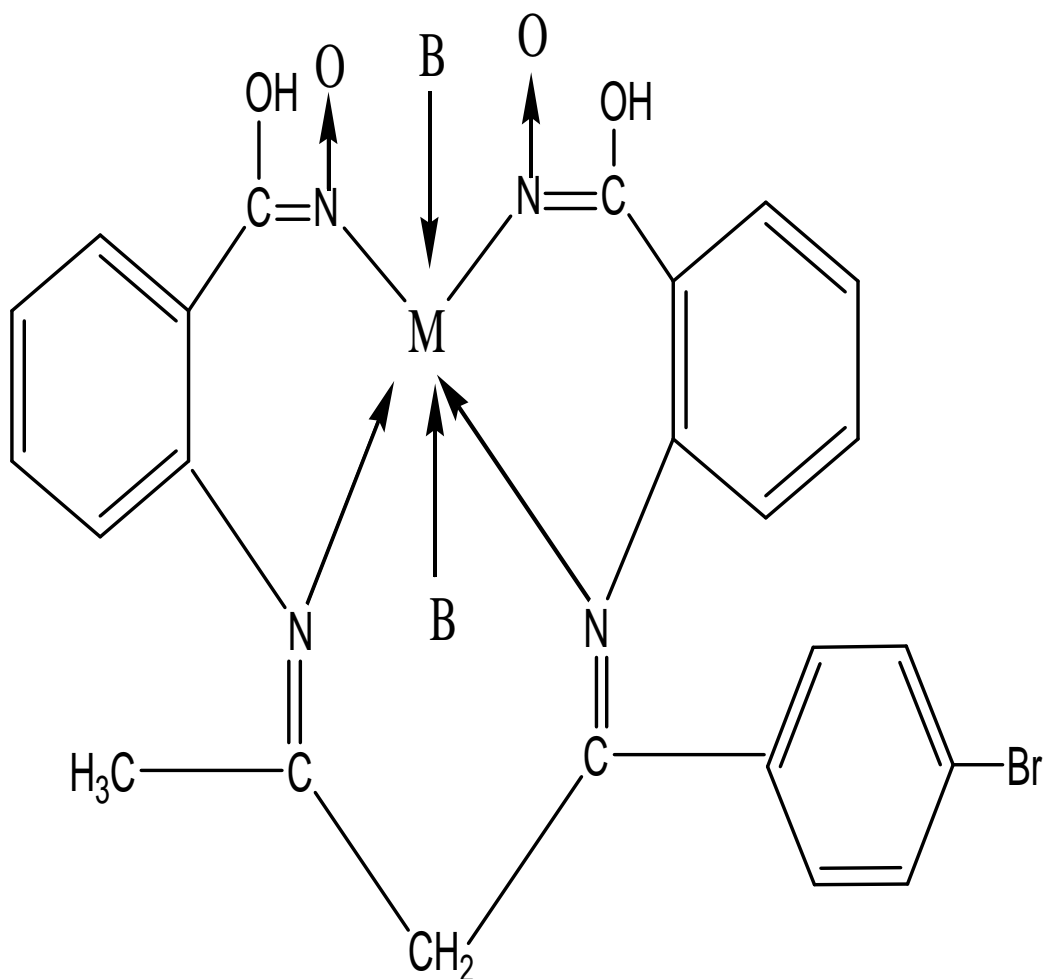


Figure 2. Structure of metal (II) complexes  
 M = Co(II) and Cu(II)  
 B = Water, ammonia and pyridine

#### 4. Conclusion

The Schiff base ligand 1,3-bis(2-imino benzohydroxamic acid)-p-bromo benzoyl acetone has been synthesized by the condensation of 2-amino benzohydroxamic acid and p-bromo benzoyl acetone in an alcoholic medium at room temperature. The Schiff base and its metal complexes were characterized by micro elemental analysis and different spectroscopic techniques. All the metal complexes have 1:1 (metal: ligand)

stoichiometry. The lower molar conductance values of investigated metal complexes in DMF at room temperature revealed their non-electrolytic nature. All the metal complexes have been found to be paramagnetic. The Schiff base ligand acts as tetradentate and coordinated through two azomethine nitrogen atoms and two oxyimino nitrogen atoms. Thus, on the basis of elemental analysis and spectral studies octahedral geometry for Co(II) complexes and distorted octahedral geometry for Cu(II) complexes were proposed.

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