# Structural Studies of Some Transition Metal Complexes with Tridentate Schiff Base

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***Abstract :*** The complexes of divalent Iron and Copper metals have been prepared with Schiff base ligand 2(5-bromo salicylalidine) imino benzoic acid in presence of bases containing nitrogen and oxygen atoms as their donor sites. The complexes on characterisation by physico-chemical methods were found to be non-electrolyte, mono-meric, paramagnetic, octahedral in geometry with general molecular formula $[M(L)(B)_3]$ where M=Iron(II) and Copper(II) cations, L=ligand and B=bases.

***IndexTerms*** - Cations, characterisation, paramagnetic, octahedral, geometry, complex, preparation, donor.

## I. INTRODUCTION

A large number of complexes of divalent transition metals have been prepared with Schiff bases as ligand in presence of aqueous and non-aqueous medium. But least work has been carried out for the formation of complexes of divalent transition metals with the Schiff bases obtained by the condensation of 2-amino benzoic acid and 5-bromo salicylaldehyde. Therefore, in this paper, I report the formation of complexes of divalent Iron and Copper metals with the Schiff base obtained by the condensation of 2-amino benzoic acid and 5-bromo salicylaldehyde in presence of bases.

## II. PREPARATION OF THE LIGAND

**(A)** **Preparation of 2(5-bromo salicylidene)imino benzoic acid**: The ligand was prepared by the condensation of 2-amino benzoic acid(anthranilic acid) and 5-bromo salicylaldehyde by the method as given by Pfeiffer and co-workers.

**Procedure:** An ethanolic solution of 2.74g of anthranilic acid was added to an ethanolic solution of 5g of 5-bromo salicylaldehyde in 1:1 molar ratio. On stirring vigorously, yellow precipitate of the Schiff base formed and filtered. It was crystallised from ethanol water mixture.

The compound is highly soluble in ethanol, acetone, ether etc.

The compound was analysed and found to contain Carbon=52.5%, Hydrogen=3.12% and Nitrogen=4.37% which corresponds to the formula $C_{14}H_{10}NO_3Br$.

## III. PREPARATION OF THE COMPLEXES

The complexes with 2(5-bromo salicylaldihyde) imino benzoic acid were prepared by the general procedure detailed hereunder:-

The acetate of a metal was dissolved in aqueous ethanolic solution. To the known weight of the metal solution was then added ethanolic solution of 2(5-bromo salicylidene)imino benzoic acid in 1:1 molar ratio followed by a few ml. of acetic acid (ph=6). The resulting solution was then refluxed on steam-bath from half and an hour to one hour till the complex precipitated out.The precipitate obtained was then filtered, washed and dried in a desiccator over KOH pellets. The complexes of this ligand were prepared using acetates of Fe(II) and Cu(II) in aqueous medium as well as in the presence of bases like ammonia, phenyl isocyanide,

quinoline and pyridine with each of the metals separately and the procedure carried out in each case was of similar nature with slight variation of time of reflux.

The complexes of Fe(II) and Cu(II) metals with the ligand were prepared separately in the presence of bases like ammonia, phenyl isocyanide, quinoline and pyridine. In both the cases, the colour of crystal were found to have different colour.

**Analytical Date of Iron(II) and Copper(II) Metal Complexes**

**Found→% (Calculated→%)**

| S.N. | Compounds | Metal | Carbon | Hydrogen | Nitrogen | Bromine |
|---|---|---|---|---|---|---|
| 1. | $[Fe(C_{14}H_8NO_3Br)(H_2O)_2]$ | 12.80 (13.08) | 38.86 (39.25) | 3.30 (3.27) | 3.36 (3.27) | 18.40 (18.69) |
| 2. | $[Fe(C_{14}H_8NO_3Br)(NH_3)_2]$ | 12.96 (13.17) | 38.90 (39.25) | 4.04 (4.00) | 13.20 (13.17) | 18.40 (18.82) |
| 3. | $[Fe(C_{14}H_8NO_3Br)(C_6H_5NC)_2]$ | 8.02 (8.19) | 61.10 (61.49) | 3.40 (3.36) | 8.28 (8.19) | 11.32 (11.71) |
| 4. | $[Fe(C_{14}H_8NO_3Br)(C_9H_7N)_2]$ | 7.10 (7.35) | 64.15 (64.65) | 3.84 (3.81) | 7.45 (7.35) | 10.10 (10.51) |
| 5. | $[Fe(C_{14}H_8NO_3Br)(C_5H_5N)_2]$ | 8.96 (9.16) | 56.90 (56.95) | 3.80 (3.76) | 9.20 (9.16) | 12.80 (13.09) |
| 6. | $[Cu(C_{14}H_8NO_3Br)(H_2O)_2]$ | 14.40 (14.58) | 38.30 (38.57) | 3.26 (3.21) | 3.28 (3.21) | 18.00 (18.36) |
| 7. | $[Cu(C_{14}H_8NO_3Br)(NH_3)_2]$ | 16.36 (16.68) | 38.40 (38.84) | 3.96 (3.93) | 13.00 (12.94) | 10.10 (10.49) |
| 8. | $[Cu(C_{14}H_8NO_3Br)(C_6H_5NC)_2]$ | 9.02 (9.19) | 60.40 (60.82) | 3.35 (3.33) | 8.16 (8.11) | 11.32 (11.58) |
| 9. | $[Cu(C_{14}H_8NO_3Br)(C_9H_7N)_2]$ | 8.10 (8.26) | 63.76 (64.02) | 3.80 (3.77) | 7.36 (7.28) | 10.10 (10.40) |
| 10. | $[Cu(C_{14}H_8NO_3Br)(C_5H_5N)_2]$ | 10.10 (10.26) | 56.10 (56.26) | 4.56 (4.52) | 9.10 (9.05) | 12.52 (12.93) |

On the basis of elemental analysis of Iron(II) and Copper(II) complexes, all the complexes have been found to be monomeric with molecular formula $[M(L)(B)_3]$ where M=Iron(II) and Copper(II) cations, L=ligand and B=bases.

**CHEMICALS REQUIRED:** Acetates of Fe(II) Cu(II), ammonia, quinoline, phenyl isocyanide, pyridine, 2-amino benzoic acid, 5-bromosalicylaldehyde, alcohol, acetone etc. were either of BDH (AR) of extra pure E-Merck quality.

## IV. METHODS OF ANALYSIS

Iron was estimated volumetrically by $K_2Cr_2O_7$ titration method.

Copper was volumetrically estimated by iodometry titration.

Bromine was gravimetrically estimated as silver bromide method.

Carbon, hydrogen and nitrogen were estimated by semi-micro combustion method.

Magnetic moment of Iron(II) and Copper(II) complexes were measured by Gouy's method and the values of magnetic moment obtained for Iron(II) and Copper(II) complexes in the range of 5.96-5.10BM and 1.90-2.10BM respectively indicates the octahedral geometry for all the complexes.

Electronic spectra of Iron(II) and Copper(II) complexes were recorded on Hitachi-320 spectrophotometer In case of Iron(II) complexes, a broad and unsymmetrical band was obtained around 10,200-10,800$cm^{-1}$ indicating octahedral geometry. In case of Copper(II) complexes, one broad and unsymmetrical band was obtained in the range of 14,600-15,200$cm^{-1}$ indicating distorted octahedral geometry for all the complexes.

**INTERPREATION OF THE I.R. SPECTRA OF THE LIGAND ($L_1H_2$):**

The IR spectrum has been recorded on Perkin Elmer Infrared Spectrophotometer using KBr pellets in the range of 4,000-200$cm^{-1}$. The assignments of bands have been made on the basis of literature quoted under reference.

The carboxylic group is made up of a carbonyl group (C=O) and a hydroxyl group (OH), and the infrared spectrum of carboxylic acids reflects both these structure units.

The absorption owing to the carbonyl stretching vibration of carboxylic acid is shifted to longer wave length. Absorption owing to bonded O-H stretching absorbs in the region 2,700$cm^{-1}$ is diagnostic of carboxylic group.

A broad and strong band near 3,500$cm^{-1}$ has been assigned due to coupled $\nu_{OH}$ frequencies. The $\nu_{OH}$ shifts from 3,500$mc^{-1}$ to 3,000$cm^{-1}$ due to strong hydrogen bonding of the two adjacent phenolic groups. In the spectrum of ligand the band appearing in the region 3,000$cm^{-1}$ is assigned due to coupled –OH while that of 1,610$cm^{-1}$ is due to azomethine while that at 1,480$cm^{-1}$ amide II $\nu_{C-N}$ and the band at 750$cm^{-1}$ is due to rocking vibration of OH group.

The broad band near 3,400$cm^{-1}$ has been assigned due to $\nu_{OH}$. Absorption owing to bonded O-H stretching frequency absorbs in the region 2,750$cm^{-1}$. Two absorptions near 1,605$cm^{-1}$ and 1,300$cm^{-1}$ are observed that are caused by the symmetric and asymmetric >C⋯⋯O stretching vibrations of the resonance stabilised carboxylate anion group.

The frequency at 1,390$cm^{-1}$ is due to bending mode of vibration of –OH group while that at 750$cm^{-1}$ is due to rocking mode of vibration of –OH of the ligand.

They form metal chelates in the deprotonated form. On complexation, the azomethine frequency shifts to lower side while the $\nu_{OH}$ band disappears showing that –OH groups have deprotonated. The presence of coordinated water in the complexes is indicated by a sharp band around 3,400$cm^{-1}$ and two somewhat weaker bands around 850$cm^{-1}$ and 710$cm^{-1}$ assigned as the $\nu_{OH}$ stretching, rocking and wagging vibrations respectively. In almost all the complexes, broad $\nu_{OH}$ vibration located at around 3,000$cm^{-1}$ - 3,400$cm^{-1}$ disappears suggesting the absence of hydrogen bonding in the complexes as well as deprotonation of hydrogen bonded OH group of the Schiff baes. The weak band in the region around 520-530$cm^{-1}$ may be due $\nu_{M-N}$ vibration. Thus, it appears that nitrogen of the Schiff bases are involved in bonding similar to Ni(II) dimethyl glyoximato. The M-N stretching frequency is of particular interest since it provides direct information about the coordination bond. Because of the relatively heavy mass of the metal and the low bond order of the co-ordinate bond, the M-N stretching vibrations may appears in the lower frequency region (430-450$cm^{-1}$).

Thus, the probable form of the ligand to form complex is as bi-anionic due to deprotonation of one –OH group present inthe salicylaldehyde moiety and one –OH group present in benzoic acid moiety. Thus the ligand acts as bianionic tridentate having one oxygen atom of –OH group of 5-bromo salicylaldehyde and one oxygen atom of carboxylic group of benzoic acid and one nitrogen atom of 2-amino benzoic acid. Thus the ligand molecule behaves like tridentate

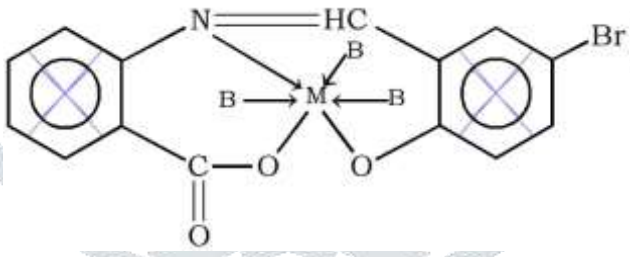
In case of aquo complexes separate band for co-ordinated $H_2O$ is obtained around 3,400cm$^{-1}$. In addition to the three fundamental modes of the free water molecules, coordinated water is expected to show three more modes of vibrations viz., asymmetric stretch, rocking and wagging modes of vibrations. The frequencies observed in the rage of 700-800cm$^{-1}$ in aquo complexes may be attributed as due to rocking mode of co-ordinated water. The rocking and metal oxygen stretching modes will become infrared active if the M-O bond is sufficiently covalent. In pyridine (above 650cm$^{-1}$), the pyridine vibrations show very little shift upon complex formation. However, those are shifted to higher frequencies around 750cm$^{-1}$ upon co-ordinated to a metal. The pyridine complexes, however, display some extra band in finger print and far infrared region. The pyridine ring stretching mode of vibration located at 990-1,020cm$^{-1}$ in complexes has been taken to be characteristic vibrations of co-ordinated pyridine molecule. The IR band at 520-530cm$^{-1}$ in the complexes are also characteristic of presence of pyridine molecule in the complexes.

In free phenyl isocyanide, a sharp and medium band obtained around 2,180cm$^{-1}$ has been shifted to 2,210cm$^{-1}$ in the complexes. This increase in the band position indicates the coordination of N-atom of isocyanide group in the bond formation with the metal ion.

In quinoline complexes, a medium and broad band obtained around 1,430cm$^{-1}$ in complexes due to ring vibration indicates the involvement of N-atom of the quinoline in the complex formation.

In case of aquo complexes, the complexes retain water molecules even at 150°c suggesting the co-ordinated nature of $H_2O$. The electrical conductance of the complexes at room temperature (30°c) falls in the range of 2-10mho which indicated that these complexes are non-electrolytic in nature.

Thus on the basis of the elemental analysis, magnetic moment measurement and spectral studies, it is suggested that the ligands from octahedral complexes with Fe(II) and Cu(II) complexes in the presence of bases like water, ammonia, phenyl isocyanide, quinoline and pyridine have been proposed octahedral geometry with the general molecular formula $[M(L)(B)_3]$




where M=Fe(II) and Cu(II) cations, L=ligand and B=bases.

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