

Preparation of Some Complexes of Iron(II) and Copper(II) Metals with Tri-dentate Derivative of Salicylaldehyde

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Abstract : Some complexes of divalent Iron and Copper metals have been prepared with tri-dentate derivative of salicylaldehyde in presence of bases containing nitrogen and oxygen atoms as their donor sites. On the characterisation of the ligand and the complexes by usual physico-chemical method, such as measurement of electrical conductance, magnetic moment, elemental analysis, electronic and IR spectral behaviour of the ligand and the complexes, all the complexes have been found to be non-electrolyte, mono-meric, paramagnetic and octahedral in geometry with general formula $[M(L)B_3]$ where $M=Fe(II)$ and $Cu(II)$ cations, $L=$ ligand and $B=$ bases.

KEY WORDS: Spectral behaviour, ligand, complex, magnetic moment, paramagnetic, mono-meric, solvent, solution, filtration, precipitate, divalent transition metals.

I. INTRODUCTION

A considerable amount of research work regarding the formation of complexes of transition metals having different oxidation states different kinds of Schiff bases have been studied in details. But least work has been carried out for the formation of complexes of divalent transition metals with tri-dentate derivative of salicylaldehyde containing hydroxamic acid as functional group in its moiety.

Therefore, in this paper, I report the preparation of some complexes of divalent Iron and Copper metals with tri-dentate derivative of salicylaldehyde due to their wide application in the field of industry, pharmacology and fertilisers.

II. EXPERIMENTAL

The Schiff base compound 2(2-hydroxy benzylidene) imino benzo hydroxamic acid has been prepared into two steps:

(A) Preparation of 2-amino benzo hydroxamic acid:

4.8g of sodium hydroxide was completely dissolved in 300ml of water and this solution was cooled under ice-bath. 41.6g of hydroxylamine hydrochloride was gradually added with constant stirring to the solution of sodium hydroxide. After that 45.2g of methyl benzoate (methyl anthranilate) (39ml, sp. Gr. 1.16) was gradually added to the resulting solution along with enough alcohol for the proper dilution of the solution. The resulting or while solution was allowed to stand for three days at room temperature. Then, the solution was distilled under the reduced pressure until sodium salt of hydroxamic acid was precipitated leaving about 100ml of mother liquor in the flask. The salt was filtered by suction and washed with ether. The filtrate was then made acidic with *dil.*HCl and then free hydroxamic acid was precipitated. The crude product was recrystallized from ether. It was light brown in colour. The melting point of the compound was recorded and found to be 149°C. The yield of the compound was found to be nearly 65%.

The compound was further analysed and found to contain carbon=55.15%, hydrogen=5.25% and nitrogen=18.45% which corresponds the molecular formula $C_7H_8N_2O_2$.

(B) Preparation of the Schiff base compound 2(2-hydroxy benzylidine) imino benzo hydroxamic acid:

This Schiff base compound has been prepared by the condensation reaction of 2-hydroxy benzaldehyde (salicylaldehyde) and 2-amino benzohydroxamic acid at reflux temperature.

Procedure: 12.4g (0.1 mole) of 2-hydroxy benzaldehyde was completely dissolved in minimum volume of ethyl alcohol and 17.4g (0.1 mole) of 2-amino benzohydroxamic acid was dissolved in glacial acetic acid. Both the solutions were mixed together gradually and the resulting solution was vigorously and continuously stirred until a brownish yellow precipitate appeared in the solution. This was then refluxed for half an hour.

A clear brownish yellow solution was obtained which on cooling produced brownish crystals of Schiff base. The compound was separated by filtration, washed with cold water, followed by a little alcohol and then recrystallized with methyl alcohol. The compound was found to be soluble in acetone and the melting point of the compound was recorded and found to be 130°C.

The compound was further analysed and found to contain carbon=65.24%, hydrogen=4.66% and nitrogen=10.95% which corresponds the molecular formula $C_{14}H_{12}N_2O_3$.

The identification of the compound was confirmed by I.R. and 1H NMR spectroscopy.

Preparation of Complexes of Iron(II) and Copper(II) metals

0.235g (0.001 mole) of Iron(II) chloride hexa hydrate was completely dissolved in minimum volume of cold water. 0.272g (0.001 mole) of the ligand 2(2-hydroxy benzylidine) imino benzo hydroxamic acid was dissolved in ethyl alcohol. Both the solution were gradually mixed together with regular shaking. After that, the resulting solution was refluxed for about 40-50 minutes on water-bath. During the course of reflux, the colour of the solution was gradually changed and faint and in some case dirty and brownish green colour crystals were separated out by allowing the solution to overnight in the cup-board. The product was separated by filtration, washed with a small amount of acetone and then dried over KOH pellets placed in a desiccator.

The complexes of divalent iron metals with the ligand have been prepared separately in presence of bases like water, ammonia, phenyl-isocyanide, quinoline, pyridine. In each case, the ratio of metal and the ligand was always kept 1:1 respectively.

For the preparation of complexes of Copper(II) metal, the similar procedure was obtained with slight variation of time of reflux and the colours of crystals obtained.

Table-1
Elemental Data of Iron(II) and Copper(II) Metals

Found→% (Calculated→%)

S.N.	Complexes	Metal	Carbon	Hydrogen	Nitrogen
1.	$[Fe(C_{14}H_{10}N_2O_3)(H_2O)_3]$	15.10 (15.38)	45.76 (46.15)	4.43 (4.39)	7.76 (7.69)
2.	$[Fe(C_{14}H_{10}N_2O_3)(NH_3)_3]$	15.32 (15.51)	46.10 (46.53)	5.20 (5.26)	19.48 (19.39)
3.	$[Fe(C_{14}H_{10}N_2O_3)(C_6H_5NC)_3]$	8.76 (9.04)	67.45 (67.85)	4.05 (4.03)	11.40 (11.30)
4.	$[Fe(C_{14}H_{10}N_2O_3)(C_9H_7N)_3]$	7.72 (8.03)	70.32 (70.58)	4.46 (4.44)	10.10 (10.04)
5.	$[Fe(C_{14}H_{10}N_2O_3)(C_5H_5N)_3]$	10.02 (10.23)	63.27 (63.61)	4.60 (4.57)	12.86 (12.79)
6.	$[Cu(C_{14}H_{10}N_2O_3)(H_2O)_3]$	16.74 (17.09)	44.88 (45.22)	4.32 (4.30)	7.66 (7.53)

7.	[Cu(C ₁₄ H ₁₀ N ₂ O ₃)(NH ₃) ₃]	16.96 (17.23)	45.20 (45.59)	5.18 (5.15)	19.12 (18.99)
8.	[Cu(C ₁₄ H ₁₀ N ₂ O ₃)(C ₆ H ₅ NC) ₃]	9.76 (10.13)	66.66 (67.03)	4.01 (3.99)	11.24 (11.17)
9.	[Cu(C ₁₄ H ₁₀ N ₂ O ₃)(C ₉ H ₇ N) ₃]	8.72 (9.01)	69.62 (69.83)	4.44 (4.40)	10.00 (9.93)
10.	[Cu(C ₁₄ H ₁₀ N ₂ O ₃)(C ₅ H ₅ N) ₃]	11.12 (11.45)	62.36 (62.75)	4.56 (4.50)	12.70 (12.62)

On the basis of the elemental analysis of the ligand and the complexes, the complexes were found to be mono-meric with general molecular formula [M(L)(B)₃] where M=Fe(II) and Cu(II) cation, L=ligand and B=bases.

CHEMICALS REQUIRED: Methyl benzoate, hydroxylamine, hydrochloride, salicylaldehyde, ethyl alcohol, acetone, Fe(II) chloride hexahydrate, Copper(II) chloride hexa hydrate, DMF, ammonia, phenyl isocyanide, quinoline, pyridine etc. All the chemicals taken were either of E. Merck extra pure or BDH(AR) quality.

ANALYTICAL METHODS: The estimation of metals and non-metals present in the ligand and the complexes has been done by standard methods:

- (i) **Copper:** Copper was volumetrically estimated by iodometry titration method.
- (ii) **Iron:** Iron is volumetrically estimated by dichromate titration method.
- (iii) **Carbon, Hydrogen and Nitrogen** have been estimated by semi-micro combustion method.

III. RESULTS AND DISCUSSION

The values of electrical conductivity for Iron(II) and Copper(II) complexes have been obtained in the range of 10-16 and 12-20Am respectively which indicate clearly non-electrolyte nature of all the complexes.

The values of magnetic moment of Fe(II) and Cu(II) complexes have been obtained 4.98-5.10BM and 1.90-2.10BM respectively indicating the octahedral nature of all the complexes.

In case of Iron(II) complexes, a broad and unsymmetrical band obtained in the range of 10,600 - 10,900cm⁻¹ due to ⁵T_{2g}→⁵E_g transition indicates octahedral geometry for all the complexes.

In case of Copper(II) complexes, a broad and unsymmetrical band obtained in the range of 15,450-15,950cm⁻¹ indicates distorted octahedral geometry for all the complexes.

Infra-red Spectra of the Ligand and the Complexes

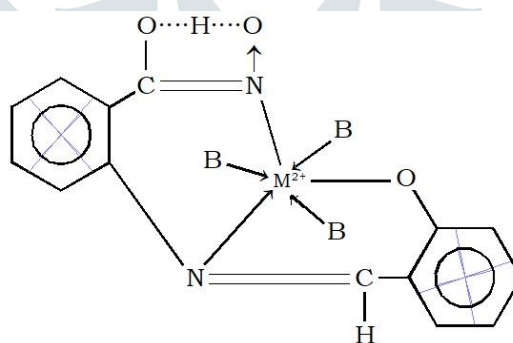
Table-2

Groups	Ligand	Complexes
Fee ν _(NH) + ν _(OH)	3460	3460
H-bonded ν _(OH)	3140	3240
ν _(C=N)	1650	1590
ν _(C-N)	1460	1480
ν _(N-O)	1090	1120

By the perusal of infra-red spectra of the ligand and the complexes, we have come to the conclusion that there are appreciable changes in ν_(OH), ν_(C=N), and ν_(N-O) frequencies of the ligand molecule after the complex formation. Remaining frequencies due to the vibration of different groups present in the ligand

molecule were intact after complex formation. The highest band around $3,460\text{cm}^{-1}$ has been obtained due to combined $\nu_{(\text{NH}+\text{OH})}$ vibrations. A strong and sharp band obtained at $3,420\text{cm}^{-1}$ in the ligand molecule due to the vibration of phenolic $-\text{OH}$ group, disappears in all the complexes indicating the deprotonation of phenolic $-\text{OH}$ group. A medium and sharp band obtained at $1,510\text{cm}^{-1}$ has been assigned due to the vibration of phenolic $\text{C}-\text{O}$ group in the ligand molecule. This band position has been shifted to $1,540\text{cm}^{-1}$ suggesting increase in bond order of $(\text{C}-\text{O})$ group in the complexes. This means that oxygen atom of phenolic $-\text{OH}$ group takes part in the bond formation with the metal cations. In the ligand molecule, a sharp band around $3,140\text{cm}^{-1}$ in the ligand molecule has been obtained due to strong hydrogen bonding. The frequency of this group has been increased to $3,240\text{cm}^{-1}$ due to weaker hydrogen bonding. This means that there is reduction in the strength of hydrogen bonding after complex formation. A broad and strong band obtained at $1,650\text{cm}^{-1}$ in the ligand molecule and $1,590\text{cm}^{-1}$ in the complexes is due to $\nu_{(\text{C}=\text{N})}$ vibration. This reduction in the frequency obtained due to $\nu_{(\text{C}=\text{N})}$ vibration indicate the participation of aldimino nitrogen atoms as well as hydroxamino nitrogen atoms in the complex formation. The increase in the frequency by 30cm^{-1} due to $\nu_{(\text{N}-\text{O})}$ vibration after complex formation also support the participation of two hydroxamino nitrogen atoms in the complex formation. There is an increase by 20cm^{-1} in the frequency obtained due to $\nu_{(\text{C}=\text{N})}$ vibration also support the participation of two aldimino nitrogen atoms in the complex formation. A sharp and weak band around $2,180\text{cm}^{-1}$ in the ligand and $2,210\text{cm}^{-1}$ in the complexes indicate the participation of nitrogen atom of phenyl-isocyanide in the complex formation. A separate band for coordinated H_2O is not obtained due to overlap of $\nu_{(\text{OH})}$ vibration. Two weak bands around 960cm^{-1} and 610cm^{-1} are obtained due to vibration of pyridine and picoline molecules. It was to be noted that there was no change in the band obtained at $1,460\text{cm}^{-1}$ due to $\nu_{(\text{NH})}$ vibration.

A broad and strong band obtained in the complexes at 450cm^{-1} confirms the coordination of nitrogen atoms in the bond formation. A weak band obtained in the complexes at 560cm^{-1} confirms the participation of the oxygen atoms in the complex formation. Thus on the basis of elemental analysis, magnetic moment, electrical conductivity, electronic transition and IR spectral behaviour, all the complexes of $\text{Fe}(\text{II})$ and $\text{Cu}(\text{II})$ metals with the ligand 2(2-hydroxy benzylidene) imino benzohydroxamic acid in presence of various bases have been suggested to be octahedral in nature as show below:



where $\text{M}=\text{Iron}(\text{II})$ and $\text{Copper}(\text{II})$ cations, $\text{B}=\text{bases}$ and $\text{L}=\text{ligand}$.

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