

Synthesis and Characterisation of Some Complexes of Cobalt(II) and Copper(II) Metals with Bi-dentate Hydroxamic Acid

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Abstract : The complexes of divalent iron with α -(*p*-nitro benzylidene) imino aceto hydroxamic acid has been prepared separately in aqueous and non-aqueous medium. The general molecular formula of the complexes has been found to be $[M(L)_2(B)_2]$, where M=Cobalt(II) and Copper(II) metals, L= α -(*p*-nitro benzylidene) imino aceto hydroxamic acid and B=bases containing oxygen and nitrogen atoms as their donor sites. On the characterisation of the complexes by usual physico-chemical methods, all the complexes have been found to be non-electrolyte, monomeric and octahedral in geometry.

KEY WORDS : Geometry, octahedral, divalent, non-electrolyte, ligand and complex.

I. INTRODUCTION

In this paper, we report the preparation of some complexes of divalent cobalt and copper metals with α -(*p*-nitro benzylidene) imino aceto hydroxamic acid in presence of bases like ammonia, quinoline, phenyl isocyanide, pyridine and α -picoline.

II. CHEMICALS REQUIRED

Acetate/chloride of iron in divalent state, α -amino aceto hydroxamic acid, *p*-nitro benzaldehyde, ethanol, methanol and some bases like ammonium hydroxide, pyridine, quinoline, phenyl isocyanide and different picolines.

III. EXPERIMENTAL

Preparation of the Ligand: A dry and cold solution of 15.1g (0.1 mole) of *p*-nitro benzaldehyde in ethanol was allowed to react with the ethanolic solutions of 9g (0.1 mole) of α -amino aceto hydroxamic acid in equimolar proportion under the reflux on a water-bath for several hours at room temperature. During the course of reflux, the whole solution was shaken well more than three times. The resulting solution on cooling under ice-bath produced a faint orange coloured solid which was separated by filtration, washed and then dried over pellets of KOH placed in a desiccator.

The compound was further analysed and found to contain C=48.32% and N=18.88% which corresponds to the expected molecular formula $C_9H_9N_3O_4$. The identity of the ligand was verified by infra-red spectroscopy.

Preparation of the Complexes: The ethanolic solution of Co(II) acetate/chloride (0.01 mole) and the ligand (0.01 mole) in molar proportion of 1:2 respectively was allowed to react in presence of bases under reflux on water bath for about two hours at room temperature. The resulting solution on crystallization produced the crystals of pinkish and dirty brown colour. The solid was then separated by filtration washed with acetone and finally dried over KOH pellets placed in a desiccator. The complexes of Co(II) cations with the ligand were prepared separately in presence of bases like water, ammonia, quinoline, phenyl isocyanide and pyridine.

For the preparation of Copper(II) metal complexes, similar procedure was adopted with slight variation of time of reflux and in case of Copper(II) metals, crystals were obtained having green and in some cases dirty green colour.

Analytical data of Cobalt(II) and Copper(II) complexes with the ligand $\alpha(p$ -nitro benzylidene) imino aceto hydroxamic acid

Table1

Found→% (Calculated→%)

S.N.	Compounds	Metal	Carbon	Hydrogen	Nitrogen
1.	Co[C ₉ H ₈ N ₃ O ₄](H ₂ O) ₂	10.40 (10.90)	39.74 (40.08)	3.73 (3.71)	15.66 (15.58)
2.	Co[C ₉ H ₈ N ₃ O ₄](NH ₃) ₂	10.46 (10.97)	39.92 (40.23)	4.10 (4.09)	20.90 (20.86)
3.	Co[C ₉ H ₈ N ₃ O ₄](C ₆ H ₅ NC) ₂	7.96 (8.30)	53.88 (54.16)	3.70 (3.66)	15.86 (15.79)
4.	Co[C ₉ H ₈ N ₃ O ₄](C ₉ H ₇ N) ₂	7.10 (7.40)	56.40 (56.77)	3.96 (3.94)	14.76 (14.71)
5.	Co[C ₉ H ₈ N ₃ O ₄](C ₅ H ₅ N) ₂	8.62 (8.91)	50.36 (50.83)	3.98 (3.93)	17.00 (16.94)
6.	Cu[C ₉ H ₈ N ₃ O ₄](H ₂ O) ₂	10.26 (11.68)	39.32 (39.74)	3.70 (3.67)	15.52 (15.45)
7.	Cu[C ₉ H ₈ N ₃ O ₄](NH ₃) ₂	11.36 (11.72)	39.28 (39.88)	4.10 (4.06)	20.76 (20.68)
8.	Cu[C ₉ H ₈ N ₃ O ₄](C ₆ H ₅ NC) ₂	8.48 (8.89)	53.42 (53.81)	3.68 (3.64)	15.76 (15.69)
9.	Cu[C ₉ H ₈ N ₃ O ₄](C ₉ H ₇ N) ₂	7.90 (8.29)	56.10 (56.43)	3.94 (3.91)	14.70 (14.63)
10.	Cu[C ₉ H ₈ N ₃ O ₄](C ₅ H ₅ N) ₂	9.10 (9.54)	50.12 (50.48)	3.92 (3.90)	16.90 (16.82)

MAGNETIC PROPERTIES OF THE COMPLEXES: The magnetic moments of the complexes were measure by Gouy's method using the [Hg(NCS)₄] as a calibrant. The values of magnetic moment obtained in the range of 4.82-5.10BM indicate octahedral geometry of all the Co(II) complexes.

The values of magnetic moment obtained in the range of 1.86-2.10BM indicate octahedral geometry for Cu(II) complexes.

IV. ELECTRONIC SPECTRA OF THE COMPLEXES

A broad and unsymmetrical band obtained around 14,200-14,800cm⁻¹ due to ²E_g→²T_{2g} transitions indicate octahedral geometry of all the Cu(II) complexes.

A broad and unsymmetrical band obtained in the range of 22,400-22,800cm⁻¹ indicates the octahedral geometry for all Co(II) complexes.

I.R. SPECTRA OF THE LIGAND AND THE COMPLEXES: In almost all the complexes, the frequencies of (OH), aldimino (C=N) and (N-O) of the ligand molecule are changed appreciably in the complexes. The strong and sharp band obtained at $3,310\text{cm}^{-1}$ due to (-OH) and (N-H) vibration of the ligand $3,310\text{cm}^{-1}$ disappears in all the complexes of the ligand and a new broad band appears in the complexes at about $3,440\text{cm}^{-1}$ confirming the presence of (NH) group even in the complexes reducing the strength of the hydrogen bonding. The disappearance of the strong band at $3,280\text{cm}^{-1}$ further suggests the deprotonation of the (OH) group i.e. (N-OH) proton located at hydroxamic acid moiety. The deprotonation of (N-OH) proton is further confirmed by the reduction in the frequency of (N-O) group of the ligand and the complexes by $20\text{-}30\text{cm}^{-1}$ due to bonding mode of vibration of $\nu_{(\text{OH})}$ group disappears in the complexes indicating the deprotonation of $\nu_{(\text{OH})}$ group. The appreciably change in the frequency of aldimino nitrogen $\nu_{(\text{C}=\text{N})}$ by the ligand and the complexes. There is reduction in the frequency of $\nu_{(\text{C}=\text{N})}$ group in almost all complexes by $50\text{-}65\text{cm}^{-1}$ indicating the coordination of the aldimino nitrogen (C=N) with metal ions to form the complexes.

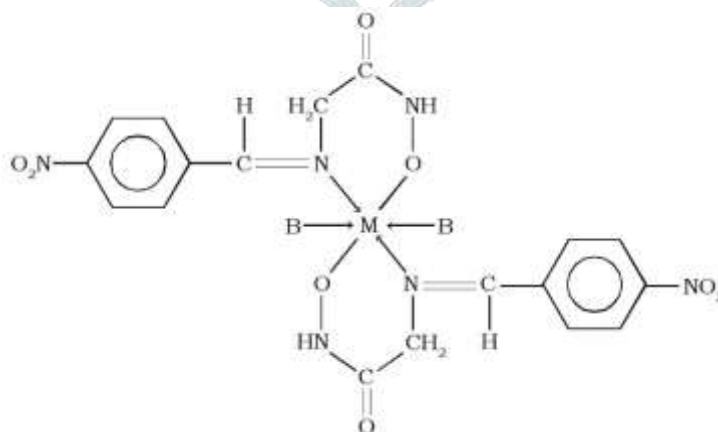
The deprotonation of (N-OH) proton and coordination of aldimino nitrogen (C=N) atom are further confirmed due to the appearance of two new bands around 560cm^{-1} and 450cm^{-1} due to $\nu_{(\text{M}-\text{O})}$ and $\nu_{(\text{M}-\text{N})}$ vibrations.

In case of aquo-complexes, separate band for coordinated H_2O is not obtained as it is overlapped by $\nu_{(\text{OH})}$ and $\nu_{(\text{NH})}$ vibrations. The frequencies obtained in the range of $700\text{-}800\text{cm}^{-1}$ in aquo-complexes may be attributed to rocking mode of coordinating water.

The amine complex displays one broad and strong band around $3,300\text{cm}^{-1}$ assignable to (NH) stretching vibration of coordinated ammonia molecule. In case of phenyl isocyanide complexes, there is an increase in the $\nu_{(\text{C}=\text{N})}$ vibration of the ligand ($2,170\text{cm}^{-1}$) and the complexes ($2,210\text{cm}^{-1}$) indicating the involvement of (NC) group in coordination. In quinoline complexes, a medium and broad band around $1,440\text{cm}^{-1}$ obtained due to ring vibration (ring breathing) indicates the involvement of N-atom of the quinoline in the complex formation.

The pyridine and picoline complexes display bands in finger print and for infra-red region. The pyridine ring breathing mode of vibration located at $930\text{-}1,060\text{cm}^{-1}$ in the complexes have been regarded as the characteristic vibrations of the coordinated pyridine and picolines molecules. The IR band at $570\text{-}580\text{cm}^{-1}$ in the complexes is also characteristic of presence of pyridine molecule in the complexes.

Thus on the basis of elemental analysis, values of electrical conductance and magnetic moments, electronic and IR spectra of the ligand and the complexes, the probable structure for $[\text{M}(\text{L})_2(\text{B})_2]$ complexes has been suggested to be octahedral, monomeric and non-electrolyte in nature.



where M=Cobalt(II) and Copper(II) cations, L=ligand and B=bases.

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