

SPECTRAL AND MAGNETIC STUDIES OF CO-ORDINATION COMPOUNDS OF Ni(II) AND Cu(II) WITH POLYDENTATE HYDROXAMIC ACID

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ABSTRACT

Studies on coordination chemistry of Ni(II) and Cu(II) are fast gaining importance due to its enormous organometallic and catalytic chemistry. The complexes of Ni(II) and Cu(II) with bidentate ligand 2,-bis(α -imino aceto hydroxamic acid) Butana, LH₂ derived from the reaction between Butane-2,3-dione and α -amino acetohydroxamic acid in alcoholic medium have been synthesized and characterized on the basis of elemental analyses, magnetic susceptibility, infrared, electronic spectral and conductivity data. The metal chelates ligand have general formula [M(L)(B)₂]. The IR observations suggest that the ligands have two proton of the hydroxamic acid moiety, one from each (N-O-H) group are lost producing binate ion. The resulting ligand, LH₂ act as dianionic tetradentate 4-nitrogen atoms of the macrocyclic ligand shifts 4- coordinations in planar framework. In which coordination occurs through equatorial mode of two Carbonylimino nitrogen and two imine nitrogen atoms with central metal ion while remaining centers of the central metal ion are satisfied by two axial coordinated molecules such as water, ammonia, quinoline, phenyl isocyanide etc. are in facial and perpendicular mode of one another. But two hydroxyl group of the hydroxamic acid combine to one another by Intramolecular hydrogen bond and formed six members chelating ring structure while imine group forming five members chelating ring with central metal ion above and below in a layer lattice complexes structure. Which both are enhancing the extra stability of the complexes. During the course of present investigation of magnetic susceptibility along with electronic and IR spectral data Indicates distorted high spin, paramagnetic Octahedral structure for the Ni(II) and Cu(II) complexes. The electrical conductance of the complexes show that these are to be non-electrolyte in nature while elemental analysis of the complexes indicate that the complexes are monomeric in nature. The stability of the macrocyclic complexes have been found to be dependent on the ring size of the cavity of the macrocyclic ligands which can be varied by changing the number of intervening atoms between two N atom of hydroxamic acid moiety and size of alkyl groups present in the terminal and intramolecular hydrogen bonding.

KeyWords-: Equatorial mode, Intervening atoms, Carbonylimino nitrogen, Dianionic tetradentate molecule, Chelate ligand, paramagnetic.

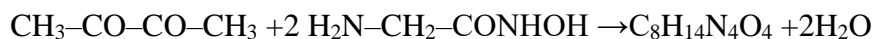
INTRODUCTION

There are strong reasons to believe that inspite of phenomenal progress in the field of macrocyclic chemistry, three still remains wide scope to isolate new macrocyclic complexes and study their physicochemical properties which will expand our horizon of understanding in several fundamental aspects enshrined with new information and facts. Consequently, in continuation of our earlier interests in the field. First of all hydroxamic was reported due to the reaction of hydroxylamine on diethyl oxalate by H. Lossen¹ in 1869. The production of violet colouration with Fe (III) and green colouration with Cu (II) are the characteristic reactions of hydroxamic acids. Hydroxamic acids are generally prepared by the reaction of hydroxylamine on organic esters or its derivatives in presence of sodium ethoxide²⁻⁵. Yoe et⁶ al have reported that hydroxamic acid behave as a bidentate chelating agent having complexing sites both of hydroxyl and carbonyl in which former loses a proton on forming a chelate. The structure of the hydroxamic acids was first brought to the attention of W.Lossen⁷⁻⁹ by the observation that the product obtained by the interaction of an isohydroxamic acid and benzoylchloride was different from the product obtained with benzohydroxamic acid and anisoyl chloride. Both acyl group in each compound were attached to the nitrogen atom of the hydroxyl amine molecule¹⁰⁻¹³. The successive acylation of hydroxyl amine each of the hydrogens of the hydroxyl amine molecule behaved differently from the other two and as a result of the proposed the hydroxy oxime structure RC (OH) = NOH. Such a structure served to explain the difference between ethyl benzohydroxamic acid C₆H₅C (OC₂H₅) = NOH and ethyl benzohydroxamate C₆H₅C (OH) = NOC₂H₅, as well as the hydrolytic product obtained with a verity of acylated and alkylated monohydroxamic acids. Various attempts to prepare compounds of the hydroxy oxime structure demonstrated their instability under conditions known to have little effect on the hydroxamic acids. To the controversy on the structure of the hydroxamic acids can be attributed the development Angeli's nitrosyl theory. In an attempt to establish the structures of these compounds Angeli¹⁴⁻¹⁶ searching for a new method for their synthesis, succeeded in preparing sodium nitrohydroxamate Na₃N₂O₃. Under certain conditions this later compound served as source of free nitrosyl NaOH. W. Lossen neglected the development of the rearrangement which bears this name either as a consequence of this complete occupation with the structure of the hydroxamic acids form a lack of interest. He was award of its similarity to the Hofmann rearrangement¹⁷⁻¹⁸. The hydroxamic acids are acidic in nature like phenols and carboxylic acids. The pka values for various hydroxamic acids have been reported in literature and these found to be of the order of 9 pka units, that is six units more acidic than amides¹⁹⁻²¹. Now we have undertaken a project for preparation of Ni(II) and Cu(II) complexes with the ligand 2,3-bis(α -imino acetohydroxamic acid) butane.

Ligand Synthesis

Preparation of 2,3-bis(α -imino acetohydroxamic acid) butane, (LH₂).

The ethanolic solution of butane-2,3-dione has been allowed to react with ethanolic solution of α -amino acetoacetic acid in 1:2 proportion under reflux on water bath for more than two hours at room temperature. The resulting solution on crystallization produced another crop of Schiff base which was then separated by filtration, washed and finally dried over KOH placed in a desiccator. The compound was further analysed and found to contain which corresponds to the molecular formulae, C₈H₁₄N₄O₄. The chemical reaction between them is given below.



Preparation of complexes

1. Preparation of complexes of Ni(II) and Cu(II) ions with the ligand 2,3-bis(α -imino acetohydroxamic acid) butane, (LH₂).

The metal acetate/chloride was dissolved in aqueous ethanolic solution. The ligand solution in ethanol was added to it with regular shaking. The metal-ligand molar ratio was always kept 1:1 respectively. The complex of Ni(II) and Cu(II) acetate / chloride were prepared with the ligand in aqueous medium in presence of bases like water, ammonia, quinoline, phenyl isocyanide and different picolines. The resulting solutions as a whole was then refluxed on a water bath for two hours at room temperature, within this period, the complexes in form of solid separated out in the solution. The complexes were separated by filtration, washed and finally dried over KOH placed in a desiccator. On the basis of analytical Data the complex were found to possess the expected general molecular formula $[M(L)(B)_2]$, B=Water, ammonia, quinoline, phenyl isocyanide, pyridine etc, and M = Ni(II), Cu(II).

RESULTS AND DISCUSSION

All the chemicals used in the present work were obtained from BDH. Glycine ethyl ester hydrochloride, hydroxylamine, hydrochloride, dimethyl formamide, ethylalcohol, quinoline, ammonia, phenyl isocyanide, pyridine and different picolines. Metal acetate / chlorides were either from BDH or Aldrich extra pure E. Merck quality. They were used without further purification.

Elemental analysis of the complexes of the Ni(II) and Cu(II) ions have been incorporated in the experimental work. The remaining following tools for the structure elucidation are being discussed below.

Elemental analysis of the ligand and the complexes

The estimation of metals, Hydrogen, carbon, and nitrogen in the complexes were carried out by standard methods. The complexes were first decomposed with a view to bringing the metals in their proper ionic solution and then they were quantitatively analytical data given below. While elemental analysis of the complexes indicate that all the complexes are monomeric in nature.

Table-1

Analytical data of the Cu(II) complexes with the ligand.

Compounds	% Analysis, found(calculated)			
	Metal	Carbon	Hydrogen	Nitrogen
$[Cu(C_8H_{14}N_4O_4)(H_2O)_2]$	19.22 (19.38)	29.20 (29.31)	4.90 (4.88)	17.20 (17.09)
$[Cu(C_8H_{14}N_4O_4)(NH_3)_2]$	19.36 (19.50)	29.32(29.49)	5.54(5.52)	25.92 (25.80)
$[Cu(C_8H_{14}N_4O_4)(C_9H_7N)_2]$	11.42(11.55)	56.60(56.77)	4.76(4.73)	15.40(15.31)
$[Cu(C_8H_{14}N_4O_4)(C_6H_5NC)_2]$	12.64(12.76)	52.92(53.06)	4.47(4.42)	16.96(16.88)
$[Cu(C_8H_{14}N_4O_4)(C_5H_5N)_2]$	14.02(14.12)	47.95(48.05)	4.92(4.89)	18.76(18.69)

Table-2

Analytical data of the Ni(II) complexes with the ligand.

Compounds	% Analysis, found(calculated)			
	Metal	Carbon	Hydrogen	Nitrogen
[Ni(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	18.10(18.19)	29.60(29.74)	4.98(4.95)	17.42(17.36)
[Ni(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	18.20(18.30)	29.80(29.93)	5.66(5.61)	26.24(26.19)
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	10.62(10.77)	57.15(57.27)	4.82(4.77)	15.48(15.42)
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	11.81(11.94)	53.40(53.56)	4.50(4.46)	17.10(17.04)
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	13.08(13.19)	48.42(48.57)	4.98(4.94)	18.96(18.88)

Magnetic behaviour of Cu(II) complexes

On the basis of the consideration of magnetic properties, Cu(II) complexes, fall into two broad classes, (1) Those having essentially temperature independent magnetic moments in the range 1.75 – 2.20 B.M. (2) Those having temperature dependent, magnetic moment values below the spin only value. In such complexes the pair of Cu(II) ions are held together by hydroxyl or carboxylate anions. There are examples in which the two Cu(II) ions are coupled together and the dimers becomes diamagnetic²². Ray and Sen²³ have studies several Cu(II) complexes and have categorised several Cu(II) complexes them into two sub-groups. (a) Complexes having magnetic moments between 1.73 and 1.84 B.M. (b) Those having magnetic moment values between 1.94 and 2.2 B.M. They assigned the former to square planar with dsp² hybridization and the latter tetrahedral or octahedral with sp³d² bonding. The absence of orbital contribution in former category has been explained by the authors on the assumption of greater quenching affect of the crystal field in the orbital moment. The orbital contribution to the magnetic moment is greater in the case of tetrahedral Cu(II) complexes than Cu(II) octahedral complexes. The magnetic moment values obtained for [Cu(L)(B)₂] complexes have been found in the range of 1.92 – 2.10 B.M. Which unambiguously suggests the high spin paramagnetic six coordinated octahedral arrangement of ligand molecules around the metal ions in complexes.

Table-3

Magnetic moment data for Cu(II) complexes with the ligand.

Complexes	colour	M _{eff} B.M.	Magnetic Nature
[Cu(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	Deep Green	2.10	Paramagnetic
[Cu(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	Light Green	2.00	Paramagnetic
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	Green	1.94	Paramagnetic
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	Green	1.96	Paramagnetic
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	Light Green	1.92	Paramagnetic

Magnetic behaviour of Ni(II) complexes

In our present investigation the value of magnetic moment for the [Ni(L)(B)₂] complexes obtained in the range of 2.90-3.00 B.M. indicate the six coordinated octahedral nature of the complexes.

Table- 4

Magnetic moment data for Ni(II) complexes with the ligand.

Complexes	colour	M _{eff} B.M.	Magnetic Nature
[Ni(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	Light green	2.98	Paramagnetic
[Ni(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	Greenish white	3.00	Paramagnetic
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	green	2.96	Paramagnetic
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	Pale-green	2.90	Paramagnetic
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	Light- green	2.94	Paramagnetic

Electrical conductance of Cu(II) complexes

The value of electrical conductance of the Cu(II) complexes with the ligand 2,3-bis(α-imino acetohydroxamic acid) butane are obtained in the range of 18-30 ohm⁻¹ cm² mol⁻¹ indicate non-electrolytic nature of the Cu(II) complexes with the ligand 2,3-bis (α-imino acetohydroxamic acid)butane. Which clearly indicates that anions are coordinated with metal atom / ions of the complexes.

Table- 5

Data of electrical conductance for the Cu(II) complexes with the ligand.

Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvent
[Cu(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	28	DMF
[Cu(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	26	DMF
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	28	DMF
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	18	DMF
[Cu(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	20	DMF

Electrical conductance of Ni(II) complexes

The values of electrical conductance obtained in the range of 14-24 ohm⁻¹ cm² mol⁻¹ indicate non-electrolyte nature of the Ni(II) complexes with the ligand 2,3-bis (α-imino acetohydroxamic acid) butane. Which clearly indicates that anions are coordinated with metal atom / ions of the complexes.

Table-6

Date of electrical conductance for the Ni(II) complexes with the ligand.

Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvent
[Ni(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	24	DMF
[Ni(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	16	DMF
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	18	DMF
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	14	DMF
[Ni(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	16	DMF

I.R. spectral behaviour of the ligand, LH₂

The sharp and broad band around 3150 cm⁻¹ has been obtained due to combined $\nu_{(\text{OH})}$ and $\nu_{(\text{NH})}$ frequencies. The $\nu_{(\text{OH})}$ of the enol form(-COH) shifts from 3500 cm⁻¹ to 3180 cm⁻¹. Free primary amines shows $\nu_{(\text{NH})}$ stretching between the range of 3450-3300 cm⁻¹ is lowered due to hydrogen bonding. A sharp and strong band at 1070 cm⁻¹ is obtained due to the vibration of $\nu_{(\text{N-O})}$ group present in hydroxamic acid moiety of the ligand. Two protons of the hydroxamic acid moiety one from each (N-O-H) group are lost producing dinegative ion. The resulting ligand LH₂ act as dianionic tetradentate molecule which coordinates through two oxime nitrogen and two imide nitrogen with the metal ions to the complexes. The ligand has different donor sites and it can form chelate ring in a number of ways. The probable mode of attachment between the metals and the ligand molecule and related data are shown below.

Table-7**I.R. spectral data of the ligand.**

I.R. band positions cm ⁻¹	Nature	Probably assignments.
3160	Strong/broad	$\nu_{(\text{OH})} + \nu_{(\text{NH})}$
2970	Broad/Weak	$\nu_{(\text{C-H})}$
1850	Broad/Strong	$\nu_{(\text{C-CH}_3)}$
1650	Broad/Strong	$\nu_{(\text{C=N})}$
1440	Broad/Weak	$\nu_{(\text{C-N})}$
1080	Broad/Strong	$\nu_{(\text{N-O})}$

I.R. spectral behaviour of the complexes

In almost all complexes $\nu_{(\text{O-H})}$ azomethine group $\nu_{(\text{C=N})}$ and $\nu_{(\text{N-O})}$ band position of the ligand molecule are appreciable affected. The broad and strong band due to vibrations of $\nu_{(\text{O-H})}$ and $\nu_{(\text{N-H})}$ of the ligand molecule located at 3150 cm⁻¹ disappears in all the complexes formed with the ligand and a new broad band appears in the complexes at about 3320 cm⁻¹ confirming the presence of at least one free (-OH) group with a very weak hydrogen bonding even in the complexes. The band position due to $\nu_{(\text{C=N})}$ and $\nu_{(\text{C-N})}$ located at around 1640 cm⁻¹ and 1420 cm⁻¹ in the ligand is also shifting to lower frequency in almost all complexes by about 60-50 cm⁻¹. This shifting of $\nu_{(\text{C=N})}$ band toward lower frequency in the complexes suggest the coordination of the two imide nitrogen of the ligand in formation of the complexes. One new band in all the complexes are obtained at 445 cm⁻¹ due to the vibration of $\nu_{(\text{M-N})}$ indicating the participation of nitrogen atom in the formation of the complexes. The two nitrogen atoms of hydroxamic acid part (-NH₂) deprotonated and two nitrogen atom of (azomethine, C=N) group are the bonding sites of the Schiff base 2,3-bis(α -iminoaceto hydroxamic acid) butane (LH₂). In case of Ni(II) complexes three electronic spectral bands around 230, 330 and 430 nm. have been obtained due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{p})$ transition, while Cu(II) complexes one broad and unsymmetrical band around 455 nm has been obtained due to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition both are supporting the octahedral nature of the complexes.

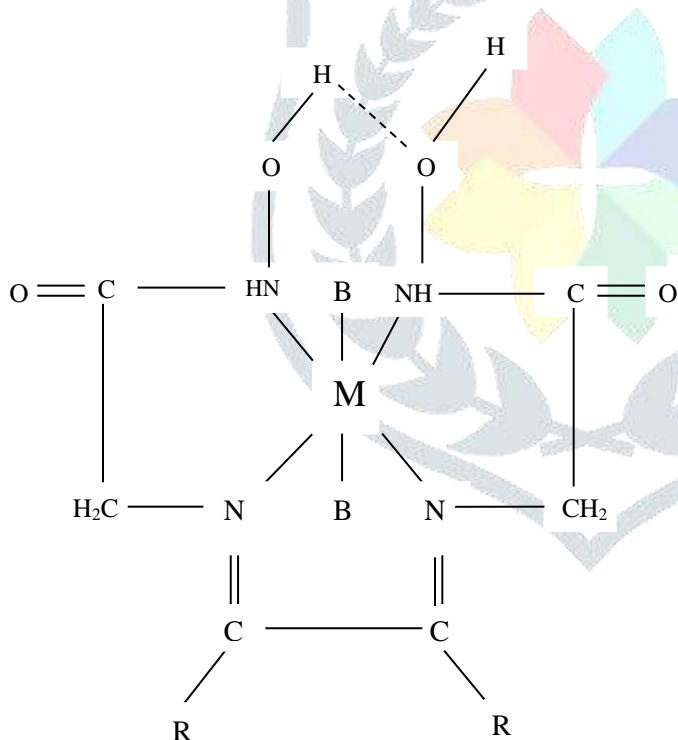
Table-8**I.R. spectral data of complexes with ligand.**

I.R. bands position cm ⁻¹	Nature	Probably assignments
3320	Strong/broad	$\nu_{(\text{OH})}$
2940	Broad/weak	$\nu_{(\text{C-H})}$
2180	Broad/weak	$\nu_{(\text{Phenyl isocyanide})}$
1590	Broad/strong	$\nu_{(\text{C=N})}$
1420	Broad/strong	$\nu_{(\text{C-M})}$
1130	Broad/strong	$\nu_{(\text{N-O})}$

CONCLUSION

Thus on the basis of above studies, it is concluded that central metal ion as Ni(II) and Cu(II) in the complexes involve bonding of imine groups with the metal centres and the macrocyclic ligand exists in dianionic form. The dianionic form of the ligand for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands, enclosing the metal ion in the macrocyclic cavity forming six members intramolecular hydrogen bonding chelating rings structure with the imide moieties above and five members chelating rings structure involving imine group below of central metal ion and both are provide the extra stability of the complexes. The remaining centres of metal ions are satisfied by two axial mode of molecules as water, ammonia, quinoline, phenyl isocyanide etc are present in facial and perpendicular mode to one another in complexes. While the central metal ion contain coordination number six with ligand, which is proposed that the geometry of the complexes are monomeric, paramagnetic, Octahedral structure.

On the basis of elemental analysis, electrical conductance, magnetic moment data, I.R. Spectra of the ligand and complexes with bonding sites of the ligand, the probable structure for the complex of the $M(L)B_2$ are suggested to be monomeric paramagnetic octahedral in nature as shown below.



Tentative monomeric octahedral structure of the complexes.

R= H, -CH₃ - C₆H₅ groups, M= Ni(II) , Cu(II) B= Water, ammonia, quinoline, phenyl, isocyanide etc.

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