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Studies of Spectral and Magnetic Behaviour of Co-Ordination Compounds of Co(II) and Ni(II) with Bidentate Hydroxamic Acid

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ABSTRACT

Recently there are strong reasons to believe that in spite of phenomenal progress in several field of coordination chemistry shows that the stereochemical considerations are gaining an increasing importance. Studies on coordination chemistry of Co(II) and Ni(II) are fast gaining importance due to its enormous organometallic and catalytic chemistry. The complexes of Co(II) and Ni(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]. 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 Co(II) and Ni(II) complexes. Elemental analysis of the complexes indicated that the complexes are monomeric while electrical conductance of the complexes show to be non-electrolyte 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- Facial mode, Macrocyclic ligand, Intervening atoms, Carbonylimino nitrogen, Ring size of cavity, Chelates.

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INTRODUCTION

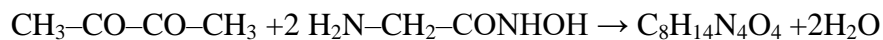
First of all hydroxamic was reported due to the reaction of hydroxylamine on diethyl oxalate by H. Lossen¹ in 1869. Hydroxamic acids are generally prepared by the reaction of hydroxylamine on organic esters or its derivatives in presence of sodium ethoxide²⁻⁵. Yoe et⁶ al have reported that hydroxamic 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 $C_6H_5C(OC_2H_5) = NOH$ and ethyl benzohydroxamate $C_6H_5C(OH) = NOC_2H_5$, as well as the hydrolytic product obtained with a variety of acylated and alkylated monohydroxamic acids. 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 $Na_3N_2O_3$. 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 aware 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 Co(II) and Ni(II) complexes with the ligand 2,3-bis(α -imino aceto hydroxamic acid) butane.

Ligand Synthesis

Preparation of 2,3-bis(α -imino aceto hydroxamic 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 desiccators. The compound

was further analysed and found to contain which corresponds to the molecular formulae, $C_8H_{14}N_4O_4$. The chemical reaction between them is given below.



Preparation of complexes.

Preparation of complexes of Co(II) and Ni(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 Co(II) and Ni(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 his 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 desiccators. 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 = Co(II), Ni(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 Co(II) and Ni(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 the 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 indicates that all the complexes are monomeric in nature.

Table-1 Analytical data of the Co(II) complexes with the ligand.

Compounds	%Analysis, found(calculated)			
	Metal	Carbon	Hydrogen	Nitrogen
[Co(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	18.10 (18.24)	29.60 (29.73)	4.98 (4.95)	17.41 (17.34)
[Co(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	18.21 (18.35)	29.78 (29.91)	5.65 (5.60)	26.25 (26.17)
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	10.64 (10.80)	57.12 (57.25)	4.80 (4.77)	15.46 (15.41)
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	11.76 (11.94)	53.40 (53.56)	4.50 (4.46)	17.10 (17.04)
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	13.08 (13.23)	48.38 (48.55)	4.98 (4.95)	18.96 (18.88)

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 Co(II) complexes.

The magnetic moment values of Co(II) (3d⁷) complexes fall into two classes. In one the magnetic moments lie in the range of 4.3-5.6 B.M. While in the other, the magnetic moments occurs in the range of 1.8-3.0 B.M. Co²⁺ ion contains three un paired electrons in the ground state and the spin only magnetic moment calculated by the formula, $\mu_s = \sqrt{n(n+2)}$ B.M. gives the value of 3.88 B.M. Any excess value of the magnetic moment over μ_s is attributed to the various degree of orbital contribution. Co(II) forms tetrahedral, square planer, and octahedral complexes and all are paramagnetic. The magnetic moment values obtained for [Co(L)(B)₂] complexes have been found in the range of 4.82 to 4.96 B.M. Which unambiguously suggest the high spin six coordinated octahedral arrangement of ligand molecules around the metal ion.

Table-3 Magnetic moment data for Co(II) complexes with the ligand.

Complexes	colour	M_{eff} B.M.	Magnetic Nature
[Co(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	Brown	4.96	Paramagnetic
[Co(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	Brown	4.90	Paramagnetic
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	Light brown	4.98	Paramagnetic
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	Light brawn	4.80	Paramagnetic
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	Pale brawn	4.86	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 Co(II) complexes

The value of electrical conductance of the Co(II) complexes with the ligand 2,3-bis(α -iminoacetohydroxamic acid) butane are obtained in the range of 8-24 ohm⁻¹ cm² mol⁻¹ indicate non-electrolytic nature. Which clearly indicates that anion is coordinated with metal atom / ions of the complexes.

Table- 5 Data of electrical conductance for the Co(II) complexes with the ligand.

Complexes	Ohm ⁻¹ cm ² mole ⁻¹	Solvent
[Co(C ₈ H ₁₄ N ₄ O ₄)(H ₂ O) ₂]	18	DMF
[Co(C ₈ H ₁₄ N ₄ O ₄)(NH ₃) ₂]	24	DMF
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₉ H ₇ N) ₂]	12	DMF
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₆ H ₅ NC) ₂]	10	DMF
[Co(C ₈ H ₁₄ N ₄ O ₄)(C ₅ H ₅ N) ₂]	08	DMF

Electrical conductance of Ni(II) complexes.

The values of electrical conductance obtained in the range of 14-24 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ 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 Data of electrical conductance for the Ni(II) complexes with the ligand.

Complexes	$\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	Solvent
$[\text{Ni}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4)(\text{H}_2\text{O})_2]$	24	DMF
$[\text{Ni}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4)(\text{NH}_3)_2]$	16	DMF
$[\text{Ni}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4)(\text{C}_9\text{H}_7\text{N})_2]$	18	DMF
$[\text{Ni}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4)(\text{C}_6\text{H}_5\text{NC})_2]$	14	DMF
$[\text{Ni}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2]$	16	DMF

I.R. spectral behaviour of the ligand

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 $3450\text{-}3300 \text{ cm}^{-1}$ 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 LH_2 act as dianionic tetradentate molecule which coordinated through two oxime nitrogen and two imide nitrogen in equatorial mode with the central metal ions in the complexes. The ligand has different donor sites and it can form chelating 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 in 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 appreciably 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 $60\text{-}50 \text{ cm}^{-1}$. 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 the Co(II) complexes one electronic spectral band around 460 nm has been obtained due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition while 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 supporting both are octahedral nature of the complexes.

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

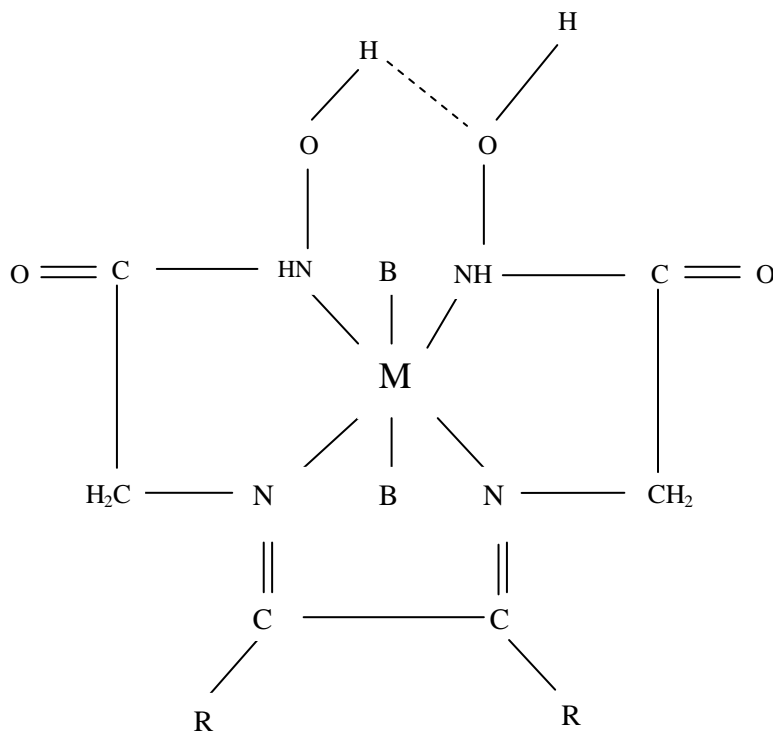
I.R. bands position in cm^{-1}	Nature	Probably assignments
3320	Strong/broad	$\nu_{(\text{OH})}$
2940	Broad/weak	$\nu_{(\text{C-H})}$
2180	Broad/weak	$\nu_{(\text{Phenyl isocyanide})}$
1590	Broad/strong	$\nu_{(\text{C=N})}$
1420	Broad/strong	$\nu_{(\text{C-M})}$
1130	Broad/strong	$\nu_{(\text{N-O})}$

CONCLUSION

Thus on the basis of above studies, it is concluded that central metal ion as Co(II) and Ni(II) in the complexes coordinated that the ligand acts as a bidentate manner and coordination is proposed through four equatorial N atom of two imine and two hydroxamic acid group of the ligand shifts 4-coordinations in planar framework. The remaining centres of central metal ions are satisfied by two axial

mode of coordinated molecules as water, ammonia, quinoline, phenyl isocyanide etc are present in facial and perpendicular mode to one another in above and below of layer lattice structure in the complexes. While two –OH group of hydroxamic acid combine to each other by intramolecular hydrogen bond and forming six members cyclic ring structure with central metal ion and imine group forming five members chelating ring which both provide the extra stability of the complexes. The central metal ion in complexes contains 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 complexes 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= Co(II) , Ni(II) B = Water, ammonia, quinoline, phenyl, isocyanide etc.

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