

HYDROXAMIC ACID: AN ANALYTICAL REAGENT FOR NUMBER OF ELEMENTS

Nitish Bhardwaj
Research Scholar
Dept. of Chemistry.
J. P. University, Chapra

ABSTRACT

Hydroxamic acid was reported by H. Lossen in 1869 due to the reaction of hydroxylamine on diethyl oxalate. 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 ethoxide.

Hydroxamic acid behaves as a bidentate chelating agent having complexing sites both of hydroxyl and carbonyl oxygen in which former loses a proton on forming a chelate.

The structure of the hydroxamic acids was first brought to the attention of W. Lossen by the observation that the product obtained by the interaction of anisohydroxamic acid and benzoyl chloride was different from the product obtained with benzohydroxamic acid and anisoyl chloride. He introduced the term 'metamers' to describe these compounds erroneously believing that both acyl groups in each compound were attached to the nitrogen atom of the hydroxyl amine molecule.

Key words : anisoyl chloride, benzoyl chloride, metamers.

INTRODUCTION

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 this, 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 benzo hydroxamate $C_6H_5-C(OH)=NOC_2H_5$, as well as the hydrolytic product obtained with a variety of acylated and alkylated mono-hydroxamic acids. He considered the α -, β - and γ -forms of dibenzoyl hydroxamate or the α - and β -forms of ethyl benzo hydroxamic acid in each instance as physically different manifestations of the same parent compound. It was at this time that he became considerably involved in a controversy on structure with

Werner, Tiemann and others. Werner presented evidence which indicated that the α - and β -forms of ethyl benzohydroxamic acid were geometric.

The hydroxamic acids of α -hydroxy acids like tartaro-, citro-, glycolo, and lacto-hydroxamic acids, all yield orange solutions in alkaline medium with nickel salts, but the complexes could not be isolated in the solid state. Cobalt (II) compounds of the unsubstituted hydroxamic acids, that have been isolated are of light pink colour having the composition CoR_2 like the corresponding nickel compounds. These dissolve in alkalis and slowly change to give a reddish brown colouration due to the formation of cobalt (II) complexes. Complex cobaltous salts with benzo-, salicyl-cinnamyl-, dihydrocinnamyl and anisyl hydroxamic acids have thus been isolated.

Hydroxamic acids are generally prepared by the reaction of hydroxylamine on organic esters or its derivatives in presence of sodium ethoxide. Benzohydroxamic acid was first introduced by Musante¹⁴ and was used as an analytical reagent for number of elements¹⁵⁻¹⁸. Chakravarty used this acid in the gravimetric analysis of Ti and Zr. Seaborg reported its utility as complexing agent and carried out separation of a number of rare-earth elements.

EXPERIMENTAL

Preparation of Ni (II) complexes with 2-amino-5-chloro benzohydroxamic acid:-

0.20 grams (0.001 mole) of the ligand, 2-amino-5-chloro benzohydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of Ni (II) chloride hexahydrate 0.23 gram (0.001 mole). Three to four drops of ammonium hydroxide was added to the resulting solution. The resulting solution thus obtained was heated under reflux on water bath for 2 hours when a greenish crystalline solid was obtained which was separated by filtration and washed with small quantity of alcohol followed by ether and dried over KOH pellets placed in desiccator. It was further analysed and found to contain.

Table – 1**Elemental analysis of Nickel (II) Complexes**

Compounds	Found %	Calculated %
Nickel	12.48	12.65
Carbon	36.10	36.23
Hydrogen	3.90	3.88
Nitrogen	18.16	18.11
Chlorine	15.12	15.31

Which corresponds to the molecular formula $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{NH}_3)_2$

Preparation of Ni (II) complexes with 2-amino-5-chloro benzohydroxamic acid:-

0.20 grams (0.001 mole) of the ligand, 2-amino-5-chloro benzohydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of Ni (II) chloride hexahydrate 0.23 gram (0.001 mole). Three to four drops of quinoline was added to the resulting solution. The resulting solution thus obtained was heated under reflux on water bath for 2 hours when a faint green crystalline solid was obtained which was separated by filtration and washed with small quantity of alcohol followed by ether and dried over KOH pellets placed in desiccator. It was further analysed and found to contain.

Table – 2

Elemental analysis of Nickel (II) Complexes

Compounds	Found %	Calculated %
Nickel	8.38	8.53
Carbon	55.56	55.83
Hydrogen	3.80	3.78
Nitrogen	12.30	12.22
Chlorine	10.14	10.32

Which corresponds to the molecular formula $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_9\text{H}_7\text{N})_2$

Preparation of Ni (II) complexes with 2-amino-5-chloro benzohydroxamic acid:-

0.20 grams (0.001 mole) of the ligand, 2-amino-5-chloro benzohydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of Ni (II) chloride hexahydrate 0.23 gram (0.001 mole). Three to four drops of phenyle- isocyanide was added to the resulting solution. The resulting solution thus obtained was heated under reflux on water bath for 2 hours when a slight green crystalline solid was obtained which was separated by filtration and washed with small quantity of alcohol followed by ether and dried over KOH pellets placed in desiccator. It was further analysed and found to contain.

Table – 3

Elemental analysis of Nickel (II) Complexes

Compounds	Found %	Calculated %
Nickel	9.12	9.23
Carbon	52.65	52.85
Hydrogen	3.48	3.46
Nitrogen	13.24	13.21
Chlorine	11.04	11.16

Which corresponds to the molecular formula $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2\text{C}_6\text{H}_5\text{NC})_2$

Preparation of Ni (II) complexes with 2-amino-5-chloro benzohydroxamic acid:-

0.20 grams (0.001 mole) of the ligand, 2-amino-5-chloro benzohydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of Ni (II) chloride hexahydrate 0.23 gram (0.001 mole). Three to four drops of pyridine was added to the resulting solution. The resulting solution thus obtained was heated under reflux on water bath for 2 hours when a light green crystalline solid was obtained which was separated by filtration and washed with small quantity of alcohol followed by ether and dried over KOH pellets placed in desiccator. It was further analysed and found to contain.

Table – 4

Elemental analysis of Nickel (II) Complexes

Compounds	Found %	Calculated %
Nickel	9.86	9.98
Carbon	48.84	49.00
Hydrogen	3.78	3.74
Nitrogen	14.36	14.29
Chlorine	11.92	12.08

Which corresponds to the molecular formula $\text{Ni}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_5\text{H}_5\text{N})_2$

RESULTS AND DISCUSSION

The structures of the complexes are proposed by the interpretation of the results of elemental analysis, magnetic moment, electrical conductance, electronic spectral behaviour of the complexes and I.R spectral nature of the ligand and the complexes undertaken for the present investigation.

The low value has been attributed to equilibrium between high spin and low spin Co(II) octahedral complexes. The high value relative to μ_s (3.88 B.M) have been attributed to orbital contribution. For several Co(II) octahedral complexes μ_{eff} has been reported in the range (2.1 to 3.7) B.M⁷⁹.

Table
Electronic conductance data of [Co(L) 2 B2] complexes:-

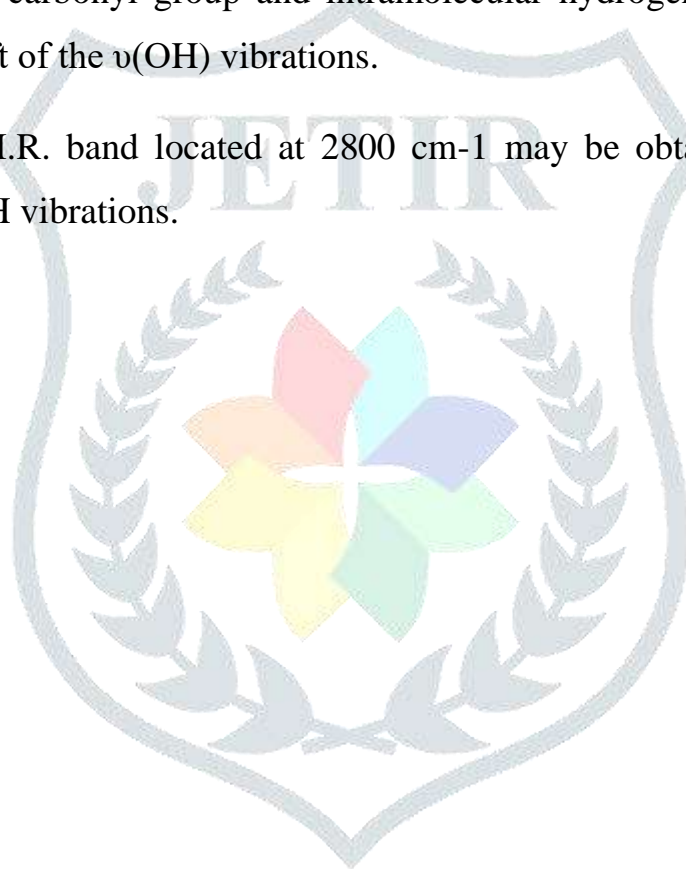
Complex	Λ_m $\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	Solvent
1. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{H}_2\text{O})_2$]	28	DMF
2. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{NH}_3)_2$]	24	DMF
3. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_9\text{H}_7\text{N})_2$] Quinoline	16	DMF
4. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_6\text{H}_5\text{NC})_2$] Phenyl isocyanide	10	DMF
5. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_5\text{H}_5\text{N})_2$] Pyridine	18	DMF
6. [$\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2 (\text{C}_5\text{H}_4\text{NCH}_3)_2$] α -picoline	20	DMF

CONCLUSION

Free primary amines show $\nu(\text{NH})$ stretching vibrations between the range 3500-3300 cm^{-1} which lowered due to hydrogen bonding. Thus the band at 3100 cm^{-1} may had been due also to $\nu(\text{NH})$ stretching frequency of the primary amine lowered due to intramolecular hydrogen bonding. Thus a good deal of overlapping between $\nu(\text{OH})$ and $\nu(\text{NH})$ vibrations occur in this region so that differentiation is not possible.

A sharp and mild band obtained at 1660 cm^{-1} has been assigned due the presence of azomethine ($>\text{C}=\text{N}-$) group in the ligand molecule. The amide group shows band due to combination of $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$ and $\nu(\text{N}-\text{H})$ groups. I.R. spectra data of the Ligand, 2-amino-5-chloro benzohydroxamic acid and its complexes of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ cations. A sharp and strong band near 3100 cm^{-1} has been assigned due to combined $\nu(\text{OH})$ and $\nu(\text{NH})$ frequencies. The $\nu(\text{OH})$ of the enol form ($-\text{C}-\text{OH}$) shifts from $3500-3100\text{ cm}^{-1}$ due to hydrogen bonding. So, there is also a chance of coupling $\nu(\text{OH})$ band with $\nu(\text{NH})$ band in spectra of the hydroxamic acid. The ligand forms intra molecular hydrogen bonding and the $-\text{OH}$ group of the hydroxamic acid part is bonded to the electron rich atom, oxygen of the carbonyl group and intramolecular hydrogen bonding may occur leading to a large shift of the $\nu(\text{OH})$ vibrations.

Thus a broad I.R. band located at 2800 cm^{-1} may be obtained due to strongly hydrogen bonded $-\text{OH}$ vibrations.



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