

# HYDROXAMIC ACID: A CLASS OF CHEMICAL COMPOUNDS

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## ABSTRACT

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. Later he realised that in 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  $\alpha$ -,  $\beta$ - and  $\gamma$ -forms of dibenzoyl hydroxamate or the  $\alpha$ - and  $\beta$ -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

**Key words** : hydroxamic acids, acylated, dibenzoyl hydroxamate, ethyl benzo hydroxamic acid.

## INTRODUCTION

Hydroxamic acids can be synthesized from aldehydes via the Angeli-Rimini reaction. A well-known hydroxamic acid reaction is the Lossen rearrangement.

Many hydroxamic acids, such as salicylhydroxamic acid, are utilized as ligands in the synthesis of metallocrowns.

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 Musante<sup>14</sup> and was used as an analytical reagent for number of elements<sup>15-18</sup>. 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.

The red and orange nickel amino hydroxamic acid complexes are diamagnetic whereas the yellowish green nickel complexes of the other hydroxamic acids are paramagnetic having magnetic moment values of 2.78 to 3.15 B.M.

The hydroxamic acids of  $\alpha$ -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<sup>39</sup>. 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.

Cobalt(III) complexes of the type  $CoR_3$  with unsubstituted hydroxamic acid could not, however, be obtained because of their instability in neutral or acid solutions. From the alkaline solution of benzo-hydroxamic acid a complex (anionic) was precipitated by the addition of a solution of Cobalt(III) bis-bigunadinium salt.

But with glycine hydroxamic acid cobaltic trisglycine hydroxamato compound has been isolated by treating hexamine cobaltic chloride with glycine hydroxamic acid. It has the composition  $Co(C_2H_5O_2N_2)_3$  and separates out as crystals from the solution. A more soluble variety of dark-red coloured compound was obtained by passing air through a suspension of cobaltous hydroxide in glycine hydroxamic acid solution and then evaporating the dark-red filtrate, from any undissolved residue, to dryness in vacuum. The two varieties like are possibly related as cis-trans isomer to each other<sup>40</sup> with  $\alpha$ -alanine hydroxamic acid

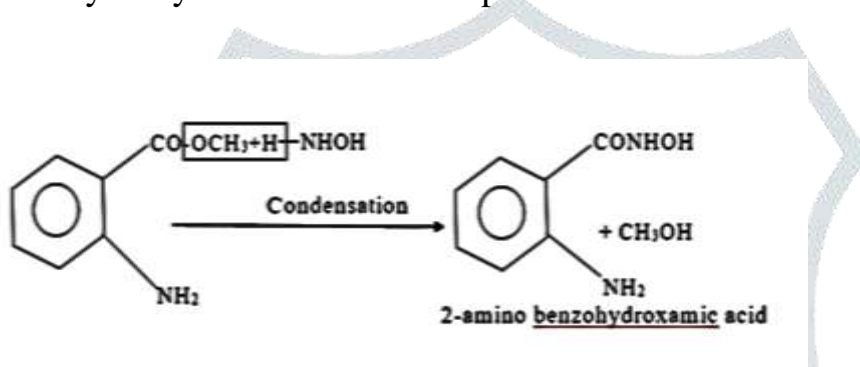
it has not been possible to isolate any Co(III) complex, though a dark-red solution results when a solution of this acid is allowed to react with hexamine cobaltic chloride.

## EXPERIMENTAL

Preparation of the ligand, 2-amino-5-chloro benzohydroxamic acid. The ligand 2-amino-5-chloro benzohydroxamic acid has been prepared in two steps:-

### Preparation of 2-amino benzohydroxamic acid:-

A.W. Scott and B.L.Wood<sup>74</sup> prepared in this compound by the interaction of methyl anthranilate and hydroxylamine at room temperature.



### Procedure:-

41.6 grams of hydroxylamine hydrochloride was gradually added with constant stirring to an ice cold solution of 48 grams of sodium hydroxide dissolved in 300 ml of water after that, 45 grams of methyl anthranilate (39 ml, sp.gr.1.16) was added to the resulting solution along with enough alcohol for the proper dilution of the solution. The whole solution was allowed to stand for three days at room temperature. Then the solution distilled under the reduced pressure until sodium salt of hydroxamic acid was precipitated leaving 100 ml of mother liquor in the flask. The salt was filtered by suction was washed with ether. The filtrate was made acidic with HCl and then free hydroxamic acid was precipitated. The crude product was recrystallised from ether. It was light brown in colour having the melting point 1490 C. The yield of the sodium salt and free hydroxamic acid obtained from the mother liquor was 60%.

The compound gave a good test for hydroxamic acid with FeCl<sub>3</sub>. It is fairly stable upto 1400C and was kept for three months at room temperature without any remarkable decomposition.

This is soluble in ether acetate, slightly soluble in either and almost insoluble in ligroin.

The compounds was analysed and found to contain.

**Table - 1**

**Elemental analysis of 2-amino-5-chloro benzohydroxamic acid**

Elements	Found %	Calculated %
Carbon	55.10	55.26
Hydrogen	5.228	5.26
Nitrogen	18.48	18.42

Which corresponds to the molecular formula as  $C_7H_7NO_3$ .

**Preparation of Co(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 aqueous-ethanolic solution of Co (II) chloride hexahydrate 0.23 gram (0.001 mole). The resulting solution was heated under reflux on water bath for 2 hours when a light brown 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 Cobalt(II) Complexes**

Compounds	Found %	Calculated %
Cobalt	12.48	12.64
Carbon	35.82	36.05
Hydrogen	3.42	3.43
Nitrogen	12.04	12.01

Chlorine	15.15	15.23
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Which corresponds to the molecular formulae  $\text{Co}(\text{C}_7\text{H}_6\text{N}_2\text{ClO}_2)_2(\text{H}_2\text{O})_2$

### Preparation of Co(II) complexes with 2-amino-5-chloro benzo hydroxamic 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 Co (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 brownish 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 Cobalt(II) Complexes

Compounds	Found %	Calculated %
Cobalt	8.44	8.56
Carbon	55.62	55.82
Hydrogen	3.78	3.77
Nitrogen	12.24	12.21
Chlorine	10.16	10.32

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

### Preparation of Co(II) complexes with 2-amino-5-chloro benzo hydroxamic 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 Co (II) chloride hexahydrate 0.23 gram (0.001 mole). Three to four drops of phenyle-isocyanid was added to the resulting solution. The resulting solution thus obtained was heated under reflux on water bath for 2 hours when a deep brown 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.

## RESULTS AND DISCUSSION

The high value relative to  $\mu_s$  (3.88 B.M) have been attributed to orbital contribution. For several Co(II) octahedral complexes  $\mu_{eff}$  has been reported in the range (2.1 to 3.7) B.M<sup>79</sup>. The low value has been attributed to equilibrium between high spin and low spin Co(II) octahedral complexes.

**Table-4**

**The magnetic moment data of [Co(L)<sub>2</sub>B<sub>2</sub>] complexes**

Complexes	Colour	$\mu_{eff}$	Magnetic Moment
1. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Chocolate	4.98	Paramagnetic
2. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	Light brown	4.90	Paramagnetic
3. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ] Quinoline	Yellowish brown	4.96	Paramagnetic
4. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ] Phenyl isocyanide	Pinkish brown	4.90	Paramagnetic
5. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ] Pyridine	Pinkish brown	4.90	Paramagnetic
6. [ Co(C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> ClO <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>4</sub> NCH <sub>3</sub> ) <sub>2</sub> ] $\alpha$ -picoline	Yellowish brown	4.92	Paramagnetic

## CONCLUSION

I.R. spectra data of the Ligand, 2-amino-5-chloro benzohydroxamic acid and its complexes of Co(II), Ni(II) and Cu(II) cations.

A sharp and strong band near 3100 cm<sup>-1</sup> has been assigned due to combined  $\nu$ (OH) and  $\nu$ (NH) frequencies. The  $\nu$ (OH) of the enol form (-C-OH) shifts from 3500-3100 cm<sup>-1</sup>

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.

Free primary amines show  $\nu(\text{NH})$  stretching vibrations between the range 3500-3300  $\text{cm}^{-1}$  which lowered due to hydrogen bonding. Thus the band at 3100  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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.

The ligand forms intra molecular hydrogen bonding and the -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  $\text{cm}^{-1}$  may be obtained due to strongly hydrogen bonded -OH vibrations.

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