

Chapter one

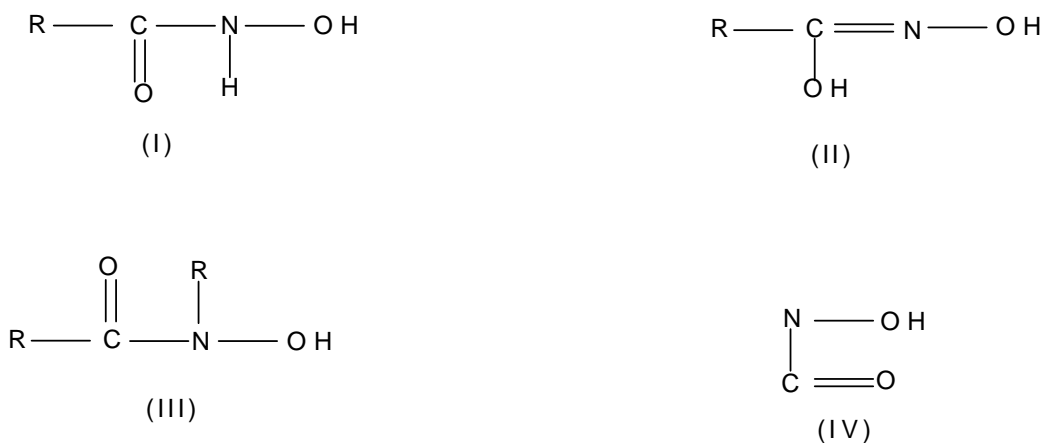
Introduction and literature review

1 Introduction

1.1 Hydroxamic Acids:

Hydroxamic acids have been known for over a century in 1868, H lossen, reported that the reaction between diethyl oxalate and hydroxyl amine yields an acidic compound which is named oxalo-hydroxamic acid later (Bauer & Exner 1947), H lossen, found that Benzoyl chloride and hydroxyl ammonium chloride gave a mixture of benzo-hydroxamic acid benzoyl benzo-hydroxamate and, di benzoyl benzo-hydroxamate (Wolf 1972).

The term hydroxamic acid stands for N-acyl derivatives of hydroxylamine and indicates most readily compound with hydroxyl amide structure (Yale 1943) fig (1.1) [1] even though, the term hydroxamic acid with acids is used commonly to denote all the mono-acyl derivatives of hydroxylamine, however tautomeric form with hydroxylimide structure (II) . Fig (1.1) exist which is termed hydroxamic acid .



Figure(1.1)

hydroxamic acids, were found to be an important chelating agent towards a large number of metal ions (Gasparini&Polodori 1976) since they possess the functional

group ($\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---N---} \\ | \\ \text{OH} \end{array}$), that fulfils the basic requirement of complex formation with metal ions replacement of the carbonyl oxygen, by Sulphur atom, the formation of a new class of hydroxamic acids was brought about (thiohydroxamic acids) (Mizukami &Nagate1968), which occurs in two tautomeric forms (V) and (VI) fig (1.2)

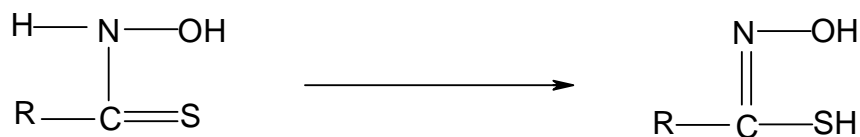


Figure (1.2)

1.1.1- structure of the hydroxamic acids

hydroxamic acids have been classified as primary(I), secondary(III) and cyclic (IV) fig(1.1) they can be represented in two tautomeric forms keto(I), enol(II)fig(1.1), or by substitution of hydrogen atom attached to the nitrogen atom in (I) by aryl or alkyl groups, N-substituted hydroxamic acid of the type(III) can be obtained structure (II) fig (1.1) is most properly termed hydroxamic acids, it constitute only a minor component of the tautomeric equilibrium mixture, although derivatives of it were known (Gasparini&Polodori 1976), this-trans isomerism in mono-alkyl hydroxamic acids have been studied spectroscopically, where, it was predicted that in the keto form Z and E-isomerism figure (1.3), can exist of rotation about C-N bond is restricted, H^1 and C^{13} .NMR studied on N-substituted hydroxamic

acid have shown that, the Z and E-isomeric ratio is solvent dependent, the Z-isomer predominate in polar solvent (Mageswaran&Fitzapatric 1989).

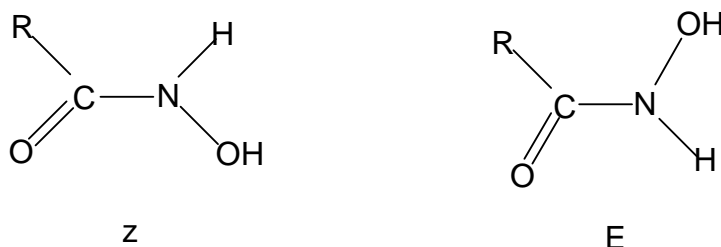


Figure (1.3)

The keto form, represents hydroxamic acids in the solid state as shown by X-ray analysis (Bauer&Exner 1974)spectral studies indicate that, the keto form is predominate in solution, UV studies on hydroxamic acid and mono –alkyl derivatives of the type (VII) and (VIII)figure (1.4) support the structure (1) keto form, and it is mono – basic acid which is predominates in acidic solution.

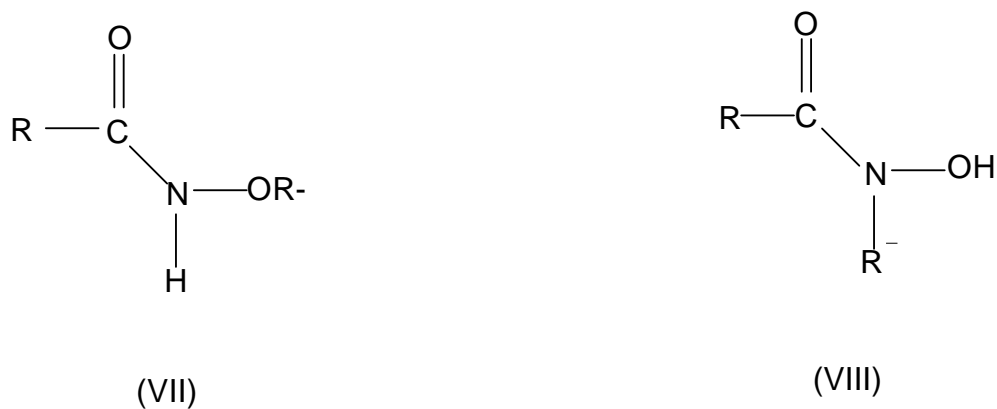


Figure (1.4)

Structure (II) fig (1.1) enol form is di –basic acid and predominate in basic solution (Heorey& Manning 1950). Most of hydroxamic acids exist in the keto form and will be hydrogen bonded (Plapinger 1959).

1.1.2-properties of hydroxamic acids:

Hydroxamic acids are white crystalline solids (Kadam&Shrivastva 1987), except iodo and nitro –substituted which are pink and light yellow respectively (Advendra&Rangon 1980), they are soluble in chloroform, hot benzene, diethyl ether, dioxane and alcohol, sparingly soluble in carbon tetra chloride, and cold benzene, they are insoluble in water, they are of low melting points and are weak acids their acidity is due to the presence of hydroxyl group (Agrawal 1980). But they are stronger acids than phenols the suppression of acidic character was attributed to intramolecular hydrogen bonding fig (1.5) as shown by infrared studies (Agrawal&Tandon 1972).

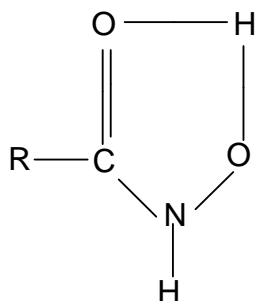


Figure (1.5)

Hydroxamic acids are capable to form inter and intra molecular hydrogen bonding in the solid state fig (1.6)

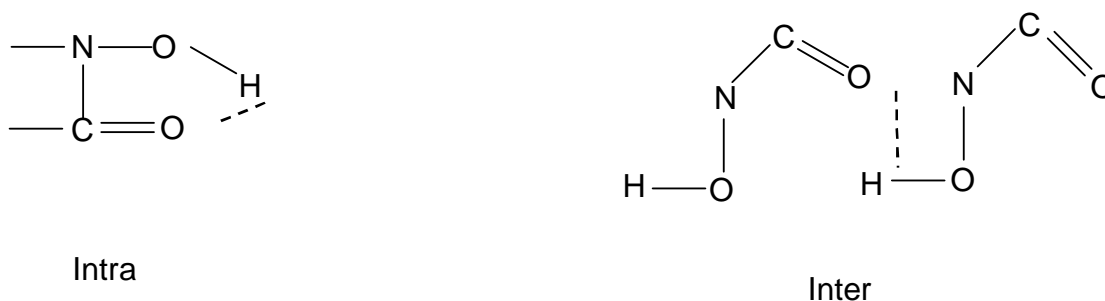


Figure (1.6)

Measurement of the ionization constant, of N-aryl-hydroxamic acid revealed that, the replacement of the hydrogen attached to the nitrogen by a phenyl group decreases the pK_a values in aqueous solution at different temperatures.



According to the measurement of pK_a values, thio-hydroxamic acids were found to be stronger acids than the corresponding oxygen compounds which in turn stronger acids than phenols. The infrared spectra of hydroxamic acids show the most characteristic bonds associated with the hydroxamic acids functional groups, those due to O-H, C=O, N-O, C-N stretching vibrations, which are generally assigned to the regions 3200, 1600, 910, 1385 cm^{-1} respectively. The position and intensity of the carbonyl and hydroxyl infrared absorption bands vary according to the type of the acid under investigation, and was affected by the type of hydrogen bonding the carbonyl absorption frequencies of cyclic hydroxamic acids are generally lower than those of the

corresponding lactams, the carbonyl absorption are shifted to a higher frequencies on alkylation, and to still higher frequencies on acylation.

1.1.3 Nomenclature:

The nomenclature based on the naming of carboxylic acids from which it was derived. In naming specific compound, the practice is to drop the (-ic) of the related acid and substituted by the latter (O) followed by hydroxamic, but this is not applicable in all cases, e.g. from caproic acid we should derive caprohydroxamic acid, from capric acid the hydroxamic acid would also be caprohydroxamic acid therefore in these and similar cases, we have to attempt to use the systematic name, hexanohydroxamic acids as the derivative of caproic acid, and decanohydroxamic acid as the derivative of capric acid. The cyclic hydroxamic acid usually derive their names from the hetero cyclic (Wolf 1972).

1.1.4 Characterization:

Hydroxamic acid have been characterized in terms of their elemental analysis, melting point, color test and spectral data which are obtained basically for their characterization, such as infra-red, U.V-Vis spectrum. In some cases proton nuclear magnetic resonance ($^1\text{H NMR}$), mass spectra and thin layer chromatography (Yadvendra, & Agrwal 1977) are also used for the characterization.

1.1.4.1 Colour test reactions:

Hydroxamic acids give characteristic colors with certain metal ions, they give violet colors with V(v) and red –violet colors with Fe(III) in acidic solution. Generally the Fe(III) complexes with hydroxamic acids are pH-dependent giving rise to different colors.

1.1.4.2 Infra red spectra:

Their infrared spectra revealed the presence of four characteristic groups O-H, C=O, N-O and C-N around 3200, 1600, 910, and 1385 cm^{-1} respectively (Palpinger 1959).

1.1.4.3-Volumetric analysis:

Monohydroxamic acid group can be titrated with alkali using phenolphthalein indicator gives dark violet color with ferric chloride.

1.1.5-preparation of hydroxamic acids:

hydroxamic acids are in general prepared by reaction of an activated acyl or aryl group with hydroxylamine in presence of an alkali as catalyst. Substrates that undergo this reaction are carboxylic acid, ester, acid chlorides, amides, lactams, acid anhydrides and imides. There are more than one method for their preparation.

- i. The reaction between an ester and hydroxylamine

This reaction takes place in absolute alcohol, and proceeds rapidly at room temperature, particularly in the presence of an equimolar quantity of sodium alkoxide (Angeli & Casteuana 1941). In the absence of an alkaline reagent, longer periods of time are required (Jones & Neuffer 1917).

- ii. The reaction between an acid anhydride or acid chloride and hydroxyl amine

Acetic anhydride and hydroxyl amine or its salt yield acetohydroxamic acid (Crismer 1892). Acid chlorides (halides) and hydroxyl amine, in presence of alkali, give, in addition to the mono-substituted hydroxamic acid, further acylated product (Heintz 1869). In some instances, this method is preferred

over other method, e.g. in the preparation of 2,4-dihydroxyl benzohydroxamic (Scott & Kears 1940).

iii. oxidation of aldoximes, amines, aldehydes ammonias, amides and nitriles

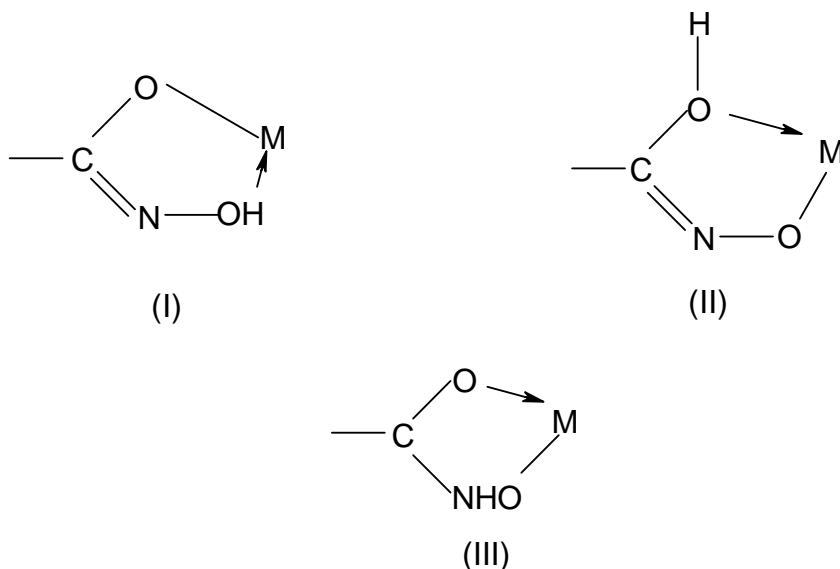
The reaction between Carro's reagent (persulphuric acid) and benzaldoxime give benzohydroxamic acid (Bamberger & Scheutz 1934). The oxidation of primary amines by persulphuric acid yields hydroxamic acid.

V-reaction between carboxylamine in presence of Raney nickel as a catalyst. Acetic acid and hydroxylamine form acetohydroxamic acid (Mumson & Connors 1972), through nickel catalysis. This catalysis occurs through a complex of nickel with acetate ion rendering the acetate more susceptible to nucleophile attack by hydroxylamine.

1.1.6 Hydroxamic acid metal complexes:

Hydroxamic acid have extraordinary complexing (Steinberg & Swidler 1965), ability towards a very great number of metal ion because they have bidentate group. The complex formation between a metal (M^{+n}) and hydroxamic acid usually take place with the replacement of hydroxylamine hydrogen by the metal ion and ring closure through the carbonyl-oxygen chelate (Agrawal 1980).

The structure of metal complexes may be represented in three different ways as shown below



Other possible structures are excluded, as they would lead to the formation of unstable four-membered rings involving the metal-nitrogen linkage.

Depending on the pH, hydroxamic acids react with metal ions with different stoichiometric ratios (Gipson, et al 1963).

Many transition metals, such as Co(II), Ni(II), Zn(II), Cu(II) and Fe(III) form stable complexes with hydroxamic acids (Mizukami & Nagata 1968).

Monohydroxamic acids form octahedral complexes with a number of metal ions coordinating via two oxygen atoms of the deprotonated hydroxamic acid group (NHO^-) (Davia & Glass 1979). The keto form of hydroxamic acids contains one easily replaceable proton (monobasic) while the enol form may dissociate two protons, behaving as a dibasic acid. The keto-enol tautomerism provides a number of sites which are available for metal ion coordination. The metal chelates of hydroxamic acids are non-ionic in nature (Ryan 1960) therefore, it is possible to extract these uncharged metal chelates with water-immiscible organic solvents. Salts of mono-hydroxamic acids have been prepared with nearly all the elements of group I, II and III of the periodic table (Brown, Mckeith & Glass 1979) together

with zirconium, thorium, cobalt, nickel and iron, the salts of iron, copper, cobalt and nickel are of special interest. Those compounds are colored and possess chelated structures. It is known that derivatives of the general formulas RCONHOR or RCOH-NOR don't give color reactions with ferric ions while compounds of the structures fig (1.7)

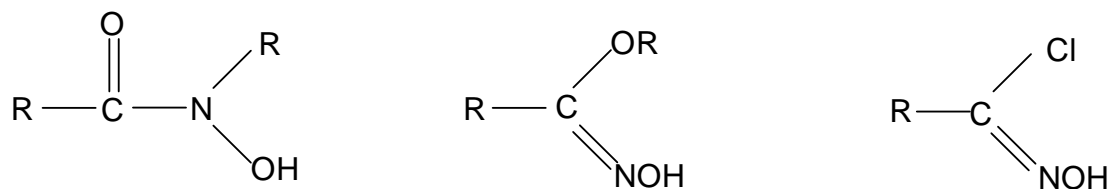


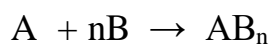
Figure (1.7)

It is apparent that, the presence of (=NOH) group is necessary for the formation of the coordination compounds.

The sodium and potassium salts of the di-hydroxamic acids found application on studying the lossen rearrangement.

N-phenyl butyrohydroxamic acid (Shukla&Tandon1972), form a divalent metal chelates with Cu(II) Ni(II) Zn(II) and Mn(II) in a metal to ligand value of 1:2. For determination of the formula of these complexes a method of continuous variation is used.

The formation (Warrenc, Volsburgh& Cooper 1941) of many complex ions can be represented by equation



Where A is a metallic ion, B may be either ion or molecule.

To determine n, solution of A and B of the same molar concentration are mixed in varying proportion and a suitable property of resulting solution is measured. The monochromatic light is a suitable property for this method the absorption of light is proportional to the concentration of the absorbing species which is one of the necessary conditions the absorbance of each solution is measured and is then plotted against the mole fraction of the ligand (A/A+B). Triangular-shaped curves are obtained. The ratio of the metal: ligand is determined from the curve where the maximum absorbance is obtained.

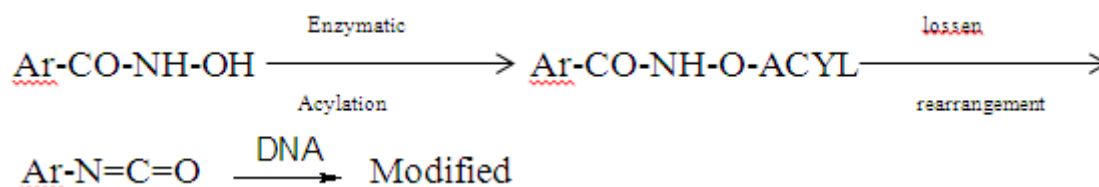
1.1.7-Photo chemical behavior of hydroxamic acids:

Till 1980, very few reports about the photo chemical liability and photo physical characteristics of hydroxamic acids were available. However, in 1982 an unusual fluorescence behavior for N-methyl anthranilohydroxamic acid were observed.

In 1988, the fluorescence of naphthalene carbohydroxamic and related amide were studied (Ewa 1991).

1.1.8-Mutagenic activity of some hydroxamic acids:

The possible mutagenic activity of hydroxamic acids has only recently been investigated in spite of their broad utility as drugs and pesticides. Enzymatic acylation of hydroxamic acid to O-ester followed by lossen rearrangements, would give isocyanates, which can serve as electrophiles for carba-moylation.



Results of the studies on the relation of chemical structure and mutagenicity of hydroxamic acids have suggested that lossen rearrangement is activation process of this class of mutagens and the presence of NH group which is required for the lossen rearrangement, is also essential for mutagenic activity (Ewa 1991).

1.1.9-Applications:

1.1.9.1-Biological application:

studies in hydroxamic acids chemistry has been stimulated by the isolation of naturally occurring compounds, found mainly in fungi, which are active as antibiotics, antitumor agents, fungitoxics, growth and cell division factors (Bianchi 1987). They also play an important role in iron uptake and metabolism (Das & Base 1984). Many synthetic hydroxamic acids also show fungicidal, anti-malaria and anti-bacterial activities and thus finds therapeutic applications (Ahmed & Sabbaro 1980). desferrioxamine is an iron –chelating drug for human use , while other compounds have been reported to inhibit stone formation in the urinary tract (Harry & Scheidt 1989). some hydroxamic acids inhibit DNA biosynthesis.

1.1.9.2 Nuclear technology:

Octanohydroxamic acid is used in the purification of uranium containing solutions, which is used in the manufacturing of nuclear grade uranium trialkylacetohydroxamic acids have been proposed as new extractant to exploited reprocessing of nuclear fuel, in the treatment of nuclear wastes, as in hydrometallurgical processes for recovery and purification of metals (Ahamed & Sabbaro 1980).

1.1.9.3 Microscopic analysis:

Oxlohydroxamic acid has been used for identification of alkaline earth elements by observing the crystals formed under the microscope. Barium gives rods, calcium pentagonal stars while strontium produces amorphous precipitate (Jasper 1990).

1.1.9.4 Detergent:

Carbohydroxamic acids used as detergent for cleaning exterior walls of building and removal of tea stain from cotton fabric (Contor 1990).

1.1.9.5 Volumetric analysis:

Salicylhydroxamic acid has been used as indicator in the chelometric titration of iron (III) at pH 3, whereas benzohydroxamic acid has been used as indicator in the titration of EDTA with iron (III) and with ascorbic acid for determining vanadium (Bianchi 1989).

1.1.9.6 Quantitative organic analysis:

Feigl utilized the color reaction given by iron(III) with hydroxamic acids for detection of carboxylic acids or anhydrides. The reaction also served for estimation of esters (Vernon&Shorassani 1978).

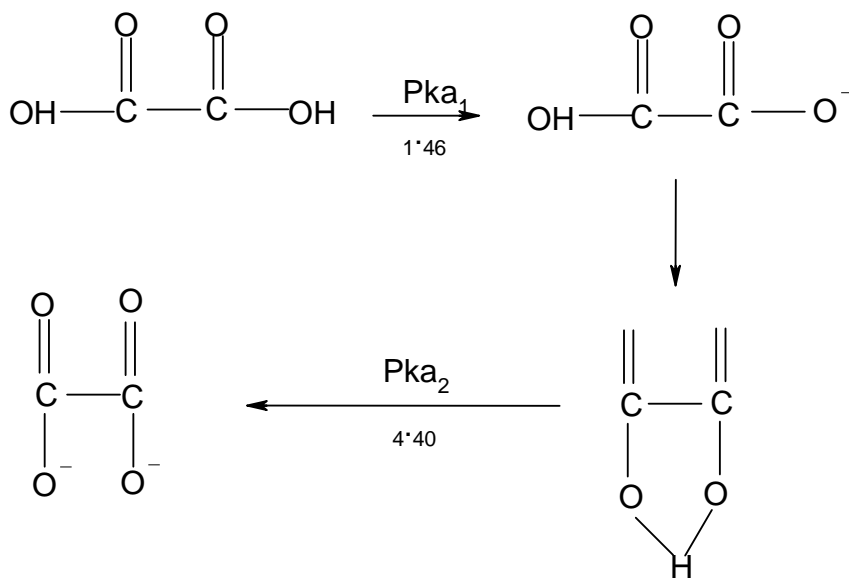
Carboxylic acids, their chlorides, anhydrides, esters. Lactones, amides, lactams and imides react with hydroxyl amine to give hydroxamic acid which yields red violet complexes with iron (III) in acidic medium (Thomas&Neilands 1960).

1.1.10 parent acids:

The carboxyl group (CO(OH)) is characteristic functional group of the organic acid .

❖ Di caroxalic acid:

The first P^{K_a} for this acid is significantly lower than atypical monocarboxalic acid, indicating that these compound form mono-anion more readily. The enhanced ease of ionization of one carboxyl group in these two diacids results from the ability of the other adjacent acid group to stabilize the negative charge of the conjugate base by hydrogen bonding.



Also the second P^{k_a} of these acid is significantly higher than typical monocarboxalic acid. This is because that second acid proton is held more tightly by the mono ionized complex via intramolecular hydrogen bonding.

1.2 The chemistry of coordination compounds

An interpretation for the reactions of co-ordination compounds, was firstly brought by Alfred Werner (Miessler & Tarr 1991). The beginning of co-ordination chemistry is marked by the discovery of cobalt (III) hexaammines $[\text{Co}(\text{NH}_3)_6]^{3+}$. A co-ordination compound is formed when an electron rich center ligand is attached to an electron deficient center (metal atom or ion) via donation of lone pair of electrons (Cotton & Wilkison 1980). So co-ordination compounds can be defined as molecules or ions for which the central ion is closely attached to other atom or groups of atoms/ions known as ligands.

A co-ordination compound would therefore contain a number of atoms or groups in the so called first co-sphere, that is directly attached to the central atom. Also the complex may contain additional atoms, that are less finally bonded in the so called second co-sphere (Gerloch & Constable 1994). Co-ordination compounds (transition metal complexes) may occur (Morrison & Henry 1967) in several types:

- i. Simple co-ordination complexes, in which the metal ions combine with mono-functional ligands in a number equal to the co-ordination numbers e.g. $[\text{Fe}(\text{CN})_6]^{-4}$
- ii. Complexes which are derived from the interaction of metal ions with poly dentate ligands, that can occupy more than one position in the co-sphere of the metal, those complexes are called chelates e.g. EDTA.
- iii. Complexes, distinguished by the presence of a central complex ion rather than a central mono-atomic ion, of which, heteropoly acids we examples (molybdophosphoric acid), which formulated as follows $\text{H}_m\text{P}_x\text{Mo}_y\text{O}_z$. Many of these complexes are extractable in organic solvents, forming a large group of Oxygen containing acids (Morrison

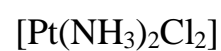
&Henry 1967). A complex compounds may be either cationic, anionic or neutral metal complexes fig(1.8)



Cationic complex



Anionic complex



Neutral complex

1.2.1 complex formation:

A complexation reaction with a metal ion, involves the replacement of one or more of coordinated solvent molecules by other nucleophilic groups, which are called ligands (Gerloch & Constable 1994). In aqueous solution a complexation reaction may be represented by the following equation



The ligand (L) can either be a neutral molecule or charged ion, and successive replacement of water molecule by the ligand (L) leads to the formation of the complexes ML_n , where n maximum number of ligands that can be attached to the central metal atom, and it has been assumed that, the complex species ML_n does not contain more than one metal ion, but under appropriate conditions binuclear or even polynuclear complex can be formed (Vogel 1957).

1.2.2 Complexing agents:

The application of Lewis electronic theory of acids and bases to the conditions of co-ordination compounds is very useful (Morrison & Henry 1967). According to Lewis acid-base reaction involves the co-ordinate covalent bond formation of complexes by a metal ion may be interpreted in terms of its tendency to fill up unoccupied orbitals and thereby achieve the stable electronic configuration of an inert gas.

The basic entities, which are characterized by possessing at least one unshared pair of electrons, are usually either neutral, as in the case of water or ammonia or negatively charged, as with cyanide or halide ions (Cotton & Wilkins 1980) .

The nature of the bonds between the acidic metal cation and the basic coordinated group, ranges from almost completely covalent as in $(\text{Fe}(\text{CN})_6)^{-4}$, to the other extreme of essentially electrostatic as in $[\text{Ca}(\text{H}_2\text{O})_6]^{+2}$, with a large number of complexes having bonds of intermediate character. The transition between electrostatic and covalent bonding may be considered in terms of the polarizabilities of the ions or groups involved. When a metal cation and a ligand approach each other, the attraction of the electron atmosphere of the latter by the metal cation induces deformation or polarization in the ligand. The cation is also polarized but to a lesser extent due to its small size polarization results in an increase in the extent of sharing of electrons, or covalent character. Ion deformation is favored by highly charged metal cation, by large ligands, and by metal ions with non-inert gas electronic configuration (Morrison & Henry 1967).

1.2.3 The ability of ligands to form complexes:

Ligand may be classified generally into two main classes:

- i. classical or simple donor ligands which act as electron pair donors to acceptor ions or molecules, and form complexes with all types of Lewis acids, metal ions or molecules e.g. H_2O , NH_3 , Cl^- , etc.
- ii. non classical ligands, π -bonding or π -acid ligands, form compounds largely if not entirely with transition metal atoms. This interaction occurs, because of the special properties of both metal and ligand the metal has d-orbitals

that can be used in bond formation, the ligand has not only donor capacity, but also has acceptor orbitals, this concept can be illustrated by comparison of an amine (:NR_3) with phosphine (:PR_3), other modes of classification include, electronic classification which depends on the number of electrons that the ligand participate on bond formation, structural classification (Cotton & Wilkison 1980), that is by the number of connections they make to the central metal atom, and classification based on the nature of the donor atoms of the ligand (Kettle 1969). The nature of the donor atom determines the properties of the complex compounds according to the coordinating atom of the ligand, the complex formation decreases in the order $\text{C} > \text{N} > \text{O} > \text{F}$, thus NH_3 coordinated before H_2O and CN^- before OH^- . Multi-dentate ligands are strongest complexing agent which forms five membered chelate rings (Cotton & Wilkison 1980).

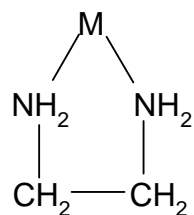


Figure (1-9)

1.2.4 The ability of metals to form complexes:

There are many factors which determine the complexing power of metals, among which the charge, the electrostatic force (Morrison, & Henry 1967), and deformability of central metal ion, polarizability of the ligand, and the dipole moment of ligand when it is a molecule. Cations are classified according to their complexation ability into the following groups (Ringbom 1963):

- i. cation with a noble gas configuration which include the alkali metals, alkaline earth metals and aluminum, which form stable complexes due to the strong electrostatic forces between small ions of high charge, the fluorine and oxygen are strongly bond than other donor atoms, water stronger than ammonia, which has smaller dipole moment, univalent, large ions(K,Rb,Cs) exist as hydrated ions in solution. Which do not form complexes, small univalent (Li, Na) form a few weak complexes with some chelating agents such as EDTA the ability of complex formation is stronger in alkaline earth metal, but decreased with increase in ionic size from(Be,Ba) the strength of the coordination bond increase greatly with the charge of the cation, many ions of high valence stable show complexing tendency similar to the cation of this class, although they do not have a noble gas configuration.
- ii. cation with completely filled d-orbitals which include Cu(I), Ag(I) and Au(I) ions which are highly deformable and the bond in their complexes are covalent.

The charge and size of the metal ion are not important, unlike the cation of the first class, but the electronegativity of metal ions and the donor atom were important.

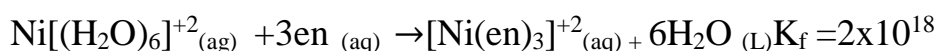
- iii. transition metal ions with incomplete sub-shells, the charge size and ionization potential, determine their ability to form complexes. The most studied is the series of the di-valent metals Mn(II), Fe(II), Co (II), Ni(II),Cu(II) And Zn(II). In which the ionic radius decreases and ionization potential increases in the same orders(Irving&Williams1948).

The complexation tendency of the metal of these series is particularly pronounced when nitrogen, carbon and sulphur are the coordinating atoms, but

less pronounced when oxygen is the coordinating atom . Covalent bonds are favored by the small ionic charge and large ionic radius, low valence states are stable in cyanide solution, whereas high valence states are stable in strong alkaline solution.

1.2.5 Chelating agents

Chelating agents are molecules having more than one donor atom which are attached directly to the central metal atom .These complexes formed chelates, whereas mono-dentate ligand form non-chelate complexes. The process by which chelate compounds are formed was forming chelation(Myers1978). Chelating compound have cyclic structure which rise from the link between the metal atom or ion with the multi- dentate ligand , which is characterized by high stability in comparison with those complexes formed by uni-dentate ligands containing the same functional groups. The additional stability is due to chelation that depend on geometric factor, rather than electronic factor(Kettle1969), consider the following reaction:



en = ethylene diamine

The difference in the formation constant is due to the chelation(Myers1978), the increase stability brought by chelation is due to increase in dentate character, which can be explained in terms of entropy effect thermodynamically, it was found that the chelating effect, in complexes formation, was due to the more favorable entropy change for the reaction involving poly-dentate ligands. The number of free moving species in the system was increased due to the replacement of water molecules with (en).

Which led to an increase in the entropy of the system (Cotton & Wilkison, 1980).

1.2.6 stability of complexes:

The stability of complexes with ionic or multidentate ligand is expected to increase as the ionic potential of the metal ion increases. For transition metal ions, with incomplete d-orbitals, the stability also depends on the number of d-electrons, i.e., on the crystal field stabilization energy, electron pairing energy, stereochemical configuration and on the metal to ligand and ligand to metal π -bonding (Majumdar 1972). Different methods for evaluation of overall stability constants for hydroxamic acids, complexes show that stability of bivalent metal chelates increase regularly from manganese to copper and there is a systematic decrease in stability from copper irrespective of the nature of the ligand used.

The metal ions are classified (Pearson 1968) as class (a) and class (b) ions according to whether they form, respectively their more stable complexes with the ligand atoms of the first periodic row, i.e. N, O and F, or with those of the second or subsequent rows. The class (a) or hard acid character of the acceptor atom is associated with small size, high positive charge and absence of valence electrons which are easily distorted, while the class (b) or soft acid character is manifested by the acceptor atom of low or zero charge, of large size or having several valence electrons which are easily distorted. The stability of the class (b) metal ion complexes decrease in the order of increasing electronegativity of the ligand atoms as $C \approx S > I > Br > Cl \approx N > O > F$.

A strongly reversed trend, although not complete, is observed with class (a) metal complexes. The simple electrostatic approach explains the stability of

many of the complexes of the metal ions, particularly of class (a) type. For class(b) metal ions, besides electrostatic contribution, other factors such as π – bonding, crystal field effect and increased covalent character to in metal ligand also play significant parts. According to π –bonding theory, in addition to σ – bonding class(a) metal ions have the potential to form ligand to metal π –bonds with the more basic metal to ligand atoms, whereas class (b) metal ions are likely to form ligand π –bonds by the overlap of the field d-orbitals with the vacant p or d orbitals of the ligand, in the latter instance the metal to ligand π – bonding increase the d-orbital splitting as the metal ion acquires a higher effective charge. This property of the ligand increase the crystal field stabilization energy compared to the ligands which have no such π –bonding tendency.

The stability of metal complexes, as well as depending on the type of metal ion and the donor atom, resets much on the base strength and the number of coordination sites of the ligand, the chelate ring size and steric and the resonance effects. Complexes with five –and six membered chelate rings are most stable .chelate complexes with four-membered rings are rare while chelate rings with more than six-membered or generally less stable. Of the former two, aliphatic chelate complexes with five-membered rings appear to be owing to favorable entropy changes (Cotton&Harris 1955).The six-membered chelate rings with conjugated double bonds or aromatic ligands are sometime more stable compared to five –membered rings, perhaps because of the release in strain by wider bond angles and resonance.

The stability decreases with the decrease in the double bond order of the chelate ring (Calvin&Wilson 1945).

1.2.7 Nomenclature of complex compound:

In a given complex compound, if the complex is salt, the cation appears first and the rest of the complex constitutes are named in the following order anions, neutral ligands .central metal ion, example $K_4[Fe(CN)_6]$ potassium hexacyano ferrate(II) .

The anionic ligands are given –O endings e.g. OH^- , hydroxo, O^{2-} , oxo, S^{2-} , thioetc while the names of the neutral ligands are not changed exceptions to this rule are H_2O , NH_3 , CO , NO ,The number of ligands of particular type is indicated by a prefix di-,tri-, tetra-, penta-, hexa-, for simple ligands for complicated ligands like EDTA the prefixes bis-,tris-,and tetrakis (two, three,four) are employed the oxidation number central metal ion is indicated by a roman number in parentheses at the end of the name of the complex. Anionic complexes have the ending –ate, if the complex is cationic or neutral complex the name is not changed e.g. cationic complex $[Ag(NH_3)_2]Cl$, diamine silver(1)chloride,neutral complex $[Ni(CO)_4]$;tetra carbonyl nickel(0).

1.3-Transition metal used in this research

1.3.1-Iron:

Electron configuration $[Ar]3d^6 4s^2$

1.3.1.1-occurrence:

Iron is chemical element with the symbol Fe, and atomic number 26. it's in the first transition series. It is most common element (by mass) forming the planet earth as a whole, forming much of earths outer and inner core.

1.3.1.2-properties:

Iron is the most widely used of all the metals, accounting for 95% of worldwide metal production. Its low cost and high strength make it, its indispensable in engineering applications and commonly used in the form of steel.

1.3.1.3-Iron compounds:

Iron forms compounds mainly in the +2 and +3 oxidation state. Traditionally, iron (II) compounds are called ferrous, and iron (III) compounds ferric-iron also occurs in higher oxidation states, an example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Numerous organometallic compounds contain formal oxidation states of +1, 0, -1, or even -2.

The iron compounds produced on the largest scale in industry are iron (II) sulfate and iron (III) chloride. Iron (II) compounds tend to be oxidized to iron (III) compounds in the air. Iron reacts with fluorine, chlorine and bromine to give corresponding ferric halides.

1.3.2 Copper:

Electron configuration: $[Ar]3d^{10} 4s^1$

1.3.2.1 Occurrence

Copper is a chemical element with the symbol Cu and atomic number 29. It is present in the earth's crust at a concentration of about 50 (ppm), and also synthesized in massive stars.

1.3.2.2 Properties

Copper is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; freshly exposed surface has a reddish – orange color. It is used as a conductor of heat and electricity, and constituent of various metal alloys.

1.3.2.3 Copper compound

Copper forms a rich variety of compounds with oxidation states +1 and +2, which are often called cuprous and cupric, respectively (Holleman & Wiberg 2001). It does not react with water, but it slowly reacts with atmospheric oxygen forming a layer of brown – black copper oxide. Copper like all metals forms coordination complexes with ligands. Many other oxyanions form complexes; these include copper (II) acetate, copper (II) nitrate, copper (II) carbonate. Copper (II) sulfate forms a blue crystalline pentahydrate.

Copper (III) is the most characteristically found in oxides. Complexes of copper (III) are also observed as intermediates in reactions of organo – copper compounds.

1.4 Objectives of the study:

- Oxalohydroxamic and benzohydroxamic acids are prepared and recrystallized .
- The synthesized acids were used as chelating agents towards two metal ions Fe(III) and Cu(II).
- Characterizing of the free ligands and complexes by their use IR techniques.

2.1-Equipments and chemicals

2.1.1-Equipments:

- Beakers.
- Conical flasks.
- Burette.
- Hot plate, stirrer.
- Condenser.
- Round bottom flasks.
- Filter papers.
- Melting point apparatus.
- IR spectrophotometer, FTIR- 8400S, shimadzu.

2.1.2-Chemicals:

- Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$)(LD Reagent)
- Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) (CDH Reagent)
- Sulphuric acid(H_2SO_4)(BDH Analar Grade)
- Methanol(MeOH 99%) (BDH Analar Grade)
- Ethanol(EtOH 99%) (BDH Analar Grade)
- Hydroxylamine hydrochloride($\text{NH}_2\text{OH} \cdot \text{HCl}$) (BDH Reagent)
- Sodium hydroxide(NaOH) (Analar Grade)
- Acetic acid(AcOH)(CDH Reagent)
- Ferric chloride hexa hydrate($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (AC Reagent)
- Copper sulfate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)(AC Reagent)
- Distilled water.

2.2-Preparation of hydroxamic acids

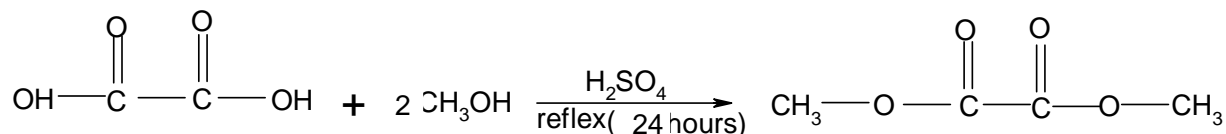
Procedure

2.2.1-Preparation of oxalohydroxamic acid:

The reaction of ester and hydroxylamine hydrochloride was adopted for the preparation of oxalohydroxamic acid (OHA)

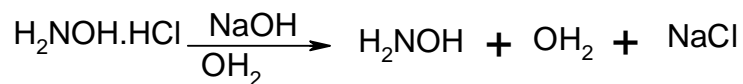
i. Preparation of dimethyl oxalate

(56.9g) 0.2 mole oxalic acid was refluxed with excess methanol (63cm³) and (2.2cm³) 0.04 mole concentrated sulphuric acid for 24 hours. The ester was filtered and dried.



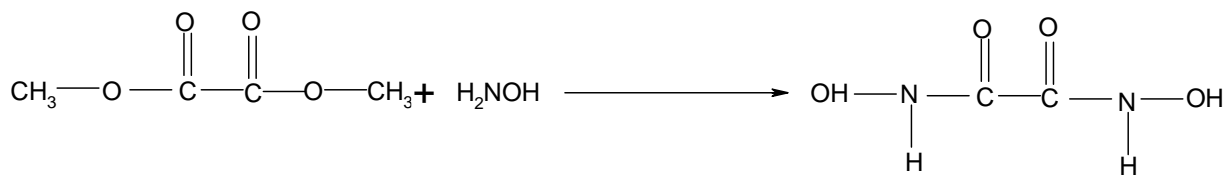
ii. Preparation of free hydroxylamine

(13.9g) 0.2 mole hydroxylamine hydrochloride was added to 10% sodium hydroxide



iii. Preparation of hydroxamic acid

Product (I) added to product (II). The mixture was stirred for 2 minute. Then the product was filtered off and dried and recrystallized by acetic acid.

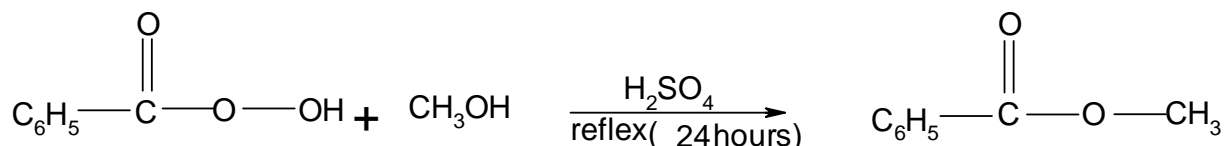


2.2.2 Preparation of benzohydroxamic acid:

The reaction of ester and hydroxylamine hydrochloride was adopted for the preparation of benzohydroxamic acid (BHA)

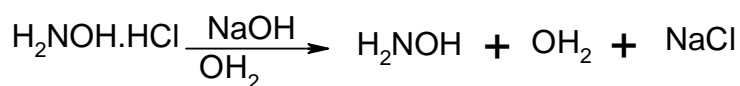
i. preparation of methyl benzoate

(56.9g) 0.2 mole benzoic acid was refluxed with excess methanol (63cm³) and (2.2cm³) 0.04 mole concentrated sulphuric acid for 24 hours. The ester was separated by diethyl ether.



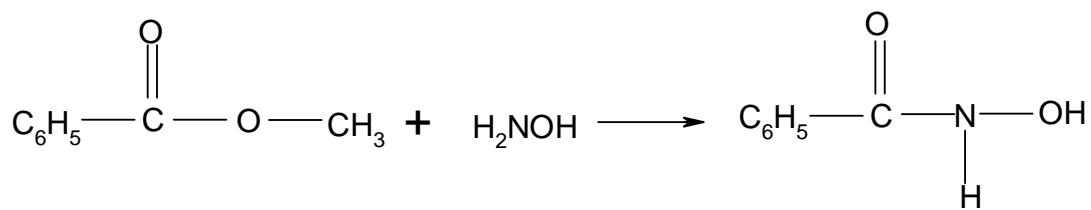
ii. Preparation of free hydroxylamine

(13.9g) 0.2 mole hydroxylamine hydrochloride was added to 10% sodium hydroxide.



iii. Preparation of hydroxamic acid

Product (I) added to product(II). The mixture was left for three days. Then the benzohydroxamic acid was filtered and dried, and recrystallized by acetic acid.



2.2.3 Identification

2.2.3.1 Melting points

In capillary tube small μg of the hydroxamic acids were introduced, into the melting point apparatus, then the degree of melting point average was adjusted, and finally the exact melting range of the oxalohydroxamic acid and benzohydroxamic acid were obtained in $123-125^\circ\text{C}$, $124-126^\circ\text{C}$ respectively .

2.2.3.2 IR data: (KBr disc), Appendix (2A): shown table (3.1)

2.2.4- Determination of molecular weight by titration method:

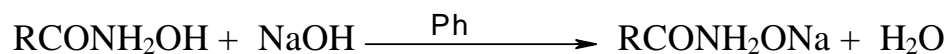
0.062g of each hydroxamic acid was dissolved in 100cm^3 ethanol, 50cm^3 of each acid was titrated against (0.1M) sodium hydroxide solution using phenolphthalein as indicator the volume of sodium hydroxide needed was 10.5 and 4.5 cm^3 , for oxalo, benzo acids respectively, from the following relation:

$$\text{MV}/1000 = \text{No of mole}$$

And No of moles of oxalohydroxamic acid = No of moles of NaOH/2

No of moles of benzohydroxamic acid = No of moles of NaOH.

As shown by the equation



The molecular weight was calculated and the results were shown in table (3.2)

2.3 Preparation of hydroxamic acid metal complexes:

Procedure

2.3.1 Fe (III) complexes:

FeCl₃.6H₂O (0.001mole) dissolved in warm water, were added to ethanolic solution of each hydroxamic acids (0.003mole), the pH of the colored solution was raised by dropwise addition of 10% sodium hydrogen carbonate solution, the red product was filtered, dried and recrystallized from methanol . The yield of the prepared Fe(III) hydroxamate was found to be 65.5, 67.9 %.

i. Identification

IR data: (KBr disc), Appendix (3A, 4A): shown in table (3.3)

2.3.2 Cu(II) complexes:

CuSO₄.5H₂O (0.001mole) dissolved in warm water, were added to ethanolic solution of each hydroxamic acids (0.003mole), the pH of the colored solution was raised by dropwise addition of 10% sodium hydrogen carbonate solution, the green product was filtered , dried and recrystallized from methanol . The yield of the prepared Cu(II) hydroxamate was found to be 80.5, 85.9%.

i. Identification

IR data: (KBr disc), Appendix (5A, 6A): shown in table (3.4)

Results and Discussion

3.1 Results

3.1.1 IR Data

Table (3.1) the infrared absorption frequencies of hydroxamic acids

Hydroxamic acids	OH	NH	C=O	C-N	N-O
Oxalo-	2748.37	3251.76	1683.74	842.83	1026.06
Benzo-	2752.23	3298.05	1614.31	898.77	1396.37

Table (3.2) the infrared absorption frequencies of Fe(III) complexes

Fe(III) complexes	O-H	N-H	C=O	C-N	N-O
Oxalo-	2804.81	3258.69	1648.37	878.69	1022.80
Benzo-	2900.74	3195.83	1596.95	914.20	1352.01

Table (3.3) the infrared absorption frequencies of Cu(II) complexes

Cu(II) complexes	O-H	N-H	C=O	C-N	N-O
Oxalo-	2804.31	3253.69	1645.17	873.69	1022.20
Benzo-	2812.02	3186.18	1604.66	923.84	1352.01

3.1.2Molecular weight by titration method

M_{wt} of benzoic acid

No of mole NaOH= $MV/1000$

$$0.1*4.5/1000 =0.00045\text{mole}$$

No of mole of NaOH = No of mole of benzoic acid

$M_{wt} =W_t / \text{No of mole}$

$$M_{wt}= 0.062/0.00045 = 137.8$$

Table (3.4) molecular weight

Titration method

Hydroxamicacids	C_1	C_2
Oxalo-	120	119.23
Benzo-	137.1	137.8

C_1 = Theoretical

C_2 = Practical

3.2 Discussion

3.2.1 general approach:

Hydroxamic acids are those compounds possessing the functional group (-C-N-OH) which fulfil the basic requirements for complex formation since it has an easily replaceable hydroxyl hydrogen, and hence they found a large application in the fields of analytical chemistry as well as medicinal and pharmaceutical applications.

3.2.2 Preparation of hydroxamic acids:

Carboxylic acids are the starting materials for the preparation of hydroxamic acids either through ester or acid or acid chloride route. It is well known that aromatic hydroxamic acids are more stable than aliphatic ones.

Oxalohydroxamic acid (OHA) and benzohydroxamic acid (BHA) have been prepared from the reaction of the methyl ester derivatives of oxalic, benzoic acids respectively with free hydroxylamine, and recrystallized by acetic acid . These acids are found to be solid at room temperature, they were identified by their melting points, which were found to be consistent with those obtained from the literature (124, 125°C) respectively, and the IR spectra shows the most characteristic band associated with the hydroxamic acids functional groups , the fundamental frequencies (cm^{-1}) of the various groups are summarized in the table(3.1).The carbonyl bands was shifted slightly, and the appearance of the hydroxyl (OH) bands at the region (2750cm^{-1}) are indicative of the occurrence of intra- and intermolecular hydrogen bonding fig (1.6).

The molecular weights were determined by titration with sodium hydroxide and the results were found in agreement with the theoretical values. The results were shown in table (3.4).

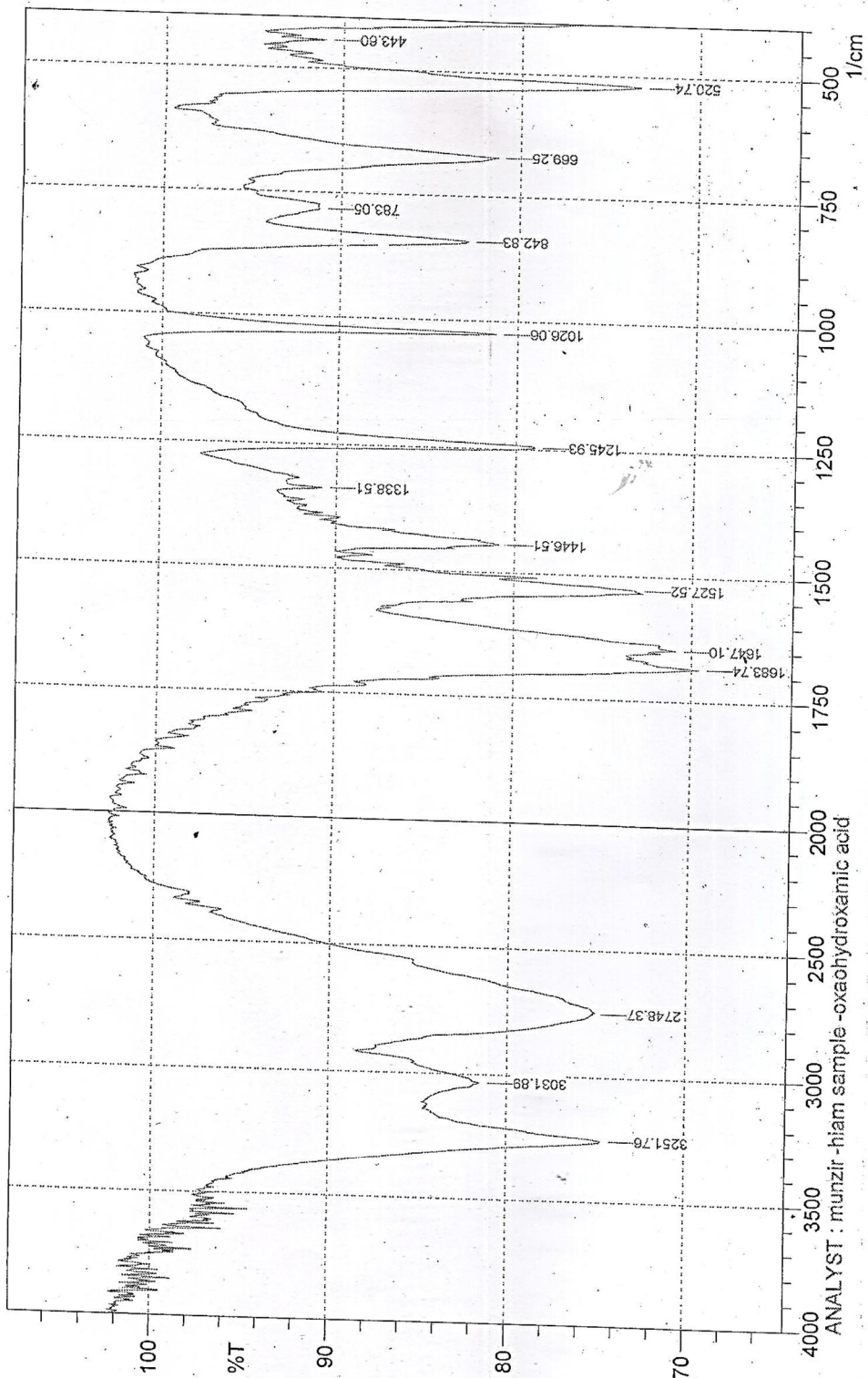
3.2.3- Metal complexes:

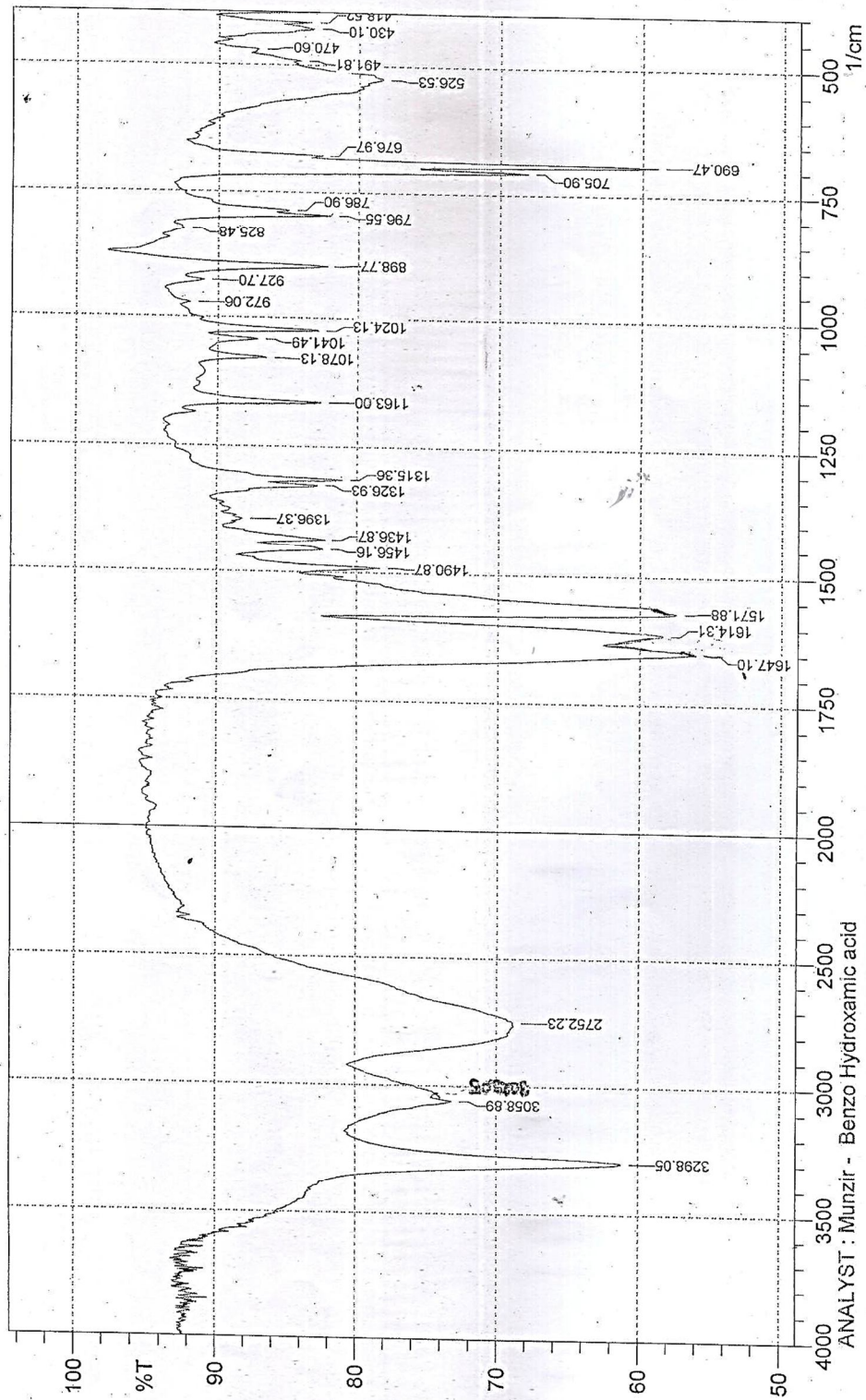
Complexes of two metal ions Cu (II) and Fe (III) were prepared by the reaction of the metal ion salts with an ethanolic solution of two different hydroxamic acid as ligands. The complexes produced were colored compounds, the color of the Fe(III) complexes was blood-red, red and that of the Cu(II) complexes was bluish-green, green with the BHA and OHA respectively.

These complexes, were characterized spectroscopically by their IR spectra, which revealed that, the carbonyl band of the free ligand was shifted slightly due to chelation, and the disappearance of the band at the region 3200 cm^{-1} , which indicates that the metal-ligand bond was formed by the release of the hydroxyl hydrogen of the free ligand. The fundamental frequencies (cm^{-1}) of the various groups are summarized in table (3.2), (3.3).

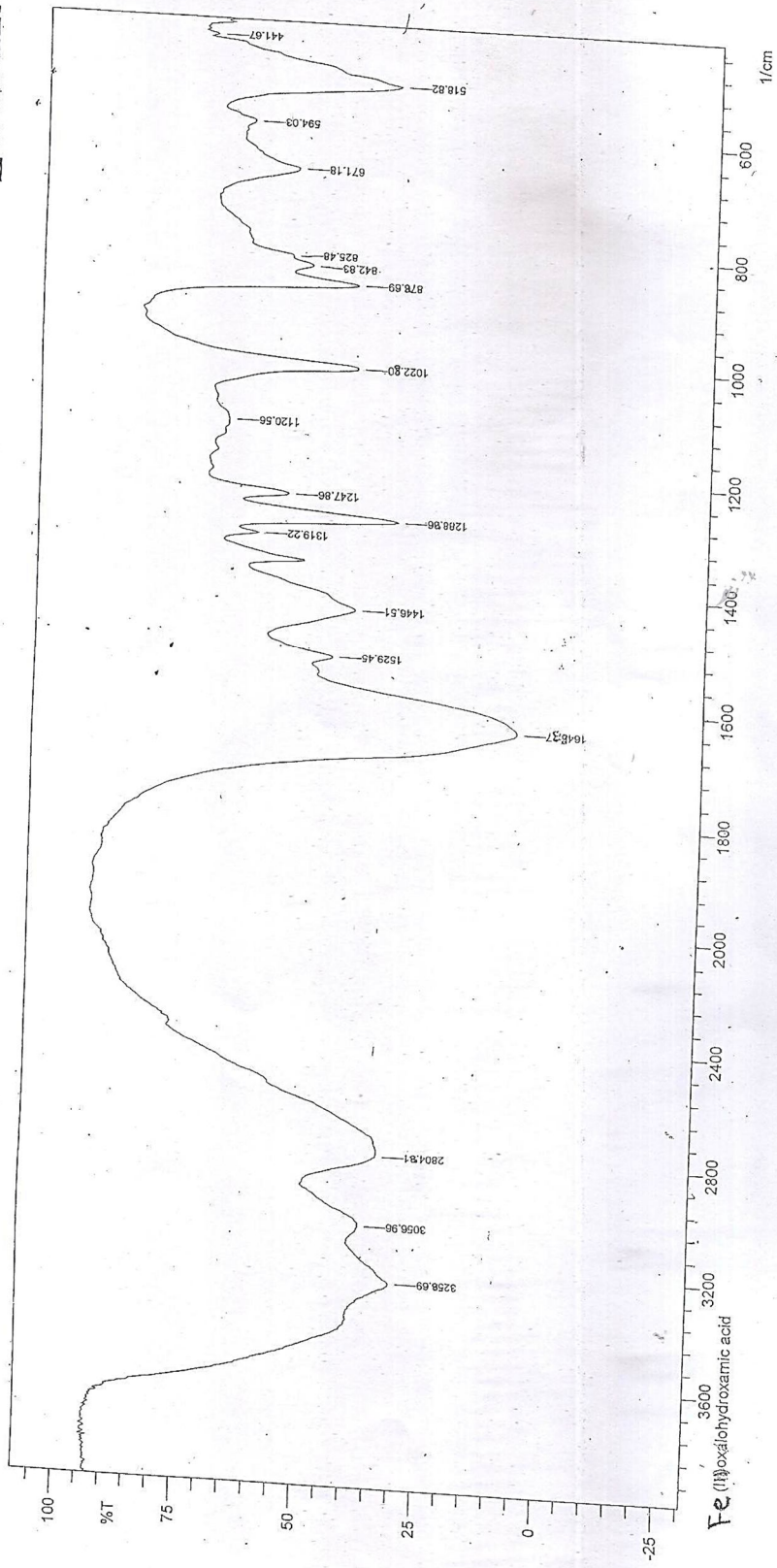
3.3 Conclusion:

- The two hydroxamic acids prepared in this work has been found to give very intensive color, as well as high percentage recovery for the other metals ions, so it can be used as an indication analytical reagents for these metals.
- Fe (III) and Cu (II) in acidic medium form red and green chelates complexes with hydroxamic acids prepared.
- The IR spectrum show the most characteristic bands associated with hydroxamic acids functional group that is due to OH, C=O, N-O and C-N.





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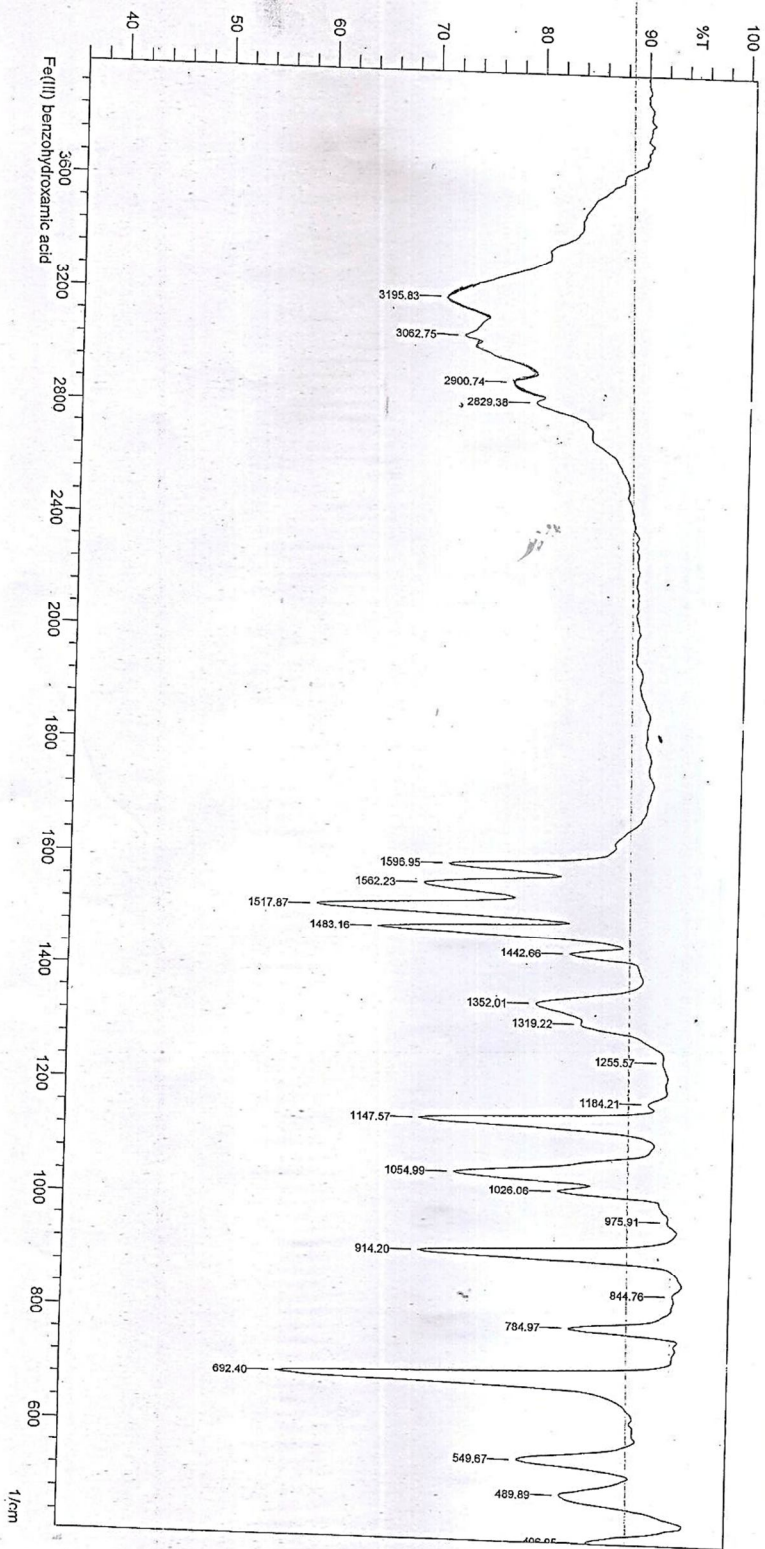
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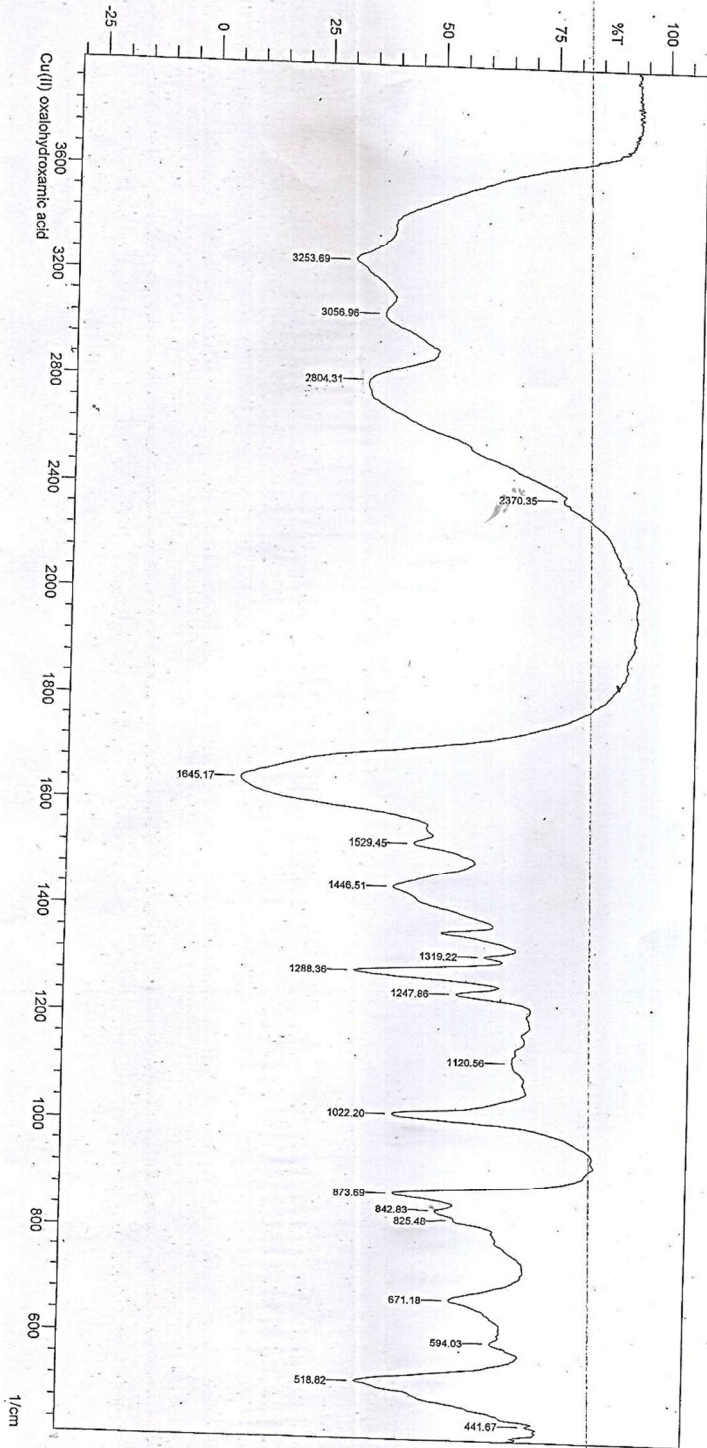


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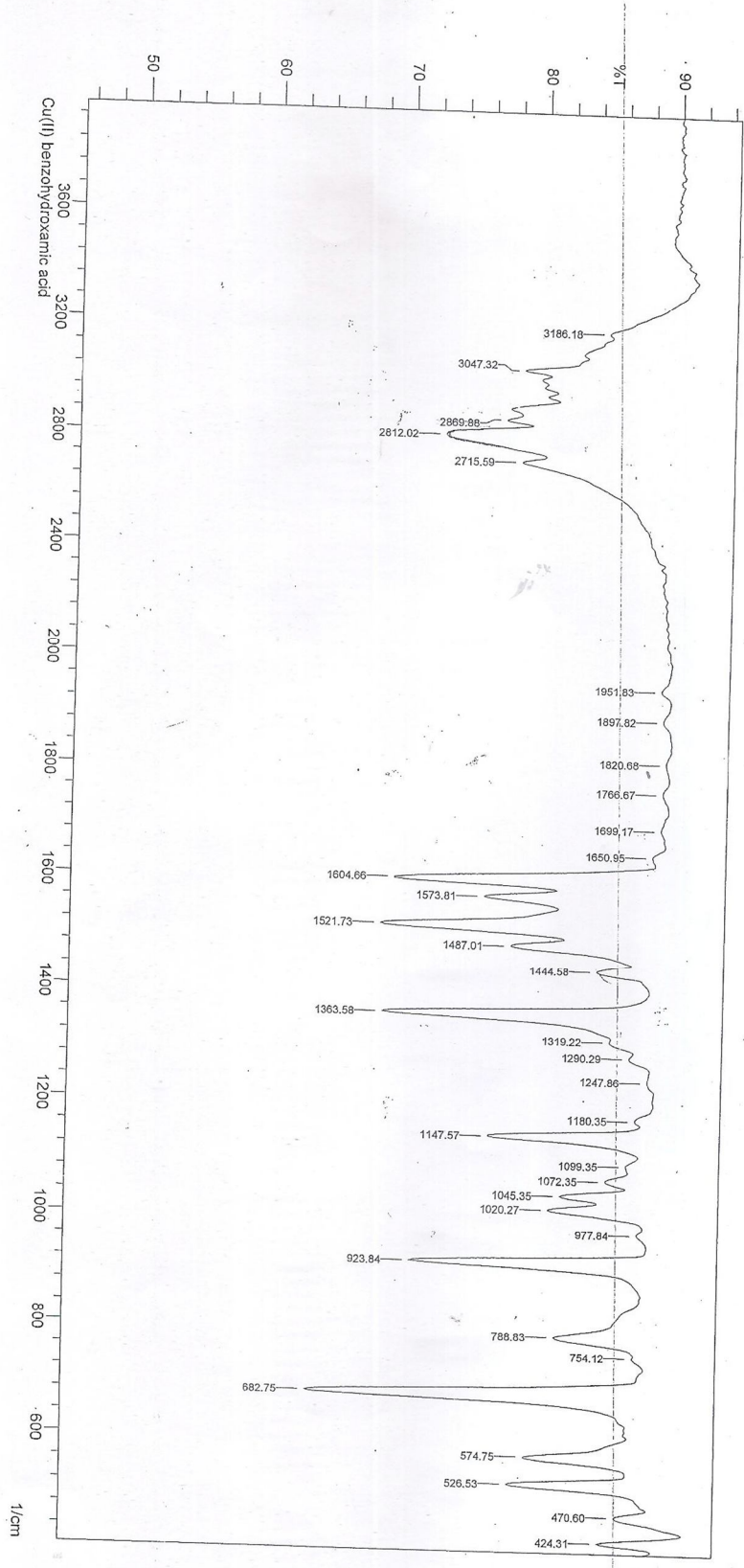
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Cu(II) oxalohydroxamic acid

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Comment:
Cu(II) benzohydroxamic acid

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