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Study of the stoichiometry of iron and vanadium nitrobenzohydroxamate complexes

Ehsan AA[1], Elmugdad AA[2], Dalia MO[3]
[1] Department of Chemistry, College Education, Wadi Alnile University, Atbara, Sudan
[2] Department of chemistry, College of Science, SUST, Khartoum, Sudan
[3] Department of Chemistry, College of Science. University of Hafr Al-batin, Hafr Al-batin, Saudi Arabia

Abstract

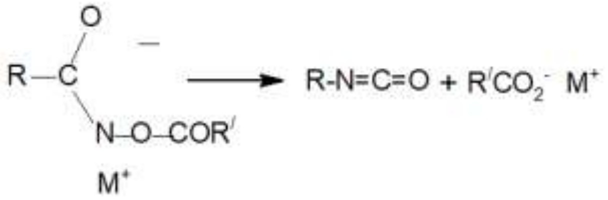
Nitrobenzohydroxamic acid was synthesized by coupling methyl nitrobenzoate with free hydroxylamine hydrochloride. The compound was recrystallized in water/acetic acid mixture and identified by m.p(211-213C^0), iron and vanadium color test and infrared spectra [showing absorption bands 3112 cm^{-1} (-- OH), 1691 cm^{-1} for(C=O) and 933 cm^{-1} for (N-O). Iron, and vanadium nitrobenzohydroxamate complexes were prepared by reacting nitrobenzohydroxamic acid with the corresponding metal salt in aqueous media at pH=3and pH=5 for Fe^{3+}, $V5^+$ complexes respectively. They show absorbance at a wavelength of maximum (λ_{max}) 420nm, 520 nm for Fe^{3+} (red), V^{5+} (dark blue) complexes respectively indicating that the metal ligand complexes were formed from both. Showing the characteristic colors. Their purity of complexes was tested by their linear relationship of concentration and absorbance.

Stoichiometry of iron and vanadium with the ligand is more level at different pH values. The results show 1:1, 1:2, for iron and 1:1, 1:2 for vanadium.

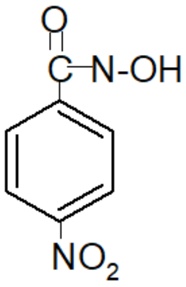
Keywords: hydroxamic acid, ligand, spectra**,** oxo-vanadate

Introduction

Hydroxamic acids are organic molecules containing the -CO-N-O- group(s) [3]. They are a class of organic acids of general formula RC (=O) N (R') OH, that have very important role in biological systems [4]. The first hydroxamic acid, oxalohydroxamic acid, was synthesized by H. Lossen [5]. Shortly thereafter, W. Lossen discovered a rearrangement [6] reaction of O-acyl derivatives of hydroxamic acids, which now bears his name**:**



Hydroxamic acids are among the most well studied compounds due to their significance in so many fields (7) that can act as O—O donor ligands with high affinities for hard cations such as Fe^{3+} [8, 9, 10]. The nitrobenzohydroxamic acid molecule possesses, apart from the reactive grouping of the hydroxamic acid.



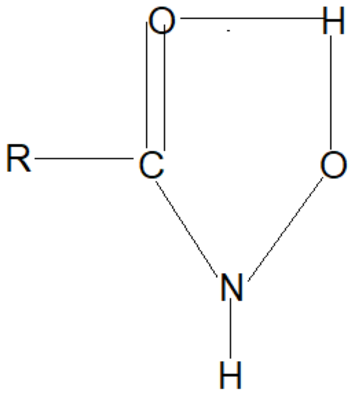


Fig 1

Hydroxamic acids are capable to form inter and intra molecular hydrogen booding in the solid state Figure (2).

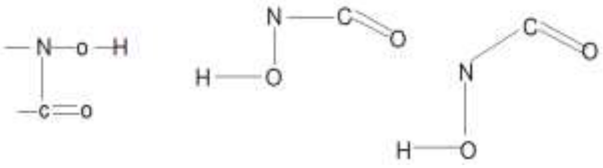
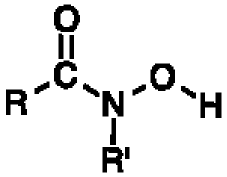


Fig 2

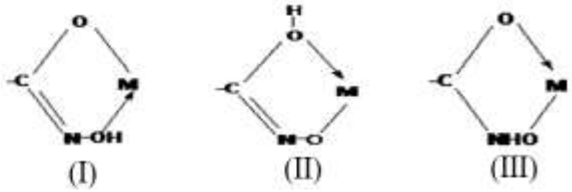
Stoichiometry is the science of measuring the quantitative proportions, or the ratio in which chemical elements stand to one another [1]. It is defined as the constrains placed on the composition of a closed system by the requirement for conservation of the amount of each atomic species and of electronic charge. These constrains take the form of linear conservation equation,



Nitrobenzohydroxamic acid has a nitrobenzoate and hydroxamic acid moieties. It is a potent chelating agent for Fe^{3+}, V^{5+}, Cu^{2+}, Co^{2+}, Ni^{2+}, etc [11]. Compounds containing the hydroxamic group [C (QO)–N (–H)–O–H)] act as chelating agents for metal ions [12].

All the hydroxamic acids are white crystalline or light yellow solids, except the iodo and nitro derivatives which are light pink, yellow, respectively. They are sparingly soluble in water, readily soluble in benzene, ethyl alcohol, dioxane, diethyl ether and chloroform. They are stable to normal storage [20]. They are of low melting points and weak acids. Then acidity is due to the presence of hydroxyl group, but they are stronger acids than phenols the suppression of acidic character was attributed to intramolecular hydrogen bonding as shown by infrared studies [21]. Hydroxamic acids act as bi-dentate ligands. They exist in two tautomeric forms (eno and keto-) of the atoms.

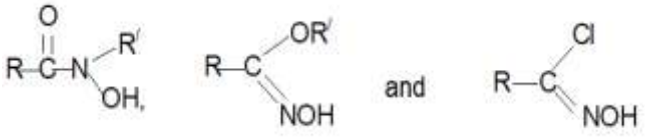
The structure of their metal complexes may represent in three different forms as shown below: (I) (II) (III)



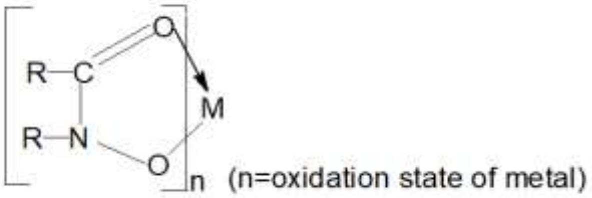
(I) (II) (III)

Fig 3

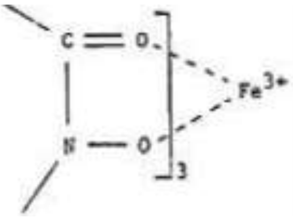
Other possible structures are excluded, as they would lead to the formation of unstable four member rings involving the metal nitrogen linkage [13]. The complex formation is believed to take place by replacement of the hydroxyl amino hydrogen by the metal ion and ring closure through the carbonyl oxygen. The resultant complex is generally neutral and forming a precipitates or soluble colored complex in aqueous solution, providing method for gravimetric analysis or solvent extraction methods with spectrophotometric finish. The most characteristic reaction is the intense red color produced by ferric chloride and dark blue color with vanadium (V). Since it is known that derivatives of the general formula RCONHOR' or RC (OH) =NOR' do not give color reactions with ferric chloride, while compounds of the structures do. It is apparent that the =NOH grouping is necessary for the formation of the coordination compound.



Complexes of monohydroxamic acids with Fe (III), Co (II) and Cu (II) are shown to coordinate via oxygen atoms of the ligand [14].



Copper (II) forms square planar complexes and vanadium (V) forms oxo-complexes. The best known of these complexes is that, with Fe (III) the beautiful red color of this compound forms the basis for the sensitive qualitative and quantitative determination of hydroxamic acids and their derivatives [15, 16].



The chemistry of nitrobenzohydroxamic acid rather than by coupling reaction, its characterization, the colour is yellow and its sparingly soluble in water, readily soluble in benzene, ethyl alcohol, diethyl ether and chloroform, melting point (211-213) C^0, its application as a ligand for complexation with iron (III) and vanadium (V).

Nitrobenzohydroxamic acids, NO2RCONHOH, form highly stable complexes with vanadium (V) in 1:1 and 1:2 molar ratios. The stability constants of the complexes were determined through spectrophotometric and potentiometric methods at various pH values and found in agreement. The hydroxamates are of interest due to their ability to form stable transition metal complexes through the formation of a five membered chelate ring [17]. Even in acid media iron (III) forms intensely colored complexes with this ligand which are useful for spectrophotometric analysis. The ability of hydroxamic acids to chelate metal ions has also found pharmaceutical applications [16].

Stoichiometry is determined by different methods: mole ratio, slope ratio and continuous variations (job's method). Mole ratio method determines the concentration of metal ion is held fixed, while the concentration of the reagent (ligand) increased stepwise. One the graph of absorbance vs. moles of reagent added, the intersection of the extrapolated linear segments determines the ratio: moles of reagent / moles of metal. In slope ratio method, two series of solutions are prepared.

In the first series various amounts of metal ion are added to a large excess of the reagent, while in the second series different quantities of reagent are added to a large excess of metal ion. The absorbance of the solutions in each series is measured and plotted vs. the concentration of the variable component.

The discovery of continuous variations method is attributed to Job [18]. who first applied it to complex formation; it is a simple and effective approach to the determination of chemical reaction.

In this method, cation and ligand solutions with identical analytical concentrations are mixed in such a way that the total volume and the total moles of reactants in each mixture is constant but the mole ratio of reactants / varies systematically (for example, 9:1, 8:2, 7:3, …, 1:9). The absorbance of each solution is then measured at a suitable wavelength and corrected for any absorbance that the mixture might exhibit if no reaction had occurred. The corrected absorbance is plotted against the volume ratio of one reactant, that is, VM/ (VM+VL), where VM is the volume of cation solution and VL is the volume of the ligand solution.

The resulting curve will show a maximum at the mole ratio corresponding to that in the complex. When the curvature is pronounced and the maximum is not apparent, the apex may be obtained by drawing tangents [19].

Materials and Methods

Chemicals

- Benzoic acid, LOBA chemie, India.
- Methanol (dried), LOBA chemie, India.
- Sulfuric acid, LOBA chemie, India.
- Carbon tetrachloride, LOBA chemie, India.
- Hydroxylamine hydrochloride, LOBA chemie, India.
- Sodium hydroxide, CDH, China.
- Ferric chloride, CDH, China.
- Ammonium Meta vanadate, CDH, China.
- Copper sulfate, LOBA chemie, India.
- Ethanol, Alwatanya ltd. Company for distillation, Sudan.
- Sodium hydrogen carbonate.
- Magnesium sulfate.

Instruments

- FTIR spectrophotometer, 84005, Shimatzu, Japan.
- PH/ion meter, 555, Corning pinnacle, Switzerland.
- UV/Vis. spectrophotometer, 6505, Jenway, England.

Methods

Preparation of nitrobenzohydroxamic acid (NBHA)

Nitrobenzohydroxamic acid was prepared by coupling of methyl nitro benzoate and free hydroxylamine left over night, acidified, the precipitate formed is filtered, recrystallized form water acetic acid mixture and identified.

Quantitative Evaluation of complex formation:

Linear relationship between metal complexes concentration and absorbance

Preparation of stock solution of nitrobenzohydroxamic acid

0.01M of nitrobenzohydroxamic acid was prepared by weighing 0.1 g, dissolved in 50ml of ethanol, transferred to 100 ml volumetric flask, the volume was completed to the mark with distilled water.

Preparation of stock solution of metals

0.01M stock solutions of Fe (III) and V (V) were prepared. 0.0290 g $FeCl_3$, 0.0230 g NH_4VO_3 were weighed out accurately, dissolved in distilled water, transferred in to 100 ml volumetric flasks, completed up to the mark with distilled water.

Preparation of standard solution of complexes

2, 4, 6, 8, 10, 12 ppm standard solutions of metal were prepared by taking 0.2, 0.4, 0.6, 0.8, 1, 1.2 ml of metal stock solution into 10 cm3 volumetric flask, then 1 ml of 0.01M nitrobenzo hydroxamic acid was added, the volume was completed to the mark with distilled water.

Preparation of blank solution

1cm3 of 0.01M nitrobenzohydroxamic acid was taken, transferred to 10 cm3 volumetric flask and completed up to the mark with distilled water.

Λmax determination

1cm3 of 0.01M nitrobenzohydroxamic acid was taken into 10 cm3 volumetric flask, and then 1 cm3 of FeCl3 was added and completed up to the mark with distilled water. The same method was applied for vanadium and copper.

Results and Discussion

Characterization of nitrobenzohydroxamic acid

- m.p (211-213)ºC.

- I.r. Spectrum (KBr); the spectra showing absorption bands: 3112 cm^{-1} (OH), 1691 cm^{-1}(C=O).

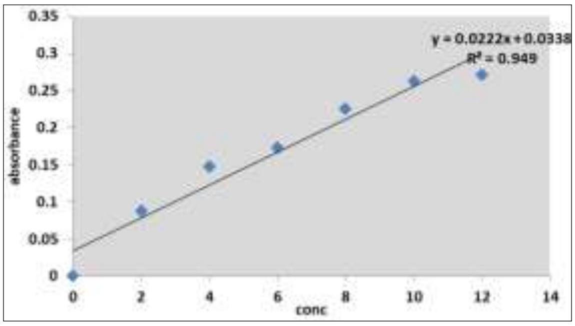


Fig 1: Calibration curve of iron Nitrobenzohydroxamate complex

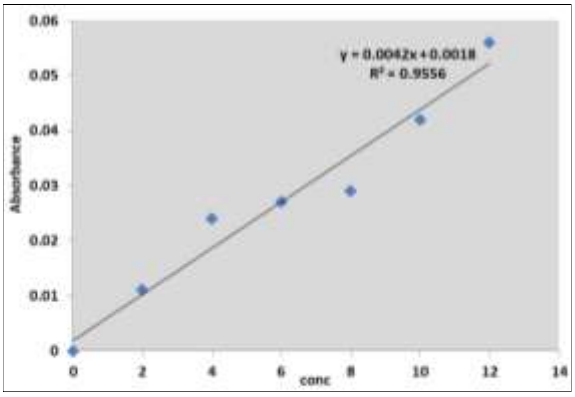


Fig 3: Calibration curve of vanadium Nitrobenzohydroxamate complex

Determination of stoichiometry of complexes using continuous variation method

Preparation of buffer solutions

- 20.32 cm^3 of 0.1M potassium chloride was mixed with 50cm^3 of 0.1M ($C_8H_5O_4K$) to obtain a solution of pH 3.0.
- 50cm^3 of 0.1M ($C_8H_5O_4K$) was mixed with 14.7cm^3 of 0.1 KCl mixed to obtain a solution of pH is equal 4.
- 50cm^3 of 0.1M ($C_8H_5O_4K$) was mixed with 22.6cm^3 of 0.1 NaOH mixed to obtain a solution of pH is equal 5.

Effect of pH on stoichiometry of iron nitrobenzohydroxamate complex at pH 3.0

Preparation of ferric chloride stock solution

2.90189g of ferric chloride (0.0107395mole) was weighed and dissolved in distilled water, then transferred to 1000 cm³ volumetric flask, then take 1cm3 and dilute to 100ml in volumetric flask, and 5 cm³ of buffer (pH = 3.0) was added, the volume was completed up to the mark with distilled water.

Preparation of nitrobenzohydroxamic acid stock solution (0.01M)

0.1g (mole) of nitrobenzohydroxamic acid was weighed and dissolved in 50.0 cm³ ethanol, then transferred to 100cm³ volumetric flask, 5cm³ of buffer was added (pH =3.0), the volume was completed up to the mark with distilled water.

Preparation of Iron nitrobenzohydroxamate complex

A series of solutions of different mole fractions of the two constituents were prepared, 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0 cm³ nitrobenzohydroxamic acid (ligand): ferric ion. The total volume of the prepared complex and the pH were kept constant.

The λmax was determined; the absorbance of each solution was recorded at the wavelength of maximum absorbance.

The same method was used for determination of stoichiometry of complexes with pH= 3, (vs. absorbance, absorbance in some time) λmax = 420 nm.

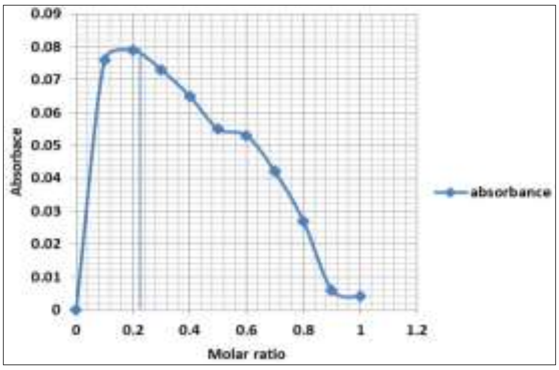


Fig 4: Stoichiometric curve of iron complex vs. absorbance at pH=3

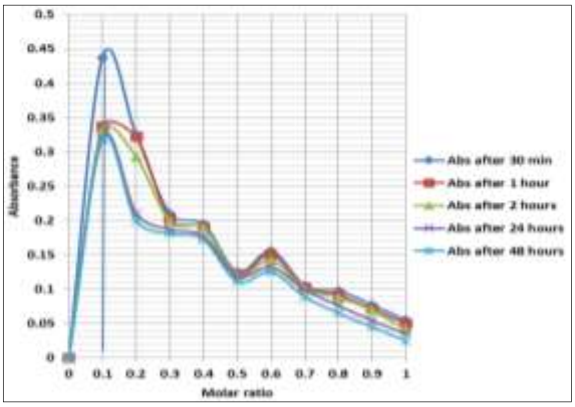


Fig 5: Stoichiometric curve of iron complex vs. absorbance in different time at pH=3

Determination of vanadium nitrobenzohydroxamate complex (at pH=5)

Preparation of ammonium-metavanadate stock solution

3.8696g ammonium-metavanadate of (mole) was weighed and dissolved in distilled water, then transferred to 1000 cm³ volumetric flask, then take 1cm3 and dilute to 100ml in volumetric flask, and 5 cm³ of buffer (pH = 5) was added, the volume was completed up to the mark with distilled water.

Preparation of nitrobenzohydroxamic acid stock solution (0.01M)

0.1g (mole) of nitrobenzohydroxamic acid was weighed and dissolved in 50.0 cm³ ethanol, then transferred to 100cm³ volumetric flask, 5cm³ of buffer was added (pH =5), the volume was completed up to the mark with distilled water.

Preparation of vanadium nitrobenzohydroxamate complex

A series of solutions of different mole fractions of the two constituents were prepared, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0 cm ³ nitrobenzohydroxamic acid (ligand): ammonium metavanadate (metal). The total volume of the prepared complex and the pH were kept consistent.

Λmax determination

Λmax. Was determined using the solution having the highest concentration, and found to be 520 n.m. The λmax was determined; the absorbance of each solution was recorded at the wavelength of maximum absorbance.

The same method was used for determination of stoichiometry of complex with pH 5 and λmax = 520 nm. (Dark blue) color was observed for both pH values.

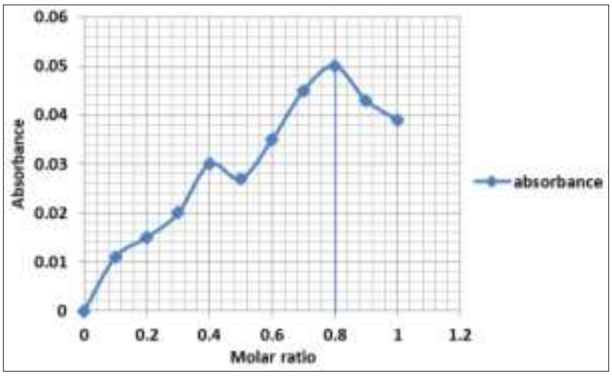


Fig 6: Stoichiometric curve of vanadium complex vs. absorbance at pH=5

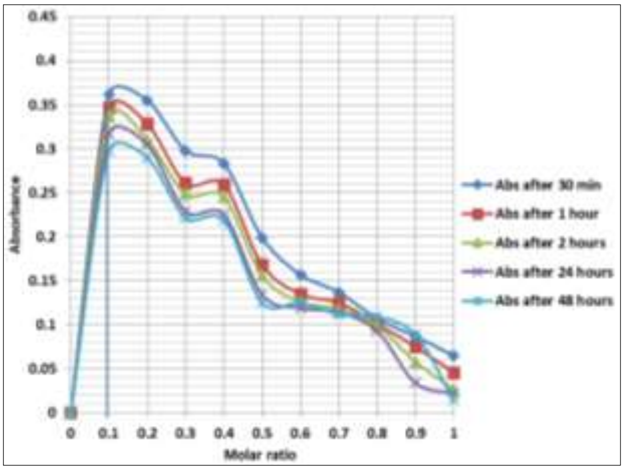


Fig 7: Stoichiometric curve of vanadium complex vs. absorbance in different time at pH=5

Discussion

Nitrobenzohydroxamic acid was smoothly prepared through the ester route method. The acid was recrystallized and identified by M.pt, complex-color test and IR spectra. Iron nitrobenzohydroxmate (red), vanadium nitrobenzohydroxmate complexes were prepared in aqueous acidic media. The complexes were air dried to form defined beautiful crystals.

UV-Visible spectroscopic measurements of the ligand with iron and vanadium complexes at different concentrations show strict linearity. This confirms that the ligand and the metal cations are complexed uniformly. The complexes for both cations were formed at pH values which are later selected for stoichometric study.

Based on complex formation, following continuous variation method; iron shows 1:2 and 1:1 stoichiometric ratios at pH 3.0. Vanadium shows 1:2 and 1:1 stoichiometric ratios at pH 5.

VO^{+3} unit and are related by a pseudo-three-fold axis.

The nitrobenzohydroxamic acid is doubly deprotonated; therefore, this dianionic ligand is coordinated as a nitrobenzohydroximate rather than the doubly deprotonated nitrobenzohydroxamate. Although all oxygen and nitrogen atoms, are bonded to vanadium, an individual ligand donates only two heteroatoms to each independent vanadium (V). The deprotonated hydroxamate nitrogen and phenolate oxygen bind to vanadium atom while the two remaining oxygen atoms bind to the second vanadium. This bonding repeats throughout the cluster forming a triangular unit with a [-V-N-O-] core.

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