



Spectrophotometric Determination of the Stoichiometry of Cobalt (II) and Copper (II) Salicylhydroxamate Complexes

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Abstract

Salicylhydroxamic acid was prepared by coupling reaction of methyl salicylate and free hydroxylamine, precipitated by acidification and recrystallized by hot water/ acetic acid it was characterized by melting point, iron and vanadium color test and FT-IR absorption bands at 3260cm^{-1} (OH), 1663cm^{-1} (C=O), and 900cm^{-1} (N-O) and $^1\text{H-NMR}$ characteristic peak of the proton of the hydroxyl group attached to the nitrogen atom in the region $9.566 - 9.762$ ppm. The shifting of the resonance signal of hydroxyl proton to lower field supports intermolecular hydrogen bonding. The peak proton of aromatic ring appears in the region $7.699 - 7.714$ ppm. The peak protons of -NH appears in the region $3.772 - 3.783$ ppm. The ^{13}C NMR spectra exhibit absorption signal due to carbonyl (C=O) group at nearly 166.118 ppm. The chemical shifts of aromatic carbons appear in the region of $133.329 - 127.148$ ppm. The complexation of salicylhydroxamic acid either with Co^{2+} or Cu^{2+} cation was both determined by continuous variation method. Spectrophotometric analysis for determination of Co^{2+} and Cu^{2+} salicylhydroxamate complexes was based on formation of colored complexes in weak acidic media. The produced colored complexes of Co^{2+} and Cu^{2+} showed maximum absorption at λ_{max} 510nm and 385nm respectively. The mole ratio of complexes were determined in different chemical environments, and found to be in ratio of 1:3 and 1:1 (M:L), respectively.

Keywords: coupling, chemical shifts, cation, buffer solution

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المستخلص

الهدف من الدراسة تحديد العلاقة الكمية الحسابية لمعقدي حمض ساليلوهيدروكسيمك مع النحاس (II) والكوبالت (II). تم تحضير حمض الساليلوهيدروكسيمك بمفاعلة التزواج بين ميثيل سالسليت مع هيدروكسيل امين الحر ومن ثم تشخيصه بنقطة الانصهار والاختبارات اللونية و مضافية الاشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون ونظير الكربون $^{13}\text{-}$. وظهر طيف الاشعة تحت الحمراء حزم الامتصاص المميزة في 3260سم^{-3} (OH)، 1663سم^{-3} (C=O) و 900سم^{-3} (NH). كما اظهر طيف الرنين النووي المغناطيسي قمة مميزة لبروتون مجموعة الهيدروكسيد المرتبطة بذرة الهيدوجين في الحيز ($9.566-9.762$ جزء من مليون جزء) وبرتون الحلقة الاروماتية في الحيز ($7.699-7.714$ جزء من مليون جزء) وقمة بروتون لمجموعة N - H في الحيز ($3.772-3.783$ جزء من مليون جزء). وظهر بروتون نظير الكربون $^{13}\text{-}$ اشعاعاً للامتصاص الناتج معه لمجموعة الكربونيل (C=O) قريباً من (166.118 جزء من مليون جزء) و الازاحة الكيميائية لكربونات الحلقة الاروماتية في الحيز ($133.329-127.148$ جزء من مليون جزء). وتم

تحديد العلاقة الحسابية لمعدي حمض ساليو هيدروكسيمك مع النحاس (II) والكوبالت (II) بطريقة الاختلافات المستمرة في وسط ضعيف الحمضية. وظهرت المعقدات الملونة لايوني Cu^{2+} و Co^{2+} الامتصاص الاقصى 385,510 نانومتر علي التتابع. والتناسب المولي للمعقدات في قيم مختلفة الاس الهيدروجين (6-1 pH) بنسبة 1:3 و 1:1 علي التتابع .

Introduction

Hydroxamic acids are hydrophilic organic compounds that can exhibit keto-enol tautomerism, and tautomers may exist either as **Z** (zusammen) or **E** (entgegen) diastereomers.(figure).

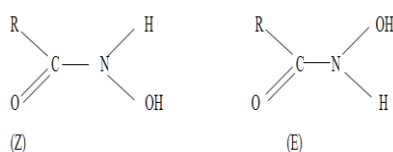


Figure 1: Z-and E-isomers of hydroxamic acid

They are much weaker acids than the structurally related carboxylic acids $\text{RC}(=\text{O})\text{OH}$, and produce hydroxamate ions. The deprotonation could be from either the nitrogen or the oxygen, making them N-acids or O-acids.

Generally, Hydroxamic acids are white or light yellow solids except iodo- nitro substituted and cinnamo- substituted which are pink and light yellow, respectively.

They are soluble in chloroform, hot benzene, diethyl ether, dioxane and ethanol and sparingly soluble in carbon tetrachloride and cold benzene but are insoluble in water, and have low melting point(Jain et al., 2005).

The hydroxamic acid grouping imparts chelating properties to this acids and its N-substituted derivatives, which serves as bidentate di-oxygen ligands toward many metal ions such as Fe (III) and Cu(II)(Chatterjee, 1978); (Chatterjee et al., 2002).The complexes formed are of highly colored nature and are very useful for the spectrophotometric and gravimetric analysis of the metal ions.(Agrawal and Patel, 1980)

The complex formation is believed to take place by replacement of the hydroxyl-

hydrogen by the metal ion and by ring closure through the carbonyl oxygen forming five member ring. The resultant complex is generally neutral which either precipitated from aqueous solution,(providing a method for gravimetric analysis) or can be extracted by organic solvent.The most characteristic reaction is the intense violet colour produced by ferric chloride.

The salicylhydroxamic acid molecule possesses, in addition to the reactive grouping of the hydroxamic acid, more functional group (OH) in a position favorable for chelation. Naturally, therefore, its presence may change to some extent the nature, stability and the colour of the complexes with respect to those of benzohydroxamic acid. The maroon cobalt compounds prepared from neutral solutions are of the type $\text{M}(\text{C}_7\text{H}_6\text{O}_3\text{N})_2$ (Musante.C.Gazz,1948).

Copper gives in a fairly ammoniacal medium, green 1:1 compounds forms oxy compounds, similar to those formed with benzohydroxamic acid, and has similar properties(Pal and Chakraborty, 1980).

Salicylhydroxamic acid is a suitable indicator in the chelatometric titration of cobalt (II) at pH 7(Seshadri, 1970).

Complexes of mono hydroxamic acids with Co (II) and Cu (II) are shown to coordinate via oxygen atoms of the ligand.(figure2)

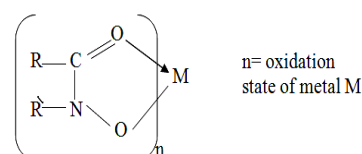


Fig 2: Structure of hydroxamic acid metal complex

Spectral and magnetic properties of Co (II) complexes indicate octahedral coordination with the metal ions forming polymeric species. Cu (II) forms square planar complexes (Niemeyer et al., 1989).

The extent to which a metal will complex with a ligand is characterized by the stability constant. If a monodentate ligand is used, that ligand binds to a metal by one donor atom only, a series of stepwise equilibria exists for the formation of metal-ligand complexes. These complexes have stoichiometry ratio of 1 to 1, 2, 3 and up to the maximum coordination number of the metal ions.

The complexation of metal ion in an aqueous solution is expressed by the following equation:



The ligand L can be either a molecule or charged ion. Other L groups can successively replace the remaining aquo groups in the complex until the complex ML_n is formed. If a metal forms a complex ion ML_n the maximum number of bound ligands is the coordination number of the metal ion. However, it is noted, that a metal ion can have more than one characteristic coordination number depending upon the valence of the central atom and upon the nature of the coordination ligand.

A ligand that is attached to the metal ion at only one point is called unidentate; water, ammonia and the halides are all unidentate ligands. Organic molecules or ions containing two or several bonding centers, i.e., donor groups, are able to replace two or more aquo or other unidentate groups from a metal ion. Such ligands are termed bi, tri, quadri, or generally multidentate. A multidentate ligand may be bound to the metal by means of two or more in such a way that a ring structure is formed. Such ring compounds are called complexes. The complexes are characterized by their

remarkably high stability compared to the compounds.

Stoichiometric is a section of chemistry that involves using relationships between reactant and/or products in chemical reaction to determine desired quantitative data. (Elkhadir, 2001). Stoichiometry is the science of measuring the quantitative proportion or math ratios in which chemical elements stand to one another. It is defined as the constraints placed on the composition of a closed system by the conservation of the amount of each atomic species and of electronic charge. These constraints take the form of linear conservation equation, which may be expressed in the form either of algebraic atom or charge in balanced equation or chemical equation

The most common techniques employed for complex ions stoichiometric studies:

The continuous variation method

The slope-ratio method

The mole-ratio method

The aim of this work is to determine the stoichiometric of complexes formed by the cation Co^{2+} and Cu^{2+} and salicylhydroxamic acid as ligand.

2. Materials and Methods

2.1 Materials

Methyl salicylate, hydroxylamine hydrochloride, ethanol, methanol, copper sulphate, cobalt nitrate, sulphuric acid, sodium hydroxide, sodium hydrogen carbonate, glacial acetic acid, diethyl ether (All chemicals reagents are of analytical grade)

2.1.2 Equipment

Electrical balance. A and D company, Ltd CE Germany FTIR300 Spectro with KBr disc UV/VIS. Spectrophotometer 6505 UV-VIS spectrophotometer, with printer hp desk jet 640 C, Jenway, England

pH meter Model 3030, Jenway, England.

N.M.R. spectrophotometer, ^1H and ^{13}C were recorded at 400 and 75 MHz respectively, on a Bruker AV – 400 Spectrometer (USA). Chemical shift for ^1H and ^{13}C spectra were recorded in ppm relative to residual proton of CDCl_3 (^1H 7.28, ^{13}C 77 ppm).

2.2 Methods

2.2.1 Preparation of salicylohydroxamic acid

The ligand was synthesized in two simple steps by the coupling reaction of free hydroxyl amine and methyl salicylate as shown in figure 3.

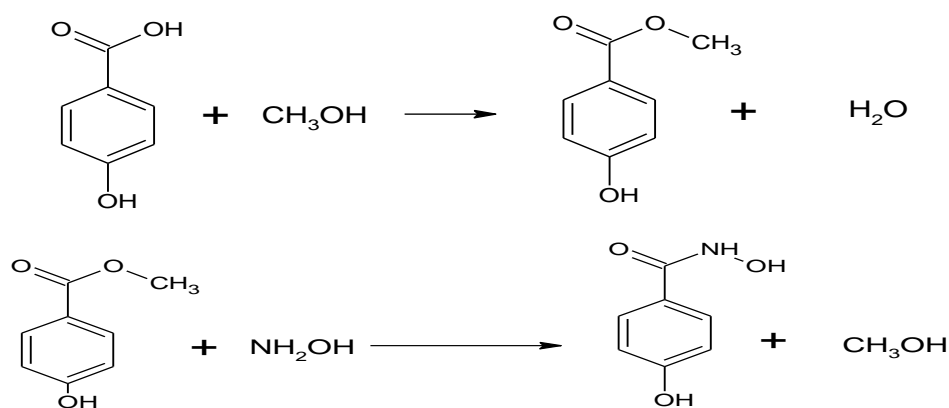


Figure 3 Synthetic routes for Ligand

2.2.2 Preparation of stock solution of metal cation (100ppm)

Stock solutions of 100ppm of cobalt and copper were prepared by weighing 0.0403, 0.0392g of CoNO_3 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ respectively. Each salt was dissolved in distilled water, transferred into 100cm^3 volumetric flask and completed to the mark with distilled water.

2.2.3 Preparation of stock solution of salicylohydroxamic acid, SHA (100ppm)

2.2.1.1 Coupling reaction of methyl salicylate and hydroxylamine

14 g (0.1mol) hydroxylamine was added to 200cm^3 12% solution of sodium hydroxide and cooled at room temperature. Then (15.2g, 0.1mol) of methyl salicylate was added in small portion with vigorous shaking after each addition to ensure complete dissolution. The mixture was allowed to stand for a period of two days until the solution became straw brown. Then acidified with addition of 2M sulphuric acid and acidity was tested by (litmus paper); then it was placed in an ice – bath at 0°C . The precipitate was filtered and recrystallized from hot water and drop of acetic acid, and the hot solution was filtered and placed in an ice – bath at 0°C again the white precipitate was collected giving yield of 15g (90%).

A stock solution of 100ppm of SHA was prepared by weighing 0.1531g, dissolved in 5cm^3 ethanol, transferred into 100cm^3 volumetric flask and completed to the mark with distilled water.

2.2.4 Preparation of standard solution of complexes (ppm)

Standard solutions of 20, 40, 60, 80, 100, 120 ppm of either cobalt or copper salicylohydroxamate complexes were prepared by taking aliquots of 2, 4, 6, 8, 10, and 12cm^3 of each of the respective metals, into separate 10cm^3 volumetric flasks. Then

1 cm³ of 0.1 M salicylhydroxamic acid was added, and the solution was diluted to the mark with distilled water.

2.2.5 Determination of stoichiometry of complexes using continuous variation method

2.2.5.1 Determination of stoichiometry of salicylhydroxamate complexes

2.2.5.2 Preparation of stock solution of metals

0.016g (0.000653 mole) of cobalt nitrate and copper sulphate was each weighed separately and dissolved in small amount of distilled water, then transferred to 50cm³ volumetric flask, 5cm³ of buffer solution (pH=7,6) were added, then the volume was diluted to the mark with distilled water.

2.2.5.3 Preparation of salicylhydroxamic acid stock solution

0.01g (0.000653 mole) of salicylhydroxamic acid was weighed and dissolved in 1.0 cm³, then transferred to 50cm³ volumetric flask, 5 cm³ of buffer solution (pH= 7,6) was added, then the volume was completed up to the mark with distilled water.

2.2.5.4 Determination of stoichiometry of cobalt- copper salicylhydroxamate complexes

A series of solutions of different mole fractions of salicylhydroxamic acid (SHA) and either cobalt or copper cation (metal) were prepared by mixing the following volume of SHA and metal 0+10, 1+9, 2+8, 3+7, 4+6, 5+5, 6+4, 7+3, 8+2, 9+1, 10+0 cm³, respectively the total number of cm³ mixed (total number of moles) as well as pH was constant for each of the solution mixtures

Salicylhydroxamic acid (ligand): ion. The total volumes of the prepared complexes and the pH were kept constant.

2.3 Characterization of salicylhydroxamic acid

2.3.1 Spot test

Ethanol solutions of salicylhydroxamic acid were added to an aqueous solution of

ferric chloride, vanadium salt separate. The two solutions of hydroxamic acids were thoroughly mixed and transferred to a watch glass for air dryness.

2.3.2 Melting Points of salicylhydroxamic acid

In this technique melting point apparatus with capillary tube was used to determine the melting points of salicylhydroxamic acid

2.3.3 Infrared spectrum of salicylhydroxamic acid

The infrared spectroscopy (IR) analysis was carried out for salicylhydroxamic acid by using JENWAY FTIR instrument with KBr disc. The spectrum obtained is shown in fig (3).

2.3.4 ¹H NMR spectrum of salicylhydroxamic acid

The nuclear magnetic resonance spectroscopy (¹H NMR) analysis was carried out for salicylhydroxamic acid by using instrument. The spectrum obtained is shown in fig (4).

2.3.5 ¹³C NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (¹³C NMR) analysis was carried out for salicylhydroxamic acid by using instrument. The spectrum obtained is shown in fig (5)

3. Results and Discussion

The salicylhydroxamic acid was prepared and characterized by the following methods:

(i) Colors test (spot test) with Fe³⁺, V⁵⁺ where positive red and violet colors were observed respectively

(ii) The melting point was carried out and found to be 170°C (lit. compared to 169-170°C)

(iii) Infrared spectral data were carried out (Fig. 4): 3260 cm⁻¹ is due to O-H stretching vibration, 1663 cm⁻¹ is assigned to the C=O of hydroxamic acid group, and a

sharp band at 900 cm^{-1} is attributed to N-O caused by stretching vibration.

(iii)The ^1H NMR spectra of salicylhydroxamic acid (Fig. 5) show the characteristic proton of the hydroxyl group attached to the nitrogen atom in the region $9.566 - 9.762$ ppm. The shifting of the resonance signal of hydroxyl proton to lower field supports intermolecular hydrogen bonding. The protons of aromatic ring appear in the region $7.699 - 7.714$ ppm. The protons of $-\text{NH}$ appear in the region $3.772 - 3.783$ ppm.

(iv)The ^{13}C NMR spectra of salicylhydroxamic acid (Fig. 6) exhibit absorption signal due to carbonyl ($\text{C}=\text{O}$) at nearly 166.118 ppm. The chemical shifts of aromatic carbons appear in the region $133.329 - 127.148$ ppm.

Complexation studies

The system obeyed Beer's law over the range of $0.1-6.5\mu\text{gml}^{-1}$, and a regression analysis equation was obtained from the calibration standard curve of cobalt and copper.

Stoichiometry of complex

The stoichiometric ratio of Co- salicylohydroxamate complex, Cu- salicylohydroxamate

complex were determined by modified Job's method of continuous variation. The mole ratio of complexes were determined in different chemical environments, and found to be in ratio of 1:3 and 1:1 M:L respectively. Similar results were obtained by O'Brien et al. (1997).

The absorbance (A) of complexes of a series of solution containing cobalt, copper (a) and SHA (b) at constant total concentration (a + b) but different concentration ratios, were measured at 510nm for cobalt and 385nm for copper. The A values were plotted against mole ratio metal (cobalt and copper) ions $a/(a + b)$. The maximum value for A was clearly obtained at $a/(a + b) = 0.11$, indicating a 1:3 and 1:1 stoichiometric ratio of Co:SHA and Cu:SHA, respectively. The accuracy of this result is possible if only a single complex is formed.

Table (1) and figure (7) shows the correlation of concentration of metals (ppm) vs absorbance of synthesized metal complexes of salicylohydroxamic acid.

Table (2) shows and figure (8) the correlation of concentration of metal complexes vs absorbance of metal complexes of salicylohydroxamic acid was synthesized to determine the stoichiometry (mole ratio) of complexes.

Table (1) Correlation of concentration of metals (ppm) vs Absorption of metal complexes of salicylohydroxamic acid

Concentration of metal ion (Cu(II) or Co(II) in (ppm)	0.0	20	40	60	80	100
Absorbance of Co(II) complexes of salicylohydroxamic acid at wavelength 510nm	0.00	0.007	0.022	0.039	0.045	0.052
Absorbance of Cu(II) complexes of salicylohydroxamic acid 385nm	0.00	0.220	0.430	0.629	0.832	0.985

Table (2) the results of mole fraction of complexes vs absorbance of synthesized metal complexes of salicylohydroxamic acid to determine stoichiometry (mole ratio) of complexes

Mole ratio of SHA:metal Co(II):SHA at pH =7, Cu(II):SHA at pH=6	0:10	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1	10:0
Mole fraction	0.0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
Absorbance of Co(II)	0.00	0.303	0.673	0.697	0.524	0.421	0.345	0.339	0.320	0.210	0.00
Absorbance of Cu(II)	0.00	0.980	0.464	0.559	0.666	0.782	0.703	0.565	0.350	0.235	0.00

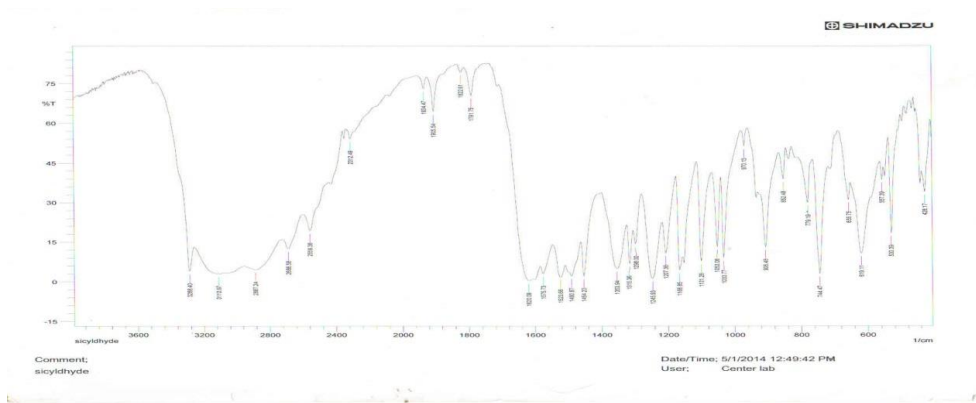
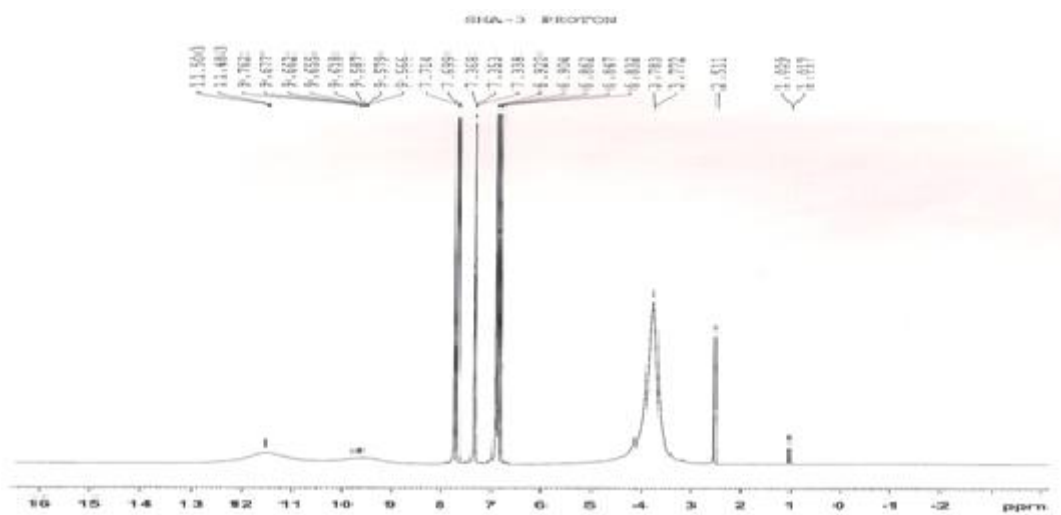


Fig (4) Infrared of salicylhydroxamic acid



Fig(5)¹H NMR of salicylhydroxamic acid

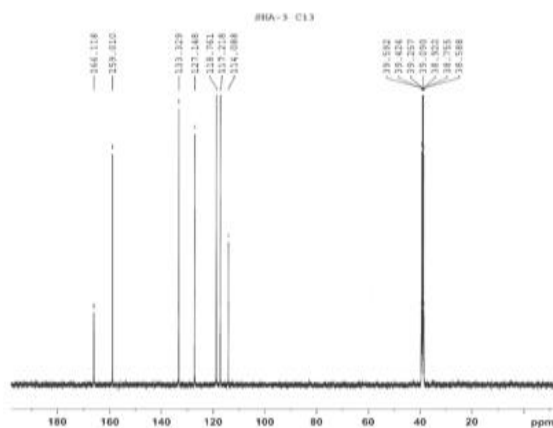


Fig (6)¹³CNMR of salicylhydroxamic acid

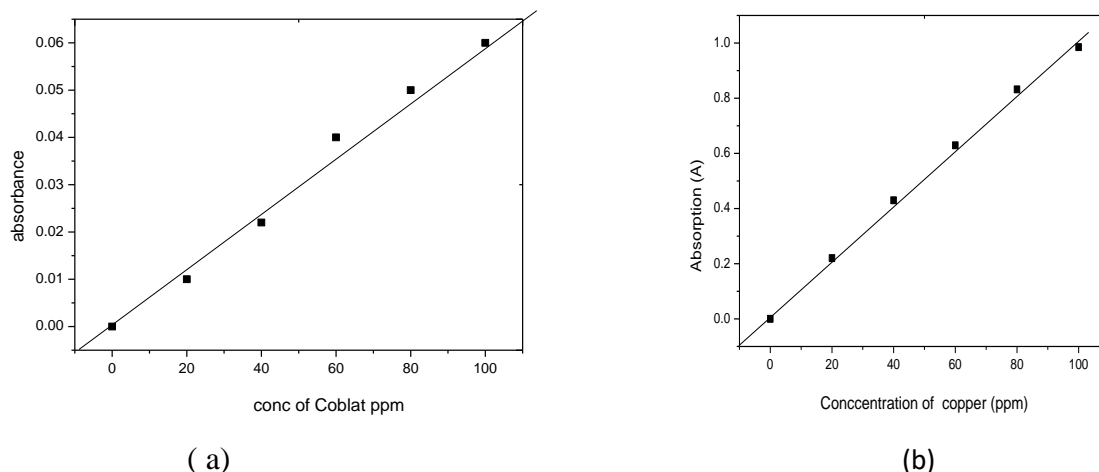


Fig (7) (a) and (b) shows the

Absorbance of Co(II), Cu(II) complexes of salicylohydroxamic acid at wavelength 510, 385nm and concentration of Co(II), Cu(II)

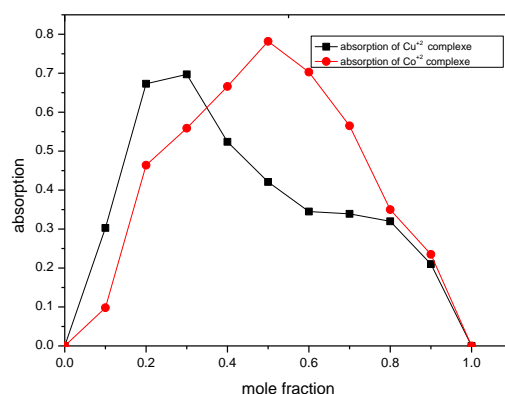


Fig.(8) shows the stoichiometry (mole ratio) of Co(II) and Cu(II) complexes with salicylohydroxamic acid

Conclusion

The complexes of salicylohydroxamic acid with Cobalt (II) and Copper (II) were successfully prepared and their complex formulas were determined spectrophotometrically by continuous variation method. The mole ratio of complexes were determined in different chemical environments, and found to be in ratio of 1:3 and 1:1 (M:L), respectively. The finding of the study has shown that the optimal condition for formation of Co(II) and Cu(II) complexes with salicylohydroxamic acid were at pH7 and pH6, respectively. Both cation were formed coordination complexes and which were selected for stoichiometry study. At pH7 (high pH) Cobalt formed octahedral

stable complex this could be explained by its coordination number 6 leaving for 1:3 number stoichiometry ratio, while copper formed square planer at pH6 by its coordination 6 leaving for 1:1 stoichiometry ratio.

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