

Preparation and Characterization of Salicylhydroxamic acid and its Complexes with Iron (III), Cobalt (II) and Manganese (II)

Leena Salah Ibrahim^{1,*}, Elmugdad Ahmed Ali², Mohammed Sulieman Ali²

Jazan University, College of Science, Chemistry Department

Sudan University of Science and Technology, College of Science, Department of Chemistry

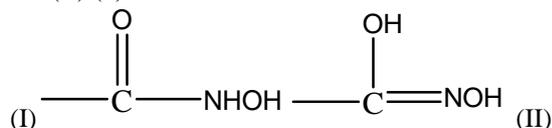
leenachem81[at]gmail.com, abotrteel74[at]gmail.com, elmugdad[at]hotmail.com

Abstract: At the present work salicylhydroxamic acid and its complexes with iron (III), cobalt (II) and manganese (II) were studied. Firstly, salicylhydroxamic acid had been prepared by the reaction of methyl salicylate and free hydroxylamine and was characterized by its melting point, (169 °C), FT-IR showed characteristics spectral bands at 3288 cm^{-1} due to (OH) stretching vibration, 1614 cm^{-1} due to (C=O) and 907 cm^{-1} due to (N-O). The ¹H NMR spectrum shows the characteristic attachment of the proton of the hydroxyl group to the nitrogen atom in the region 11.41 – 12.20 ppm, the appearance of protons of aromatic ring in the region 6.83 – 7.832 ppm. Iron (III), cobalt (II) and manganese (II) salicylhydroxamate complexes were prepared by reacting salicylhydroxamic acids with corresponding metal salts. The compounds were characterized using elemental analysis, spectral (infrared, UV-Vis), TGA and magnetic susceptibility. The purity of the complexes was confirmed by CHN analysis. The result indicates that the reaction between iron (III) and cobalt (II) with SHA (salicylhydroxamic acid) at 1:2 molar ratio but with manganese (II) was 1:1 molar ratio. They show absorbance at a wavelength of maximum (λ_{max}) 470nm, 351 nm and 300 nm for Fe³⁺, Mn²⁺ and Co²⁺ respectively indicating that the metal ligand complexes were formed. The complexes were characterized by FT-IR characteristics spectral which showed bands at 1597- 1601 cm^{-1} (C=O) and 915-925 cm^{-1} (N-O), TGA thermogram of all complexes has shown three characteristics mass loss and residue mass as metal oxide. The spectral study analysis reveals that all complexes coordinated to the metal via oxygen atoms (O, O) in bidentate to form octahedral for [Fe (SHA)₂.Cl₂]₂H₂O, tetrahedral for [Co (SHA)₂]₂H₂O and square pyramidal geometry for [Mn (SHA)Cl.H₂O]₂H₂O.

Keywords: Salicylhydroxamic acid, Iron (III), Cobalt (II), Manganese (II), Magnetic Moment

1. Introduction

Hydroxamic acids are organic molecules containing the -CO-N-O- group (s) (1). The structure of hydroxamic acid was first noted by W. Lossen who observed that the product obtained by the reaction of anisohydroxamic acid and benzoyl chloride was different from the product produced by the reaction of benzohydroxamic acid and anisoylchloride (2). Evidence for the existence of hydroxamic acids in tautomeric forms, keto form, structure (I) and enol form, structure (II) (3)



They have been classified into three groups: primary hydroxamic acid, secondary hydroxamic acid and cyclic hydroxamic acid. They are able to coordinate metal ions with very high affinity because having bidentate functional grouping (4). Their ability to act as metal chelators constitutes the basis of their use (i) as flotation agents in extractive metallurgy and (ii) their employment in many biological applications. Recently preparation, Characterization of different hydroxamic acids and its metal complexes had extensively studied (5-9)

The main objective of this study is the synthesis of hydroxamic acid by coupling reaction, its characterization and its application as a ligand for complexation with iron (III) and Co (II) and Mn (II). Hydroxamic acids having one or

more -CONHOH groups have been extensively studied as a consequence of their biological importance which is related with their ability to form metal ion complexes. These acids are important also due to their pharmacological, toxicological and pathological properties. Besides, they have a great number of applications in analytical chemistry (10-12).

2. Materials and Method

2.1 Materials

Salicylic acid, methanol (MeOH), sulphuric acid, hydroxylamine hydrochloride, ferric chloride FeCl₃, and Co (NO₃)₂·6H₂O cobalt nitrite hex hydrate, MnCl₂·4H₂O manganese chloride tetra hydrate, sodium hydroxide pellets (NaOH), sodium hydrogen carbonate (NaHCO₃), glacial acetic acid, diethyl ether, were obtained from CDH chemical Ltd, China (all chemicals were analytical grade).

2.2 Instruments

- FTIR spectrophotometer, 84005, Shimadzu, Japan.
- UV/Vis. spectrophotometer, 6505, Jenway, England
- Melting point electrical, type (Gallenkamp, England) Griffin Melting point Apparatus model 9100.
- Elemental Analyzer FLASH EA1112 series, CHNS-O.
- Bruker AMX-300 NMR spectrometer.
- Shimadzu Thermogravimetric Analyzer (TGA-50).

2.3 Methods

2.3.1 Preparation of salicylhydroxamic acid

The ligand was prepared in two steps, step one the methyl salicylate was prepared by the esterification of salicylic acid with methanol in this reaction 28g (0.2 mol) of salicylic acid, 81cm³ of methanol and 8cm³ of concentrated sulfuric acid were mixed and step two by the coupling reaction of hydroxylamine and methyl salicylate. 13.9 g (0.2mol) of hydroxyl amine was weighed and added to 200cm³ of 10% sodium hydroxide solution and cooled at room temperature. Then 152.3g (0.1mol) of methyl salicylate was added in small portions with vigorous shaking after each addition to ensure complete dissolution. The mixture was allowed to stand for 36 hours. Then it was acidified with 2M sulphuric acid and cooled. The precipitate was filtered, recrystallized from hot water containing a drop of acetic acid, re-cooled and filtered; white precipitate collected and weighed, the yield was 14g.

2.3.2 Preparation of Fe (III), Co (II) and Mn (II) -salicyl hydroxamate complexes

In two separate 100cm³ beakers, 1.53g of salicylhydroxamic acid was weighed and dissolved in 5cm³ ethanol. In another separate beaker, 1.62 g of ferric chloride, 2.9g of cobalt nitrite hexahydrate, and 1.9 g of manganese chloride tetra hydrate were weighed and dissolved with distilled water respectively. The two solutions were mixed using (10%) (NaHCO₃) to raise the pH, the reddish brown, brown and white precipitate was formed for Fe (II), Co and Mn complexes respectively, which were filtered, washed with methanol to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether.

3. Characterization of salicylhydroxamic acid and their metal complexes

3.1 Colour test

0.2 g of salicylhydroxamic acid was dissolved in ethanolic solutions and was added to an aqueous solution of ferric chloride, and the developed color was observed and reported.

3.2 Melting Points of hydroxamic acids

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

3.3 CHN Elemental analysis

Carbon, hydrogen, and nitrogen contents were determined on CHNS/O analyzer

3.4 ¹H NMR spectrum of hydroxamic acids

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

3.5 Infrared spectrum of hydroxamic acids

The infrared spectroscopy (IR) analysis was carried out for salicylhydroxamic acid by using JENWAY FTIR instrument with KBr disc. The spectrum obtained was shown in fig (2) (3) (4) (5).

3.6 wave length and absorption were determined on UV/VIS. spectrophotometer 6505 with printer HP desk jet 640C.

3.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Simultaneous Thermal Analyzer Netzsch STA449 F3 Jupiter. The analysis was carried out under nitrogen gas flow from 20°C to 900°C at a heating rate of 10°C/min.

3.8 Faraday balance (CAHN-7600) Scientific Magnetic Balance was used to determine magnetic Susceptibility.

4. Results and Discussion

4.1 Characterization of salicylhydroxamic acid

(i) The salicylhydroxamic acid was prepared and characterized by its melting point (169°C) conforming with the literature value and by its colours test with iron (III) and cobalt (II), Mn (II) giving reddish brown and brown and white colours respectively.

(ii) Infrared Spectroscopy (IR) of hydroxamic acid

The infrared spectra of absorption bands of ligand SHA shows a strong band at 1614 cm⁻¹ due to (C=O) and 3288 cm⁻¹ due to (O-H) the (C-N) and (N-O) bands occur as a sharp peak in the ranges 1354, 907cm⁻¹ respectively.

(iii) The ¹H NMR spectrum of hydroxamic acids (fig. 1) under investigation shows the characteristic of the proton of the hydroxyl group attached to the nitrogen atom in the region 11.41 – 12.20 ppm, aromatic ring appear in the region 6.82 – 7.83 ppm.

4.2 Characterization of salicylhydroxamic acid metal complexes:

The results of the elemental analysis and physical characteristics of the synthesized compounds are listed in Table 1. The purity of the complexes was confirmed based on the CHN analysis and IR spectrum.

(i) Infrared Spectroscopy (IR) of the complexes:

The differences of the SHA and their metal complexes spectra are being confirmed from Figure 2. Hence, by comparing the ligand and the metal complexes spectrum obtained, From the infrared data shown on Table 2. The shifting of (C=O) to a lower wave number appeared at 1597-1601 cm⁻¹ indicating the involvement of C=O during complexation (13). The involvement of C=O during complexation supported by the appearance of new band M-O at 479-489 cm⁻¹ (14). In addition, Band at 3288cm⁻¹ assigned to (O-H) in SHA disappeared on the metal complexes bands suggesting that -OH are involved during

the complexation. The medium band at 915, 925 and 923cm⁻¹ in, [Co (SHA)₂] H₂O, [Fe (SHA)₂.Cl₂] 2H₂O and [Mn (SHA)Cl. H₂O] H₂O, ascribed to (N-O) (15). The shifting of (C=O) to lower wave number and disappearance of (O-H) in the metal complexes suggesting that the bonding of SHA to the metal salts via oxygen atoms of carbonyl and hydroxyl group.

Table 2: Infrared spectral data for complexes:

Compounds	C=O (cm ⁻¹)	C- N (cm ⁻¹)	N-O (cm ⁻¹)	Pr (OH) (cm ⁻¹)
[Co (SHA) ₂] H ₂ O	1597	1342	915	3323
[Mn (SHA)Cl. H ₂ O] H ₂ O	1601	1312	925	3396
[Fe (SHA) ₂ .Cl ₂] 2H ₂ O	1600	1312	923	3404

Table 1: Physical data for metals complex

Compounds	Molecular Weight	Colour	C	H	N
[Co (SHA) ₂] H ₂ O	383.226	brown	43.87 (44.65)	3.16 (4.36)	7.13 (7.52)
[Mn (SHA)Cl.H ₂ O]H ₂ O	297.	White	30.072 (30.81)	3.6 (2.57)	5.00 (4.96)
[Fe (SHA) ₂ .Cl ₂]2H ₂ O	469.057	Reddish brown	32.37 (35.7)	3.05 (3.01)	5.33 (5.9)

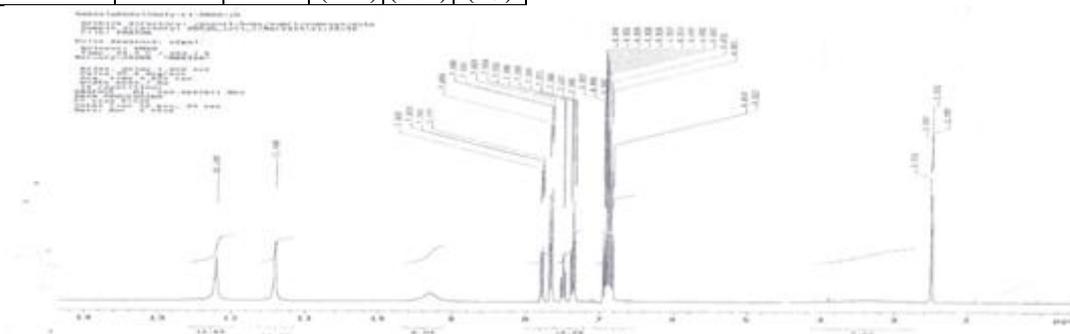


Figure 1: NMR spectra of salicyhydroxamic acid

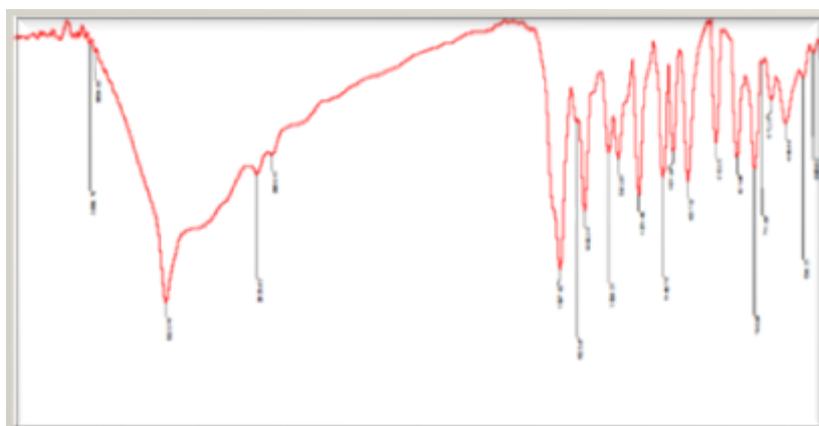


Figure 2: Infrared of Salicylic hydroxamic acid

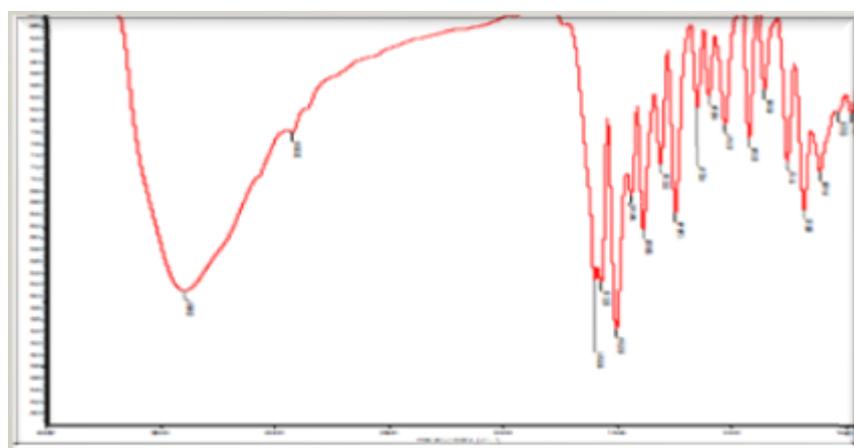


Figure 3: Infrared of Co (II) hydroxamate complex

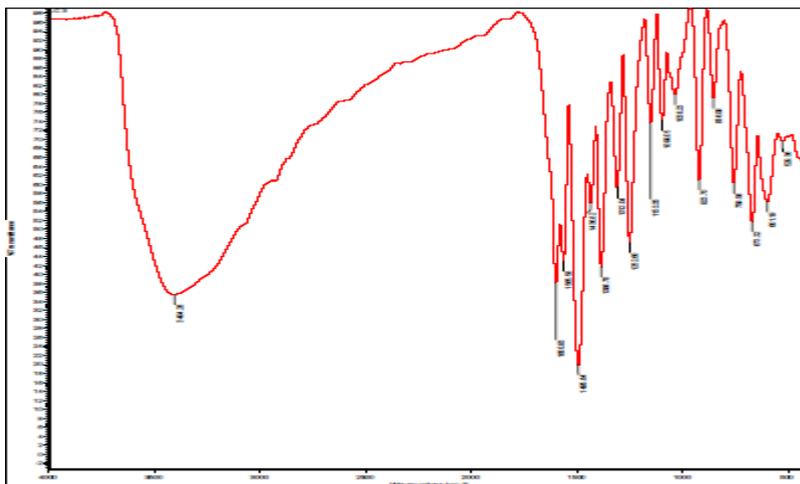


Figure 4: Infrared of Fe (III) hydroxamate complex

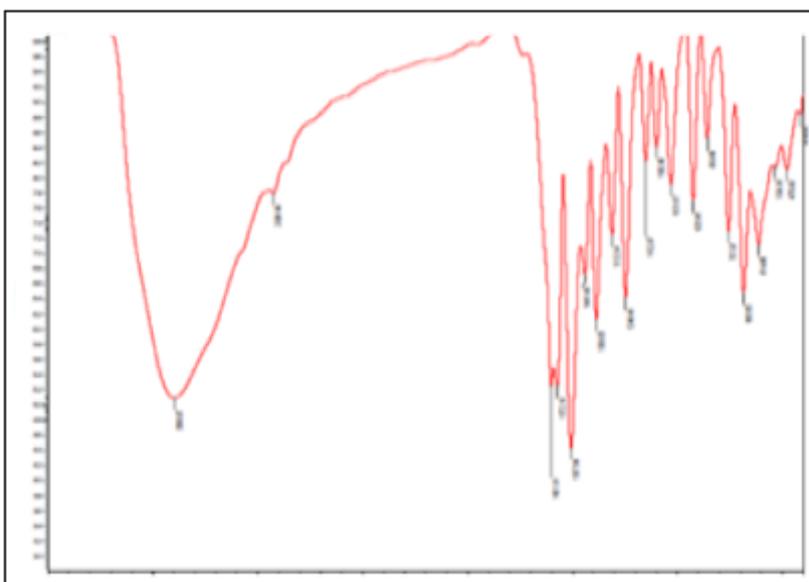


Figure 5: Infrared of Mn (II) hydroxamate complex

(ii) Thermogravimetric analysis (TGA)

The simultaneous TGA analysis of Fe (III), Co (II), Mn (II) complexes were done from ambient temperature to 1000°. The TGA thermograms were shown in Figures 6, 7 and 8. In the Thermogravimetric analysis result of these complexes, the mass loss occurred in two to three stage until the complex is destroyed and the metal oxide is formed. In Mn (II) complexes there is a relatively small mass change (6 %) start before 100 C° due to loss of moisture and the solvent, the first degradation step in the range 100—240 C° due to loss (11.6 %) of hydration water and coordinated water. dehydration take place and molecules of crystallization water were eliminated. for this complex the second step decomposition took place around 240 -500C° (50%) deterioration of the chloride and hydroxamic acid molecule.

and the last decomposition step of complexes in the range of 500 -900C° due to formation of MnO. Fe (III) the first degradation step in the range 100—240 C° due to loss (13.53 %) of two molecule hydration water, for this complex the second step decomposition took place around 240 -500C° (56%) deterioration of the chloride and hydroxamic acid molecule. and the last decomposition step of complexes in the range of 500 -900C° due to formation of Fe₂O₃. Co (II) the first degradation step in the range 100—240 C° due to loss (4. %) of hydration water, for this complex the second step decomposition took place around 240 -500C° (56%) deterioration of the chloride and hydroxamic acid molecule. and the last decomposition step of complexes in the range of 500 900C° due to formation of cobalt oxide.

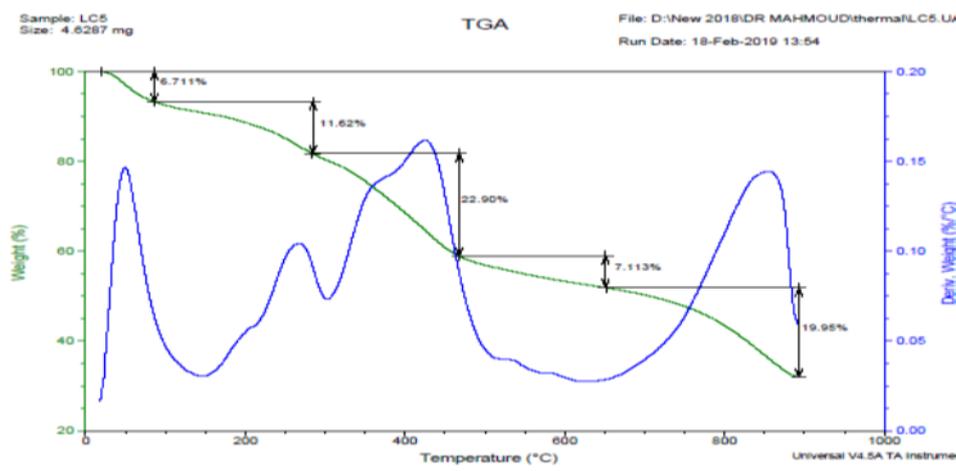


Figure 6: TGA of Mn (II) hydroxamate complex

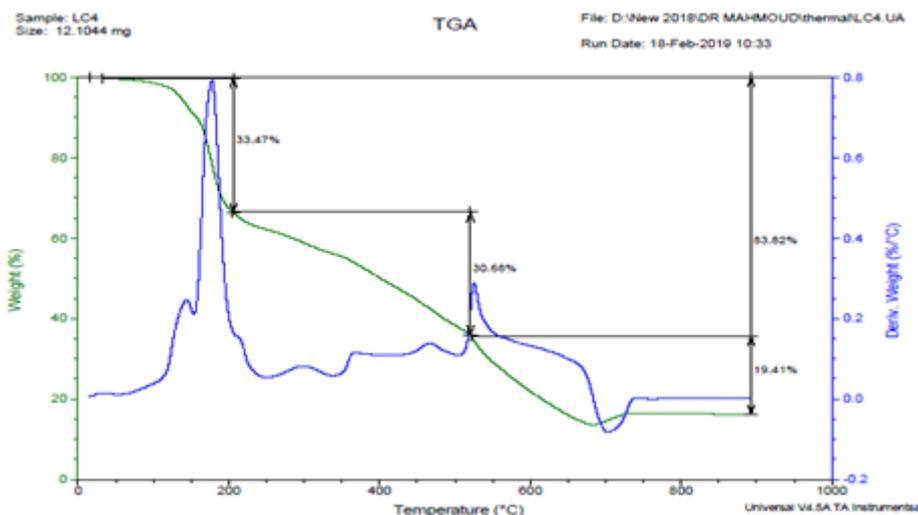


Figure 7: TGA of Co (II) hydroxamate complex

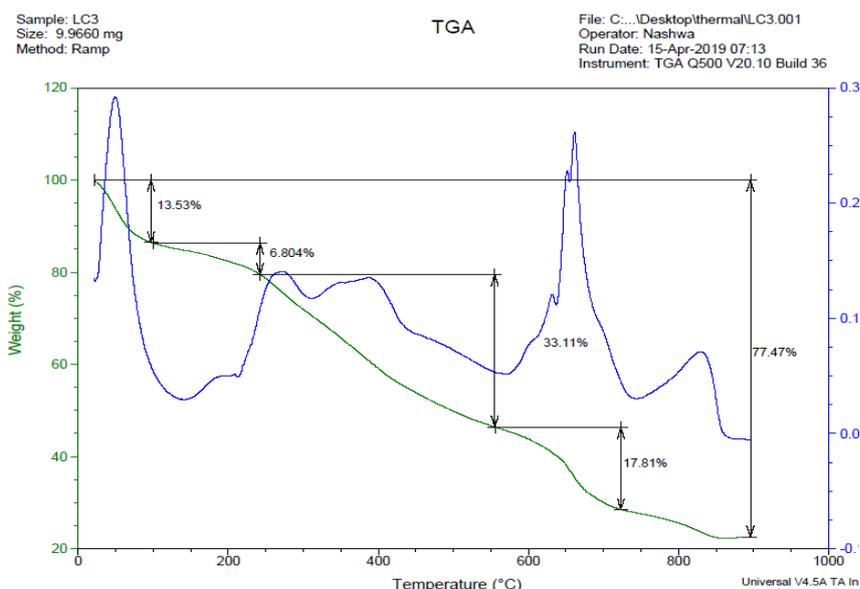


Figure 8: TGA of Fe (III) hydroxamate complex

(iii) Magnetic Moment

Since the Fe (III), Co (II) and Mn (II) complexes are paramagnetic, The magnetic susceptibility value of Fe (III), Co (II) and Mn (II) complexes are 6, 1.8 and 6.8. B.M., respectively. Octahedral geometry was proposed for [Fe

(SHA₂)₂.Cl₂] 2H₂O and tetrahedral for [Co (SHA)₂] H₂O. Square pyramidal geometry was proposed for [Mn (SHA)Cl.H₂O]H₂O referred to the value obtained from the magnetic susceptibility balance (16)

5. Conclusion

At the present work Preparation, and characterization of Salicylhydroxamic acid and its complexes with iron (III), cobalt (II) and manganese (II) was studied. salicylhydroxamic acid had been prepared by the reaction of methyl salicylate and free hydroxylamine and was characterized using its melting point, FT-IR Spectroscopic and ^1H NMR spectrum. Iron (III), cobalt (II) and manganese (II) salicylhydroxamate complexes were prepared by reacting salicylhydroxamic acids with corresponding metal salts. The compounds were characterized using elemental analysis, spectral (infrared, UV-Vis), TGA and magnetic susceptibility. The purity of the complexes was confirmed by CHN analysis. The spectral study analysis reveals that all complexes coordinated to the metal via oxygen atoms (O, O) in bidentate to form octahedral for $[\text{Fe}(\text{SHA})_2\text{Cl}_2]2\text{H}_2\text{O}$, tetrahedral for $[\text{Co}(\text{SHA})_2]\text{H}_2\text{O}$ and square pyramidal geometry for $[\text{Mn}(\text{SHA})\text{Cl}.\text{H}_2\text{O}]\text{H}_2\text{O}$.

References

- [1] Lipczynska-kochany.E, The photolability of hydroxamic acids and its importance to the human environment; J. The Science of the Total Environment, (1991).100, 469-482.
- [2] Yale, H. L., "The hydroxamic acids" Chem. Rev. Shell Development Company, California, 209 (1943).3. Sandler, S. R. and Kara, W., "Organic functional groups preparation, Academic Press, London (1972).
- [3] Sandler, S. R. and Kara, W., "Organic functional groups preparation" Vol. 3, Academic Press, London (1972).
- [4] Agrawal Y, Patel S. Hydroxamic acids: reagents for the solvent extraction and spectrophotometric determination of metals. Reviews in analytical chemistry.1980; 4:237-278.
- [5] Randa, B. A., Elmugdad, A. A., (2016), Stoichiometry Study of Iron and Vanadium Salicylhydroxamate Complexes, SUST Journal of Natural and Medical Sciences (JNMS) vol. 18 (2) 2017
- [6] Rehab A, Elmugdad AA, A Azize ME, (2018) (Preparation, and analyses of cinnamon hydroxamic acid and its complexes with iron (III) and vanadium (V), International Journal of Multidisciplinary Research and Development, 5 (11): 16-21.
- [7] Ehsan AA, Elmugdad AA, Dalia MO, (2020) Study of the stoichiometry of iron and vanadium nitrobenzohydroxamate complexes International Journal of Multidisciplinary Research and Development, 7 (3):86-90.
- [8] Ehsan AA, Elmugdad AA, Dalia MO, (2020) Preparation, characterization of N: Phenyl B: Nitrobenzohydroxamic acid and its iron (III) and copper (II) complexes, International Journal of Multidisciplinary Research and Development, 7 (3): 91-96
- [9] Nehal FA Mohammed, El mugdad AA, Ahmad EEM, (2020) Synthesis and characterization of hydroxamated polyacrylamide, International Journal of Multidisciplinary Research and Development, 6 (12):131-135
- [10] Chatterjee, B., "Donor properties of hydroxamicacids" Coordination Chemistry Review, Elsevier Scientific Publishing Company, Amsterdam (1978).26, 281-303.
- [11] Barbara, K., Henry, K. and Etelka, F., "hydroxamicandaminohydroxamic acids and their complexes with metal ions"Coordination Chemistry Review, Elsevier Science Publishers B.V., Amsterdam (1992)114, 169-200.
- [12] Kirk, O., "Encyclopedia of chemical technology" ³rd. edn. vol. 2, John Wiley and Sons, New York (1978).
- [13] Shankar, B., R. Tomar, R. Kumar, M. Godhara, and V. K. Sharma. Antimicrobial Activity of Newly Synthesized Hydroxamic Acid of Pyrimidine-5-carboxylic Acid and Its Complexes with Cu (II), Ni (II), Co (II) and Zn (II) Metal Ions. *Journal of Chemical and Pharmaceutical Research*.2014. 6 (5): 925-930.
- [14] Shotor, S. N. M., K. Kassim, H. Bahron, A. M. Tajuddin, F. Z. Yusof, C. J. Marmion, and N. F. Rajab. 2010. *In-Vitro* Cytotoxicity Studies of Vanadyl Complexes with Hydroxamic Acid Series. *International Conference on Science and Social Research (CSSR)*.Kuala Lumpur, Malaysia. 5-7 2010.doi: 10.1109/CSSR.2010.5773735.
- [15] Haratake, M., M. Fukunaga, M. Ono, and Nakayama, M. Synthesis of Vanadium (IV, V) Hydroxamic Acid Complexes And in Vivo Assessment of Their Insulin-Like Activity. *Journal of Biological Inorganic Chemistry*. 2005.10 (3): 250-258.doi: 10.1007/s00775-005-0634-8.
- [16] Vanco, J., J. Marek, Z. Travnicek, E. Racanska, J.Muselik, and O. Svajlenova. Synthesis, Structural Characterization, Antiradical and Antidiabetic Activities of Copper (II) and Zinc (II) Schiff Base Complexes Derived from Salicylaldehyde and b-alanine. *Journal of Inorganic Biochemistry*.2008. 102 (4): 595-605.