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Preparation, and analyses of cinnamon hydroxamic acid and its complexes with iron (III) and vanadium (V)

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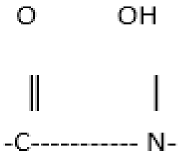
Abstract
Cinnamon hydroxamic acid had been prepared by coupling reaction of methyl cinnamate and free hydroxylamine and was characterized by melting point. (145 ºC), iron and vanadium color test, FT-IR characteristics spectral bands at 3260cm^{-1} (OH),1663 cm^{-1} (C=O) and 900 cm^{-1} (N-O). The ^{1}H NMR spectrum shows the characteristic attachment of the proton of the hydroxyl group to the nitrogen atom in the region 9.045 – 9.229 ppm, the shift of the resonance signal of hydroxyl proton to lower field to support intermolecular hydrogen bonding, the appearance of protons of aromatic ring in the region 7.071 – 8.32 ppm, and the appearance of protons of – CH_3 group in the region 2.322 – 2.346 ppm. The ^{13}C NMR spectra exhibit absorption signal due to carbonyl (C=O) nearly 165 ppm. The chemical shifts of aromatic carbons appear in the region 123.43 – 149.21 ppm. Beside these signals, a singlet signal nearly 21 ppm appeared which corresponding to carbon atom of alkyl group. Iron (III) and vanadium (V) cinnamon hydroxamate complexes were prepared by reacting cinnamon hydroxamic acids with corresponding metal salts at pH 3 media. Showing the characteristic colors. They show absorbance at a wavelength of maximum (λ_{max}) 480nm, 520 nm for Fe^{3+},V^{5+} complexes respectively indicating that the metal ligand complexes were formed from both. The complexes were characterized by FT-IR characteristics spectral bands at cm^{-1} (OH),1663 cm^{-1} (C=O) and 900 cm^{-1} (N-O), the ^{1}H NMR spectrum of Fe (III) cinnamon hydroxamate complexes showed the characteristic at7.2-7.3 the appearance of protons of – CH_3 group, and ^{1}H NMR spectra of V (V) - cinnamon hydroxamate complexes in under investigation showed the characteristic at 6,7.5-8. 4 due to the protons of aromatic ring appear in the region.
The^{13}C NMR spectra exhibit absorption the chemical shifts of aromatic carbons appear in the region 122.7 – 139.21 ppm.

Keywords: intermolecular, cinnamon hydroxamic acid, resonance, chemical shifts, coupling

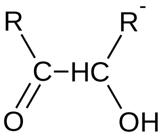
1. Introduction

Hydroxamic acids are known at have the bidentate functional group [1].



$$-\overset{\overset{O}{\|}}{C}\text{-----------}\overset{\overset{OH}{|}}{N}-$$

This functional group makes complexes with different metal ions and forms a family of chelating agents. They have the general formula:



Where R and R` could be hydrogen, alkyl or aryl group.

Hydroxamic acids are important chelating agents having complexing ability towards a very great number of metal ions. They have been known for more than a century. They belong to a group of organic compounds, which are derived from hydroxylamine. They are known compounds having the bidentate functional grouping. They form a family of chelating reagents, which are used in colorimetry.

Hydroxamic acids are weak organic acids used as commercial flotation

reagents in extractive metallurgical, inhibitors for copper corrosion.

Most hydroxamic acids will be hydrogen bonded and exist in the keto form, bonded to a transition metal through the oxygen atom. They have been classified into three groups: primary hydroxamic acid, secondary hydroxamic acid and cyclic hydroxamic acid.

Hydroxamic acids have particular affinities for ‘hard’ cations such as Fe (III), Np (IV), and Pu (IV) [2, 3], which they form five-membered chelate rings. On acid hydrolysis of free hydroxamic acids, hydroxylamine and the parent carboxylic acid are formed [4]. Metal ions bound to hydroxamates also hydrolyze [5].

The chelating ability of hydroxamic acids has been used to link pharmaceutically useful ions such as radioactive or paramagnetic ions to monoclonal antibodies that direct the ion to a desired target tissue for tumor or tissue imaging or therapy purposes. The use of hydroxamate coordination polymers as molecular magnets [6] has also been explored [7]. Owing to all these applications, the coordination chemistry of hydroxamates has evoked much interest [8, 9, 10].

The main goal 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 vanadium (V)

2. Materials and Methods

2.1 Materials

Hydroxylamine hydrochloride, cinnamic acid ethanol (EtOH), methanol (MeOH), ferric chloride hex hydrate, ($FeCl_3.6H_2O$)] and ammonium metavandategrade), sulphuric acid,, sodium hydroxide pellets (NaOH), sodium hydrogen carbonate ($NaHCO_3$), glacial acetic acid, diethyl ether, were obtained from CDH chemical Ltd, Chaina (all chemicals were analytical grade)

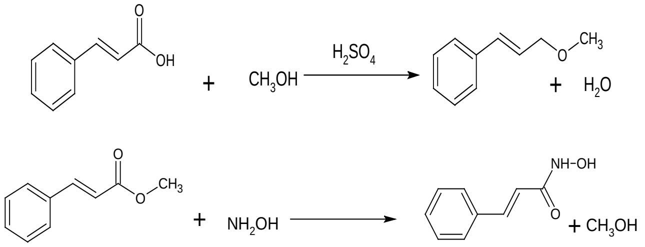
2.2 Instruments

Electrical balance, (A and D company, Ltd CE Germany). FTIR 300 spectrometer with KBr disc, (Shimatzu. Japan), UV/VIS. spectrophotometer 6505 with printer HP desk jet 640C, (Jenway, England).Melting point electrical, type (Gallenkamp, England), serial No. MFB, 600.100F, APP.NO2CO117, pH meter Model 3030 (Jenway, England).

2.3 Methods

2.3.1 Preparation of the cinnamon hydroxamic acid

The ligand was prepared in two simple steps, step one the reaction of cinnamic acid with methanol and step two by the coupling reaction of hydroxylamine and methyl cinnamate as shown in Scheme 1.



Scheme 1 Preparation route for cinnamon hydroxamic acid

14 g (0.1mol) hydroxyl amine was weighed and added to 200cm^3 of 12% sodium hydroxide solution and cooled to room temperature. Then16.2g (0.1mol) of methylcinnamate was added in small portions with vigorous shaking after each addition to ensure complete dissolution. The mixture was allowed to stand for two days. Then it was acidified with2M sulphuric acid (litmus paper) and coolest in an ice – bath at 0 ^{0}C. The precipitate was filtered, recrystallized from hot water containing a drop of acetic acid, filtered and recooled in an ice – bath at 0 ^{0}C as white precipitate collected and weighed giving 5g (60%).

2.3.2 Preparation of Fe (III) and V (V) - cinnamon hydroxamate complexes

In two separate 100cm^3 beakers, 1g of cinnamon hydroxamic acid was weighed and dissolved in 5cm^3 ethanol. In another separate beaker, 0.29 g of ferric chloride, and 0.229 g of ammonium Meta vanadate were weighed and dissolved with distilled water. The two solutions were mixed, their pH was adjusted, with pHmeter using (5%) sodium hydroxide until the pH became 3 for iron (III)- cinnamon hydroxamate and 5for vanadium(V)- cinnamon hydroxamate complexes, and then cooled in an ice – bath at 0 ^{0}C. The dark violet precipitate crystals were filtered, washed several times with 50% (v/v) methanol-water to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether, dried in desiccator over $Cacl_2$, collected and weighed to giving 5g and8g, respectively.

2.3.3 Characterization of cinnamon hydroxamic acid

2.3.3.1 Spot test

Ethanolic solutions of cinnamon hydroxamic, were added to an aqueous solutions of ferric chloride, vanadium salt sparate. The two solutions of hydroxamic acids were thoroughly mixed and transferred to a watch glass for air dryness.

2.3.3.2 Melting Points of hydroxamic acids

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

2.3.3.3 Infrared spectrum of hydroxamic acids

The infrared spectroscopy (IR) analysis was carried out for cinnamon hydroxamic acidby using JENWAY FTIR instrument with KBr disc. The spectrum obtained is shown in fig (1) (4), (5).

2.3.3.4 ^{1}H NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (1H NMR) analysis was carried out for Cinnamon hydroxamic acid and Fe (III)-, V (V) - cinnamon hydroxamate complexes by using instrument. The spectrum obtained is shown in fig (2), (6), (7), respectively.

2.3.3.4 ^{13}C NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (13C NMR) analysis was carried out for Cinnamon hydroxamic acid and Fe (III)-, V (V) - cinnamon hydroxamate complexes by using instrument. The spectrum obtained is shown in fig (3), (8), (9), respectively.

3. Results and Discussion

3.1 Characterization of cinnamon hydroxamic acid

i) The cinnamon hydroxamic acid was prepared and identified by its melting point (114°C) conforming with the literature value and by its colours spot test with iron(III) and vanadium(V) giving red and violet colours respectively
ii) The of the prepared ligand Infrared spectral data are shows characteristic absorption bands at 3260 cm^{-1} due to O-H stretching vibration, 1663 cm^{-1} is assigned for the C=O of hydroxamic acid group, A sharp band at 900 cm^{-1} attributed to N-O by stretching vibration(fig.1).
iii) The ^{1}H NMR spectrum of hydroxamic acids (fig. 2) under investigation shows the characteristic of the proton of the hydroxyl group attached to the nitrogen atom in the region 9.045 – 9.229 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 7.071 – 8.32 ppm. The protons of – CH_3 group appear in the region 2.322 – 2.346 ppm.

iv) The ^{13}C NMR spectra (fig. 3) exhibit absorption signal due to carbonyl (C=O) nearly 165 ppm. The chemical shifts of aromatic carbons appear in the region 123.43 – 149.21 ppm. Beside these signals, a singlet signal nearly 121 ppm appeared which corresponding to carbon atom of alkyl group.

3.2 Characterization of Fe (III)-, V (V) - cinnamon hydroxamate complexes

i) IR spectrum(KBr); the spectra showing absorption bands(fig. 4,5) : 3176.54 cm^{-1} due to O-H stretching vibration, 1639cm^{-1} is assigned for the C=O of hydroxamic acid group, A sharp band at 970 cm^{-1} attributed to N-O by stretching vibration. The band at 756 cm^{-1} attributed to C-N.

ii) The ^{1}H NMR spectra of Fe (III) cinnamon hydroxamate complexes in (fig. 6) showed the characteristic at7.2-7.3, and ^{1}H NMR spectra of V (V) - cinnamon hydroxamate complexes in (fig. 7) under investigation showed the characteristic at 6, 7.5-8. 4 due to the protons of aromatic ring appear in the region

iii) The ^{13}C NMR spectra exhibit absorption (8,9) the chemical shifts of aromatic carbons appear in the region 122.7 – 139.21 ppm.

4. Conclusion

The complexes of cinnamon hydroxamic acid with Fe (III) and V (V) were successfully prepared and characterized. The complexes of iron (III) was accomplish by displacement of hydrogen o O-NH group of cation NOH by the cation forming a five member ring of stable iron (III) cinnamon hydroxamate

The finding of the study has shown that the optimal condition for formation of Fe (III) and V(V) complexes with cinnamon hydroxamic acid were at pH5 and pH3.

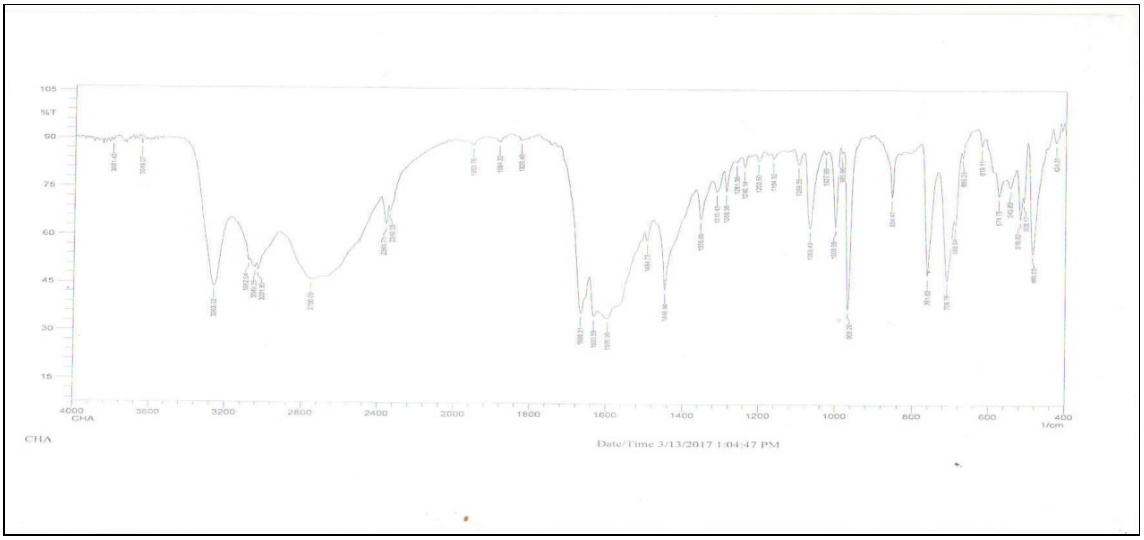


Fig 1: Infrared of cinnamon hydroxamic acid

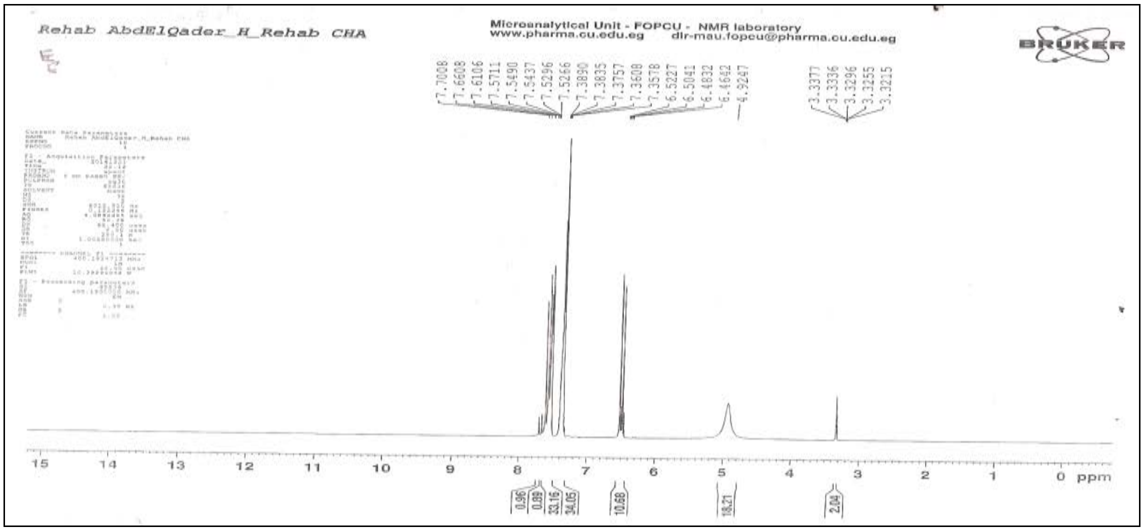


Fig 2: ^{1}HNMR of cinnamon hydroxamic acid

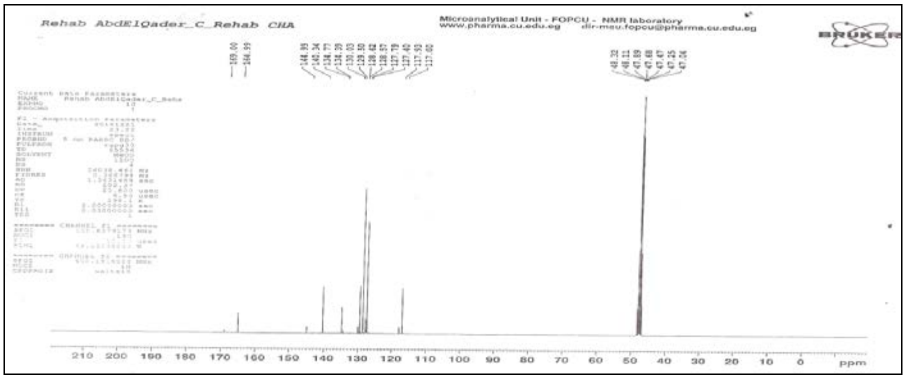


Fig 3: ^{13}C of cinnamon hydroxamic acid

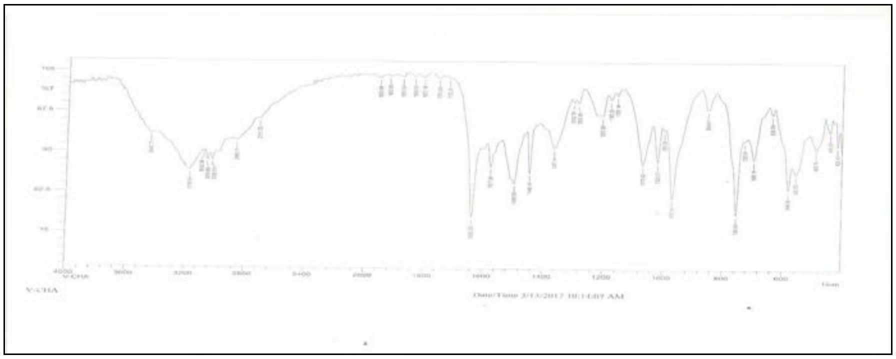


Fig 4: Infrared of V (V) - cinnamon hydroxamatecomplex

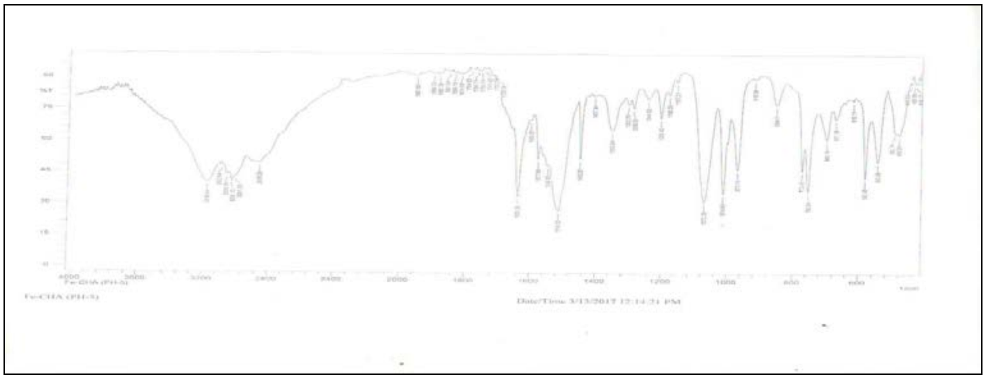


Fig 5: Infrared of Fe (III) - cinnamon hydroxamate complex

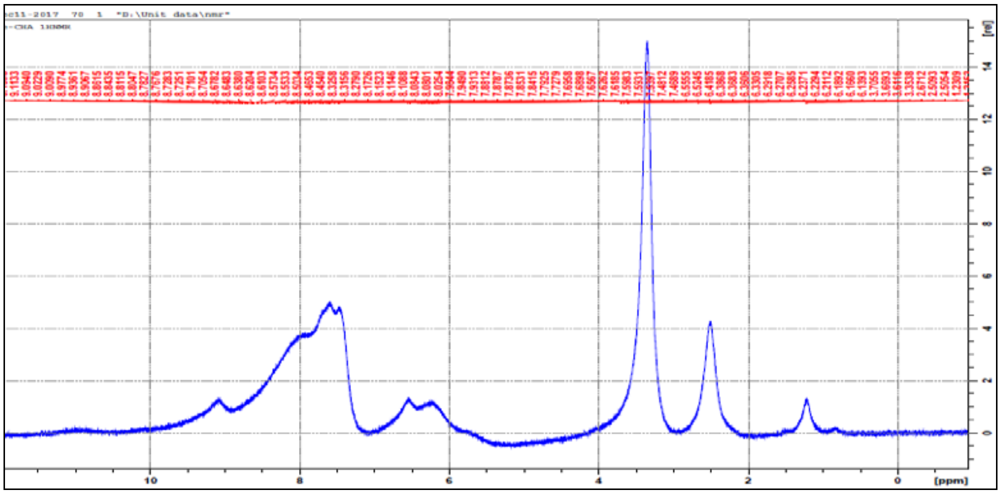


Fig 6: ^{1}HNMR of Fe (III) - cinnamon hydroxamate complex

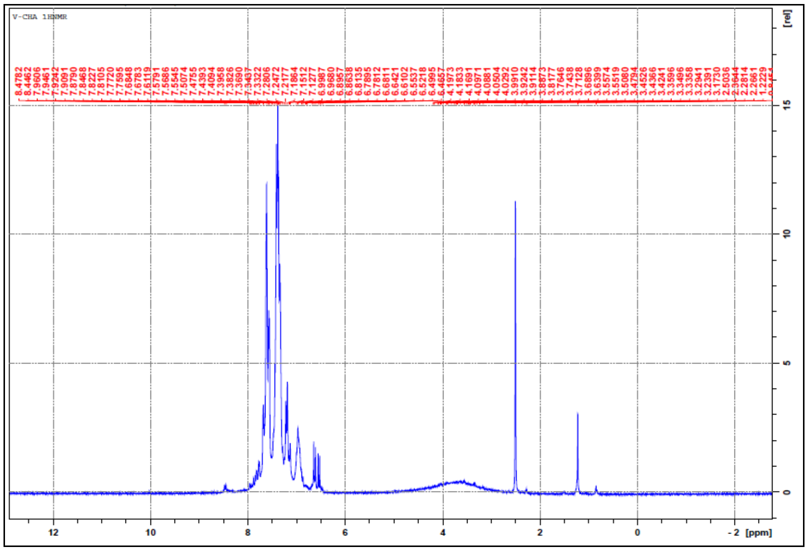


Fig 7: ^{1}HNMR of V (V) - cinnamon hydroxamate complex

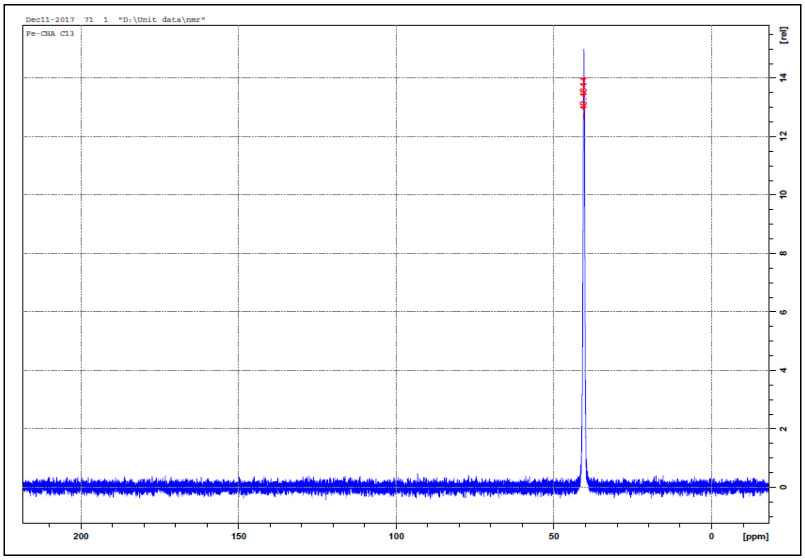


Fig 8: ^{13}C of Fe(III) - cinnamon hydroxamate complex

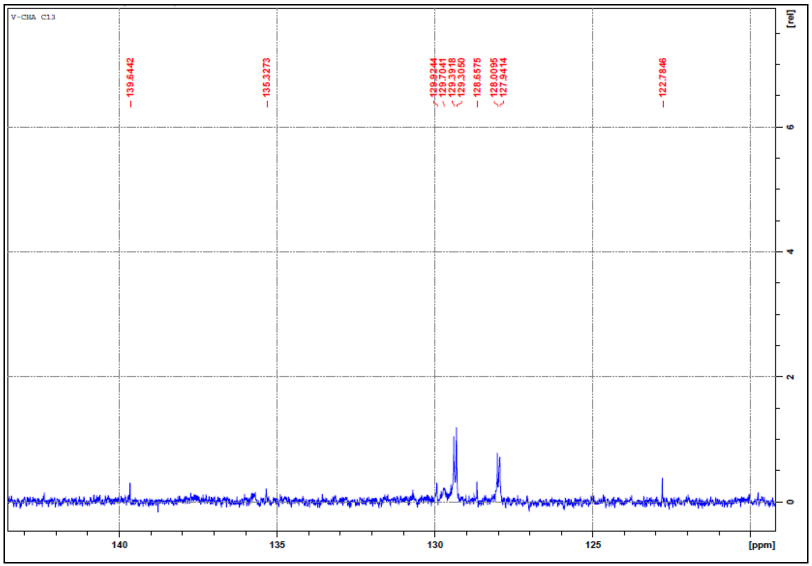


Fig 9: ^{13} C of V (V) - cinnamon hydroxamate complex

5. Acknowledgment

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