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Synthesis and Characterization of Cr (III)-Ascorbic acid Complex

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ABSTRACT: Ascorbic acid is a powerful antioxidant because of its ability to eliminate free radicals generated by the body. The ability of this compound to protect the body cells and its components from radicals has been proven. In this work, a complex of Cr (III) ascorbate was synthesized through the reaction of ascorbic acid and Chromium (III) chloride. The nature of the coordination between chromium ion and ascorbic acid was studied. The complex was characterized by UV-Visible, Infrared and ^{1}H NMR spectroscopy. The yield, melting point and solubility of the complex were determined. The solubility parameter suggested that the complex is mildly polar. Electronic spectrum of the complex showed ligand to metal charge transfer (LMCT) and d-d transition. FTIR spectrum of the complex showed a shift to lower frequency for C=O and OH functional groups. Spectroscopic characterization suggested the involvement of carbonyl and 2 hydroxyl group of ascorbic acid ligand in coordination with chromium (III) ion to form the complex. A tridentate geometry was proposed for the complex based on the spectroscopic studies. The Ascorbic acid behaved as a bidentate ligand towards Cr (III) ion. Finally, the ability of ascorbic acid to extract Cr (III) ions from environment or biological system is hereby assured.. The application of ascorbic acid in Cr chelation therapy is hereby recommended.

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Metals have an esteem place in medicinal chemistry. Transition metals represent the d-block elements which fall in between groups 3-12 on the periodic table. A characteristic of these metals is that they easily lose electron to form positively charged ions which tends to be soluble in biological fluids. It is in the cationic form that metals play their role in biology (Saddam *et al.*, 207). The broad range of coordination numbers and geometries, available redox states, thermodynamic and kinetic characteristic of cationic metal ions and ligands offer the medicinal inorganic chemist a large variety of reactivities to be exploited. Among the natural sciences, medicinal inorganic chemistry is still considered a young discipline by many, but this is contrary to the historically proven use of metals in pharmaceutical potions, which traces back to the ancient civilization of Mesoptamia, Egypt, India and China (Orvig and Abram, 1999; Thompson and Orvig, 2006). However, a wide range of biological activities such as antibacterial, antifungal, antitumor, antiviral and antioxidant activities are exhibited by organic compounds and their metal complexes (Otuokere *et al*., 2021; Otuokere and Robert, 2020; Otuokere *et al*., 2020; Otuokere and Amadi, 2017; Otuokere *et al*., 2017; Sokwaibe and Otuokere, 2016;Onyenze *et al*., 2016). Chromium is widely used in many industries. Some of these industries include electroplating, pulp producing, water cooling, tanning, as well as ore and petroleum refining industries. It exists in two stable oxidation states, that is, Cr (III) and Cr (VI) ions. Cr (VI) ion is considered more toxic relative to Cr (III) ion. Thus, Cr (VI) exerts many harmful effects in human. It induces cancer and mutation in living cells, damages DNA protein cross-links and causes the single-strand breaks. On the other Cr(III) is relatively less or non-toxic, hence it is listed as an essential element for good health, as well as nutritious to many organisms (Park *et al*., 2008; Aroua *et al*., 2007). Recently, Cr (III) oxidation toCr (VI) in biological systems came into consideration as a possible reason of antidiabetic activities of some Cr (III) complexes. The specific interaction of Cr(III) ions with cellular insulin receptors are caused by intra or extracellular oxidations of Cr(III) to Cr(VI)

compounds, which act as protein tyrosine phosphatase (PTP) inhibitors (Ewais *et al*., 2009). Chromium is also essential for metabolism of higher animals; for example, impaired carbohydrate metabolism seen Chromium-deficient humans can be corrected by administration of small amount of the metal. Cr (III) is identified and partially characterized as the glucose tolerance factor (GTF) believed to be essential for the normal disposition of glucose loads (Gabriel and Salifoglou, 2005). Meanwhile, research has proven that coordination of Cr(III) ion and other antioxidant bioactive ligands such as morin exhibited a more powerful antioxidant activity compared tomorin molecule alone Qadeer, and Shahabuddin, 2014).

Ascorbic acid or Vitamin C is a naturally occurring organic compound with antioxidant properties found in both plants and animals. It functions as a redox buffer which can reduce, and thereby neutralize reactive oxygen species (Fadime, 2017). Ascorbic acid is a potent reducing agent and scavenger of free radicals in biological systems Duarte and Lunec, 2005). It is involved in the first line of antioxidant defense, protecting lipid membranes and proteins from oxidative damage. As a water soluble molecule, ascorbic acid can work both inside and outside the cells, and can neutralize free radical and prevent cell damage. It is an excellent source of electrons for free radicals that are seeking electron to regain their stability. It tends to donate electrons to free radicals and quench their reactivity (Rouhier *et al*, 2008; Bindhumol *et al*., 2003). In addition, it has been demonstrated that coordination of metals like Pt (II) ion and ascorbic acid showed an improved pharmaceutical activity and reduced toxic effects (Malcolm *et al*., 1999).The chemical structure of ascorbic acid is shown in Figure 1

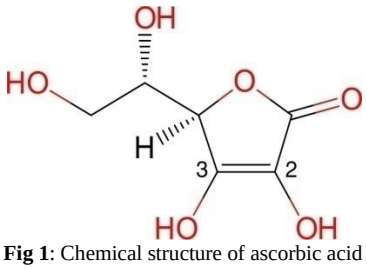


Fig 1: Chemical structure of ascorbic acid

Considering the brilliant properties presented by both Cr (III) ion and ascorbic acid, it becomes interesting to note that to the best of our knowledge that the report on coordination behavior of Cr (III)towards ascorbic acidis scanty. Therefore, the present study is aimed at synthesizing, characterizing Cr (III)-Ascorbic acid Complex

MATERIALS AND METHODS

Materials: All chemicals used for this study were of analytical grade and were used without further purification. The metal salt, chromium (III) chloride, ascorbic acid were obtained from British Drug House Chemical limited, poole, England. Both reagents were weighed with an accuracy of ±0.0001g. The UV/Visible spectroscopy of ascorbic acid and its chromium complex were evaluated in the range of 200 – 800nm using a UV/Visible spectrophotometer (Labomed Incorporated). The Infrared spectra were recorded on an Agilent Cary 630 FTIR Spectrophotometer. The ^{1}HNMR spectra were recorded on an Agilent 400mHz NMR spectrophotometer.

Synthesis of Chromium (III) ascorbic acidcomplex: 17.613g (0.1mol) of ascorbic acid was dissolved 100ml of distilled water. After 5 minutes of continuous stirring, 250ml of absolute (99.5%) ethanol was added to the solution of 15.840g of chromium (III) chloride whichwas then added to the ascorbic acid solution and stirred continuously for 25minutes. The mixture was allowed to settle for 24 hours and the decanted to separate the colourless upper layer from the settled precipitate. The precipitate was placed in the water bath for 1 hour, after which it was completely dried in a desiccator. After drying, the dark grey coloured chromiu (III) ascorbate complex was weighed. The yield was recorded.

RESULTS AND DISCUSSION

The results of the physical properties, UV-Visible, IR spectral and proton NMR spectral data of ascorbic acid and its chromium (III) complex are shown in Tables 1, 2, 3 and 4 respectively. The UV-Visible, IR and proton NMR spectral of ascorbic acid and its chromium (III) complex are shown in Figures 2a,2b,3a, 3b, 4a and 4b respectively.

Table 1: Colour, yield, melting point and solubility of ascorbic acid and its Cr(III) complex

Ligand/complex	Melting Point (°C)	Colour	Solubility				Yield (%)
			Ethanol	Acetic acid	Hexane	H_2O	
Ascorbic acid	190	White	Sparingly soluble	Sparingly soluble	insoluble	Soluble	-
Cr(III) ascobate Complex	110	Dark Grey	Insoluble	Sparingly soluble	Insoluble	Slightly soluble	83

The change in colour from white to dark grey reported in Table 1 suggested the formation of complex because transition metal complexes are coloured.The melting point of the ligand was 190 ℃ while that of

the chromium (III) complex was 110℃. This decrease in melting point is an indication that co-ordination has taken place (Narendra and Parashuram, 2017).The ligand was soluble in water, sparingly soluble in acetic acid and insoluble in non-polar solvents such as hexane as shown in Table 1. On the other hand, the complex was only slightly soluble in water, sparingly soluble inacetic acid but remains insoluble in non-polar solvents. This entails that both ascorbic acid and its chromium (III) complex are polar but the complex is less polar than the ligand.

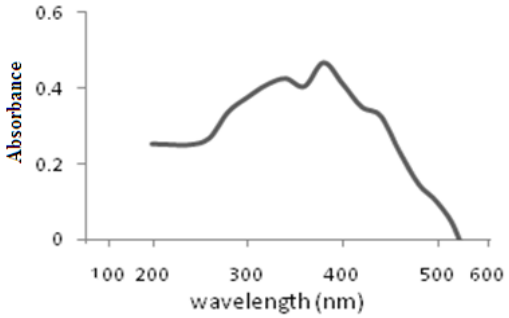


Fig 2a: Electronicspectrum of Ascorbic acid

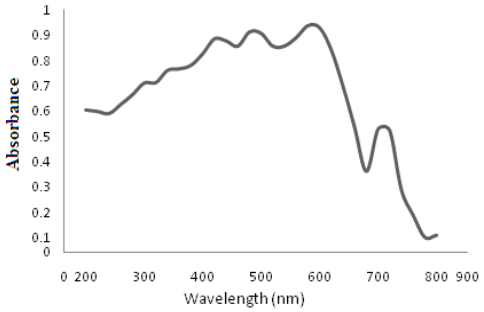


Fig 2b: Electronic spectrum of Cr (III) ascorbatecomplex

The absorbance maxima at wavelength 320 and 360nm was attributed to the transition (n - π*). This suggested that the non-bonding (n) lone pairs of electrons in the oxygen of the keto-group in the ligand was involve in transition. This is otherwise regarded as intra-ligand charge transfer (ILCT). The band at 420, 480, and 580nm in the chromium (III) complex spectrum was assigned to ligand-metal charge transfer (LMCT) (Narayanachar *et al*., 2013). This band suggested that coordination actually occurred. Finally, the band that appeared at 720nm was attributed to d-d transition which is of E-T_2 type from Orgel diagram. This is also suggestive of a tetrahedral geometry (Lever, 1984).

Table 2: Electronic/absorption spectra data of Ascorbic acid and its chromium (III) complex

Ligand/complex	Solvent	Wavelength (nm)	Assignment
Ascorbic acid	Water	320	ILCT (n - π*)
		360	ILCT (n - π*)
Cr(III) ascobate complex	Water	300	ILCT (n - π*)
		340	ILCT (n - π*)
		420	LMCT
		480	LMCT
		580	LMCT
		720	E-T_2

ILCT = Intra-ligand charge transfer, LMCT = ligand-Metal charge transferE-T_2 (d-d transition from Orgel Diagram)

The IR spectra provided valuable information on the nature of functional group of the synthesized metal complex. The spectrum of the ligand which showed C=O band in the region 1751.8 cm^{-1} was shifted to lower frequency region in the spectrum of the chromium(III) complex (1740 cm^{-1}) indicating that co-ordination has taken place (Nakamoto, 1997). The above shift can be attributed to increase in electron density which leadto the increase of the C=O bond length and consequently slowed down the vibration frequency. This observation is consistent with the Dewar-Chatt model of bonding in metal carbonyls (Onyenze *et al*., 2016). The observation of a peak at 3406.8 cm^{-1} in the ascorbic acid spectrum is assigned to OH functional group.

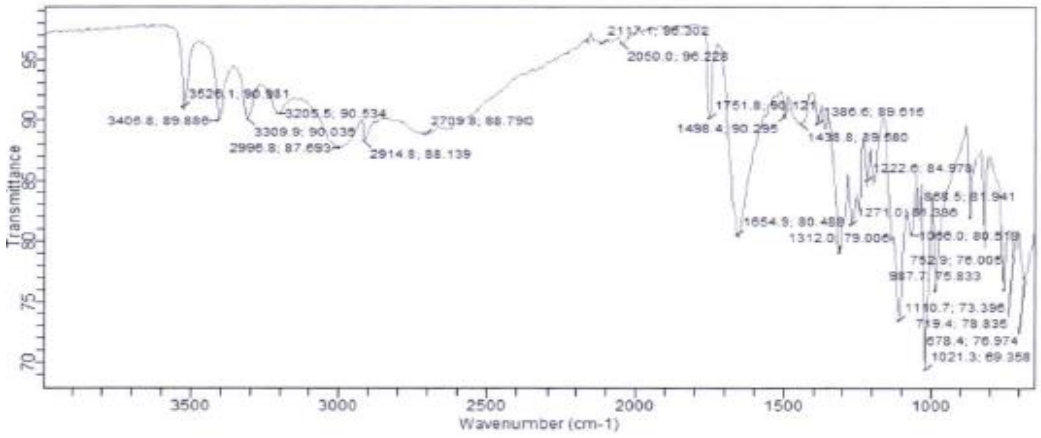


Fig3a: FT-IR spectrum of Ascorbic acid

Table 3: Selected infrared spectral data of ascorbic acid and its chromium (III) complex

	Frequencies (cm^{-1})				
Ligand/complex	OH Stretch	C=O Stretch	C-O Stretch	C=C Stretch	CH_2Stretch
Ascobic acid	3406.8	1751.8	1066.0	1498.4	1386.6
Cr(III) ascobate	3354.6	1740.0	1066.0	1498.4	1360.4

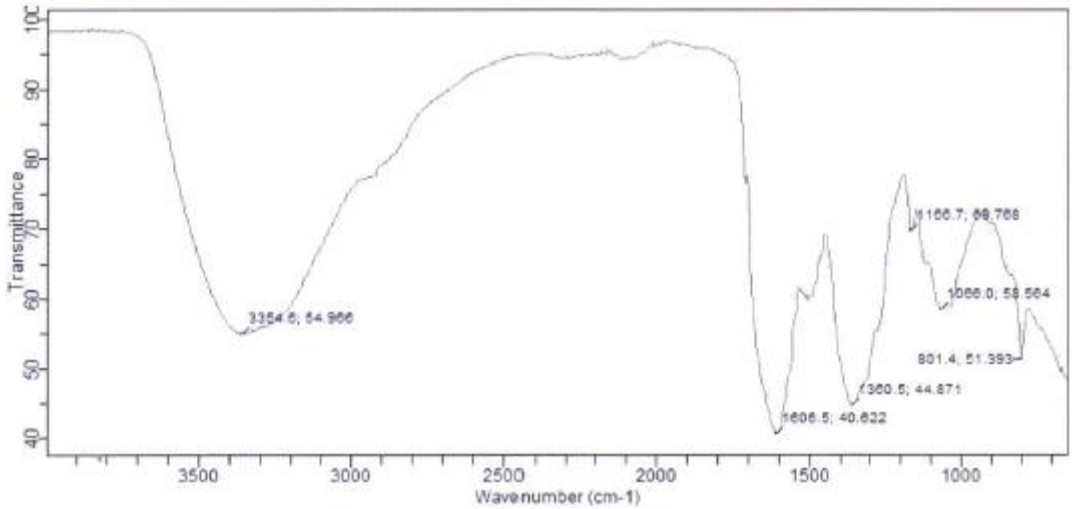


Fig 3b: FT-IR spectrum of Cr (III)ascorbate complex

This peak was shifted to lower frequency in the chromium (III) complex (3354.6 cm^{-1}) indicating coordination. Furthermore, it was observed that the C-O peak in chromium (III) complex and that in the ligand spectrum were observed in the same frequency which indicated that the coordination did not affect the hetero-oxygen atom in the five member ascorbic acid ring.

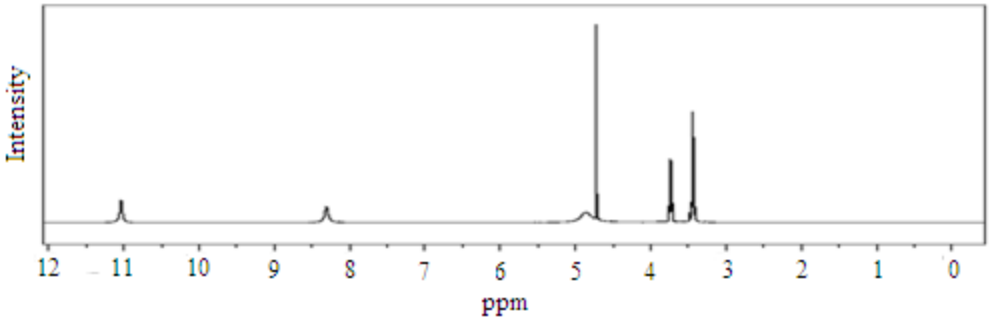
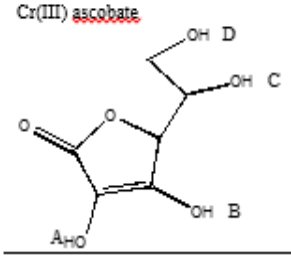


Fig 4a: Proton NMR spectrum of Ascorbic acid

Table 4: Selected proton NMR spectra data of Ascorbic acid and its chromium (III) complex

Ligand/complex	OH A	OH B	OH C	CH	CH_2
Ascorbic acid	11.03	8.31	4.86	3.73	3.43
Cr(III) ascobate	Absent	Absent	4.97	3.73	3.43



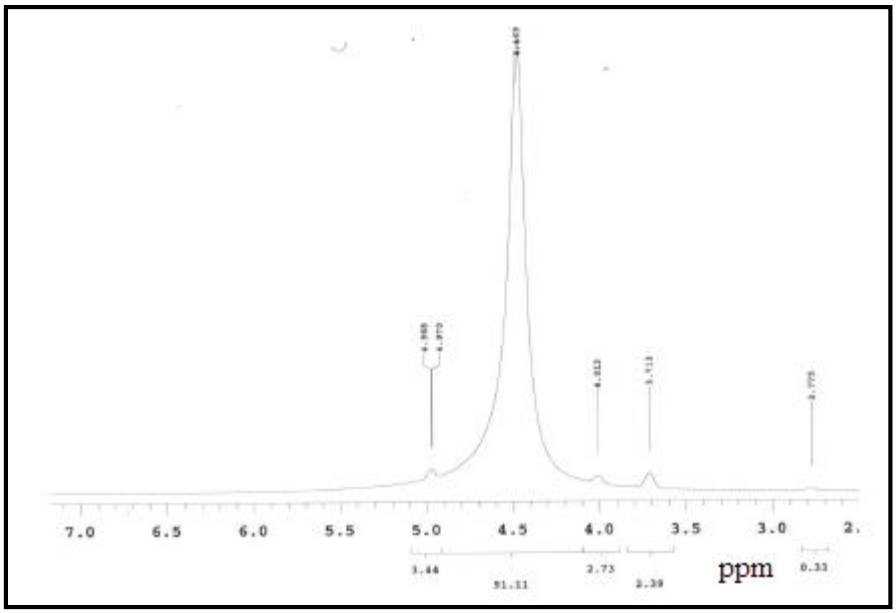


Fig 3b: Proton NMR spectrum of Cr (III) ascorbate complex

From the result in Table 4, it was observed that two protons signals present in the spectrum of the ligand were absent in the H NMR spectrum of the complex. This is a strong indication that the ligand may have coordinated with chromium ion through the deprotonated hydroxyl group at A and B position of the ascorbic acid (Kleszczewska, 1999). This spectroscopic study revealed that enolized form of ascorbic acid can act as a bidentate ligand. Based on the spectroscopic results, a tentative structure of [Cr (III)ascorbate] was proposed in Figure 5.

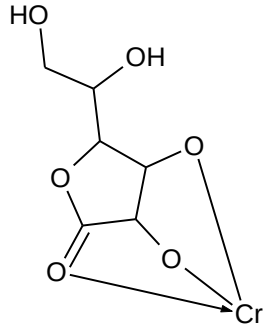


Fig 5: Proposed structure of chromiumascorbate complex

*Conclusion***:** Chromium (II) ascorbate complex was successfully synthesized. The ability of ascorbic acid as a ligand to sequestrate Cr (III) ion is hereby assured. These spectroscopic studies showed that coordination occurred through carbonyl and 2 hydroxyl groups of the ascorbic acid ligand. Finally, the ability of ascorbic acidto extract Cr (III) ions from environment or biological system is hereby assured.The application of ascorbic acid in Cr chelation therapy is hereby recommended.

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