Coordination Chemistry of Vitamin C. Part III.* Interaction of L-Ascorbic Acid With Al(III), La(III), and Pb(II) Ions. Evidence for Metal Chelate Formation in the Solid and Aqueous Solution

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ABSTRACT

The interaction of L-ascorbic acid with Al(III), La(III), and Pb(II) has been investigated in aqueous solution at pH = 6–7. The solid salts of the type Al(L-ascorbate)$_3$, La(L-ascorbate$_3$ · $4H_2O$ and Pb(L-ascorbate)$_2$ · $2H_2O$ were isolated and characterized by ^{13}C NMR and Fourier Transform infrared (FT-IR) spectroscopy.

Spectroscopic evidence suggested that in aqueous solution, metal chelation can occur through ascorbate anion O-3 and O-2 atoms, whereas in the solid state metal coordination is through the O-1, O-3 and O-2, O-3 of the acid anions as well as the H_2O molecules. The aggregation of the Pb(II)- and La(III)-ascorbate salts occur via the carbonyl O-1 atom, while association of the Al(III)-ascorbate would be through other anion donor groups. The structural properties of these metal-ascorbate complexes are different in the solid and aqueous solution.

INTRODUCTION

In our recent reports [1, 2], the interaction of L-ascorbic acid with the alkaline earth, zinc group, and manganese ions were investigated both in the crystalline solid and aqueous solution. It was pointed out that the acid anion chelation will occur with Zn(II) and Mn(II) ions through the O-3 and O-2 atoms in aqueous solution, while the alkaline earth and other zinc group metal ions bind via the negatively-charged O-3

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* For parts 1 and 2, see references 1 and 2.

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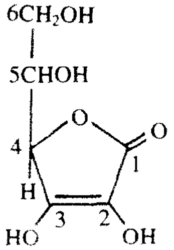

SCHEME 1. L-Ascorbic acid.

atom (inner-sphere) or through the H_2O (outer-sphere) molecule [1, 2]. However, in the solid state the acid anion uses most of its donor groups in metal-ligand bindings and produces three-dimensional polymeric structures [3–5]. In the view of the literature reports, which have suggested that it is difficult for metal chelate formation with ascorbate anion to occur in aqueous solution [6–8], the present study was undertaken.

In this work, the interaction of L-ascorbic acid with Al(III), La(III), and Pb(II) ions has been investigated both in the solid and aqueous solution using ^{13}C NMR and FT-IR spectroscopy that have not been previously reported. A comparison has been made between the spectroscopic properties of these metal ascorbate complexes and those of the other structurally identified metal-ascorbate salts [1, 2]. This comparison allowed us to detect the characteristic feature of each structural type of compound synthesized here and to establish a correlation between the spectral changes and the binding mode used by ascorbic acid (Scheme 1) in these metal-ascorbate complexes.

EXPERIMENTAL

Materials and Methods

L-ascorbic acid was purchased from Aldrich Chemical Co. and was used as supplied. D_2O (99.90%) was from Cambridge Isotopic Laboratories. Other chemicals were reagent grade and were used without further purification.

Synthesis of Al(III)-, La(III), and Pb(II)-Ascorbate Salts. The metal-ascorbate salts were prepared by the addition of the metal ion salts ($Al(NO_3)_3$, $La_2(CO_3)_3$, or $PbCO_3$), 1 mmol in H_2O (20 ml) to a hot solution of L-ascorbic acid 1 mmol in H_2O (20 ml) and the pH of solution was adjusted to 6–7 by the addition of NaOH (0.1 M). After cooling the solution, acetone (30 ml) was added to bring down the precipitate. This was filtered off and washed with acetone several times and dried in a desiccator over $CaCl_2$. The analytical results showed the composition of Al(L-ascorbate)$_3$, La(L-ascorbate)$_3 \cdot 4H_2O$, and Pb(L-ascorbate)$_2 \cdot 2H_2O$. The metal-ascorbate salts are slightly soluble in hot water and not soluble in common organic solvents.

Physical Measurements. The ^{13}C NMR spectra were recorded on a Bruker WH-80 MHz instrument with D_2O solution containing dioxane as reference. The FT-IR spectra were recorded on a DIGILAB FTS-15/C Fourier Transform infrared interferometer equipped with HgCdTe (nitrogen cooled) detector and KBr beam splitter. The spectra were taken as KBr pellets with resolution of 2–4 cm^{-1}. The solution spectra were recorded in D_2O, using AgI window. The pH and pD of solution was adjusted to 6–7, using a microelectrode and an Orion Research Model 721 pH meter.

RESULTS AND DISCUSSION

^{13}C NMR Spectra

The ^{13}C NMR spectra of the Al(III)-, La(III)-, and Pb(II)-ascorbate salts are compared with those of the free acid and Na-ascorbate in D_2O; the results are shown in Figure 1 and Table 1. Upon acid ionization, drastic changes were observed in the ^{13}C NMR spectrum of the acid anion, which are the results of acid O(3)—H group deprotonation (Fig. 1 and Table 1). The observed spectral changes were related to the lengthening of the C-2—C-3, C-3—C-4, C-1—O-1, and C-2—O-2 and the shortening of the C-1—C-2 and C-3—O-3 bonds, in the monoanion salt [5]. The effect of the acid ionization on the ^{13}C NMR spectra of the L-ascorbic acid has been studied in detail in the literature [9, 10].

On comparing the ^{13}C NMR spectra of the Al(III)-, La(III), and Pb(II)-ascorbate complexes with those of the Na-salt, the C-2 chemical shift of the acid anion exhibited downfield shift at 116.60 ppm in Al(III)-, at 115.98 ppm in La(III)-, and at 120 ppm in the Pb(II)-ascorbate complexes in D_2O solution (Fig. 1 and Table 1). The C-3 chemical shift of the free acid at 156.07 ppm also exhibited major downfield shifts in the spectra of the acid anion and the aluminum, lanthanum, and lead-ascorbate salts (Fig. 1). The observed downfield shifts of the C-2 and C-3 chemical shifts are indicative of the metal chelation through the acid anion O-2 and O-3 atoms in aqueous solution. Similar metal chelate formation was observed for the Zn(II)-ascorbate, where the C-2 and C-3 chemical shifts of the free acid was observed at 122.45 and at 174.37 ppm, respectively [2]. On the other hand, the C-2 chemical shift of the free anion was observed at a similar position as for the Na-ascorbate salt (113.85 ppm) in the spectra of the alkaline earth metal-ascorbate salts, which the unidentate metal-ascorbate binding via negatively charged O-3 atom was predominant in aqueous solution [1]. These findings are consistent with the extra stability associated with the 1:1 Al(III)- and Pb(II)-ascorbate complexes with respect to those of the alkaline earth metal-ascorbate species formed in aqueous solutions [11]. Metal-ascorbate chelate formation was also found in the solution studies of several organometallic tin and titanium ascorbate complexes [12] as well as in the cobalt(III)tetrammine ascorbate compounds [13]. However, in the solid state a unique form of a metal-chelation through O-5 and C-2 atoms was found in the crystal structures of the antitumor Pt(II)amine-ascorbate complexes [14].

FT-IR Spectra

The assignments of the vibrational frequencies of ascorbic acid and its metal ion salts have been previously reported [1, 2, 15]. Based on the intermolecular O...O and O...H distances found in the crystal structure of the ascorbic acid [16], the eight sharp absorption bands observed at 3500–2700 cm^{-1} in the infrared spectrum of the free acid were assigned to the eight hydrogen bonded OH stretching groups [1, 2, 15].

Upon Al(III), La(III), and Pb(II) ions interaction, the free acid OH stretching vibrations were replaced by a broad and strong (unresolved) band centered at about

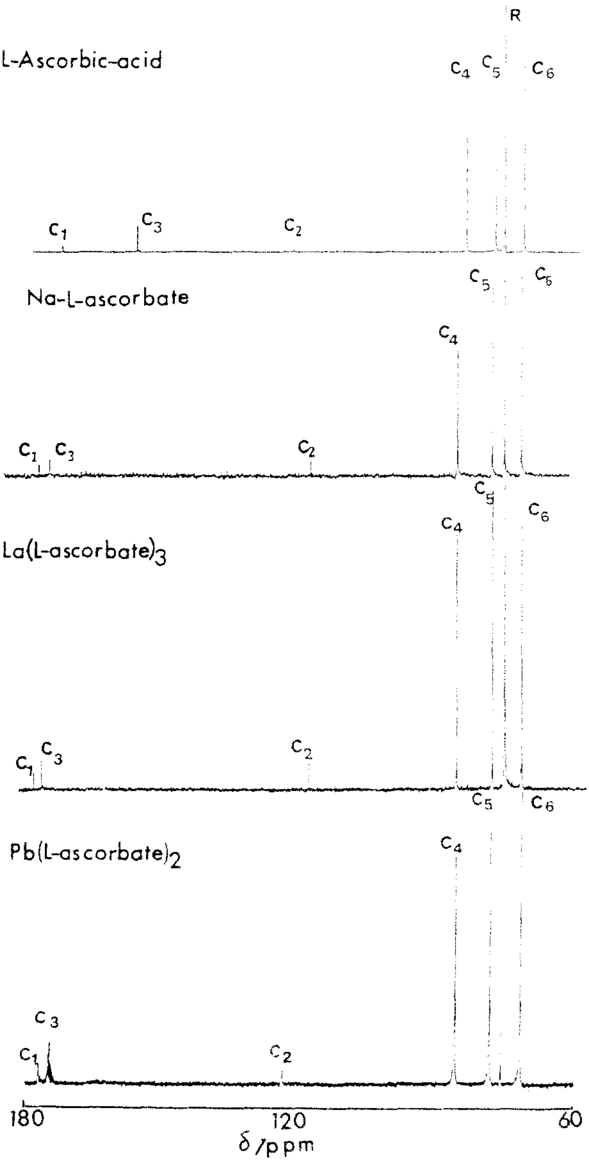

FIGURE 1. ^{13}C NMR spectra of L-ascorbic acid and its metal ion salts in D_2O solution.

3200 cm^{-1}. The broadening and shifting of the acid OH stretching bands in the spectra of these metal-ascorbate salts are indicative of the participation of the ascorbate anion OH groups in metal-ligand bondings. Similar spectral changes were observed in the spectra of the alkaline earth and zinc group metal ascorbate salts, where the acid anion binding was through O-3 and O(2)—H groups [1, 2]. It should be noted that the infrared spectra of these metal-ascorbate complexes were substantially different from that of the Na-ascorbate salt in the region of 3500–3000 cm^{-1}. The dissimilarities observed are due to the different binding modes of the sodium

TABLE 1. ^{13}C NMR Chemical Shifts (ppm) for L-Ascorbic Acid and Its Metal Ion Salts in D_2O Solution

Compounds	C-1	C-3	C-2	C-4	C-5	C-6
L-ascorbic acid	173.79	156.07	118.51	76.87	69.66	62.80
Na-ascorbate	178.09	176.34	113.85	79.28	70.46	63.46
Al(ascorbate)$_3$	175.95	176.12	116.60	79.18	70.40	63.41
La(ascorbate)$_3 \cdot 3H_2O$	176.88	175.46	115.98	78.46	70.55	62.87
Pb(ascorbate)$_2 \cdot 2H_2O$	176.27	175.12	120.00	78.73	70.26	62.89

Dioxane was used as reference (67.40 ppm).

ions with respect to the aluminium, lanthanum, and lead ions, in these metal-ascorbate salts.

Due to the overlapping of the ascorbate OH stretching frequencies with the water OH stretching vibrations in the region of 3500–3000 cm^{-1} and the acid anion carbonyl and double bond stretchings with the H_2O bending mode in the region of 1700–1600 cm^{-1}, it is difficult to locate any absorption band related to the metal bonded H_2O molecules. However, a shoulder band at 1640 cm^{-1} in the spectrum of the La(III)-ascorbate salt can be attributed to the bending mode of the coordinated H_2O molecules (Fig. 2).

The free ascorbic acid C-1=O stretching vibration [15] was observed as a band with medium intensity at 1753 cm^{-1} and shifted towards a lower frequency and split into two components in the spectra of the La(III)- and Pb(II)-ascorbate salts (Fig. 2). Similarly, the strong bands at 1670 and 1650 cm^{-1} in the free acid, which are assigned to the strongly coupled carbonyl and C=C stretchings [1, 2, 15] were shifted towards lower frequencies upon aluminium, lanthanum, and lead ion interaction (Fig. 2). The observed spectral changes are indicative of the participation of the C-1=O group in metal-ascorbate binding. It is important to note that the spectral features of the carbonyl band of the free acid at 1753 cm^{-1} was different for the Al(III)-, La(III)-, and Pb(II)-ascorbate salts (Fig. 2). The carbonyl band was split into two components at 1720, 1780 cm^{-1} for the La(III) and at 1717, 1790 cm^{-1} for the Pb(II) complexes, whereas it was observed at 1725 cm^{-1} in the spectrum of the Al(III) salt (Fig. 2). The dissimilarities observed in the spectra of the aluminium salt with respect to the lanthanum and lead complexes are related to the aggregation of the La(III)- and Pb(II)-ascorbate salts through bridging carbonyl groups, while such aggregation of the Al(III)-ascorbate could occur through other anion donor groups (not the carbonyl group). Similar splitting of the carbonyl stretching vibration was observed in the IR spectra of the cobalt(III)-ammine-ascorbate complexes, which was due to the polymerization of the cobalt(III)ammine-ascorbates through the carbonyl C-1=O groups (13).

A broad band with medium intensity centered at 1350 cm^{-1} in the spectra of the Al(III), La(III), and Pb(III)-ascorbate salts, absent in the free ascorbic acid (Fig. 2), is assigned to the C-3—O$^-$ stretching vibrations [1, 2]. The broadening of this band in the spectra of these metal ion ascorbate salts (particularly in the aluminum salt) can be attributed to the participation of the O-3 atom in metal-ligand binding. The broadening of this band was also observed in the spectra of the alkaline earth and zinc group metal-ascorbate salts, which was related to the presence of the metal—O-3 binding [1, 2]. Several absorption bands in the region of 1300–900 cm^{-1} of the free acid spectrum (Fig. 2), which are assigned to the binding modes of the O(2)—H, O(5)—H, and O(6)—H as well as the ring C-O and C-C stretching vibrations [1, 2, 15] exhibited marked spectral changes (loss of intensities and shiftings), upon Al(III), La(III), and Pb(II) coordination. The observed spectral changes are indicative of the participation of the acid anion OH and C-O groups in metal-ascorbate complexation. Similar behaviors were observed in the spectra of the structurally known Ca-ascorbate salt [1], where the direct metal-OH and metal-carbonyl bindings were observed [5].

The ring skeletal deformations C-C-C and C-O-C modes [1, 2, 15] of the free acid were observed as several weak absorption bands in the region of 900–500 cm^{-1} and showed shifting and intensity changes in the spectra of the aluminium, lanthanum, and lead ascorbate salts (Fig. 2). The observed spectral modifications are due to the acid ionization and the metal ion coordination [1, 2].

Solution Spectra

The infrared spectra of the L-ascorbic acid and its metal ion complexes have been studied in the region of 1900–1300 cm^{-1} in D_2O solution. Marked spectral similarities were observed between the solid and solution spectra of the metal-ascorbate salts in this region. The carbonyl C-1=O and the C=C stretching bands of the free acid at 1750–1650 cm^{-1} shifted towards lower frequencies in the solution spectra of the Al(III)-, La(III), and Pb(II)-ascorbate complexes. This is indicative of the acid ionization and the participation of the anion carbonyl group in the metal-ligand binding. It should be noted that the acid carbonyl stretching vibration at 1750 cm^{-1} (D_2O) was observed at about 1700 cm^{-1} in the spectrum of the Na-salt (monoanion) and at 1720 cm^{-1} in the spectra of the aluminium-, lanthanum-, and lead-ascorbate salts in D_2O solution. The larger shift of the carbonyl stretching band towards a lower frequency in the sodium salt ($\Delta\bar{\nu} = 50$ cm^{-1}) with respect to these metal-ascorbates ($\Delta\bar{\nu} = 30$ cm^{-1}) could be related to the formation of an intramolecular O(2)-H . . . O=(1)-C network, which was suggested to be present in the acid

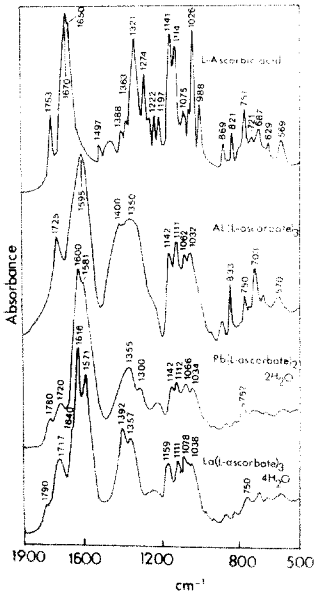

FIGURE 2. FT-IR spectra of L-ascorbic acid and its Al(III), La(III), and Pb(II) ion salts in the region of 1900–500 cm^{-1}.

anion in aqueous solution [6]. However, this intramolecular H-bonding will be broken upon Al(III), La(III), and Pb(II) ion coordination. Similarly, in aqueous solution the broadening of the C-3—O^- stretching band at 1350 cm^{-1} was observed in the spectra of the aluminium-, lanthanum-, and lead-ascorbate complexes, which has not occurred in the Na-ascorbate salt. This can be interpreted in terms of the involvement of the O-3 atom in metal-ascorbate binding for the Al(III), La(III), and Pb(II) complexes, which is not the case for the alkali metal-ascorbate salts, in aqueous solution.

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