



pH-Independent decomposition reactions of L-ascorbic acid in aqueous metal solutions—I. Formation and structures of Co^{II} and Gd^{III} oxalates

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Abstract—The reactions of L-ascorbic acid in aqueous Co^{II} and Gd^{III} solutions were investigated at pH values of 2, 6 and 12. IR spectral studies revealed that the initially formed metal-ascorbates slowly decompose to the solid oxalate complexes in a pH-independent manner. The compositions of the cobalt oxalates were defined as CoC₂O₄·2H₂O and those of Gd^{III} showed variations due to the stereochemical changes in the precursor ascorbate complexes related to pH. X-ray crystal analyses were performed and the structure of Gd₂(C₂O₄)₃·6H₂O is reported for the first time. © 1997 Elsevier Science Ltd

Keywords: L-ascorbic acid; metal-ascorbate complexes; cobalt oxalate; gadolinium oxalate.

The most important chemical characteristics of vitamin C (L-ascorbic acid) are its redox properties. In aerobic conditions, the stable oxidation product is dehydroascorbic acid (DHA) [1]. As a two-electron reducing agent, L-ascorbic acid (AA) can react with various metal ions that have suitable reduction potentials. The rate of oxidation of ascorbate in aqueous solution and the tendency towards complexation has been shown to be pH and catalytic metal dependent [2–6]. When heated in aqueous acidic solutions, evolution of carbon dioxide occurs by the anaerobic degradation of ascorbic acid [7]. A recent EPR study has revealed that the reaction of Cr^{VI} with ascorbate produces carbon-based radicals, including CO₂⁻ as reactive intermediates, independently of the buffer and oxygen [8]. In alkaline solutions, it has long been known that *in vitro* decomposition of DHA leads to the formation of oxalic acid and trihydroxy butyric acid under aerobic or anaerobic conditions [9]. *In vivo*, oxalate is a non-metabolizable end product of AA metabolism [10,11]. However, the kinetics of oxalate

metabolism and the factors that modulate oxalate biosynthesis are largely unexplored.

Considerable effort is being expended on the biological activity and applications of the metal salts and complexes of this water-soluble vitamin. There still remains controversy about the structures of the complexes both in aqueous solution and the solid state. The complexes are weaker than those with other chelating ligands [12] and moreover, isolation of the analytically pure compounds from solution is difficult due to the instability of the ascorbate anion to oxidation. Only a few of such compounds have been analyzed by X-ray crystallography [13–15], solution studies [16–23] and solid-state IR spectra [17–23].

As mentioned above, most of the research on AA chemistry has been related with its redox phenomena. The lack of degradation data in the presence of metal ions needs to be fulfilled. In view of these facts, we aimed to investigate the effects of Co^{II} and Gd^{III} ions, representative of transition and lanthanide metals, on the decomposition of L-ascorbic acid in aqueous solution. X-ray diffraction studies have been carried out to identify the structures and here we report the crystal structure of Gd₂(C₂O₄)₃·6H₂O for the first time.

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EXPERIMENTAL

General

Reactions were conducted in deionized/deoxygenated water at a ligand to metal ratio of 10:3. The data indicated that more than 2 equiv. of AA are needed for the complete conversion and chelation of the metal. Each experiment was started from freshly prepared solutions and oxygen-free conditions were provided by passing nitrogen through the system.

The appropriate quantity of AA (Merck) was dissolved in water and pH of this solution was adjusted to the desired value (6 and 12) by the controlled addition of NaOH solution and to 2 by adding HNO₃. The solutions containing metal salts were prepared by dissolving Gd(NO₃)₃·6H₂O (prepared from Gd₂O₃) and Co(NO₃)₃·6H₂O (BDH) in water. The reaction mixture obtained by the addition of the metal solution to the acid solution was kept at room conditions for a few weeks in closed vessels.

A second set of experiments were carried out by following the same procedure but refluxing the mixture at ~60°C for 3 h. Then acetone was added to start precipitation and the resulting solution was kept in the refrigerator. The compounds produced on

standing a week or more were dried in vacuum and analyzed. They were insoluble in water and also in common organic solvents.

Measurements

Carbon and hydrogen analyses were performed by a LECO CHNS-932 elemental analyzer. IR spectra of the compounds were recorded on a Mattson 1000 FTIR spectrophotometer using KBr disks at a resolution of 2 cm⁻¹.

X-ray crystallography

Details are given in Table 1.

RESULTS

Table 2 summarizes the results of the chemical analyses of the products obtained in 2 weeks at different pH values. Regardless of the type of procedure described in the experimental part, the product composition was nearly the same.

On addition of acetone to the refluxed solutions, a

Table 1. Crystal data

GdC ₃ H ₆ O ₉	Mo-K _α radiation
$M_r = 343.33$	$\lambda = 0.71073$
Monoclinic	Cell parameters from 25 reflections
$P2_1/a$	$\theta = 9-18^\circ$
$a = 10.075(1) \text{ \AA}$	$\mu = 6.83 \text{ mm}^{-1}$
$b = 9.634(1) \text{ \AA}$	$T = 298 \text{ K}$
$c = 11.049(1) \text{ \AA}$	Plate
$\beta = 65.8(1)^\circ$	$0.32 \times 0.12 \times 0.08 \text{ mm}$
$V = 978.4(1) \text{ \AA}^3$	Colorless
$Z = 4$	
$D_x = 2.33 \text{ mg m}^{-3}$	
Data collection	
Enraf-Nonius CAD-4 Diffractometer	$\theta_{\max} = 26.3^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 12$
Absorption correction: psi scan	$k = -12 \rightarrow 12$
(North, Phillips & Matthews, 1968) [24]	$l = -12 \rightarrow 13$
$T_{\min} = 0.905, T_{\max} = 0.998$	Three standard reflections
4198 measured reflections	monitored every 250 reflections
4198 independent reflections	frequency: 120 min
4198 observed reflections	intensity decay: 1%
$[F_o > 3\sigma(F_o)]$	$R_{\text{int}} = 0.025$
Refinement	
Refinement on F	$(\Delta/\sigma)_{\max} = 0.01$
$R = 0.055$	$\Delta\rho_{\max} = 0.11 \text{ e \AA}^{-3}$
$wR = 0.067$	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
$S = 1.08$	Extinction correction: none
4198 reflections	Atomic scattering factors
118 parameters	from <i>International Tables</i>
$w = 1/\sigma(F^2)$	for <i>X-ray Crystallography</i>
$\sigma(F^2) = \{\sigma(I)^2 + (0.04F^2)^2\}^{1/2}$	(1974, Vol. IV)

Table 2. Analytical results (%) for the oxalato complexes^a

Metal	Reaction pH	C	H	Precipitate composition
Co ²⁺	2	—	—	No precipitate
	6	13.2 (13.1)	2.1 (2.2)	CoC ₂ O ₄ ·2H ₂ O
	12	13.3 (13.1)	2.1 (2.2)	CoC ₂ O ₄ ·2H ₂ O
Gd ³⁺	2	10.6 (10.5)	1.4 (1.8)	Gd ₂ (C ₂ O ₄)·6H ₂ O
	6	12.1 (11.7)	0.95 (0.66)	Gd ₂ (C ₂ O ₄) ₃ ·2H ₂ O
	12	12.5 (11.7)	0.9 (0.66)	Gd ₂ (C ₂ O ₄) ₃ ·2H ₂ O

^a Values in parentheses are calculated values.

gelatinous precipitate was formed. The IR spectrum of this initially formed product was different than the others developed in a week or more.

Precipitations started at pH values of greater than 3 with Co^{II} and at all pH values studied with Gd^{III}. The acidity of the medium had almost no effect on the composition of the cobalt complexes. In all investigated cases the final products collected were defined as CoC₂O₄·2H₂O. The pink-brown Co^{II} oxalates were stable in solution. However, the X-ray crystal data for the isolated solids could not be accumulated even with the capillary technique. The apparently crystalline CoC₂O₄·2H₂O transmuted to an amorphous structure in 2 h at room temperature, probably due to loss of surface water leading to a collapse of the lattice as for La₂(C₂O₄)₃·10H₂O [25].

With Gd^{III}, the composition of the oxalates showed variations in their water content. The crystals obtained at pH = 6 were very fine and not suitable for X-ray analysis. Those obtained at pH = 12 were amorphous.

The crystal structure of Gd₂(C₂O₄)₃·6H₂O prepared at low pH values was resolved. Bond lengths and angles are given in Table 3 and the atomic numbering scheme in Fig. 1. The crystal packing is shown in Fig. 2. The symmetry-related gadolinium atoms are linked by planar bridging oxalate ligands, forming a polymeric network. Each Gd atom is coordinated to six oxygens belonging to three different oxalate anions and to three oxygens of water molecules. Symmetry-equivalent oxygens of the oxalates chelate the neighboring Gd ions. The polyhedron of nine oxygen atoms is a tricapped trigonal prism with one rectangular face slightly distorted. Gd, O(3), O(8) and O(6) form the equatorial plane while O(2), O(1), O(9) and O(5), O(4), O(7) are situated at the corners. O(1), O(9), O(7) and O(4) atoms lie in a nonplanar arrangement diverging from the best least-squares plane by 0.130(6), -0.137(8), 0.135(7) and -0.129(7) Å. The H atoms are covalently bonded to O(9), O(4) and

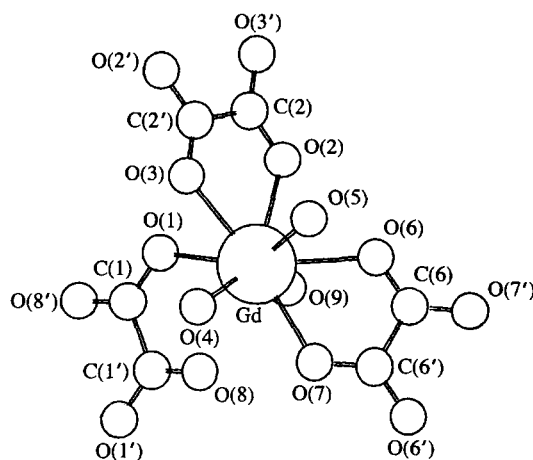


Fig. 1. The structure of Gd^{III} oxalate trihydrate with the atom-numbering scheme.

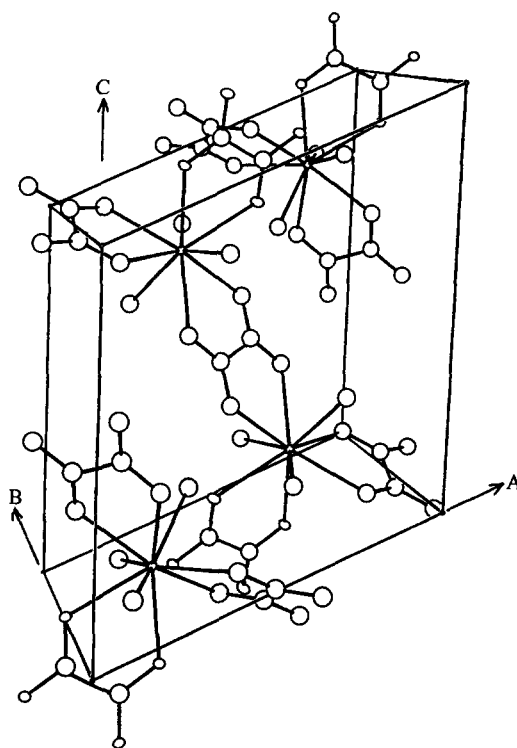


Fig. 2. Perspective view of Gd^{III} oxalate trihydrate.

O(5). The bridging oxalate ligands form five-membered planar rings and the rings are twisted with respect to each other. The bond lengths and angles of the oxalate ligand are not significantly different from those of the free oxalate ion [26]. The mean C—O and C—C distances [1.254(5) and 1.540(6) Å] and the mean C—C—O angles [116.68(7)°] are similar to the mean values of the free oxalate [1.2534(17), 1.5740(24) Å and 116.86(14)°, respectively]. It

Table 3. Bond lengths (Å) and angles (°)

Gd—O(1)	2.445(9)	Gd—O(7)	2.416(6)
Gd—O(1)	2.445(9)	Gd—O(7)	2.416(6)
Gd—O(2)	2.405(7)	Gd—O(8)	2.536(8)
Gd—O(3)	2.478(8)	Gd—O(9)	2.429(8)
Gd—O(4)	2.415(6)	C(1)—O(1)	1.264(5)
Gd—O(5)	2.475(8)	C(2)—O(2)	1.250(6)
Gd—O(6)	2.469(9)	C(6)—O(6)	1.252(5)
C(2')—O(3)	1.258(5)	C(6')—O(7)	1.246(6)
C(2')—O(8)	1.246(5)	C(1')—C(1)	1.533(6)
C(2')—C(2)	1.542(6)	C(6')—C(6)	1.545(6)
O(1)—Gd—O(2)	82.4(5)	O(3)—Gd—O(9)	128.5(6)
O(1)—Gd—O(3)	69.8(7)	O(4)—Gd—O(5)	72.8(5)
O(1)—Gd—O(4)	94.7(6)	O(4)—Gd—O(6)	127.7(6)
O(1)—Gd—O(5)	141.9(8)	O(4)—Gd—O(7)	73.8(5)
O(1)—Gd—O(6)	136.8(6)	O(4)—Gd—O(8)	69.8(6)
O(1)—Gd—O(7)	130.5(7)	O(4)—Gd—O(9)	143.9(4)
O(1)—Gd—O(8)	64.4(6)	O(5)—Gd—O(6)	69.5(4)
O(1)—Gd—O(9)	71.9(7)	O(5)—Gd—O(7)	81.4(5)
O(2)—Gd—O(3)	66.4(4)	O(5)—Gd—O(8)	135.9(7)
O(2)—Gd—O(4)	137.2(5)	O(5)—Gd—O(9)	137.1(5)
O(2)—Gd—O(5)	83.4(4)	O(6)—Gd—O(7)	66.1(4)
O(2)—Gd—O(6)	71.7(5)	O(6)—Gd—O(8)	118.5(4)
O(2)—Gd—O(7)	137.8(6)	O(6)—Gd—O(9)	68.5(5)
O(2)—Gd—O(8)	140.6(6)	O(7)—Gd—O(8)	66.5(5)
O(2)—Gd—O(9)	75.6(6)	O(7)—Gd—O(9)	89.5(6)
O(3)—Gd—O(4)	72.5(5)	O(8)—Gd—O(9)	74.3(4)
O(3)—Gd—O(5)	72.1(4)	C(1)—O(1)—Gd	122.7(5)
O(3)—Gd—O(6)	125.2(5)	C(2)—O(2)—Gd	121.4(4)
O(3)—Gd—O(7)	141.9(6)	C(6)—O(6)—Gd	119.1(5)
O(3)—Gd—O(8)	116.3(5)	C(1')—C(1)—O(1)	116.1(8)
C(1)—C(1')—O(8)	117.1(7)	C(2)—C(2')—O(3)	117.0(8)
C(2')—C(2)—O(2)	116.7(7)	C(6')—C(6)—O(6)	116.8(8)
Gd—O(3)—C(2')	118.3(7)	C(6)—C(6')—O(7)	116.4(5)
Gd—O(7)—C(6')	121.5(4)	Gd—O(8)—C(1')	119.5(5)
O(1)—C(1)—O(8')	126.8(6)	O(2)—C(2)—O(3')	126.3(5)
O(6)—C(6)—O(7')	126.8(6)		

appears that the chelates are not considerably constrained, however, the interatomic distances such as O(6)···H(52) [2.412(5)], O(1)···H(92) [2.535(5)] and O(8)···H(41) [2.534(5)] Å may indicate possible hydrogen bonds leading to the variations in the values of Gd—O bond distances [vary in the range 2.405(7)–2.536(8) Å, average 2.452(7) Å] and O—Gd—O bond angles in the chelates [vary in the range 64.4(6)–66.4(4)°]. Each of the A [Gd—O(2)—C(2)—C(2')—O(3)], B [Gd—O(1)—C(1)—C(1')—O(8)] and C [Gd—O(6)—C(6)—C(6')—O(7)] moieties are planar. The gadolinium atoms lies 0.0156(4), 0.0115(4) and –0.0086(4) Å from the best-least squares planes of A, B and C, respectively. The planes are also twisted with respect to each other, the dihedral angles between them being A—B = 35.3(3), A—C = 103.8(2) and B—C = 135.2(2)°.

Data collection, cell refinement and data reduction: MoIEN [27]. Structure solution: SHELXS86 [28]. Structure refinement MoIEN. Molecular Graphics: ORTEP II [29].

DISCUSSION

The assignments of vibrational frequencies of L-ascorbic acid and complexes are presented in Table 4. Referring to earlier studies [17–23,30,31], it is possible to ascribe the important bands of the initially precipitated products as characteristics of metal ascorbate complexes. In the 2600–3550 cm⁻¹ region, the free acid OH stretching vibrations were replaced by a strong band indicating the rupture of inter- and intramolecular hydrogen bonds on complex formation. This strong band is due to the stretching of the undissociated O—H groups of the acid and the O—H stretching vibration of coordinated water. The changes in the positions of the bands upon complexation with Co^{II} and Gd^{III} ions can be followed from Table 4. For the cobalt complex, the free acid O(3)—H bending vibration at 1220–1230 cm⁻¹ disappeared and C(3)—O stretching at 1387 cm⁻¹ appeared as a sharp peak. The free acid C=O stretching at 1753 cm⁻¹ showed a 115 cm⁻¹ red shift and broadened. There

are also several absorption bands in the region of $1300\text{--}900\text{ cm}^{-1}$ of the free acid spectrum that undergo intensity and position changes. These spectral modifications reveal that complexation mainly occurs through the O(3) atom and the carbonyl oxygen, accompanied with some contribution of the other atoms. On moving to high pH values, the intensity of the C=O peak increased; the intensities of the peaks between $1300\text{--}900\text{ cm}^{-1}$ and C(3)—O decreased. This observation indicates that O(2) atom and the oxygens on the glycolic side chain interact with the metal at high pH.

For the Gd^{III} complex, the free acid $\nu(\text{C}=\text{O})$ shifted to 1623 cm^{-1} and appeared as a very strong band, $\delta[\text{O}(2)\text{—H}]$ shifted to 1352 cm^{-1} and a very sharp peak at 1391 cm^{-1} assigned to $\nu[\text{C}(3)\text{—O}]$ was observed. No splitting in the carbonyl stretching was noted as reported for $\text{La}(\text{asc})_3 \cdot 4\text{H}_2\text{O}$ [23]. The major variations with increasing pH were the intensity rise at 1391 cm^{-1} , the intensity loss at 1159 cm^{-1} and a $\sim 13\text{ cm}^{-1}$ shift to higher wavenumbers in the carbonyl band, suggesting that the most important interaction is through the O(3) atom even at high pH values. It is also possible that the deprotonation of AA in strongly alkaline medium creates new dentating sites on the glycolic side chain and on the lactone ring. The coordination of the ascorbate anions in the solid state has been previously reported [15,32] to occur over various positions forming three-dimensional polymeric structures, however, there is no information about the complexation of AA with Gd^{III}.

In the solution phase, metal ascorbates slowly decomposed to the solid oxalate complexes at room temperature and also in the refrigerator. As the decomposition proceeded a successive spectral continuum was obtained (Fig. 3). The characteristic vibrations of the cobalt oxalate complex $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ produced in *ca* 2 weeks are represented in Table 5. The positions and intensities of $\nu_a(\text{C}=\text{O})$, $\nu_s(\text{C—O})$ and $\delta(\text{O—C}=\text{O})$ resemble to those of ionic oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, and is dissimilar from those of chelate and bridging-monodentate and -bidentate coordinations [33,34].

Details of IR bands in the $1800\text{--}1200\text{ cm}^{-1}$ region are also indicative of the tetradentate nature of the oxalate in the gadolinium complex. There are several examples of polynuclear tetradentate oxalate complexes in the literature where four oxygen atoms of a single oxalate group interact equally with two metal ions [33–35]. Table 5 summarizes some characteristic peaks of the Gd-oxalates produced by the decomposition of Gd-ascorbates. The two important bands of $\nu_a(\text{C}=\text{O})$ and $\nu_s(\text{C—O})$ appeared at 1645 and 1330 cm^{-1} with shoulders at 1708 and 1368 cm^{-1} , respectively. Another strong peak at 810 cm^{-1} has been assigned to $\delta(\text{OCO})$ coupled with $\nu(\text{OMO})$.

The structural difference between the oxalate complexes of Gd^{III} formed at various pH values is presumably the consequence of the differing stereochemistry of the precursor ascorbate complexes.

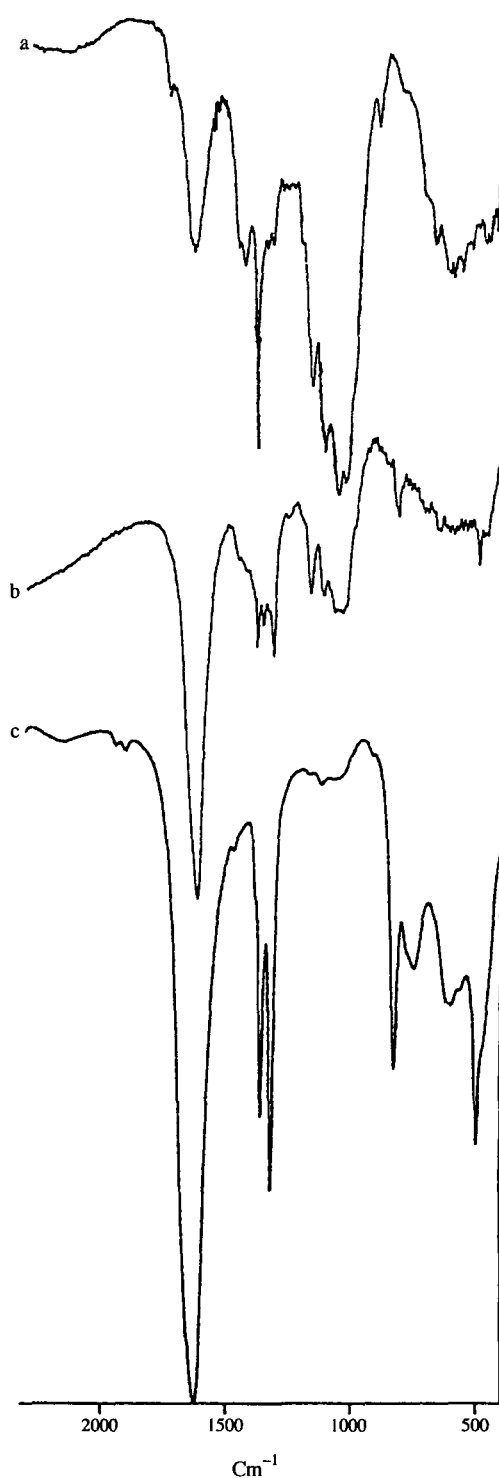


Fig. 3. IR spectra at various stages of decomposition: (a) the initial Co-ascorbate complex precipitated with acetone, (b) the product after 2 days standing, (c) final decomposition product after 2 weeks.

On moving to high pH values, vibrations between 3582 and 2864 cm^{-1} corresponding to hydrogen bonds underwent modifications and a single broad band at

Table 4. IR spectral data for L-ascorbic acid and complexes^a (cm⁻¹)

L-AA	Co-asc	Gd-asc	Assignments
3550–3100s	—	—	$\nu(\text{OH})$, intermolecular hydrogen bonding
2750–2600s	—	—	$\nu(\text{OH})$, intramolecular hydrogen bonding
	3423b	3413b	$\nu(\text{OH})$, of the undissociated acid and water O—H
2915m,sp	2921m	2964sh	$\nu(\text{C—H})$
2860vw	2858w		
1753s	1638m	1623vs	$\nu_{\text{as}}(\text{C=O})$
1670vs	overlapped by the C=O peak		$\nu(\text{C=C})$ coupled to C=O and coordinated water
1645vs			
—	1387sp	1391sp	$\nu[\text{C}(3)\text{—O}]$
1325s	1330w	1352s	$\delta[\text{O}(2)\text{—H}]$
1220–1230m	—	—	$\delta[\text{O}(3)\text{—H}]$
1200–900	1200–900	1200–900	$\delta[\text{O}(5)\text{—H}]$, $\delta[\text{O}(6)\text{—H}]$, $\nu(\text{C—O})$ ring, $\nu(\text{C—C})$ ring, ring def. (C—C—C) and (C—O—C)
900–500	900–500	900–500	$\nu(\text{M—O})$, crystal water

^a Prepared at pH = 6 and precipitated by acetone.

Abbreviations: sh: shoulder, w: weak, s: strong, vs: very strong, m: medium, b: broad, sp: sharp.

Table 5. IR spectral data for Co^{II} and Gd^{III} oxalates

Co-ox ^b	Gd-ox ^a	Gd-ox ^b	Gd-ox ^c	Assignment
3377vs	3582s	3423b	3455b	
	3403vs			
	3210sh			$\nu(\text{O—H})$, hydrogen bonding
2934sh	2934v	2934v	2928v	
2857sh	2864v	2864v	2851v	
1638vs	1708s	1720sh	1678sh	$\nu_{\text{a}}(\text{C=O})$
	1645vs	1631vs	1638s	
—	—	1482v	1482v	$\nu_{\text{s}}(\text{C=O})$
1362s	1368sh	1339sh	1387sp	
1324s	1330s	1324m	1324m	
829m	810s	803m	803m	$\delta(\text{O—C=O}) + \nu(\text{M—O})$

a, *b* and *c* denote to complexes at pH = 2, 6 and 12, respectively. Abbreviations: sh: shoulder, w: weak, vw: very weak, s: strong, vs: very strong, m: medium, b: broad, sp: sharp.

ca 3430 cm⁻¹ was observed with a loss in intensity. $\nu_{\text{a}}(\text{C=O})$ showed position shifts. The most significant change was in the $\nu_{\text{s}}(\text{C—O})$ mode which became a sharp peak at 1387 cm⁻¹. A new band at 1482 cm⁻¹ suggestive of a chelate type coordination of the oxalate was noted [33]. These observed spectral changes reveal that the modifications in the binding character of the ascorbate to the metal related to pH results in the variation of the coordination number and the geometry of the Gd^{III} ion in the oxalate complex.

CONCLUSIONS

The results might be of importance in view of bringing some new information about the possible role of trace metals on the endogenous oxalate production as a consequence of the ascorbic acid metabolism. Stud-

ies with other metal ions are in progress and will be presented in subsequent reports.

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