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Decomposition of Ascorbic Acid in the Presence of Cadmium Ions Leads to Formation of a Polymeric Cadmium Oxalate Species with Peculiar Structural Features

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Slow decomposition of L-ascorbic acid, carried out under aerobic conditions and in the presence of cadmium ions, results in formation of a crystalline product that is highly insoluble in water. This compound has been identified as a cadmium oxalate polymeric species with formula $Cd(C_2O_4)\cdot 3H_2O$. The crystal structure of this compound is described. Relevant crystal data are the following: $C_4H_{12}O_{14}Cd_2$, fw = 508.94; triclinic; space group $P1$ (No. 1); $a = 6.010(1)$ Å, $b = 6.668(1)$ Å, $c = 8.498(1)$ Å; $\alpha = 74.64(1)°$, $\beta = 74.25(1)°$, $\gamma = 80.91(1)°$; $V = 314.7(5)$ Å^3; $Z = 1$.

The interactions of L-ascorbic acid with metals have been extensively reviewed by Davies.[1] However, despite intense investigations, very few metal ascorbate complexes have been isolated until now in the solid state; regrettably, most of them are reluctant to form crystals suitable for X-ray analysis.[2]

This issue is further complicated by the propensity of L-ascorbic acid to undergo oxidative degradation. The complex pathways of L-ascorbic acid transformations, both in acidic and alkaline milieu, have been studied by several authors and partially elucidated. It was shown that the rate of oxidation of L-ascorbic acid to dehydroascorbic acid (DHA) in aqueous solution and the tendency toward complexation depend both on pH and on the presence (and nature) of metal ions.[3−7] When an ascorbic acid solution is heated in acidic medium, carbon dioxide forms by anaerobic degradation.[8] Decomposition of DHA, in alkaline solutions, produces oxalic acid and trihydroxybutyric acid in both aerobic and anaerobic conditions.[9]

It is remarkable that oxalate represents one of the main end-products of the degradation pathways, under both oxidative and nonoxidative conditions. Indeed, Simpson et al. demonstrated that 2,3-L-diketogulonate (2,3-DKG) is a key intermediate of ascorbic acid catabolism, while oxalate and L-erythrulose are the final degradation products regardless of which compound was used as the starting material.[10]

A recent work by Ünaleroglu et al. specifically addressed the effects of the presence of cobalt(II) and gadolinium(III) ions on the degradation process of L-ascorbic acid.[11] Interestingly these authors found that decomposition of L-ascorbic acid, carried out under various solution conditions, leads to slow formation of highly insoluble cobalt(II) and gadolinium(III) oxalates. The crystal structure of the gadolinium oxalate complex $Gd_2(C_2O_4)_3\cdot 6H_2O$ was solved by X-ray diffraction.[11] Notably, in this structure, symmetry-related gadolinium atoms are linked by planar bridging oxalate ligands, forming a polymeric network. Each gadolinium atom is coordinated to six oxygens belonging to three different oxalate anions and to three oxygens of water molecules.

We report here on the reaction of L-ascorbic acid with cadmium ions, at equimolar ratios, performed under mildly acidic conditions (pH 5). Although three different cadmium salts were employed, namely, $Cd(NO_3)_2$, $CdSO_4$, and $CdCl_2$, similar results were obtained in all cases, regardless of the nature of the anion. The course of the reaction is peculiar. At room temperature, a water-soluble yellow compound slowly forms with time, probably associated with formation of the six-membered δ lactone R-345, which is characteristic of L-ascorbic acid degradation.[12] Heating the solution to 60

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(1) Davies, M. B. *Polyhedron* **1992**, *11* (3), 285.
(2) Arendse, M.; Anderson, G. K.; Rath, N. P. *Inorg. Chem.* **1999**, *38*, 5864.
(3) Dixon, D. A.; Sadler, N. P.; Dasgupta, T. P. *J. Chem. Soc., Dalton Trans.* **1993**, 3489.
(4) Taqui Khan, M. M.; Shukla, R. S. *Polyhedron* **1991**, *10*, 2711.
(5) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90* (22), 6011.
(6) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1969**, *91* (17), 4468.
(7) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89* (16), 4176.
(8) Finholt, P.; Paulssen, R. B.; Alsos, I.; Higuchi, T. *J. Pharm. Sci.* **1965**, *54*, 124.
(9) Herbert, R. W.; Hirst, E. L.; Percival, E. G. V.; Reynolds, R. J. W.; Smith, F. *J. Chem. Soc.* **1933**, 1270.
(10) Simpson, G. L. W.; Ortwerth, B. J. *Biochim. Biophys. Acta* **2000**, *1501*, 12.
(11) Ünaleroglu, C.; Zümreoglu-Karan, B.; Zencir, Y.; Hökelek, T. *Polyhedron* **1997**, *16*, 2155.
(12) Kimoto, E.; Tanaka, H.; Ohmoto, T.; Choami, M. *Anal. Biochem.* **1993**, *214*, 38.

10.1021/ic025598l CCC: $22.00

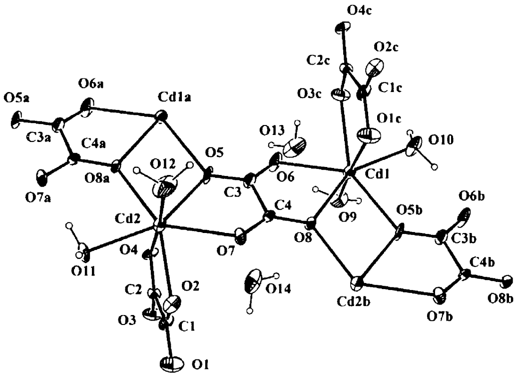

Figure 1. ORTEP drawing of part of the layered structure of $Cd_2(C_2O_4)_2 \cdot 6H_2O$ with 50% probability ellipsoids. Symmetry operations, denoted by the trailing letter in atomic labels, are (a) $x + 1, y, z$; (b) $x - 1, y, z$; (c) $x - 1, y, z + 1$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Cd_2(C_2O_4)_2 \cdot 6H_2O^a$

Bond Distances			
$Cd(1)-O(1)^{III}$	2.303(11)	$Cd(2)-O(4)$	2.299(8)
$Cd(1)-O(9)$	2.220(8)	$Cd(2)-O(12)$	2.396(12)
$Cd(1)-O(3)^{III}$	2.376(7)	$Cd(2)-O(2)$	2.337(7)
$Cd(1)-O(6)$	2.341(7)	$Cd(2)-O(7)$	2.393(7)
$Cd(1)-O(8)$	2.346(6)	$Cd(2)-O(5)$	2.381(7)
$Cd(1)-O(5)^{II}$	2.432(6)	$Cd(2)-O(8)^{I}$	2.331(6)
$Cd(1)-O(10)$	2.320(9)	$Cd(2)-O(11)$	2.382(7)
Bond Angles			
$O(1)^{III}-Cd(1)-O(9)$	172.8(4)	$O(4)-Cd(2)-O(12)$	174.9(4)
$O(1)^{III}-Cd(1)-O(3)^{III}$	69.2(3)	$O(4)-Cd(2)-O(2)$	73.2(2)
$O(6)-Cd(1)-O(8)$	70.8(2)	$O(7)-Cd(2)-O(5)$	67.6(2)
$O(8)-Cd(1)-O(5)^{II}$	70.1(2)	$O(5)-Cd(2)-O(8)^{I}$	71.3(2)
$O(5)^{II}-Cd(1)-O(10)$	81.1(3)	$O(8)^{I}-Cd(2)-O(11)$	81.5(3)
$O(10)-Cd(1)-O(3)^{III}$	74.8(3)	$O(2)-Cd(2)-O(11)$	78.1(3)
$O(3)^{III}-Cd(1)-O(6)$	75.0(3)	$O(2)-Cd(2)-O(7)$	72.2(2)

[a] Symmetry transformations used to generate equivalent atoms: *I*, $x+1, y, z$; *II*, $x-1, y, z$; *III*, $x-1, y, z+1$.

°C results in a faster appearance of this yellow product. On aging, after a few days, large colorless crystals, suitable for X-ray analysis, separate from the yellow solution. These crystals are insoluble in water and in common organic solvents. Elemental analysis revealed that the crystalline material corresponds to cadmium oxalate with the formula $Cd(C_2O_4) \cdot 3H_2O$. Overall, these observations suggest that decomposition of L-ascorbic acid in the presence of cadmium ions resembles the decomposition process described by Ünaleroglu et al. in the presence of cobalt(II) or gadolinium(III) ions.

The crystal structure, solved by X-ray diffraction methods, consists of two-dimensional arrays formed by the $Cd_2(C_2O_4)_2 \cdot 6H_2O$ repeat unit, where both of the symmetry-independent cadmium atoms are in a seven-coordinate environment of five oxalate and two water oxygens (Figure 1). Two water molecules of the repeat unit are uncoordinated and are involved in the hydrogen bond network present in the structure. Values of selected bond lengths and angles are reported in Table 1. The coordination geometry about each metal atom is approximately that of a pentagonal bipyramid with a water and an oxalate oxygen in the apical positions. Half of the planar oxalate anions provide donor atoms in the equatorial positions of the bipyramids. These anions form chains in the structure linking pairs of cadmium atoms at a distance of 6.10 Å, as well as pairs at 3.87 Å via bridging oxygens from different oxalate groups (Figure 1). The other oxalates in the structure chelate cadmium atoms belonging to different chains, through an apical and an equatorial site, yielding a layered structure. The present structure appears to be definitely different from that of $Gd_2(C_2O_4)_3 \cdot 6H_2O$[11] and related compounds,[13] although these also present polymeric networks. In fact, all of the metal atoms in the latter structures are symmetry-related and form comparable distances, all above 6 Å.

Attempts were made to prepare crystalline $Cd_2(C_2O_4)_2 \cdot 6H_2O$ starting directly from cadmium sulfate and oxalic acid; yet, these attempts failed due to rapid precipitation of cadmium oxalate. Thus, it is probable that under the present solution conditions decomposition of ascorbate and concomitant slow release of oxalate specifically favor the formation of the peculiar cadmium oxalate polymeric compound. We argue that a similar mechanism is operative in the formation of the gadolinium oxalate complex described by Ünaleroglu. It is likely that the metal directs both the L-ascorbic acid decomposition and the formation of the polymeric crystalline lattice.

We believe that such mechanisms may present some degree of generality and might be relevant for the formation of insoluble oxalate complexes also within biological systems (e.g., calcium oxalate). Studies are under way to assess the role of various metal ions on L-ascorbic acid decomposition and on the formation of polymeric metal oxalate compounds.

L-Ascorbic acid (5 mmol) was reacted with equimolar amounts of $CdCl_2$, $Cd(NO_3)_2$, or $CdSO_4$ in 20 mL of deionized water. The reaction was carried out either at room temperature or at 60 °C. In all cases, independently of the nature of the anion, a characteristic yellow color appeared within a few hours at RT; crystals formed in a few days. Anal. Calcd for $C_2H_6CdO_7$: C, 9.43; H, 2.36. Found: C, 9.46; H, 2.25.

Crystals appropriate for X-ray diffraction were obtained in the form of colorless elongated plates from solutions containing cadmium sulfate and sodium ascorbate. Accurate lattice constants were measured from the angular settings of 60 reflections with $15° < \theta < 40°$, collected with a crystal mounted on a P4 Bruker-AXS diffractometer, using Cu Kα radiation ($\lambda = 1.54184$ Å). Intensity data in the $3-27°$ θ range were measured on a Enraf-Nonius CAD4 diffractometer, with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (ψ scans, $T_{min/max} = 0.596/0.998$). The structure was solved by direct methods and heavy atom techniques, with SIR[14] and SHELXL 93,[15] and was refined by full-matrix least

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(13) Trollet, D.; Roméro, S.; Mosset, A.; Trombe, J. C. *Polyhedron* **1998**, *17*, 3977.

(14) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(15) Sheldrick, G. M. *SHELXL 93*, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1993.

squares on F^2. In the final cycles all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were given an overall isotropic temperature factor. The H atom positions were refined, with restraints on the O−H distances and the H−O−H angles. A correction for the extinction effect was applied, and the absolute structure was assigned, based on Flack's test.[16] Crystal data for **1** are as follows: $C_4H_{12}O_{14}Cd_2$, fw = 508.94; colorless plates; triclinic; space group $P1$ (No. 1); $a = 6.010(1)$ Å, $b = 6.668(1)$ Å, $c = 8.498(1)$ Å; $\alpha = 74.64(1)°$, $\beta = 74.25(1)°$, $\gamma = 80.91(1)°$; $V = 314.7(5)$ Å^3; $Z = 1$; $D_{calc} = 2.685$ g cm^{-3}; μ(Mo Kα) = 3.45 mm^{-1}; R1= 0.024, wR2 = 0.061.

Supporting Information Available: Crystallographic tables and CIF file. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(16) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.