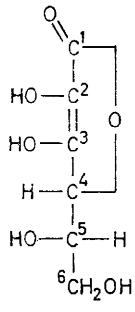
Crystal Structure of Thallium(I) L-Ascorbate

By **David L. Hughes**,* A.R.C. Unit of Structural Chemistry (University College, London), Inveresk House, 346 Strand, London WC2R 0HG

Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, $a = 10{\cdot}883(7)$, $b = 18{\cdot}598(6)$, $c = 8{\cdot}066(3)$ Å. There are two molecules per asymmetric unit, related by a pseudo-two-fold axis parallel with the a axis. The two thallium(I) ions are 4·05 Å apart and bridged by oxygen atoms. Co-ordination about the cations is typically asymmetric, involving only three and four oxygen atoms (from four anions); in each case the oxygens are grouped on one side of the thallium ion. Each ascorbate anion comprises a γ-lactone ring and an acyclic side-chain at C(**4**) (of the hexose skeleton); the anions are very similar and resemble the anion of sodium ascorbate. The lactone rings both appear planar. The O(**3**) atoms, each only 2·58 Å from a thallium ion, are pushed considerably out of the ring planes. The conformations about the C(**6**) atoms form the major difference between the anions; these conformations probably result from molecular packing and a complicated hydrogen-bonding system which, with the Tl · · · O interactions, holds the crystal as a lattice polymer.

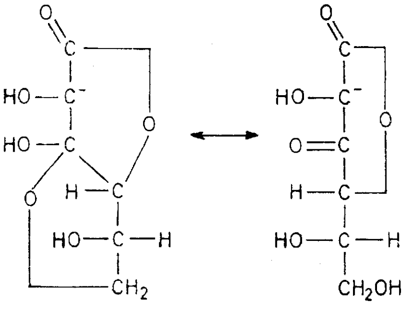
The structure was solved from diffractometer data by the heavy-atom method, and refined by block-diagonal, and finally full-matrix, least-squares methods to R 0·076 for 1253 reflections. The absolute configuration was assigned by comparison with L-ascorbic acid, the precursor of this compound.

ASCORBALAMIC acid is an ascorbigen-like compound extracted from several common vegetables and fruits.[1] Attempts to synthesise this compound have been made by the C–C coupling reaction of an L-alanine derivative with an 'ascorbic' moiety.[2] One reagent prepared from L-ascorbic acid, (I), for the latter purpose was thallium(I) ascorbate, in which the formation of a carbanion [(II) and (III)] was considered possible. The crystal structure analysis of thallium(I) ascorbate was undertaken to determine the nature of the Tl^+ ion co-ordination and the form of the anion, and thus the potential of this compound as a coupling agent.



(I)

(showing hexose skeleton numbering scheme)



(II) (III)

The results of the structure analysis would also afford a further comparison of thallium(I) co-ordination patterns with those of alkali metals;[3] the structure of sodium ascorbate has been determined by Hvoslef.[4]

EXPERIMENTAL

Thallium(I) L-ascorbate was prepared by Laird and Synge.[2] L-Ascorbic acid (0·83 g) was titrated to pH 6 in water (4 ml) using *ca.* 1M-thallium(I) hydroxide [from a solution of thallium(I) ethoxide in water]. On evaporation and cooling, a crystalline product (0·72 g) resulted; this was recrystallised from water to large white translucent masses (Found: C, 19·3; H, 1·85; O, 25·5; Tl, 53·4. $C_6H_7O_6Tl$ requires C, 19·0; H, 1·85; O, 25·3; Tl, 53·9%).

Crystals were cut to suitable sizes, and the one selected for intensity measurements was a rectangular prism $0{\cdot}25 \times 0{\cdot}09 \times 0{\cdot}15$ mm³.

Crystal Data.—$C_6H_7O_6Tl$, $M = 379{\cdot}5$, Orthorhombic, $a = 10{\cdot}883(7)$, $b = 18{\cdot}598(6)$, $c = 8{\cdot}066(3)$ Å, $U = 1632{\cdot}5$ Å³, $D_c = 3{\cdot}09$, $Z = 8$, $D_m \gg 2{\cdot}0$, $F(000) = 1376$. Space group $P2_12_12_1$, from absent spectra; there are thus two molecules of thallium(I) ascorbate per asymmetric unit. Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 198{\cdot}9$ cm^{-1} (1 Å $\equiv 10^{-10}$m). Four-circle diffractometer observations.

Preliminary cell dimensions and the space group were determined from Weissenberg and precession photographs. More accurate cell dimensions were obtained by least-squares refinement from χ, ϕ, and $2\theta_{\alpha1}$ settings of 21 reflections on a Picker four-circle automatic diffractometer, with Mo-K radiation.

1253 intensity data, to $2\theta = 45°$, were then measured on this instrument (with Zr-filter and pulse-height analyser) by use of the θ—2θ scan technique with a 2θ scan rate of 0·5° min^{-1}, and a 2θ scan range of $(2\theta_{\alpha1} - 0{\cdot}5)°$ to $(2\theta_{\alpha2} + 0{\cdot}7)°$. 250 (*i.e.* 20%) of these reflections were 'unobserved,' having $I < 2\sigma_I$ where $\sigma_I^2 = T + (b_1 + b_2) \, . \, (T_s/50)^2$, and T = scan count, b_1 and b_2 are background counts (each for 25 s), and T_s = scan time. Lorentz and polarisation factors were applied. Absorption corrections were made by use of an adaptation of Ahmed and Singh's NRC 3 program;[5,6] the transmission factor is calculated from the m-point Gaussian integration formula described by Busing and Levy.[7]

Intensities were scaled with respect to three standard reflections, indices (0,10,1), (3,7,2), and (1,2,3), measured regularly throughout the data collection. The 'standard' measurements showed considerable fluctuations in their intensities, the scale factor varying from 1·0 to 0·94 to 1·53, but the crystal showed no signs of decomposition.

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* *Present address:* Molecular Structures Department, Rothamsted Experimental Station, Harpenden AL5 2JQ.

[1] R. Couchman, J. Eagles, M. P. Hegarty, W. M. Laird, R. Self, and R. L. M. Synge, *Phytochem.*, 1973, **12**, 707.

[2] W. M. Laird, J. J. Sexton, and R. L. M. Synge, unpublished work.

[3] D. L. Hughes and M. R. Truter, *J.C.S. Dalton*, 1972, 2214.

[4] J. Hvoslef, *Acta Cryst.*, 1969, **B25**, 2214.

[5] F. R. Ahmed and P. Singh, Program NRC 3 of 'NRC Crystallographic Programs for the IBM 360 System.'

[6] X-RAY ARC: IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson (see also ref. 3).

[7] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

Structure amplitudes were then calculated.

Structure Analysis.—The structure was determined by the heavy-atom method. A Patterson synthesis showed clearly all the vector peaks corresponding to the two independent thallium ions in the asymmetric unit. After refinement of the co-ordinates and anisotropic temperature factors of the thallium ions, and calculation of structure factors (R 0·16), a Fourier difference synthesis showed all the carbon and oxygen atom positions of the ascorbate anions.

The structure was refined by block-diagonal least-squares methods, with minimisation of $\Sigma w(|F_o| - |F_c|)^2$, *i.e.* $\Sigma w\Delta^2$, for the 1003 observed reflection data; w was initially determined from the counting statistics, $\sigma_c^2 = B \,.\, \sigma_I^2/4 \,.\, I \,.\, Lp$ (where B is the absorption factor and Lp the Lorentz-polarisation factor). The scattering factors for thallium(I), carbon, and oxygen were taken from ref. 8. The thermal parameters of the thallium ions were refined anisotropically; the other atoms were treated isotropically.

As refinement progressed the data set was extended to include all 1253 planes, the scattering factors for the thallium ions were adjusted for anomalous dispersion,[8] and the weighting scheme was altered to one in which the average values of $w\Delta^2$ over ten ranges of $|F_o|$ values approximated to unity; finally, $w = 1/\sigma^2$ and $\sigma^2 = \sigma_c^2\,(-0.795 + 0.315|F_o| - 0.00487|F_o|^2 + 0.000035|F_o|^3)$;[9] in the final cycles, full-matrix least-squares methods were employed.

The two ascorbate ions were found to be very similar, each comprising a γ-lactone ring with an acyclic side-chain at the C(**4**) atom (of the hexose skeleton).* In each anion, the two carbon atoms of the side-chain, and C(**4**), all have approximately tetrahedral bonding arrangements, *i.e.* sp^3 hybridisation, and therefore, assuming a C–H bond of 1·0 Å, the co-ordinates of the hydrogen atoms bonded to these atoms could be estimated. The parameters of eight hydrogen atoms, each with B = 6·0 Å^2, were not refined, but were included in the $|F_c|$ calculations in the final cycles of refinement. The hydrogen atomic scattering factors were from ref. 10.

Bijvoet's method[11] did not distinguish the absolute configuration of this structure. The thallium(I) ions are overwhelmingly dominant in scattering power so that the structure approximates to one of only thallium(I) ions, where Friedel's law will be obeyed.[12] However, since the compound was prepared from L-ascorbic acid, whose two asymmetric carbon atoms, C(**4**) and C(**5**) of the hexose skeleton, have known configurations, the absolute configuration was assigned by the method of comparison.

Refinement was concluded with R 0·076 for all data, and 0·060 for the observed data; correspondingly, (weighted) R' 0·078 and 0·072.

A final Fourier difference synthesis showed peaks of up to 1·5 eÅ^{-3}, primarily around the thallium ions. It was not feasible to look for the remaining hydrogen atoms.

TABLE 1

Atomic positional (fractional ×10^4) and thermal parameters * with estimated standard deviations in parentheses. The absolute configuration is defined with respect to a right-handed system of axes

	X	Y	Z	B/Å^2
Tl(1)	16(1)	3433(1)	3170(2)	*
Tl(2)	−505(1)	1373(1)	1709(2)	*
C(1)	1075(35)	3362(20)	−1986(46)	4·22(81)
C(2)	779(28)	2933(17)	−658(39)	2·42(65)
C(3)	−439(27)	2913(16)	−556(36)	1·97(39)
C(4)	−1033(30)	3359(18)	−1899(43)	3·24(68)
C(5)	−1784(28)	4036(17)	−1370(37)	2·59(67)
C(6)	−2218(31)	4414(20)	−2893(43)	3·83(80)
O(1)	2130(19)	3537(13)	−2617(25)	3·34(47)
O(2)	1576(21)	2586(14)	341(29)	4·41(55)
O(3)	−1127(19)	2614(12)	545(24)	3·21(45)
O(4)	90(20)	3640(13)	−2837(26)	3·94(49)
O(5)	−1058(20)	4510(13)	−395(26)	3·66(49)
O(6)	−3141(23)	4936(14)	−2489(33)	5·66(67)
C(11)	1405(33)	1479(20)	6685(47)	4·03(76)
C(12)	939(30)	1976(18)	5654(41)	2·82(68)
C(13)	−232(26)	2005(16)	5566(37)	2·26(62)
C(14)	−654(29)	1467(17)	6918(39)	2·98(65)
C(15)	−1538(30)	863(19)	6268(41)	3·35(76)
C(16)	−1804(39)	355(25)	7688(53)	5·56(106)
O(11)	2454(18)	1248(12)	7126(26)	3·45(48)
O(12)	1760(20)	2340(12)	4507(26)	3·53(47)
O(13)	−998(20)	2346(12)	4599(26)	3·65(49)
O(14)	453(20)	1165(13)	7575(26)	3·81(51)
O(15)	−895(21)	440(13)	5001(28)	3·99(51)
O(16)	−2439(28)	712(19)	8954(39)	8·10(91)
H(4)	−1580	3040	−2620	6·0
H(5)	−2520	3880	−700	6·0
H(61)	−2580	4040	−3700	6·0
H(62)	−1510	4640	−3480	6·0
H(14)	−1110	1740	7830	6·0
H(15)	−2290	1090	5820	6·0
H(161)	−1000	130	8080	6·0
H(162)	−2300	−70	7200	6·0

* Isotropic thermal parameters are from the expression $\exp[-B(\sin^2\theta/\lambda^2)]$. For the thallium ions, anisotropic vibration parameters are in the form: $\exp[-2\pi^2 \,.\, 10^{-4}(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl(1)	352(8)	408(9)	606(9)	−40(7)	11(9)	32(8)
Tl(2)	473(9)	488(10)	616(10)	115(8)	27(9)	49(9)

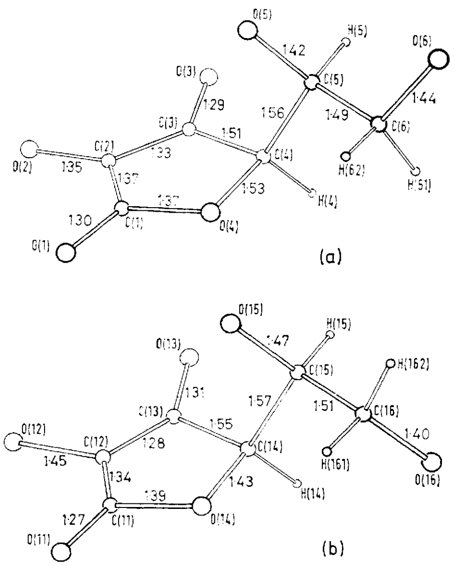

FIGURE 1 (a) Anion (A) and (b) anion (B) showing the atomic designations and bond lengths (Å). Mean standard deviations C–C 0·044 and C–O 0·038 Å

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* Throughout, bold arabic numbers in parentheses refer to formula (I), whereas ordinary arabic numbers refer to Figure 1, *etc.*

[8] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

[9] D. W. J. Cruickshank, in 'Computing Methods in Crystallography,' Pergamon Press, Oxford, 1965, p. 114.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[11] J. M. Bijvoet, *K. ned. Akad. Wet.*, 1949, *B*, **52**, 313.

[12] Y. Okaya and R. Pepinsky, in 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 275.

The final atomic parameters are in Table 1; with the conventional right-hand system of axes, the atomic co-ordinates describe the correct absolute configuration of the ascorbate anions (see Figure 1). The measured and calculated structure amplitudes are recorded in Supplementary Publication No. SUP 20742 (10 pp., 1 microfiche).*

Computing.—Most of the computing in this structure determination was on the IBM 1130 computer of this laboratory, using programs of the X-RAY ARC system.[6] The full-matrix least-squares refinement, and the final calculations of bond lengths and angles with standard deviations from a full correlation matrix, were computed on the IBM 360/65I system at University College, London.[13]

DISCUSSION

There are two crystallographically independent formula units of thallium(I) ascorbate in this crystal. The carbon atoms of the hexose chain, C(**1**)—(**6**) in carbohydrate convention (I), and their corresponding oxygen atoms O(**1**)—(**6**), are numbered C(1)—(6) and O(1)—(6) in ascorbate anion (A), and C(11)—(16) and O(11)—(16) in the other anion (B). The two anions and the two thallium ions Tl(1) and Tl(2) form the crystal chemical unit, c.c.u., in this discussion; atoms in symmetry-related units are identified by superscripts listed in Table 2. Figure 1 shows the designations of the atoms, and the bond lengths in the two anions. The Tl · · · O interactions, and distances to adjoining anions are included in Figure 2.

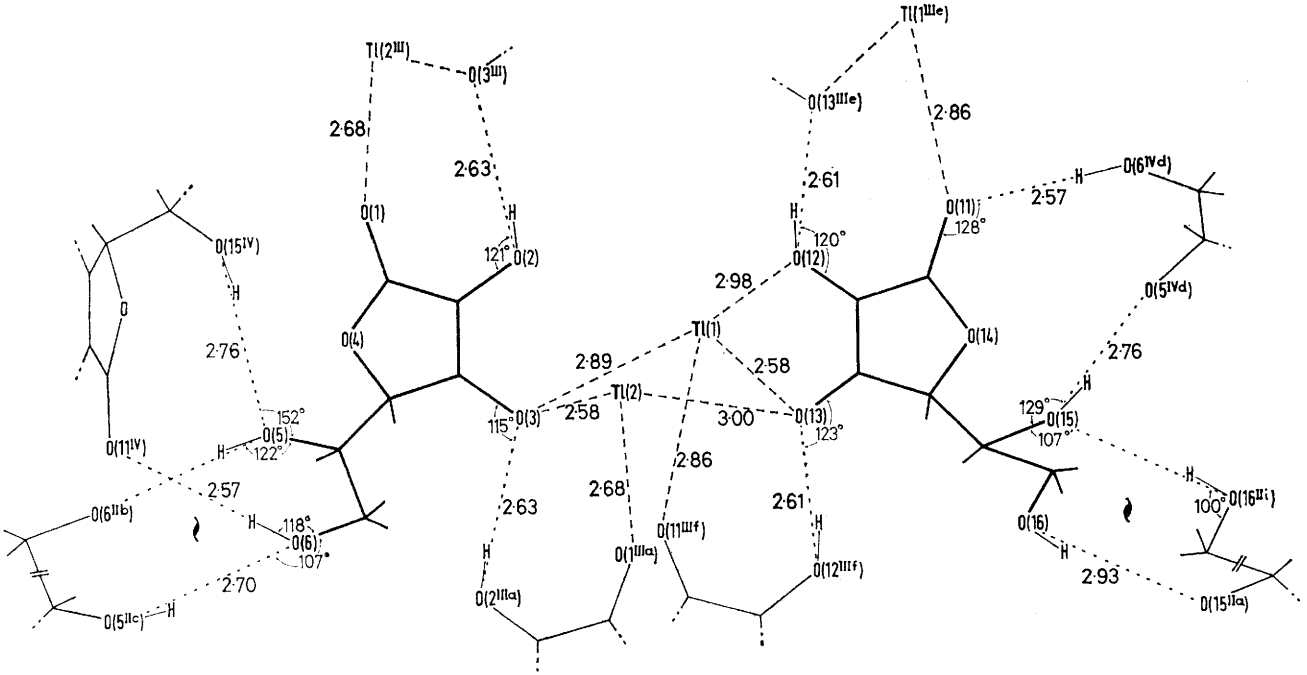

FIGURE 2 Shortest interanionic O · · · O distances and the corresponding C–O · · · O angles, all Tl · · · O contacts <3·00 Å, and estimated approximate directions of O–H bonds

The anions (A) and (B) are related by a pseudo-two-fold axis parallel to the *a* axis and passing between the pairs of enediol oxygen atoms, O(**2**) and O(**3**), and between the two Tl$^+$ ions, at *ca.* $y = 0{\cdot}243$, $z = 0{\cdot}247$ Å (Figure 3). The pseudo-symmetry is broken only in the acyclic side-chains of the anions; the conformations about the C(**5**) atoms are very similar, but in anion (A), C(6)–O(6) is *trans* (*i.e. anti*) with respect to C(5)–C(4) whereas, in (B), C(16)–O(16) is *trans* to C(15)–O(15) and *gauche* to C(15)–C(14) (Figure 1).

TABLE 2

Designations of molecules related to the crystal chemical unit (*x*,*y*,*z*) by symmetry and translation operations. Roman superscripts refer to symmetry operations:

I	x, y, z	III	$\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$
II	$\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	IV	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

Translations from these co-ordinates (x',y',z') are indicated by lower-case superscripts:

a	$x' - 1, y', z'$	f	$x' - 1, y', z' + 1$
b	$x' - 1, y' + 1, z'$	g	$x', y', z' - 1$
c	$x' - 1, y' + 1, z' - 1$	h	$x' + 1, y', z'$
d	$x', y' - 1, z'$	i	$x' - 1, y', z' - 1$
e	$x', y', z' + 1$	j	$x', y' + 1, z'$

Environments of the Thallium Ions.—The two thallium ions are separated by 4·05 Å, and are bridged by two oxygen atoms; similar separations between thallium atoms bridged by single electron-donating atoms are found in both Tl^{I} and Tl^{III} complexes.[3,14-17] Tl(1) has

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[13] IBM 360 programs: NUCLS (full-matrix least-squares program) by R. J. Doedens and J. A. Ibers; ORFFE (molecular dimensions and errors program) by W. R. Busing, K. O. Martin, and H. A. Levy.

[14] H. Luth and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 1287.

[15] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.* (*A*), 1967, 648.

[16] L. H. W. Verhoef and J. C. A. Boeyens, *Acta Cryst.*, 1968, **B24**, 1262.

[17] L. H. W. Verhoef and J. C. A. Boeyens, *Acta Cryst.*, 1969, **B25**, 607.

four oxygen atoms within a radius of 3·0 Å; Tl(2) has only three closely neighbouring oxygen atoms. These and other atoms <3·70 Å from the thallium ions are listed in Table 3. There are no Tl $\cdots$ C interactions and thus the possibility of an ascorbate carbanion cannot be considered.

TABLE 3

Distances (Å) of thallium ions from adjacent atoms. Mean estimated standard deviation 0·023 Å

Tl(1) $\cdots$ O(13)	2·576	Tl(2) $\cdots$ O(3)	2·582
Tl(1) $\cdots$ O(11$^{\mathrm{IIIf}}$)	2·860	Tl(2) $\cdots$ O(1$^{\mathrm{IIIa}}$)	2·681
Tl(1) $\cdots$ O(3)	2·889	Tl(2) $\cdots$ O(13)	2·999
Tl(1) $\cdots$ O(12)	2·983		
Tl(1) $\cdots$ O(4$^{\mathrm{Ie}}$)	3·244	Tl(2) $\cdots$ O(15)	3·200
Tl(1) $\cdots$ O(2)	3·252	Tl(2) $\cdots$ O(16$^{\mathrm{Ig}}$)	3·299
Tl(1) $\cdots$ O(16$^{\mathrm{IIIe}}$)	3·625	Tl(2) $\cdots$ O(2)	3·382
Tl(1) $\cdots$ O(5)	3·693	Tl(2) $\cdots$ O(14$^{\mathrm{Ig}}$)	3·515
Tl(1) $\cdots$ O(6$^{\mathrm{IIb}}$)	3·693	Tl(2) $\cdots$ O(6$^{\mathrm{III}}$)	3·597

As in other thallium(I) complexes,[3,18–20] there is a wide range of Tl $\cdots$ O distances, but in all cases, there is a distinct break between those of <3·00 Å and those of >3·20 Å. The limit of the thallium(I) ion–oxygen co-ordination distance is thus assumed to be *ca.* 3·00 Å.

For each of the thallium ions, the co-ordinated oxygens are distinctly on one side of the cation [Table 4, planes (*A*) and (*B*)]. The closest atoms on the opposite side of the cations are *ca.* 3.6 Å from the Tl^+ ions. Oxygen atoms at distances 3·2—3·5 Å from the cations are approximately equidistant with the cations from the mean planes.

Each thallium ion appears to occupy an ovoid bounded by several oxygen atoms. The nucleus is at the broader end of the ovoid; the 6d^2 lone-pair electrons occupy the narrower end and prevent spherical co-ordination about the thallium ion.

The oxygen atoms closest to the thallium ions (Figure 2) are those which are thought to share the anionic charges (see later), *viz.* the O(**3**) atoms [Tl(1) $\cdots$ O(13) and Tl(2) $\cdots$ O(3) both 2·58 Å] and O(**1**) atoms from neighbouring units [Tl(1) $\cdots$ O(11$^{\mathrm{IIIf}}$) 2·86 Å and Tl(2) $\cdots$ O(1$^{\mathrm{IIIa}}$) 2·68 Å]. The O(**3**) atoms also have weaker interactions with the other cation [Tl(1) $\cdots$ O(3) 2·89 and Tl(2) $\cdots$ O(13) 3·00 Å] and thus bridge the pair of thallium ions in pseudo-two-fold symmetry. O(12) interacts with Tl(1) (2·98 Å) but the corresponding O(2) $\cdots$ Tl(2) distance is somewhat greater (3·38 Å). In contrast to sodium ascorbate,[4] the O(**5**) and O(**6**) atoms do not co-ordinate with the cations; it is assumed that this follows from there being limited space around the thallium ions available for co-ordination, and that the charged oxygen atoms are preferred.

The bridging interactions of the thallium ions with anionic oxygen atoms are remarkably similar to those found in salicylato-(1,10-phenanthroline)thallium(I),[3] where the shorter and longer Tl $\cdots$ O contacts were 2·65 and 3·00 Å.

Ascorbate Anions.—The numbering of the atoms and the bond lengths of the ascorbate anions are in Figure 1; the valence angles are in Table 5. The two anions do not differ significantly in their dimensions, the largest differences appearing in distances and angles *ca.* 2σ from the mean values.

TABLE 4

Mean planes

(*a*) Equations of mean planes, in the form: $lX + mY + nZ = p$, where *X*, *Y*, and *Z* are co-ordinates, (Å), referred to the *a*, *b*, and *c* axes

Plane	*l*	*m*	*n*	*p*
(A): O(3), O(12), O(13), O(11$^{\mathrm{IIIf}}$)	−0·5157	−0·8470	0·1291	−3·618
(*B*): O(3), O(1$^{\mathrm{IIIa}}$), O(13)	−0·6850	0·7152	0·1387	4·378
(*C*): C(1)—(4), O(4)	0·0165	0·8030	0·5956	4·079
(*D*): C(1), C(2), C(4), O(1), O(4)	0·0219	0·8054	0·5922	4·101
(*E*): C(2), C(3), O(2), O(3)	0·0433	0·8173	0·5745	4·169
(*F*): C(11), C(13), C(14), O(14)	0·0503	0·7304	0·6810	5·765
(*G*): C(11), C(13), O(12)	0·0575	0·7313	0·6795	5·764
(*H*): C(11), C(12), C(14), O(11), O(14)	0·0565	0·7062	0·7057	5·853
(*I*): C(12), C(13), O(12), O(13)	0·0162	0·7923	0·6097	5·699

(*b*) Deviations, (Å), of atoms from the mean planes.

Plane (*A*):

Tl(1) −1·47, O(2) −1·30, O(3) 0·19, O(5) −2·93, O(12) −0·59, O(13) 0·96, O(4$^{\mathrm{Ie}}$) −1·42, O(6$^{\mathrm{IIb}}$) −3·05, O(11$^{\mathrm{IIIf}}$) −0·56, O(16$^{\mathrm{IIIe}}$) −4·47

Plane (*B*):

Tl(2) −1·98, O(2) −2·08, O(15) −2·57, O(16$^{\mathrm{Ig}}$) −1·73, O(6$^{\mathrm{III}}$) −5·40, O(14$^{\mathrm{Ig}}$) −3·44

Plane (*C*):

Tl(1) 2·57, Tl(2) −1·22, C(1) 0·007, C(2) −0·0, C(3) −0·004, C(4) 0·007, C(5) 1·259, O(1) −0·015, O(2) −0·025, O(3) 0·067, O(4) −0·003

Plane (*D*):

C(1) 0·012, C(2) −0·003, C(3) −0·014, C(4) −0·001, O(1) −0·002, O(2) −0·027, O(3) 0·049, O(4) −0·001

Plane (*E*):

C(1) 0·072, C(2) 0·022, C(3) −0·020, C(4) 0·009, O(2) −0·006, O(3) 0·005

Plane (*F*):

Tl(1) 0·64, Tl(2) −2·99, C(11) −0·007, C(12) 0·077, C(13) 0·004, C(14) −0·007, C(15) −1·234, O(11) −0·021, O(12) −0·014, O(13) −0·107, O(14) 0·004

Plane (*G*):

C(12) 0·082

Plane (*H*):

C(11) −0·018, C(12) 0·019, C(13) −0·065, C(14) −0·028, O(11) −0·006, O(12) −0·105, O(13) −0·215, O(14) 0·018

Plane (*I*):

C(11) −0·206, C(12) 0·011, C(13) −0·010, C(14) −0·145, O(12) −0·002, O(13) 0·002

Angle between the normals to planes (*C*) and (*F*) 6·7°.

The anions' dimensions are compared (Table 5) with results for L-ascorbic acid,[21] D-isoascorbic acid,[22] and the anion of sodium ascorbate;[4] from the trends in dimen-

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[18] J. K. Fawcett, V. Kocman, S. C. Nyburg, and R. J. O'Brien, *Chem. Comm.*, 1970, 1213.

[19] N. C. Webb, personal communication (see also ref. 3).

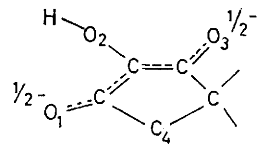
[20] M. Alleaume and D. Hickel, *J. C. S. Chem. Comm.*, 1972, 175.

[21] J. Hvoslef, *Acta Cryst.*, 1968, **B24**, 23.

[22] N. Azarnia, H. M. Berman, and R. D. Rosenstein, *Acta Cryst.*, 1972, **B28**, 2157; R. D. Rosenstein, personal communication.

sions, the thallium and sodium salts are shown here to have very similar anions.

The conjugation effects of shortening and lengthening the bonds in the chain O(**1**)=C(**1**)-C(**2**)=C(**3**)-O(**3**) are evident and in agreement with the theory[23] that the protolytic hydrogen atom was at O(**3**) and the negative charge is shared between the O(**1**) and O(**3**) atoms. The overall bonding scheme may thus be described as approaching the system (IV). The O(**2**) and O(**4**) atoms have $2p_z$ orbitals which can overlap with the π-orbitals of the conjugative scheme and thus the C(**2**)-O(**2**) and C(**1**)-O(**4**) bonds are shorter than normal C-O single bonds.



(IV)

TABLE 5

Comparison of bond lengths (Å) and angles (°), in thallium(I) ascorbate and related compounds

	Thallium(I) ascorbate				L-Ascorbic acid		
	Anion				Molecule		
	(A)	(B)	Mean	Sodium ascorbate	(A)	(B)	D-Isoascorbic acid
(*a*) Distances							
C(**1**)-O(**1**)	1·30	1·27	1·28	1·233	1·218	1·213	1·200
C(**1**)-C(**2**)	1·37	1·34	1·36	1·416	1·457	1·448	1·446
C(**1**)-O(**4**)	1·37	1·39	1·38	1·358	1·352	1·358	1·365
C(**2**)-O(**2**)	1·35	1·45	1·40	1·384	1·361	1·362	1·340
C(**2**)-C(**3**)	1·33	1·28	1·30	1·373	1·341	1·335	1·331
C(**3**)-O(**3**)	1·29	1·31	1·30	1·287	1·327	1·326	1·329
C(**3**)-C(**4**)	1·51	1·55	1·53	1·516	1·493	1·494	1·493
C(**4**)-O(**4**)	1·53	1·43	1·48	1·448	1·441	1·448	1·437
C(**4**)-C(**5**)	1·56	1·57	1·56	1·536	1·521	1·521	1·531
C(**5**)-O(**5**)	1·42	1·47	1·44	1·410	1·421	1·434	1·416
C(**5**)-C(**6**)	1·49	1·51	1·50	1·503	1·521	1·521	1·520
C(**6**)-O(**6**)	1·44	1·40	1·42	1·423	1·434	1·429	1·428
Mean σ	0·040	0·041	0·028	0·006	0·004	0·004	0·005
(*b*) Angles							
O(**1**)-C(**1**)-C(**2**)	131	138	135	129·0	128·4	129·7	128·8
O(**1**)-C(**1**)-O(**4**)	114	113	113	120·4	121·9	120·9	121·7
C(**2**)-C(**1**)-O(**4**)	115	109	112	110·6	109·6	109·4	109·4
C(**1**)-C(**2**)-O(**2**)	126	119	123	121·6	124·7	124·5	124·5
C(**1**)-C(**2**)-C(**3**)	107	116	112	109·5	107·5	108·1	107·1
O(**2**)-C(**2**)-C(**3**)	126	124	125	128·7	127·7	127·3	128·4
C(**2**)-C(**3**)-O(**3**)	129	134	132	131·3	133·7	133·3	132·8
C(**2**)-C(**3**)-C(**4**)	112	103	107	105·8	109·4	109·5	110·9
O(**3**)-C(**3**)-C(**4**)	119	123	121	122·9	116·9	117·2	116·3
C(**3**)-C(**4**)-O(**4**)	102	105	103	105·2	104·2	103·7	102·9
C(**3**)-C(**4**)-C(**5**)	118	114	116	116·1	114·8	114·8	114·0
O(**4**)-C(**4**)-C(**5**)	106	111	109	110·3	110·5	110·3	111·7
C(**4**)-C(**5**)-O(**5**)	111	109	110	113·4	111·6	111·8	108·2
C(**4**)-C(**5**)-C(**6**)	109	108	108	110·1	112·5	112·8	112·5
O(**5**)-C(**5**)-C(**6**)	110	106	108	108·5	106·1	107·6	111·6
C(**5**)-C(**6**)-O(**6**)	111	111	111	108·5	108·1	107·8	110·9
C(**1**)-O(**4**)-C(**4**)	104	106	105	108·0	109·2	109·0	109·6
Mean σ	2·8	2·9	2·0	0·4	0·25	0·25	0·3

Several mean planes are described in Table 4. In anion (A), the five-membered lactone ring [plane (*C*)] appears planar, and atoms O(1) and O(2) are not significantly out of the plane. O(3) is 0·07 Å above the ring plane, the displacement caused, presumably, by the proximity of Tl(2), 1·22 Å below the plane. The lactone group [plane (*D*)] forms a good plane in anion (A). In the enediol group, [plane (*E*)], there is a dihedral angle of 5·6° about the C(2)-C(3) bond.

Excluding C(12), the ring of anion (B) forms a good plane (*F*) and O(11) and O(12) lie in this plane; C(12) is 0·08 Å displaced from this plane and its co-ordinates must appear suspect. Plane (*G*) describes further the displacement of C(12), and planes (*H*) and (*I*) are of the lactone and enediol groups which include C(12).

As in anion (A), O(13) is pushed out of the ring plane by 0·11 Å, by the proximity of Tl(1).

The differences in the acyclic side-chains of the two anions have been mentioned. The conformations about C(**5**) [Figure 4(a)] are very similar and resemble closely the conformations in other ascorbate groups (except, of course, D-isoascorbic acid). Newman projections along the C(**5**)-C(**6**) bonds of the several ascorbate groups are shown in Figure 4(b). With respect to the C(**5**)-O(**5**) bond, the C(**6**)-O(**6**) bond is *trans* for L-ascorbic acid and for anion (A), but *gauche* for the sodium ascorbate anion, D-isoascorbic acid, and anion (B). The determining factors for these arrangements are assumed to be the packing and hydrogen-bonding schemes.

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[23] H. von Euler and B. Eistert, 'Chemie und Biochemie der Reduktone und Reduktonate,' Ferdinand Enke, Stuttgart, 1957, p. 205.

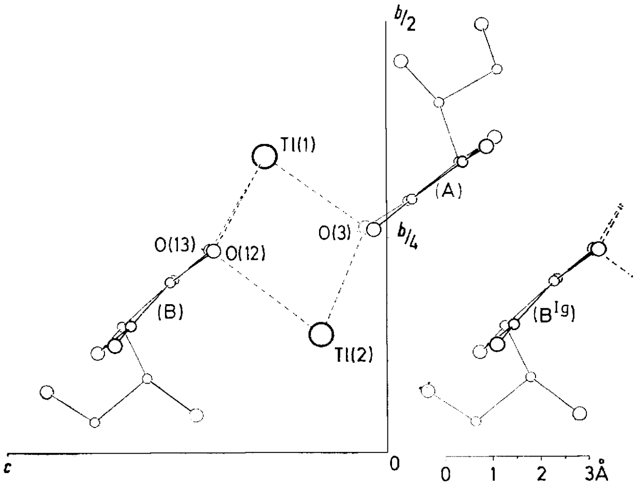

FIGURE 3 Projection down the *a* axis, showing the pseudo-two-fold symmetry. The planes of the lactone rings are almost perpendicular to the projection plane

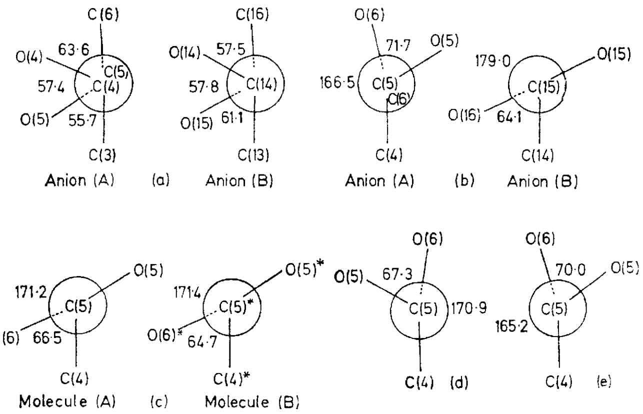

FIGURE 4 Comparison of the conformations in the acyclic side-chains. Newman projections show the dihedral angles about (a) the C(**4**)–C(**5**) bonds of the thallium(I) ascorbate anions; and the C(**5**)–C(**6**) bonds of (b) thallium(I) ascorbate, (c) L-ascorbic acid, (d) D-isoascorbic acid, and (e) sodium ascorbate

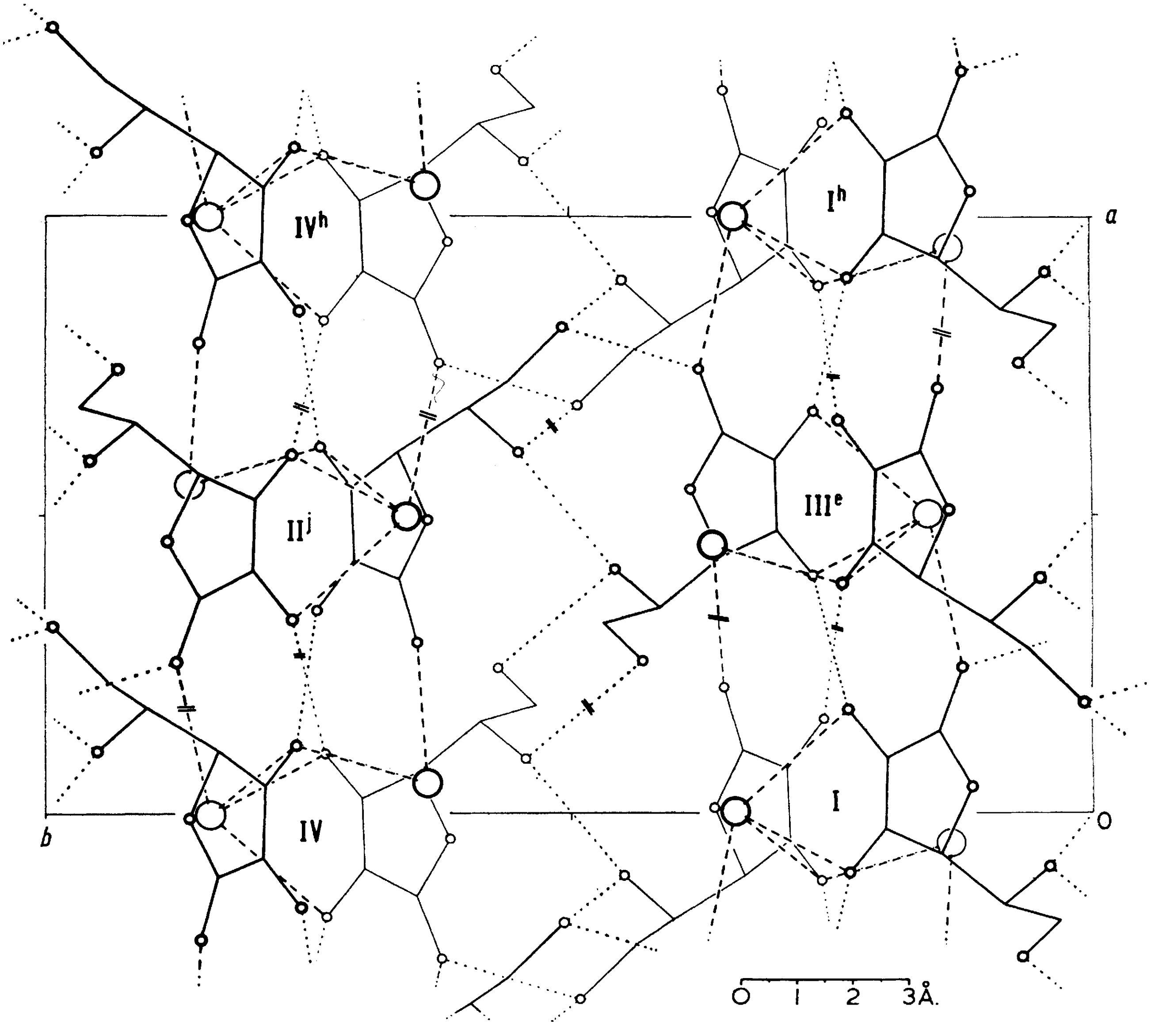

FIGURE 5 Projection down the *c* axis showing all hydrogen bonds (dotted lines) and Tl · · · O interactions (broken lines). Large circles represent thallium ions, small ones oxygen atoms

Hydrogen Bonding and Molecular Packing.—The alcoholic hydrogen atoms have not been located in this structure.

The conformations of the side-chains do not permit the formation of intramolecular hydrogen bonds, and the shortest O · · · O distances, O(4) · · · O(5) 2·84 and O(14) · · · O(15) 2·88 Å, correspond to normal van der Waals' interactions.

The shortest intermolecular O · · · O distances are shown in Figure 2 and are all thought to represent hydrogen bonding situations. The direction of the O(6)–H bond must be almost coincident with the O(6) · · · O(11^{IV}) line since this O · · · O contact is only 2·57 Å and O(11) is of a carbonyl group; hence the approximate directions of the other O–H bonds in the side-chains can be deduced. Similarly, the O(2)–H bonds should lie approximately towards the negatively charged O(3′) atoms (Figure 2).

This complicated system of hydrogen bonding, together with the co-ordination of the thallium ions with oxygens of several anions, connect thallium ascorbate units in all directions. Hence, in the crystalline form, this compound may be described as a lattice polymer. Figure 3, a projection almost perpendicular to the planes of the anions, shows a pair of anions, (A) and (B^{Ig}), related by a pseudo-two-fold axis. The lactone ring planes are *ca*. 3·3 Å apart; the minimum interatomic distances between these anions are C(1) · · · C(12^{Ig}) 3·21 Å and O(1) · · · O(12^{Ig}) 3·24 Å, and are normal van der Waals' distances.

A projection of the unit cell down the *c* axis (Figure 5) shows the crystal-packing arrangements. All hydrogen bonds and Tl · · · O interactions are shown.

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