tivity, contains 10 mg of cyclodecapeptide **2**. The next fraction was chromatographed again over Sephadex LH 60 to yield 378 mg (39%) of **1**: mp 266–267 °C; R_f A 0.44, B 0.09, C 0.48; $[\alpha]^{25}{}_D$ −149.5° (*c* 0.5, DMF). The FD mass spectrum exhibits a peak at m/e = 505. Anal. Calcd for $C_{27}H_{31}N_5O_5$ (505.58): C, 64.14; H, 6.18; N, 13.85; O, 15.82. Found: C, 63.5; H, 6.0; N, 13.8; O, 15.5.

The cyclodecapeptide **2** was prepared via fragment condensation (Scheme II) as well as via cyclodimerization.[38-40]

H-Pro-Phe-Gly-Phe-Gly-OCH$_3$ (13). Deprotection of the N terminus as described above (see **12**) yields a hygroscopic product: yield, 3.28 g (91%); mp 210–212 °C. R_f A 0.45, B 0.02, C 0.27; $[\alpha]^{25}{}_D$ −64.5° (*c* 1, DMF).

Boc-Pro-Phe-Gly-Phe-Gly-Pro-Phe-Gly-Phe-Gly-OMe (14).[5] **11** (222 mg, 0.35 mmol) was dissolved in 20 mL of DMF and treated at 0 °C under stirring with 0.18 mL (0.35 mmol) of 14% sodium nitrite in water and 0.06 mL of concentrated HCl. After 30 min it was neutralized with 0.08 mL of NMM. A solution of 200 mg (0.35 mmol) of **14** in 10 mL of DMF, neutralized with 0.04 mL of NMM, was added within 1 h at 0 °C and stirred for 24 h at room temperature. The solvent was evaporated, and the residue was stirred for 2 h with 5 g of mixed-bed ion exchanger in about 50 mL of methanol/water. The filtrate was evaporated and the residue chromatographed (Sephadex LH 20, DMF) to yield 200 mg (50%): mp 135–138 °C; R_f A 0.59, B 0.04, C 0.77; $[\alpha]^{25}{}_D$ −33.2° (*c* 1, DMF). Anal. Calcd for $C_{60}H_{74}N_{10}O_{13}$ (1143.31): C, 63.04; H, 6.52; N, 12.25. Found: C, 63.33; H, 6.60; N, 12.06.

Boc-Pro-Phe-Gly-Phe-Gly-Pro-Phe-Gly-Phe-Gly-N$_2$H$_3$ (15). The hydrazinolysis was performed as described under **11**. From 115 mg (0.1 mmol) of **14** was obtained 85 mg (74%) of **15**: mp 149–153 °C; R_f A 0.47, B 0, C 0.60; $[\alpha]^{25}{}_D$ −53.0° (*c* 1, DMF).

H-Pro-Phe-Gly-Phe-Gly-Pro-Phe-Gly-Phe-Gly-N$_2$H$_3$·2HCl (16). N-Deprotection was performed as described under **12** from 286 mg (0.25 mmol) of **15**. During the reaction some absolute methanol was added to dissolve the precipitate of the product: yield, 266 mg (96%); mp 180 °C; R_f A 0.34, B 0.03, C 0.24.

***cyclo*(Pro-Phe-Gly-Phe-Gly)$_2$ (2). Via Fragment Condensation.** **17** (245 mg, 0.22 mmol) was cyclized, worked up, and purified as described under **1**; yield: 82 mg (37%); mp 174–175 °C; R_f *a* 0.03, B 0.48, C 0.59; $[\alpha]^{25}{}_D$ −122.8° (*c* 0.5, DMF). Anal. Calcd for $C_{54}H_{62}N_{10}O_{10}$ (M_r 1011.16): C, 64.14; H, 6.18; N, 13.85; O, 15.82. Found: C, 62.4; H, 6.2; N, 13.5; O, 15.8. The deviation in the elemental analysis is caused by a small amount of an impurity, which could not be separated via chromatography. The field desorption mass spectrum shows a peak at m/e = 1011 but a further very small peak at m/e = 976.

Via Cyclodimerization. **12** (3.45 g, 6.0 mmol) was dissolved in 35 mL of DMF (0.1 mol/L) and cyclized as described under **1** but without further dilution by DMF. The gel chromatographic fraction (Sephadex LH 20, DMF) was chromatographed again separately (Sephadex LH 60, DMF) to yield 229 mg (7.6%) of **1** and 156 mg (5.2%) of **2**. **2** is identical in all physical properties with **2** obtained via fragment condensation. Also, the impurity mentioned above was present.

Acknowledgment. The heteronuclear shift correlations and the INEPT spectra have been performed in Oxford in the laboratory of Dr. Ray Freeman. R.S. is deeply indebted to Dr. Freeman and his group, especially Dr. G. A. Morris and T. H. Mareci, for their continuous advice and their generous hospitality; R.S. thanks the DAAD for a travelling grant. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Dr. H. J. Veith, University Darmstadt, for running the mass spectra. We further acknowledge Dr. E. Grell, Max-Planck-Institut für Biophysik, Frankfurt, for the use of his CD apparatus. We also acknowledge the Hoechst AG for support.

Registry No. **1**, 61898-89-3; **2**, 82247-64-1; **3**, 4192-12-5; **4**, 7625-57-2; **5**, 25616-33-5; **6**, 7625-59-4; **7**, 66876-50-4; **8**, 66876-51-5; **9**, 15761-39-4; **10**, 82265-53-0; **11**, 82265-54-1; **12**, 82247-65-2; **13**, 82247-66-3; **14**, 82247-67-4; **15**, 82247-68-5; **16**, 82247-69-6.

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The H_3O^+ Cation: Molecular Structure of an Oxonium–Macrocyclic Polyether Complex

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Received October 6, 1981

Abstract: The oxonium ion has been isolated as a discrete entity by inclusion into a macrocyclic cavity. The structure of the complex formed by a tetracarboxylic 18-crown-6 ligand with H_3O^+ has been determined by X-ray crystallography ($P2_12_12_1$; a = 10.526 (2), b = 14.325 (2), and c = 15.234 (2) Å). The structure was solved by direct methods and refined to R = 0.048 for 1957 ($I \geq 2\sigma(I)$) reflections. Hydrogen atoms were located on a Fourier difference map. The overall shape of the ligand is similar to that found in related complexes, as two carboxylic acid groups extend on both sides of the pseudoplanar macrocycle. The H_3O^+ cation is anchored in the center of the cavity by three $OH^+\cdots O$ hydrogen bonds (2.67, 2.73, and 2.74 Å) whereas the chloride counterion is H bonded to three carboxylic acid groups 5.5 Å away from the cation. The pyramidal geometry found for the oxonium cation in the present molecular complex shows this conformation to be the most stable in an ion-solvating environment.

The oxonium ion, H_3O^+, has remained a hypothetical molecule for many years. Its existence, first postulated in 1907,[1] was better accepted with the development of the acid–base theory of Brønsted and Lowry.[2] Nevertheless, its occurrence was the subject of many discussions until various physical methods allowed it to be identified unambiguously.[3] The first structural information on H_3O^+ came from spectroscopic studies. ^{1}H NMR spectroscopy brought the proof of the equivalence of the three protons in oxonium perchlorate,[4] and infrared spectroscopy of monohydrated strong

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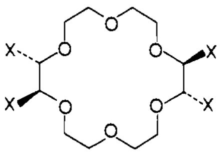
Table I. Crystal Data of the Complex

anal. for $C_{16}H_{27}O_{15}Cl$ (M_r 494.9)	
calcd	C, 38.83; H, 5.50
found	C, 38.20; H, 5.40
space group	$P2_12_12_1$, $Z = 4$
cell constants	$a = 10.526$ (2), $b = 14.325$ (2), and $c = 15.234$ (2) Å; $V = 2297$ Å^3

acids showed evidence for a pyramidal configuration.[5] The H_3O^+ structure was also inferred from the crystal structures of strong acids monohydrates,[6] but hydrogen atoms were localized only in the structure of oxonium perchlorate.[7]

Although there has been a controversy in this journal recently about the geometry of this cation,[8-10] relevant ab initio calculations[10] and solution[8,9] and solid-state[7,11] experiments now all agree with a *pyramidal geometry*. However, the strong tendency of H_3O^+ to form higher aggregates[12] has restricted the media to excess of superacid[8,12] or ionic crystals of acid monohydrates.[6,7,11] For instance, when hydrated forms (H_3O^+, $(H_2O)_n$) are observed, complex ions having one very short O–O distance (2.4–2.6 Å) exist as discrete entities.[13] These difficulties may be overcome by inclusion of the cation in a polar organic shell of appropriate size. Such a complex formation with a macrocyclic polyether ligand has been demonstrated on the basis of infrared spectroscopic measurements.[14] Indeed, macrocyclic polyethers form stable and selective complexes with various metallic as well as organic cations.[15] In particular, the tetracarboxylic 18-crown-6 ligand (**1**) containing two (*R*,*R*)-tartaric acid residues is a very strong



1, X = COOH

cation complexing agent, displaying a thousandfold increase in efficiency over the parent unsubstituted macrocyle.[16]

Here we report the crystal and molecular structure of an inclusion complex of H_3O^+ with this ligand. Evidence for complex formation came from pH data;[16] subsequent microanalysis supported this hypothesis, and the single-crystal X-ray analysis confirms this assumption.

Experimental Section

Stable crystals of the **1**·H_3OCl complex were obtained by slow evaporation of an ca 1 M HCl solution of the ligand. A single crystal of nearly cylindrical dimensions was fixed in a Lindemann capillary. Space group determination and data collection were performed on a Nonius CAD 4 diffractometer with graphite monochromatized Cu Kα radiation. Crystallographic data are summarized in Table I. The three-dimensional diffraction data set consists of 1957 independent and significant reflections ($I \geq 2\sigma(I)$) measured within a sphere of radius $\sin\theta/\lambda = 0.5617$ Å^{-1} ($\theta < 60°$) by using the $\theta/2\theta$ scan technique. A ψ scan showed the absorption effect to be weak (dispersion less than 7% on intensities, μR - 0.6), and no correction was made on the data set. Three reflections were measured every hour during data collection and showed no more than 10% decay. Anomalous dispersion effects were corrected by using the values of f' and f'' taken from ref 17.

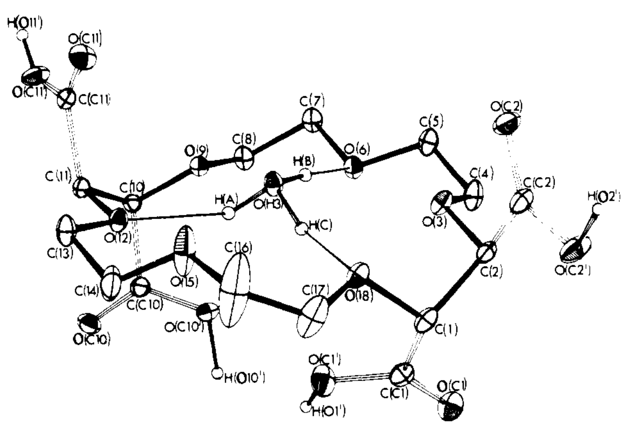


Figure 1. Perspective view and numbering scheme of the **1**·H_3O^+ molecular cation. The macrocyclic ring is visualized by dark sticks, and oxygen atoms are indicated by octant shading. Cl^- and the methylene H atoms are omitted for clarity.

The structure was solved by direct methods. A total of 24 of the 32 non-hydrogen atoms were localized on the best *E* map. The remaining atoms were found on a subsequent Fourier synthesis. Positional and thermal parameters were then refined by full-matrix least-squares analysis. All but H atoms bound to the agitated C(16)–C(17) fragment (B = 14.9 and 7.5) and to the carboxylic oxygen O(C2′) appeared as the highest peaks of a difference Fourier map (0.25–0.13 e/Å^3 on a relative scale, background below 0.1 e/Å^3). H(O2′) appeared at 0.09 e/Å^3. With the oxonium ion being firmly bound (B(O(H3)) = 3.9), its hydrogen atoms H(A, B, C) appeared unambigously contrasted on the map, at 0.22, 0.15, and 0.14 e/Å^3. These atoms were introduced in the refinement with thermal factors $B_H = 1.6B - 2$, where B holds for the atom bearing the hydrogen atom(s). Three cycles were then carried out on all nonhydrogen atoms, with anisotropic temperature factors. For the last cycle, no parameter shift was greater than 0.1 esd. At this stage, changing the coordinates to their centrosymmetric ones resulted in a 0.008 decrease of the *R* factor, in agreement with the known absolute configuration of **1**, which was synthesized from (*R*,*R*)-tartaric acid without racemization.[16]

Finally, two last refinement cycles including the positional parameters of H(A, B, C) were undertaken. No residual shift, except $z(H(B))$ (0.4 esd), was greater than 0.14 esd. The agreement factors $R = \sum||F_o| - |F_c||/\sum F_o|$ and $R_w = \{\sum_w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$ with $w = 1/\sigma^2(F)$ reached respectively 0.048 and 0.074. The atomic positional and thermal parameters are listed in Table II. Table III contains the calculated intramolecular bond lengths and angles of the ligand. Selected torsion angles are showh in Table IV.

Description of the Structure and Discussion

The three-dimensional structure of the complex cation is shown in Figure 1, with the numbering scheme used in the Experimental Section.

In the ligand, the geometrical features of tartaric acid[18] are retained. The four carboxylic acid groups are found to be planar within experimental error and show the typical asymetry in C–O bond length and C–C–O angles of COOH groups (Table III). Each group approaches coplanarity with the nearest ring-ether oxygen atom while maintaining an axial relationship with its neighbor (Table IV). Thus, two functional groups extend on both

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Table II. Positional[a] and Thermal[b] Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Cl	1.1783 (1)	0.7817 (1)	0.90184 (8)	0.0098 (1)	0.00791 (8)	0.00408 (5)	−0.0018 (2)	−0.0015 (2)	0.0013 (1)
O(3)	0.6743 (4)	0.9166 (2)	0.7567 (2)	0.0125 (4)	0.0042 (2)	0.0037 (1)	−0.0027 (5)	0.0029 (4)	−0.0015 (3)
O(6)	0.8631 (4)	0.9458 (2)	0.6339 (2)	0.0122 (4)	0.0044 (2)	0.0042 (1)	0.0028 (5)	0.0037 (4)	0.0017 (3)
O(9)	0.9902 (3)	0.7987 (2)	0.5579 (2)	0.0083 (3)	0.0040 (2)	0.0038 (1)	0.0002 (4)	0.0011 (4)	0.0004 (3)
O(12)	0.9435 (3)	0.6281 (2)	0.6259 (2)	0.0104 (3)	0.0033 (1)	0.0041 (1)	−0.0010 (4)	0.0026 (4)	−0.0002 (3)
O(15)	0.7442 (6)	0.5885 (3)	0.7375 (3)	0.0302 (7)	0.0042 (2)	0.0122 (3)	0.0019 (7)	0.0259 (7)	0.0002 (4)
O(18)	0.6634 (3)	0.7447 (2)	0.8231 (2)	0.0094 (3)	0.0046 (2)	0.0041 (1)	−0.0037 (4)	0.0023 (4)	−0.0017 (3)
O(C1)	0.8512 (4)	0.9082 (3)	0.9448 (3)	0.0122 (4)	0.0066 (2)	0.0071 (2)	−0.0046 (6)	0.0003 (6)	−0.0034 (4)
O(C1')	0.8982 (4)	0.7776 (3)	0.8704 (3)	0.0083 (3)	0.0091 (3)	0.0097 (3)	0.0019 (6)	−0.0013 (6)	−0.0056 (5)
O(C2)	0.4226 (4)	0.8741 (3)	0.7626 (2)	0.0118 (4)	0.0091 (3)	0.0035 (1)	0.0002 (6)	−0.0013 (5)	−0.0019 (4)
O(C2')	0.4256 (4)	0.8782 (3)	0.9087 (2)	0.0113 (4)	0.0121 (3)	0.0035 (1)	−0.0047 (7)	0.0030 (4)	−0.0031 (4)
O(C10)	1.2612 (4)	0.6861 (3)	0.6495 (3)	0.0125 (4)	0.0060 (2)	0.0066 (2)	0.0017 (5)	−0.0066 (5)	0.0009 (4)
O(C10')	1.1194 (4)	0.7874 (3)	0.7043 (2)	0.0166 (5)	0.0066 (2)	0.0040 (2)	0.0041 (6)	−0.0052 (5)	−0.0015 (3)
O(C11)	0.8380 (3)	0.6202 (3)	0.4611 (3)	0.0077 (3)	0.0092 (3)	0.0058 (2)	−0.0008 (6)	−0.0015 (5)	0.0008 (4)
O(C11')	1.0260 (4)	0.6436 (3)	0.3999 (2)	0.0094 (4)	0.0129 (3)	0.0031 (1)	−0.0014 (7)	0.0007 (4)	−0.0028 (4)
O(H3)	0.7841 (3)	0.7671 (2)	0.6654 (2)	0.0094 (3)	0.0039 (2)	0.0047 (1)	0.0010 (4)	0.0034 (4)	0.0008 (3)
C(C1)	0.8188 (5)	0.8399 (4)	0.9032 (3)	0.0102 (5)	0.0059 (3)	0.0040 (2)	−0.0029 (7)	0.0007 (7)	−0.0008 (4)
C(C2)	0.4804 (5)	0.8831 (4)	0.8312 (3)	0.0096 (5)	0.0068 (3)	0.0035 (2)	−0.0020 (7)	0.0027 (6)	−0.0025 (5)
C(C10)	1.1678 (5)	0.7335 (3)	0.6429 (3)	0.0104 (5)	0.0041 (2)	0.0042 (2)	−0.0006 (7)	−0.0019 (6)	−0.0001 (4)
C(C11)	0.9490 (5)	0.6327 (4)	0.4654 (3)	0.0094 (5)	0.0045 (2)	0.0040 (2)	0.0010 (7)	−0.0010 (6)	−0.0019 (4)
C(1)	0.6828 (5)	0.8194 (4)	0.8821 (3)	0.0108 (5)	0.0056 (3)	0.0034 (2)	−0.0027 (7)	0.0034 (6)	−0.0013 (4)
C(2)	0.6188 (5)	0.9030 (4)	0.8400 (3)	0.0091 (5)	0.0053 (3)	0.0030 (2)	−0.0003 (6)	0.0015 (6)	−0.0024 (4)
C(4)	0.7224 (7)	1.0060 (4)	0.7404 (4)	0.0150 (7)	0.0039 (2)	0.0072 (3)	−0.0003 (8)	0.0060 (9)	−0.0017 (5)
C(5)	0.7669 (6)	1.0132 (3)	0.6495 (4)	0.0129 (6)	0.0033 (2)	0.0060 (3)	0.0022 (7)	0.0035 (8)	0.0014 (5)
C(7)	0.9139 (6)	0.9529 (4)	0.5468 (3)	0.0122 (6)	0.0043 (2)	0.0048 (2)	0.0012 (7)	0.0050 (7)	0.0026 (4)
C(8)	1.0292 (5)	0.8940 (3)	0.5422 (3)	0.0112 (5)	0.0042 (2)	0.0047 (2)	−0.0003 (7)	0.0043 (6)	0.0023 (4)
C(10)	1.0868 (4)	0.7320 (3)	0.5595 (3)	0.0075 (4)	0.0045 (2)	0.0032 (2)	0.0004 (6)	0.0001 (5)	0.0003 (4)
C(11)	1.0235 (5)	0.6393 (3)	0.5515 (3)	0.0078 (4)	0.0048 (2)	0.0036 (2)	0.0023 (6)	0.0007 (6)	−0.0014 (4)
C(13)	0.8985 (6)	0.5350 (3)	0.6429 (4)	0.0131 (6)	0.0031 (2)	0.0072 (3)	−0.0015 (7)	0.0046 (9)	−0.0007 (5)
C(14)	0.8374 (9)	0.5319 (4)	0.7294 (5)	0.0270 (12)	0.0054 (3)	0.0080 (4)	−0.0058 (12)	0.0043 (13)	0.0042 (6)
C(16)	0.6665 (12)	0.5844 (6)	0.8115 (7)	0.0619 (16)	0.0063 (4)	0.0210 (6)	−0.0102 (16)	0.0593 (12)	−0.0016 (9)
C(17)	0.6494 (8)	0.6540 (4)	0.8600 (4)	0.0278 (10)	0.0053 (3)	0.0067 (3)	−0.0108 (9)	0.0162 (9)	−0.0013 (5)
H(A)	0.856 (4)	0.738 (3)	0.672 (3)	4.0000					
H(B)	0.787 (5)	0.817 (3)	0.651 (3)	4.0000					
H(C)	0.760 (5)	0.769 (3)	0.737 (3)	4.0000					
H(O1')	0.971	0.781	0.879	8.6000					
H(O2')	0.324	0.852	0.902	7.6000					
H(O10')	1.176	0.793	0.768	6.7000					
H(O11')	1.012	0.643	0.350	7.0000					
H(1)	0.637	0.814	0.926	4.4000					
H(2)	0.629	0.961	0.875	4.2000					
H(4)	0.678	1.049	0.758	6.6000					
H(4')	0.795	1.025	0.781	6.6000					
H(5)	0.812	1.084	0.643	5.5000					
H(5')	0.695	1.008	0.596	5.5000					
H(7)	0.840	0.920	0.500	5.4000					
H(7')	0.941	1.025	0.537	5.4000					
H(8)	1.090	0.896	0.484	4.6000					
H(8')	1.098	0.910	0.596	4.6000					
H(10)	1.148	0.742	0.512	4.0000					
H(11)	1.078	0.596	0.551	4.1000					
H(13)	0.980	0.484	0.635	6.3000					
H(13')	0.832	0.516	0.598	6.3000					
H(14)	0.812	0.471	0.748	10.2000					
H(14')	0.902	0.559	0.770	10.2000					
H(17)	0.590	0.635	0.904	9.8000					

[a] Fractional atomic coordinates. [b] The form of the anisotropic thermal parameter is $\exp(-B_{1,1}h^2 + B_{2,2}k^2 + B_{3,3}l^2 + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)$.

sides of the pseudoplanar macroring; the face complexing the cation is slightly more open. Similar behavior has been found in the ethylenediammonium complex of **1**.[19] Furthermore, this structure and those of the potassium[20] and strontium[21] complexes of similar ligands have shown that when the cation matches the cavity size, the macrocycle is in a relaxed conformation. Here, the cation is probably too small, and therefore the ring is in a more strained conformation involving a highly disordered and pseudoeclipsed O(15)–C(16)–C(17)–O(18) fragment (see Tables II and IV).

The oxonium ion is located on the central axis normal to the ring, 0.61 Å above the plane defined by O(6), O(12), and O(18) to which it is bound, and 0.34 Å above the plane of the remaining ether oxygens. Thus H_3O^+ is bound to the farthest plane and penetrates, deeper into the cavity than the larger NH_4^+, which lies at 0.75 and 1.25 Å, respectively, from the planes formed by the bonded and nonbonded 18-crown-6 heteroatoms.[22] Three slightly bifurcated hydrogen bonds anchor the cation in the cavity (O(6,12,18)···O(H3) distances of 2.734 (5), 2.672 (4), and 2.737

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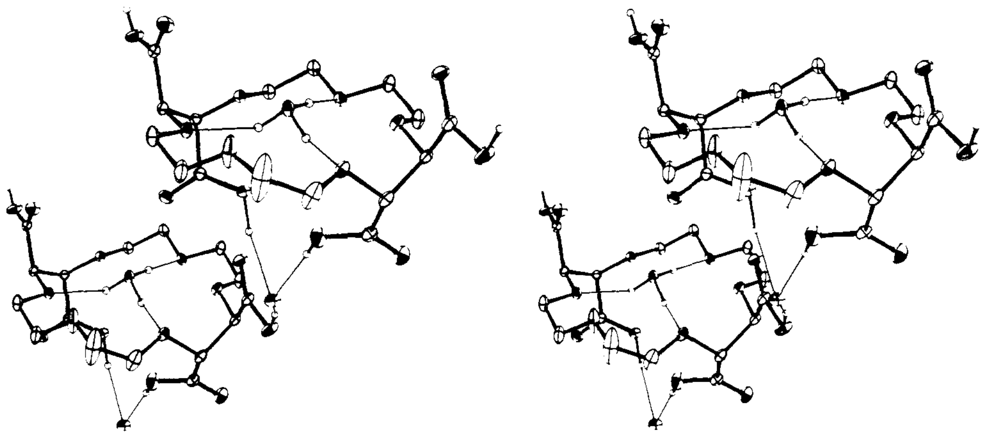

Figure 2. Stereoview of the packing along [100] and coordination of the chloride anion.

Table III. Ligand Intramolecular Bond Lengths (Å) and Valence Angles (Deg) with Their Estimated Standard Deviations

		O(18)-C(1)-C(2)	105.4 (4)
		C(C1)-C(1)-C(2)	111.2 (4)
		C(C1)-C(1)-O(18)	115.1 (4)
		O(C1')-C(C1)-C(1)	113.0 (5)
C(1)-C(2)	1.516 (7)	O(C1')-C(C1)-O(C1)	124.3 (5)
C(1)-C(C1)	1.496 (7)	C(1)-C(C1)-O(C1)	122.6 (5)
C(C1)-O(C1)	1.214 (6)	C(1)-C(2)-O(3)	107.8 (4)
C(C1)-O(C1')	1.321 (6)	C(1)-C(2)-C(C2)	108.7 (4)
C(2)-C(C2)	1.491 (7)	O(3)-C(2)-C(C2)	110.6 (4)
C(C2)-O(C2)	1.216 (6)	C(2)-C(C2)-O(C2)	125.9 (5)
C(C2)-O(C2')	1.316 (6)	O(C2')-C(C2)-O(C2)	123.1 (5)
C(2)-O(3)	1.411 (5)	O(C2')-C(C2)-C(2)	111.0 (5)
O(3)-C(4)	1.399 (6)	C(2)-O(3)-C(4)	115.9 (4)
C(4)-C(5)	1.465 (8)	O(3)-C(4)-C(5)	110.4 (4)
C(5)-O(6)	1.419 (6)	C(4)-C(5)-O(6)	109.7 (4)
O(6)-C(7)	1.435 (5)	C(5)-O(6)-C(7)	111.8 (4)
C(7)-C(8)	1.480 (7)	O(6)-C(7)-C(8)	108.0 (4)
C(8)-O(9)	1.446 (5)	C(7)-C(8)-O(9)	107.3 (4)
O(9)-C(10)	1.395 (5)	C(8)-O(9)-C(10)	116.3 (3)
C(10)-C(C10)	1.530 (6)	O(9)-C(10)-C(11)	106.4 (4)
C(C10)-O(C10)	1.199 (6)	O(9)-C(10)-C(C10)	114.3 (4)
C(C10)-O(C10')	1.317 (6)	C(11)-C(10)-C(C10)	109.2 (4)
C(10)-C(11)	1.491 (6)	C(10)-C(C10)-O(C10)	121.2 (4)
C(11)-C(C11)	1.532 (6)	O(C10')-C(C10)-O(C10)	126.1 (4)
C(C11)-O(C11)	1.184 (6)	O(C10')-C(C10)-C(10)	112.5 (4)
C(C11)-O(C11')	1.295 (6)	C(10)-C(11)-C(C11)	110.7 (4)
C(11)-O(12)	1.421 (5)	C(10)-C(11)-O(12)	107.5 (3)
O(12)-C(13)	1.439 (5)	C(C11)-C(11)-O(12)	111.9 (4)
C(13)-C(14)	1.467 (9)	C(11)-C(C11)-O(C11)	124.2 (5)
C(14)-O(15)	1.279 (9)	O(C11')-C(C11)-O(C11)	126.4 (5)
O(15)-C(16)	1.394 (9)	O(C11')-C(C11)-C(11)	109.4 (5)
C(16)-C(17)	1.254 (10)	C(11)-O(12)-C(13)	116.3 (3)
O(17)-O(18)	1.423 (6)	O(12)-C(13)-C(14)	109.5 (4)
O(18)-C(1)	1.412 (5)	C(13)-C(14)-O(15)	113.9 (6)
		C(14)-O(15)-C(16)	120.1 (8)
		O(15)-C(16)-C(17)	121.7 (7)
		C(16)-C(17)-O(18)	118.7 (6)
		C(17)-O(18)-C(1)	117.2 (4)

Table IV. Selected Torsion Angles (Deg) with Their Standard Deviations

O(18)-C(1)-C(2)-O(3)	−57.8 (6)
C(1)-C(2)-O(3)-C(4)	−126.0 (7)
C(2)-O(3)-C(4)-C(5)	−175.0 (7)
O(3)-C(4)-C(5)-O(6)	−59.1 (8)
C(4)-C(5)-O(6)-C(7)	−177.3 (6)
C(5)-O(6)-C(7)-C(8)	168.8 (7)
O(6)-C(7)-C(8)-O(9)	62.6 (6)
C(7)-C(8)-O(9)-C(10)	−177.7 (7)
C(8)-O(9)-C(10)-C(11)	−164.7 (6)
O(9)-C(10)-C(11)-O(12)	−62.3 (6)
C(10)-C(11)-O(12)-C(13)	−164.8 (5)
C(11)-O(12)-C(13)-C(14)	169.8 (7)
O(12)-C(13)-C(14)-O(15)	58.3 (9)
C(13)-C(14)-O(15)-C(16)	171.3 (10)
C(14)-O(15)-C(16)-C(17)	123.6 (12)
O(15)-C(16)-C(17)-O(18)	26.0 (14)
C(16)-C(17)-O(18)-C(1)	−170.0 (12)
O(18)-C(1)-C(C1)-O(C1')	−7.1 (8)
O(18)-C(1)-C(C1)-O(C1)	171.5 (8)
C(2)-C(1)-C(C1)-O(C1)	51.9 (8)
C(C1)-C(1)-C(2)-C(C2)	−172.7 (7)
O(3)-C(2)-C(C2)-O(C2)	4.0 (8)
O(3)-C(2)-C(C2)-O(C2')	−174.6 (7)
C(1)-C(2)-C(C2)-O(C2)	−114.1 (8)
O(9)-C(10)-C(C10)-O(C10')	10.2 (6)
O(9)-C(10)-C(C10)-O(C10)	−172.9 (6)
C(11)-C(10)-C(C10)-O(C10)	68.0 (6)
C(C10)-C(10)-C(11)-C(C11)	−176.0 (6)
O(12)-C(11)-C(C11)-O(C11)	0.3 (8)
O(12)-C(11)-C(C11)-O(C11')	179.8 (7)
C(10)-C(11)-C(C11)-O(C11')	60.0 (7)

(4) Å), and further stabilization may arise from ion–dipolar interactions (O(3,9,15)···O(H3) distances of 2.756 (4), 2.803 (5), and 2.815 (6) Å.

H_3O^+ has a *pyramidal* geometry, the oxygen atom being 0.33 (3) Å from the plane of the H atoms. This result is significant although the OH bond lengths (0.82 (6), 0.89 (5), and 1.01 (5) Å) and HOH valence angles (95 (5)°, 102 (5)°, and 120 (5)°) are widely spread. Several factors may account for this dispersion: Hydrogen atoms have a very weak X-ray diffracting power, and their electron density often does not match the nucleus. Furthermore, the H_3O^+ pyramid is rocked in the crown in such a way that H(A) and H(C) are within the O(6)–O(12)–O(18)–O(H3) tetrahedron, whereas H(B) is on the outside (Figure 1).

In the unit cell, the chloride counterion is sandwiched between the two carboxylic acid residues extending from the face opposite to that where H_3O^+ is bound (O(Cl',C10')···Cl^- distances of 2.99 (4) and 3.07 (3) Å); a third COOH···Cl^- hydrogen bond comes from the neighboring ligand along the [100] vector (O(C2')···Cl^- = 2.95(8) Å). The Cl^-–O(H3) axis (5.5 Å) is nearly perpendicular to the crown mean plane (see Figure 2). The crystal packing forces are completed by an intermolecular O(C11')···O(C2) hydrogen bond.

Conclusion

The present structure together with previous work on related complexes[16,19–21] shows that the tartaric acid moieties maintain a remarkably constant conformation, giving two lateral appendages that extend on both faces of the crown. Such a conformation allows secondary interactions with a bound molecular cation to occur.

The oxonium cation has been isolated in a macrocyclic polyether core, thereby preventing the aggregation commonly found in the structures of acid polyhydrates.[13] All previous X-ray and neutron data on H_3O^+ were performed on ionic crystals of strong acid monohydrates,[6,7,11] and theoretical or solution studies on the geometry of this cation in relation to its environment are not obvious. The pyramidal conformation found in the present structure allows this geometry to be generalized to ion-solvating media.

Registry No. 1·H_3OCl, 77027-22-6.