A Novel Crown-Ether Stabilized Oxonium Halogenochalcogenate(IV): $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The title compound $[H_7O_3$(bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ (**1**) was isolated from a solution of $SeBr_4$ and dibenzo-30-crown-10 in CH_3CN/CH_2Cl_2 containing a small amount of hydrobromic acid. During the reaction the crown ether is brominated by HBr.

The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 17.688(11)$, $b = 14.921(6)$, $c = 20.521(12)$ Å, $\beta = 97.71(5)^\circ$, and $Z = 4$. **1** is a novel example in the series of supramolecular halogenochalcogeno acids prepared in our group in which different oxonium cations are stabilized and encapsulated by crown ethers. Especially in this class of superacids complexation by cyclic polyethers offers covenient and variable possibilities for the controlled synthesis of oxonium cations. In the present case the large dibenzo-30-crown-10 ring systems are able to stabilize trinuclear $[H_7O_3]^+$ cations within their cavities. Besides the macromolecular cations and some dichloromethane solvent molecules, the crystal structure of **1** contains molecular $[Se_2Br_9]^-$ ions with approximate D_{3h} symmetry, each consisting of two face-sharing $SeBr_6$ octahedra.

Key words: Crystal Structure, Chalcogenates, Oxonium Ions, Crown Ether

Introduction

The structural properties of halogenochalcogenates(IV) can be related to the cubane structures of the tetrahalides. Adding halides results in a stepwise degradation by nucleophilic attack of the tetrameric structure leading to the tri-, di- and monomeric species $[Q_3X_{13}]^-$, $[Q_2X_{10}]^{2-}$ and $[QX_6]^{2-}$, all based on QX_6-octahedra as building blocks (Q = Se, Te; X = Cl, Br). In the oligomeric species the octahedra are connected *via* common edges. Their structures and properties are well known [1 – 3]. The size of the resulting anions mainly depends on the solvent, the concentration of the halides and the size of the counterions, respectively.

The presence of anions that do not fit into this scheme of decomposition indicate complex equilibria in solution. The formation of the monomeric $[QX_5]^-$ anions *e.g.* in the compounds $[C_8H_8S_2N][TeCl_5]\cdot 1.5C_4H_8O_2$ [4] may be caused by ligand exchange in solution. The compounds $[PCl_4]_n[TeCl_5]_n$ [5, 6] and $[H_9O_4]_n[Te_2Cl_9]_n$ [7] contain polymeric anionic species. The $[TeCl_5]_n^{n-}$ anion consists of $TeCl_6$ octahedra connected *via* common edges whereas in the $[Te_2Cl_9]_n^{n-}$ anion $TeCl_6$ octahedra are alternatingly connected *via* common edges and corners.

In solvents containing aqueous hydrogen halides the chalcogen tetrahalides form halogeno chalcogeno acids. They can be classified as superacids and are completely dissociated in solutions as well as in the solid state. Thus they should be described as oxonium halogenochalcogenates(IV). In more concentrated solutions of these systems the oxonium ions form clusters such as $[H_7O_3]^+$ or $[H_9O_4]^+$. So far crystalline compounds such as $[H_9O_4]_2[TeBr_6]$ [3], $[H_7O_3]_2[TeI_6]\cdot 2H_2O$ [8], $[H_9O_4][TeCl_4OH]\cdot H_2O$ [7], $[H_9O_4][Te_3Br_{13}]$ [3] and $[H_9O_4]_n[Te_2Cl_9]_n$ [7] have been reported. Organic molecules with electron donating groups can be used to stabilize oxonium ions. For instance in the compounds $[H_3O][TeBr_5]\cdot 3C_4H_8O_2$ [9] and $[H_5O_2][Te_2Cl_9]\cdot 2C_4H_8O_2$ [10] the oxonium cations are coordinated by three 1,4-dioxane molecules. If the electron donating group is more basic than H_2O the protonated organic molecules can be isolated as counter ions of the halogenochalcogenates(IV). This

was shown for *e.g.* $[(CH_3)_2SOH]_2[TeCl_6]\cdot 2(CH_3)_2SO$ and $[(CH_3)_2CHC(NH_2)(OH)][Te_3Cl_3]\cdot(CH_3)_2CHCN$ [2, 11].

Utilization of crown ethers is another convenient method to stabilize oxonium cations in halogenochalcogenates. Compounds within this class of materials which have been prepared include $[H_3O$(dibenzo-18-crown-6)$][Te_2Br_9]$ [10], $[H_3O$(dibromo-benzo-15-crown-5)$]_2[SeBr_6]$ [17], $[H_3O$(benzo-18-crown-6)$]_2[Te_2Br_{10}]$ $[H_5O_2$(dibenzo-24-crown-8)$]_2[Te_2Br_{10}]$ [18] and $[H_5O_2$(bis-dibromo-dibenzo-24-crown-8)$]_2[Se_3Br_8]$ [19, 20]. They have been synthezised and characterized in our research group.

Here we report the novel compound $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ (**1**) where the oxonium ions are encapsulated by especially large crown ether ligands.

Experimental Section

Synthesis

$[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5\ CH_2Cl_2$: 0.5 g $SeBr_4$ (1.254 mmol) was dissolved in a mixture of 5 ml CH_3CN/CH_2Cl_2 and HBr (0.07 ml, 48%). The solution is heated and dibenzo-30-crown-10 (12.5 mg, 0.024 mmol) was added. After cooling down to −18 °C red crystals suitable for single crystal X-ray diffraction have been obtained by careful recrystallization, m. p.: 95 °C.

Crystal structure determination

For the data collections single crystals of the compound were measured on a SIEMENS P3 four-circle diffractometer under a nitrogen atmosphere. The space group was determined from systematic absences and intensity statistics. $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5\ CH_2Cl_2$ crystallizes in space group $P2_1/n$. The structure solution was achieved *via* direct methods using the SHELXTL PLUS software [12]; full-matrix least-squares refinements were carried out using the SHELXL-93 programme. The starting coordinates of the Se and Br atoms were obtained from the initial E-maps, all other non-hydrogen atoms were derived from subsequent difference Fourier syntheses. Se, Br, Cl, O, and C atoms were refined with anisotropic displacement parameters. All atoms are on general positions of the space group.

Aromatic and aliphatic hydrogen atom positions in the organic part were calculated at idealized coordinates and were refined in a restrained system coupled to the adjacent carbon atoms. The approximate coordinates of the H atoms in the oxonium cations could be obtained from careful evaluation of the final difference Fourier maps. They were fully in accordance with chemical arguments considering the assignment of the H_3O group to O(3W) and considering the hydrogen bridge system to the crown ether oxygen atoms. However, they were not refined independently, but rigidly coupled to O(1W) (as H_2O), O(2W) (as H_2O), and O(3W) (as pyramidal H_3O) with a fixed O-H distance of 0.90 Å.

Table 1. Crystal data and details of structure refinement for $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5\ CH_2Cl_2$ (**1**).

Empirical formula	$C_{29.5}O_{13}H_{46}Br_{13}Cl_3Se_2$ (**1**)
Formula weight	1870.20 g/mol
Temperature	153(2) K
Diffractometer	SIEMENS P3
Wavelength	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
Unit cell dimensions	$a = 17.688(11)$ Å
	$b = 14.921(6)$ Å
	$c = 20.521(12)$ Å
	$\beta = 97.71(5)^\circ$
Volume	5372(1) Å^3
Z	4
Density (calculated)	2.314 g/cm^3
Crystal size	$0.03 \times 0.04 \times 0.20$ mm^3
Theta range for data collection	4.0 to 54.0°
Index ranges	$0 \le h \le 18$,
	$0 \le k \le 15$,
	$-23 \le l \le 21$
Reflections collected	6759
Independent reflections	2648
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2648 / 0 / 401
Goodness-of-fit on F^2	0.970
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0782$, $wR2 = 0.1266$
R Indices (all data)	$R1 = 0.2263$, $wR2 = 0.1849$
Largest diff. peak and hole	1.715 and −1.135 eÅ^{-3}

Besides the well-defined system of $[Se_2Br_9]^-$ anions and supramolecular crown ether-oxonium cations the crystal contains a rather ill-defined region of dichloromethane solvate molecules strongly disordered over two sites. In addition, on both sites the Cl atoms of the CH_2Cl_2 species are disordered internally so that a precise localization was difficult. Even at the data collection temperature of 153 K partial loss of crystal solvent from these disordered sites could not be avoided. So, according to the refinement of the occupational factors, a residual content of 1.5 CH_2Cl_2 per formula unit was assumed throughout the structure determination.

The parameters of the data collection as well as details of the structure solution and refinement are summarized in Table 1.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-247194 for $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-

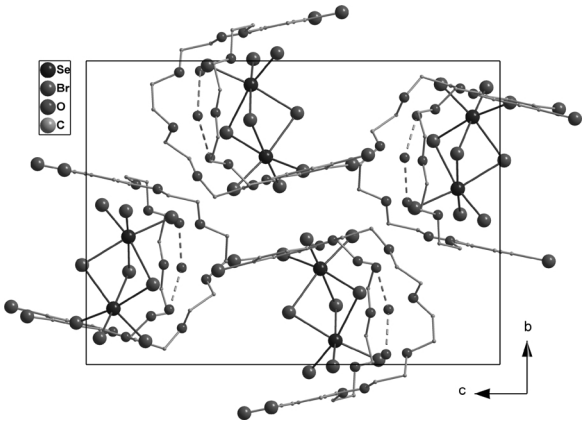

Fig. 1. Projection of the unit cell in $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ along [100], hydrogen atoms omitted.

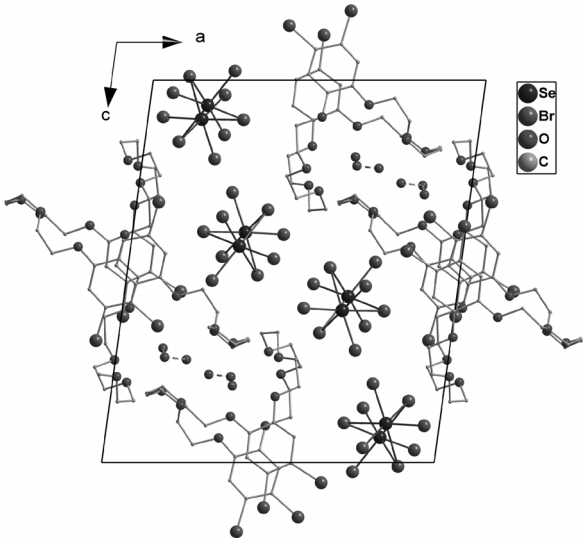

Fig. 2. Projection of the unit cell in $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ along [010], hydrogen atoms omitted.

10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Results and Discussion

The crystal structure of $[H_7O_3$(bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ (**1**) consists of a supramolecular arrangement of molecular $[Se_2Br_9]^-$ anions and $[H_7O_3$(bis-dibromo-dibenzo-30-crown-10)$]^+$ cations. In addition the crystals contain some dichlormethane solvent molecules in a disordered manner. Fig. 1 shows a projection of the unit cell along [100], in Fig. 2 the projection along [010] gives a more detailed view on the cations.

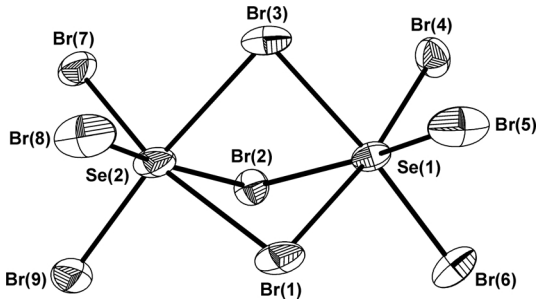

Fig. 3. Dimeric $[Se_2Br_9]^-$ anion in $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ in an ellipsoidal representation (50% probability).

The dinuclear anionic unit is formed by condensation of two axially distorted octahedral $SeBr_6$ entities *via* a common face of three bromine atoms. The anion has D_{3h} symmetry (see Fig. 3). The average Se-Br bond length in **1** (2.602 Å, for details see Table 2) is comparable to the mean Se-Br bond length in the $[SeBr_6]^{2-}$ anion [*e.g.* 14] with 2.565 Å. The Se-$Br_{(term)}$ bond lengths (mean value 2.41 Å) are significantly shorter than the Se-μ_2Br values (mean 2.79 Å). These data are in good accordance with other known Se-Br distances for terminal and bridging μ_2 bonds [1]. Moreover the single distances show a clear correlation between the Se-Br bond lengths trans to each other (*e.g.* the longest bridge bond Se(2)-Br(1) is trans to the shortest terminal bond Se(2)-Br(7), Table 2). This phenomenon is well known for hypervalent systems of the present kind and is well in accordance with the three-centre-four-electron model.

The short bonds of the terminal bromine atoms to the selenium atoms result in larger mutual repulsion of the bromine atoms resulting in an expansion of the $Br_{(term)}$-Se-$Br_{(term)}$ bond angles (mean 94.2°) and a compression of the μ_2Br-Se-μ_2Br bond angles (mean 81.9°). The structure within the terminal $SeBr_3$ units is similar to the one found in tetrameric $[SeBr_4]_4$ [16]. In the limiting case of an ionic description the anion in **1** can be regarded as $[(SeBr_3^+)_2(Br^-)_3]$. This is analogous to the formulation of the tetrabromide $[(SeBr_3^+)_4Br_4]$.

It is highly interesting to observe a number of rather short intermolecular Br···Br contacts with distances

Table 2. Bond lengths [Å] and angles [°] with standard deviations for $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$ (**1**).

Se(1)-Br(1)	2.732(4)	Se(2)-Br(1)	2.902(5)	Br(3)-Se(1)-Br(5)	89.9(2)	Br(7)-Se(2)-Br(8)	94.2(2)
Se(1)-Br(2)	2.810(4)	Se(2)-Br(2)	2.748(4)	Br(3)-Se(1)-Br(6)	174.9(2)	Br(7)-Se(2)-Br(9)	94.2(2)
Se(1)-Br(3)	2.737(4)	Se(2)-Br(3)	2.811(5)	Br(4)-Se(1)-Br(5)	94.5(2)	Br(8)-Se(2)-Br(9)	94.6(2)
Se(1)-Br(4)	2.440(4)	Se(2)-Br(7)	2.372(5)	Br(4)-Se(1)-Br(6)	94.1(2)		
Se(1)-Br(5)	2.410(5)	Se(2)-Br(8)	2.418(5)	H_7O_3 cation:			
Se(1)-Br(6)	2.433(5)	Se(2)-Br(9)	2.407(5)	O(1W)···O(3W)	2.477(22)	O(2W)···O(4)	2.757(21)
Se(1)···Se(2)	3.623(5)	Br(2)···Br(9)	3.698(5)	O(1W)···O(1)	3.076(23)	O(2W)···O(5)	3.087(21)
Br(1)···Br(2)	3.653(5)	Br(3)···Br(4)	3.639(5)	O(1W)···O(2)	2.807(25)	O(2W)···O(6)	2.841(21)
Br(1)···Br(3)	3.677(5)	Br(3)···Br(5)	3.645(5)	O(1W)···O(3)	3.046(24)	O(2W)···O(7)	3.125(22)
Br(1)···Br(5)	3.705(6)	Br(3)···Br(7)	3.670(5)	O(1W)···O(9)	2.872(27)	O(3W)···O(3)	3.453(23)
Br(1)···Br(8)	3.913(6)	Br(3)···Br(8)	3.721(5)	O(1W)···O(10)	3.059(24)	O(3W)···O(8)	2.654(21)
Br(1)···Br(9)	3.934(6)	Br(4)···Br(5)	3.560(5)	O(2W)···O(3W)	2.487(22)	O(3W)···O(9)	3.173(25)
Br(2)···Br(3)	3.695(5)	Br(4)···Br(6)	3.567(5)	O(1W)-O(3W)-O(2W)	119.2(8)	O(3W)-O(2W)-O(4)	113.3(7)
Br(2)···Br(4)	3.737(5)	Br(5)···Br(6)	3.534(6)	O(1W)-O(3W)-O(8)	116.1(8)	O(3W)-O(2W)-O(6)	128.5(8)
Br(2)···Br(6)	3.796(5)	Br(7)···Br(8)	3.508(6)	O(2W)-O(3W)-O(8)	111.8(8)	O(2)-O(1W)-O(9)	154.4(9)
Br(2)···Br(7)	3.631(5)	Br(7)···Br(9)	3.501(5)	O(3)-O(3W)-O(8)	173.8(8)	O(3W)-O(1W)-O(9)	72.4(7)
Br(8)···Br(9)	3.543(7)			O(4)-O(2W)-O(6)	107.4(7)	O(3W)-O(1W)-O(2)	132.4(8)
intermolecular distances:				H(1W)-O(1W)	0.900	H(1W)···O(2)	2.154
Br(1)···Br(11a)	3.453(4)	Br(6)···Br(6d)	3.613(7)	H(2W)-O(1W)	0.900	H(2W)···O(9)	2.314
Br(2)···Br(9b)	3.913(5)	Br(3)···Br(10d)	3.857(5)	H(3W)-O(3W)	1.200	H(3W)···O(1W)	1.324
Br(7)···Br(12c)	3.348(4)			H(4W)-O(3W)	1.100	H(4W)···O(2W)	1.418
Se(1)-Br(1)-Se(2)	80.0(2)	Br(5)-Se(1)-Br(6)	93.7(2)	H(5W)-O(3W)	0.930	H(5W)···O(8)	1.750
Se(1)-Br(2)-Se(2)	81.4(2)	Br(1)-Se(2)-Br(2)	80.6(2)	H(6W)-O(2W)	0.900	H(6W)···O(6)	1.994
Se(1)-Br(3)-Se(2)	81.6(2)	Br(1)-Se(2)-Br(3)	80.1(1)	H(7W)-O(2W)	0.900	H(7W)···O(4)	1.870
Br(1)-Se(1)-Br(2)	82.5(2)	Br(1)-Se(2)-Br(7)	166.9(2)	H(1W)-O(1W)-H(2W)	86.7	H(4W)-O(2W)-H(7W)	107.1
Br(1)-Se(1)-Br(3)	84.5(1)	Br(1)-Se(2)-Br(8)	94.3(2)	H(1W)-O(1W)-H(3W)	136.3	H(3W)-O(3W)-H(4W)	104.6
Br(1)-Se(1)-Br(4)	171.0(2)	Br(1)-Se(2)-Br(9)	95.2(2)	H(2W)-O(1W)-H(3W)	113.2	H(3W)-O(3W)-H(5W)	106.5
Br(1)-Se(1)-Br(5)	92.0(2)	Br(2)-Se(2)-Br(3)	83.4(2)	H(4W)-O(2W)-H(6W)	107.4	H(4W)-O(3W)-H(5W)	109.2
Br(1)-Se(1)-Br(6)	91.9(2)	Br(2)-Se(2)-Br(7)	90.1(2)	H(6W)-O(2W)-H(7W)	111.8		
Br(2)-Se(1)-Br(3)	83.6(2)	Br(2)-Se(2)-Br(8)	172.4(2)	O(1W)-H(1W)···O(2)	129.2	O(3W)-H(5W)···O(8)	166.3
Br(2)-Se(1)-Br(4)	90.5(2)	Br(2)-Se(2)-Br(9)	91.4(2)	O(1W)-H(2W)···O(9)	120.2	O(2W)-H(6W)···O(8)	156.3
Br(2)-Se(1)-Br(5)	171.8(2)	Br(3)-Se(2)-Br(7)	89.8(2)	O(3W)-H(3W)···O(1W)	158.5	O(2W)-H(7W)···O(4)	168.4
Br(2)-Se(1)-Br(6)	92.5(1)	Br(3)-Se(2)-Br(8)	90.5(2)	O(3W)-H(4W)···O(2W)	161.3		
Br(3)-Se(1)-Br(4)	89.2(2)	Br(3)-Se(2)-Br(9)	173.5(2)				

Symmetry transformations used to generate equivalent atoms: a) $x+1/2,-y+1/2,z+1/2$; b) $-x+1,-y+2,-z+1$; c) $x+1,y+1,z$; d) $-x+1,-y+1,-z+1$.

well below the formal sum of van der Waals radii for bromine (Table 2). As in a number of other halogenochalcogenates (*e. g.* [1]) this is an indication of significant charge transfer bonding interactions between different molecular units. In **1** the most significant interactions are between the $[Se_2Br_9]^-$ units and Br atoms of the brominated crown ether molecules, the smallest distance of 3.340 Å being between Br(7) and Br(12c), (Table 2).

The hydrophilic cavity within the thirty-membered macrocycle of (bis-dibromo-dibenzo-30-crown-10) is large enough to encapsulate a $[H_7O_3]^+$ cation (see Fig. 4). The central oxonium oxygen atom is coordinated pyramidally by two water molecules and a crown ether oxygen. The O···O distances (mean 2.48 Å) for O(1W)···O(3W) and O(2W)···O(3W) (Table 2) are typical for $[H_7O_3]^+$ entities. The distance between the central oxonium oxygen and the crown-ether acceptor oxygen atom O(8) is 2.654 Å. Thus, the $[H_7O_3]^+$ entity can be regarded as a distorted $[H_3O]^+$ cation surrounded by two water molecules. This description is supported by the qualitative location of the hydrogen atoms in the $[H_7O_3]^+$ unit, clearly showing three H atoms in bonding distance to O(3W). Moreover, the O···O hydrogen bond distances from the outer water molecules O(1W) and O(2W) of the $[H_7O_3]^+$ unit to crown ether oxygen atoms are normal $OH_{(water)}\cdots O$ values (2.76 Å, 2.84 Å, 2.81 Å, 2.87 Å, see Table 2) in contrast to the shorter value of 2.65 Å for O(3W)···O(8) typical for $OH_{(oxonium)}\cdots O$.

Evidently, the 30-membered crown ether tries to optimize its fold for a favorable encapsulation of the

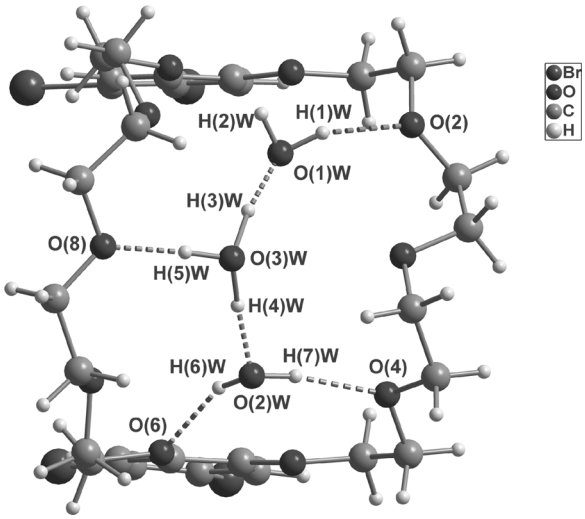

Fig. 4. $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$]^+$ cation in $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5\ CH_2Cl_2$.

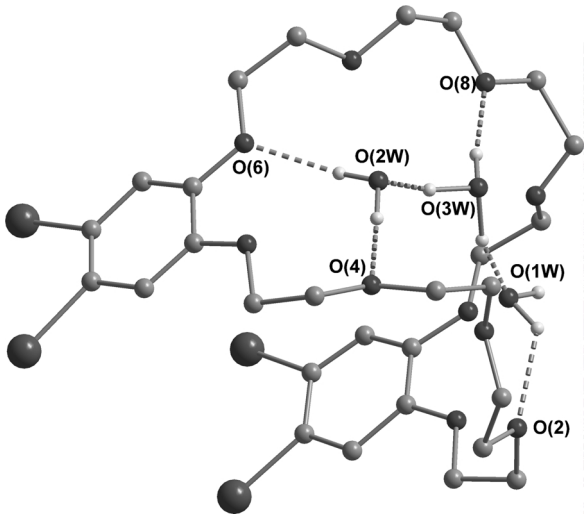

Fig. 5. Illustration of the twisting in the $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$]^+$ cation in $[H_7O_3$(Bis-dibromo-dibenzo-30-crown-10)$][Se_2Br_9]\cdot 1.5CH_2Cl_2$.

$[H_7O_3{}^+]$ entity, maximizing the hydrogen bond stabilization. As shown in Fig. 5, the polyether molecule has to twist into a very special conformation. Even this optimization leaves some unfavorable details: The angles at O(1W) sharing three H atoms between its acceptor and donor oxygen atoms exhibit large differences with 154.4(9)° (O(2)-O(1W)-O(9)), 72.4(7)° (O(3W)-O(1W)-O(9)) and 132.4(8)° (O(3W)-O(1W)-O(2)), indicating strongly non-linear hydrogen bonds.

Within the crown ether the individual C-O-C and O-C-C bond angles differ significantly from usual values (114.8° and 108.2°). The mean values however are comparable (114.7° and 105.5°).

Conclusion

The present compound extends the series of known oxonium halogenochalocogenates to an especially large 30-membered cyclic polyether as multidentate ligand to the oxonium cation. The modes of crown ether coordination, together with their substitution patterns, offer convenient possibilities for the design of oxonium cation size and configuration. Considering the series of the crown members of this class, *e.g.* $[H_3O][TeBr_5] \cdot 3C_4H_8O_2$ [9] and $[H_5O_2][Te_2Cl_9] \cdot 2C_4H_8O_2$ [10], $[H_3O$(dibenzo-18-crown-6)$][Te_2Br_9]$ [10], $[H_3O$(dibromo-benzo-15-crown-5)$]_2[SeBr_6]$ [17], $[H_3O$(benzo-18-crown-6)$]_2[Te_2Br_{10}]$ $[H_5O_2$(dibenzo-24-crown-8)$]_2[Te_2Br_{10}]$ [18], and $[H_5O_2$(Bis-dibromo-dibenzo-24-crown-8)$]_2[Se_3Br_8]$ [19, 20] a size-selective stabilization of larger homologues of the oxonium cations by the larger crown ethers is evident.

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