

Structure of Dibenzocrown Ethers and Their H-bonded Adducts. 3. Isolation of Oxonium Ions by Biphenyl-20-crown-6 and [1.5]Dibenzo-18-Crown-6 In Complexes with $[\text{NbF}_6]^-$ and $[\text{TaF}_6]^-$

EDUARD V. GANIN¹, VLADIMIR O. GELMBOLDT², LARISA V. KOROEVA², MARINA S. FONARI^{3,*}, YURII A. SIMONOV³, JANUSZ LIPKOWSKI⁴, SERGEI A. KOTLYAR⁵ and GERBERT L. KAMALOV⁵

¹Odessa State Environmental University, Ministry of Education and Science of Ukraine, Lvovskaya str., 15, 65016, Odessa, Ukraine; ²Physico-Chemical Institute of Environment and Human Protection, Ministry of Education and Science of Ukraine and National Academy of Sciences of Ukraine, Preobrazhenskaya str., 3, 65026, Odessa, Ukraine; ³Institute of Applied Physics, Academy of Sciences of Moldova, Academy str., 5, MD, 2028, Chisinau, Moldova; ⁴Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka, 44/52, Warsaw, Poland; ⁵A.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, 650080, Odessa, Ukraine

(Received: 29 November 2005; in final form: 14 March 2006)

Key words: complexes with oxonium ions, dibenzocrown ethers, hexafluoroniobate and hexafluorotantalate anions, hydrogen bonding, IR spectra and crystal structure, synthesis

Abstract

The reaction of Nb_2O_5 and Ta_2O_5 with an aqueous solution of hydrofluoric acid, HF in the presence of biphenyl-20-crown-6 (BP20C6, L^1) or [1.5]dibenzo-18-crown-6 ([1.5]DB18C6, L^2) results in the complexes $[L^1 \cdot (\text{H}_3\text{O})][\text{NbF}_6]$ (**1**), $[L^1 (\text{H}_3\text{O})][\text{TaF}_6]$ (**2**), $[2L^2 \cdot (\text{H}_7\text{O}_3)][\text{NbF}_6]$ (**3**) and $[2L^2 \cdot (\text{H}_7\text{O}_3)][\text{TaF}_6]$ (**4**). Complexes **1–4** were identified by the elemental and X-ray structural analysis and IR spectroscopy. Complexes **1** and **2** are isostructural, with the H_3O^+ oxonium ion embedded in one crown molecule *via* $\text{OH} \cdots \text{O}$ hydrogen bonds. Complexes **3** and **4** represent the supramolecular isomers distinctive by the crown conformations and crystal packing, with the $(\text{H}_7\text{O}_3)^+$ cation enclosed in the cage of two crown molecules. Being poor H-bond acceptors, NbF_6^- and TaF_6^- anions do not compete with the crown oxygen atoms for the oxonium hydrogen atoms, but are involved in the numerous $\text{C-H} \cdots \text{F}$ short contacts responsible for the extended supramolecular architectures in all cases. A change of crown ethers' conformation in complexes **1–4** and a correlation between the degree of proton hydration and an accessibility of the crown ether oxygen atoms is observed.

Introduction

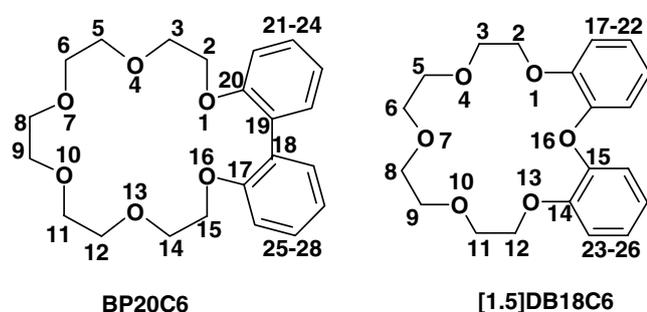
An interest to the chemistry of complexes of Nb(V) and Ta(V) fluorides is essentially connected with the development of suitable methods of concentration (separation) of these elements, the processes being based on the recrystallization or extraction of the proper complexes from acidic aqueous solutions [1]. So far there is no any data in the literature concerning the structure and properties of the products of Nb(V) and Ta(V) fluorocomplexes interaction with the crown ethers in aqueous solutions [2], and a very few structurally studied complexes of Nb(V) and Ta(V) fluorides are known where they present in the forms of $[\text{NbF}_6]^-$ [3, 4] and $[\text{TaF}_6]^-$ [5, 6] monoanions. Meantime taking into account the

complexing properties of the crown ethers, such data could be useful from the viewpoint of simulating the types of interaction in the extraction systems with the participation of neutral oxygen-containing extragents. The recent investigations [7] permit to forecast a «fixation» of H_3O^+ hydroxonium ion by crown ethers in the forms of the «extractable» fluorometallate complexes. Moreover, the results of work [8] indicate that in the series of crown ethers the most effective interaction with the proton donor component is realized in the cases of 18 and 20-membered cyclic polyethers containing six oxygen atoms.

In this work we wish to examine the «host–guest» complexes formed as a result of interaction between the products of Nb_2O_5 and Ta_2O_5 reaction with an aqueous hydrofluoric acid in the presence of biphenyl-20-crown-6 (BP20C6) and [1.5]dibenzo-18-crown-6 ([1.5]DB18C6).

* Author for correspondence. E-mail: fonari.xray@phys.asm.md

The specific structural features of these crown ethers are, on the one hand, a presence of the conformationally rigid biphenyl or diphenyloxy fragments, and, on the other hand, a different ratio of the so called “aromatic” and “aliphatic” oxygen atoms (2:4 and 3:3, respectively) (Scheme 1).



Scheme 1. Structural formulas of studied crown ethers (with the atomic numbering).

In [9], which is the first article of this cycle, we have shown the ability of these two crown ethers to interact with the amidosulfuric acid, $\text{H}_2\text{NSO}_2\text{OH}$. In the proper 1:1 adducts the amidosulfuric acid molecule in a zwitterion form coordinates to three alternative crown ether oxygen atoms in a near-ideal “tripod” arrangement *via* $\text{NH} \cdots \text{O}$ hydrogen bonds. That results in the different conformations of the crown molecules in the complexes and in the pure forms. In the second article, [10] we have revealed that [1.5]DB18C6 forms (*via* $\text{NH} \cdots \text{O}_{\text{crown}}$ and/or $\text{CH} \cdots \text{O}_{\text{crown}}$ hydrogen bonds) the H-bonded supramolecular complexes with 3-nitro-1H-1,2,4-triazole (1:1), 2,4(1H,3H)-pyrimidinedithione (1:1), 1,2,5-oxadiazole-3,4-diamine monohydrate (1:1:1), ethanedithioamide (1:1) and 1,2-hydrazinedicarbothioamide (2:3). In the all cases, the competition of the O-containing macrocyclic H-acceptor with H-acceptor (O and S) centers in the mentioned neutral molecules results in the substitution of all or part of supramolecular homosynthons by the heterosynthons and as a consequence, in the changing of supramolecular architecture.

To the best of our knowledge, Cambridge Structural Database [11] does not contain yet any complexes of [1.5]DB18C6 and BP20C6 crowns with the cations or being built on the cation–anion type interactions. Only very few examples of the complexes of the BP20C6 close derivatives with the metal [12] or organic cations [13] were found, which are sustained by ion–dipole interactions or charge-assisted hydrogen bonds.

A significant amount of studied crown ethers’ complexes with the hydrated proton (oxonium ions, $\text{H}(\text{H}_2\text{O})_n^+$, $n = 1$ to ca. 20) [14] shows that crown ethers act as excellent acceptors for strong, charge-assisted H-bonds with oxonium ions and a choice of the crown ether and a counter-ion has a decisive influence on the composition of oxonium ion stabilized in the crystal. The decisive factor is an accessibility of the crown oxygens for the interaction with the oxonium

cation, while the counter-ion should be (i) sterically inaccessible and (ii) a poor H-acceptor in comparison with the crown ether. A series of oxonium-containing crown complexes of the composition $[\text{CE} \cdot \text{H}(\text{H}_2\text{O})_n^+ \cdot \text{An}]$ (where CE – crown ether, An – halogen-containing anion, $n = 1$ and 2), are summarized in the Supplementary Table 1S. The analysis of these structures shows that predominantly 18C6 and its benzo-, dicyclohexano- and tetracarboxylic derivatives are highly selective for H_3O^+ because of the size and symmetry fit between them, allowing the inclusion of the oxonium ion within the 18-membered crown ether cavity with the formation of three strong $\text{OH} \cdots \text{O}$ hydrogen bonds [15a–u]. Less in size benzo-15C5 and 12C4 are also capable to fix oxonium ion either in a sandwich mode [15v], or through additional contact with the anion [15w], while the large in size dibenzo-30C10 is capable to display simultaneously two H_3O^+ cations inside the cavity [15x]. In contrary, the fixation of the H_7O_3^+ cation by crown ether is relatively uncommon and only two examples are known so far, where H_7O_3^+ oxonium cations alternate with crown ether in the hydrogen-bonded chains with the long-range interactions to the anions [15j].

In this article we report the synthesis, spectroscopic and structural studies of four complexes isolated from the reaction system M_2O_5 ($\text{M} = \text{Nb}, \text{Ta}$) – $\text{HF} - \text{H}_2\text{O} - \text{L}$, where L^1 – BP20C6 and L^2 – [1.5]DB18C6.

Experimental

Dibenzocrown ethers, BP20C6 (L^1) and [1.5]DB18C6 (L^2) were obtained as described in [9]. Complexes $[\text{L}^1(\text{H}_3\text{O})][\text{NbF}_6]$ (**1**), $[\text{L}^1(\text{H}_3\text{O})][\text{TaF}_6]$ (**2**), $[\text{L}^2(\text{H}_7\text{O}_3)][\text{NbF}_6]$ (**3**) and $[\text{L}^2(\text{H}_7\text{O}_3)][\text{TaF}_6]$ (**4**) were obtained by the interaction of the corresponding oxides with the 40% aqueous HF and the further treatment of the resulting solution by BP20C6 or [1.5]DB18C6. All complexes were analyzed for C, H and F in a Perkin Elmer 240 °C instrument. IR spectra (Table 1) of the complexes (samples as suspensions in Nujol mulls between KRS-5 windows) were measured on Specord 75-IR spectrometer in the range 4000–400 cm^{-1} .

Synthesis of $[\text{BP20C6}(\text{H}_3\text{O})][\text{NbF}_6]$ (**1**) Nb_2O_5 (133 mg, 0.5 mmol) was dissolved in 10 ml of 45% hydrofluoric acid. The resulting solution was evaporated up to 2 ml, and BP20C6 (388 mg, 1 mmol) in 5 ml of methanol was added, then the mixture was stored to crystallize at a room temperature and spontaneous evaporation of solvents. Colorless transparent crystals M.P. 114–116 °C (decomp.). Found, C, 43.06; H, 5.03; F, 18.61 for $\text{C}_{22}\text{H}_{31}\text{F}_6\text{NbO}_7$. Calculated, %: C, 43.01; H, 5.03; F, 18.61.

Synthesis of $[\text{BP20C6}(\text{H}_3\text{O})][\text{TaF}_6]$ (**2**) was carried out analogously to (**1**) from Ta_2O_5 (221 mg, 0.5 mmol) and BP20C6 (388 mg, 1 mmol). Colorless transparent crystals M.P. 155–157 °C (decomp.). Found, C, 37.57; H, 4.48; F, 18.19 for $\text{C}_{22}\text{H}_{31}\text{F}_6\text{TaO}_7$. Calculated, %: C, 37.62; H, 4.45; F, 16.23.

Table 1. IR spectral characteristics for ligands BP20C6 (L¹) and [1.5]DB18C6 (L²), and complexes [L¹(H₃O)][NbF₆] (**1**), [L¹(H₃O)][TaF₆] (**2**), [2L²(H₇O₃)][NbF₆] (**3**) and [2L²(H₇O₃)][TaF₆] (**4**)

L ¹	1	2	L ²	3	4	Assignment
				3480 m.br.	3470 sh. 3440 m. br.	$\nu(\text{H}_3\text{O}^+)$ ($\nu_1 + \nu_3$), $\nu(\text{H}_2\text{O})$
	3220 m.br. 3030 m.br.	3200 m.br. 3060 m.br.		3310 sh. 3235 sh. 3065 m.br.	3310 m. br. 3290 sh.	
				1670 sh. 1655 m.br. 1635 sh.	1685 sh. 1670 m.br. 1620 sh.	$\delta(\text{HOH})$
1585 m.	1590 m.	1577 m.	1595 sh. 1575 m.	1590 m. 1570 sh.	1585 m. 1565 sh.	$\nu(\text{CC})_{\text{Ar}}$
1555 sh.	1550 m.	1550 m.	1545 m.	1550 sh.	1550 sh.	
1510 sh.	1500 m.	1500 m.	1505 sh. 1320 sh.	1500 sh.	1500 sh.	$\omega(\text{CH}_2)$
1300 sh.	1295 sh.	1295 m.	1285 sh.	1280 sh.	1280 sh.	
1255 s.	1240 s.	1240 s.	1255 m.			$\nu_{\text{s,as}}(\text{ArOC})$, $\tau(\text{CH}_2)$
1220 s.	1220 s.	1220 s.	1230 m.	1230 s.	1230 s.	
1180 sh.	1175 sh.	1175 sh.	1190 s.	1185 s.	1185 s.	
1125 sh.	1125 sh.	1130 m.	1120 sh.			
1090 v.s.	1095 v.s. 1075 v.s.	1095 sh. 1075 v.s.	1105 s. 1075 sh.	1110 s. 1085 s.	1110 s. 1085 s.	$\nu_{\text{as}}(\text{COC})$
1055 s.	1045 s.	1055 s.	1050 sh.	1050 m.	1050 sh.	$\nu(\text{CC})_{\text{Cr}}$, $\rho(\text{CH}_2)$
1040 s.	1030 sh.	1030 sh.	1040 m. 1020 m.	1030 m.	1025 m.	
1000 sh.	1000 sh.	1000 sh.	1000 sh.	1000 sh.	1005 sh.	$\nu_{\text{s}}(\text{COC})$
955 m.	955 v.s.	955 v.s.	955 m.	935 s.	935 s.	
910 str.	910 sh.	900 sh.		915 m.	915 sh.	$\nu_{\text{resp.}}$, $\nu(\text{C-O})$, (CH_2)
895 m.	880 sh.	880 sh.	895 m.			
835 m.			840 m.	830 m.	830 m.	
820 m.	820 m.	825 sh.				
799 m.	790 sh.	790 sh.	795 m.	780 m.	780 m.	
745 m.	745 m.	745 m.	755 m.	740 s.	740 sh.	$\delta(\text{CH})_{\text{Ar}}$, $\gamma(\text{H}_2\text{O})$
	720 sh. 588 s.	720 sh.	730 m.	715 m. 595 s.	720 sh.	$\nu(\text{NbF})$
		565 s.			560 s.	$\nu(\text{TaF})$

Note: w – weak, m – medium, s – strong, v – very, sh – shoulder, br – broad.

Synthesis of [2[1.5]DB18C6·(H₇O₃)][NbF₆] (**3**) was carried out analogously to (**1**) from Nb₂O₅ (133 mg, 0.5 mmol) and [1.5]DB18C6·(360 mg, 1 mmol). Colorless transparent crystals M.P. 155–157 °C (decomp.). Found, C, 48.89; H, 5.65; F, 11.56 for C₄₀H₅₅F₆NbO₁₅. Calculated, %: C, 48.89; H, 5.64; F, 11.60.

Synthesis of [2[1.5]DB18C6·(H₇O₃)][TaF₆] (**4**) was carried out analogously to (**1**) from Ta₂O₅ (221 mg, 0.5 mmol) and [1.5]DB18C6·(360 mg, 1 mmol). Colorless transparent crystals M.P. 165–166 °C (decomp.). Found, C, 44.83; H, 5.22; F, 10.69 for C₄₀H₅₅F₆TaO₁₅. Calculated, %: C, 44.87; H, 5.18; F, 10.65.

Data collection and structure refinement

The X-ray intensity data for complexes **1–4** were recorded at 123 K with a Nonius Kappa CCD four-circle diffractometer equipped with graphite monochromatic MoK_α radiation using ω -2 θ rotation scan mode [16]. Final unit cell dimensions and positional data were

obtained and refined on the entire data set. Integration and scaling resulted in a data set corrected for Lorentz and polarization effects using DENZO [17]. The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK [17]. The structure solution and refinement proceeded similarly using SHELX-97 program package [18] for all structures. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full-matrix least squares method on F^2). In complexes **1** and **2** the oxygen atom of oxonium cation is disordered over two positions with the occupancies equal to 0.646(8) and 0.354(8) in **1**, and 0.66(1) and 0.34(1) in **2**, correspondingly. The minor components of oxonium oxygen atom were refined isotropically in both complexes. In complex **3** the oxonium ion occupies the position on the two-fold axis being equally disordered. C-bound H atoms were placed in calculated positions, with C–H distances of 0.93 or 0.97 Å, and were treated using a riding-model approximation, with

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H-atoms of water molecules and oxonium ions were determined from a difference Fourier map and were then allowed to refine isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ and O–H distances subjected to DFIX restraints.

The X-ray data and the details of the refinement for four complexes are summarized in Table 2, selected bond distances and angles – in Table 3, torsion angles – in Table 4.

Results and discussion

The oxonium cations and water molecules are registered in the IR spectra of complexes **1–4** by the bands of $\nu(\text{OH})$ and $\delta(\text{HOH})$ vibrations of average intensity (Table 1) in the two regions, 3480–3030 and 1685–1620 cm^{-1} , respectively, and the diffused contours of the last ones agree with the fact of the system of $\text{OH} \cdots \text{O}$ hydrogen bonding [19]. The comparative analysis of the IR spectra for complexes **1–4** with those for the corresponding ligands in the area of the conformationally sensitive vibrations of the macrocycles (1300–800 cm^{-1}) permits to conclude the crucial changing of the conformation of macrocycle due to the complex formation. Thus, in the spectra of complexes **1** and **2** (Table 1) the splitting of the intense band $\nu_{\text{as}}(\text{COC})$ of the initial BP20C6 (1090 cm^{-1}) on two components (1095 and 1080 cm^{-1}) is observed, and the bands of $\nu_{\text{s}}(\text{COC})$ vibrations at 1000 and 955 cm^{-1}

change in intensity. Instead of the intense band of $\nu_{\text{as}}(\text{COC})$ with the maximum at 1105 cm^{-1} and the shoulder at 1075 cm^{-1} observed in the spectrum of [1.5]DB18C6 (**L**²), the intense doublets with the maxima at 1110 and 1085 cm^{-1} in the spectra of complexes **3** and **4** are registered. In the area of $\nu_{\text{s}}(\text{COC})$ vibrations for these complexes the intensification and low-frequency (bathochromic) shift ($\sim 20 \text{ cm}^{-1}$) of the ligand band at 955 cm^{-1} (Table 1) was found, with practically unchanged position of the ligand band at 1000 cm^{-1} . The stretching vibrations $\nu(\text{M–F})$ for hexafluorometallate monoanions [19] in the spectra of complexes **1** and **2** become apparent in the form of very intense bands at 588 and 565 cm^{-1} , respectively, while in the spectra of complexes **3** and **4** these vibrations are registered at 595 and 560 cm^{-1} .

As it is evident from Table 2, complexes **1** and **2** are isostructural, so the structural discussion will be carried out only for complex **1**, while Tables 2–5 contain the essential geometric and hydrogen bonding parameters for both complexes. Complexes **3** and **4** have the same composition, $[\text{L}^2(\text{H}_7\text{O}_3)][\text{MF}_6]$ ($\text{M} = \text{Nb}, \text{Ta}$), but differ by the unit cell dimensions. Although they crystallize in the same monoclinic crystal system, and structure solution for both of them was found in the same space group $C2/c$, the asymmetric unit of **4** represents the four-time increased content of **3**. Below we will show the distinctive features between these two supramolecular isomers.

The NbF_6^- anions in complexes **1** and **3** adopt the usual octahedral geometry with Nb–F distances ranging

Table 2. Crystallographic data for complexes **1–4**

Compound	1	2	3	4
Composition	$\text{C}_{22}\text{H}_{31}\text{F}_6\text{NbO}_7$	$\text{C}_{22}\text{H}_{31}\text{F}_6\text{TaO}_7$	$\text{C}_{40}\text{H}_{55}\text{F}_6\text{NbO}_{15}$	$\text{C}_{40}\text{H}_{55}\text{F}_6\text{O}_{15}\text{Ta}$
Formula weight	614.38	702.42	982.75	1070.79
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$C2/c$
<i>a</i> (Å)	9.550(2)	9.562(2)	15.795(3)	43.185(4)
<i>b</i> (Å)	10.653(2)	10.677(2)	17.179(3)	18.044(6)
<i>c</i> (Å)	24.937(5)	24.989(5)	17.392(3)	23.756(7)
β (°)	90.02(3)	90.08(3)	109.61(3)	105.18(2)
<i>V</i> (Å ³)	2537.0(9)	2551.2(9)	4445.5(14)	17865.6(8)
<i>Z</i>	4	4	4	16
<i>D</i> _{calc} (g cm ⁻³)	1.609	1.829	1.468	1.592
μ (mm ⁻¹)	0.558	4.391	0.362	2.552
<i>F</i> (000)	1256	1384	2040	8672
Reflections collected/unique	15401/4448	13752/4334	15672/4368	55738/17557
	[<i>R</i> _(int) = 0.0255]	[<i>R</i> _(int) = 0.0328]	[<i>R</i> _(int) = 0.0509]	[<i>R</i> _(int) = 0.0668]
Reflections with <i>I</i> > 2σ(<i>I</i>)	4167	4096	3937	13319
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4448/6/339	4334/6/339	4368/9/296	17557/9/1161
Goodness-of-fit on <i>F</i> ²	1.015	1.021	1.077	1.048
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0285, 0.0816	0.0237, 0.0598	0.0448, 0.0986	0.0461, 0.0812
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0323, 0.0838	0.0264, 0.0612	0.0547, 0.1026	0.0736, 0.0878
Largest diff. peak and hole e (Å ⁻³)	0.276/–0.471	0.531/–0.858	0.308/–0.655	1.125/–1.565

Table 3. Bond lengths and angles in the coordination polyhedra of the NbF₆⁻ and TaF₆⁻ anions in complexes 1–4

<i>Bond lengths</i>			
1			
Nb(1)–F(1)	1.879(2)	Nb(1)–F(4)	1.890(2)
Nb(1)–F(2)	1.890(1)	Nb(1)–F(5)	1.881(2)
Nb(1)–F(3)	1.885(2)	Nb(1)–F(6)	1.891(2)
<i>Bond angles</i>			
F(1)–Nb(1)–F(2)	178.9(1)	F(2)–Nb(1)–F(6)	90.0(1)
F(1)–Nb(1)–F(3)	91.5(1)	F(3)–Nb(1)–F(4)	176.7(1)
F(1)–Nb(1)–F(4)	91.3(1)	F(3)–Nb(1)–F(5)	92.0(1)
F(1)–Nb(1)–F(5)	90.4(1)	F(4)–Nb(1)–F(5)	89.8(1)
F(1)–Nb(1)–F(6)	89.1(1)	F(3)–Nb(1)–F(6)	89.5(1)
F(2)–Nb(1)–F(3)	87.9(1)	F(4)–Nb(1)–F(6)	88.8(1)
F(2)–Nb(1)–F(4)	89.3(1)	F(5)–Nb(1)–F(6)	178.5(17)
F(2)–Nb(1)–F(5)	90.5(1)		
<i>Bond lengths</i>			
3			
Nb(1)–F(1)	1.867(2)	Nb(1)–F(3)	1.876(2)
Nb(1)–F(2)	1.876(2)		
<i>Bond angles</i>			
F(1) ^l –Nb(1)–F(1)	179.8(2)	F(3)–Nb(1)–F(2)	177.6(1)
F(1) ^l –Nb(1)–F(3)	89.0(1)	F(3) ⁱ –Nb(1)–F(2)	89.4(1)
F(1)–Nb(1)–F(3)	90.9(1)	F(1)–Nb(1)–F(2) ⁱ	89.0(1)
F(3)–Nb(1)–F(3) ⁱ	91.8(1)	F(2)–Nb(1)–F(2) ⁱ	89.5(1)
F(1)–Nb(1)–F(2)	91.2(1)		
<i>Bond lengths</i>			
2			
Ta(1)–F(1)	1.890(2)	Ta(1)–F(4)	1.896(2)
Ta(1)–F(2)	1.899(2)	Ta(1)–F(5)	1.891(2)
Ta(1)–F(3)	1.896(2)	Ta(1)–F(6)	1.901(2)
<i>Bond angles</i>			
F(1)–Ta(1)–F(2)	179.0(1)	F(2)–Ta(1)–F(6)	90.0(1)
F(1)–Ta(1)–F(3)	91.5(1)	F(3)–Ta(1)–F(4)	176.8(1)
F(1)–Ta(1)–F(4)	91.1(1)	F(3)–Ta(1)–F(5)	91.9(1)
F(1)–Ta(1)–F(5)	90.1(1)	F(3)–Ta(1)–F(6)	89.4(1)
F(1)–Ta(1)–F(6)	89.3(1)	F(4)–Ta(1)–F(5)	89.9(1)
F(2)–Ta(1)–F(3)	87.9(1)	F(4)–Ta(1)–F(6)	88.7(1)
F(2)–Ta(1)–F(4)	89.6(1)	F(5)–Ta(1)–F(6)	178.5(1)
F(2)–Ta(1)–F(5)	90.7(1)		
<i>Bond lengths</i>			
4			
Ta(1)–F(1)	1.892(3)	Ta(2)–F(21)	1.886(2)
Ta(1)–F(2)	1.888(4)	Ta(2)–F(22)	1.893(2)
Ta(1)–F(3)	1.888(4)	Ta(2)–F(23)	1.895(2)
Ta(1)–F(4)	1.895(2)		
Ta(3)–F(31)	1.859(3)	Ta(3)–F(34)	1.874(3)
Ta(3)–F(32)	1.868(3)	Ta(3)–F(35)	1.883(3)
Ta(3)–F(33)	1.874(3)	Ta(3)–F(36)	1.890(3)
<i>Bond angles</i>			
F(2)–Ta(1)–F(3)	180.0(1)	F(21)–Ta(2)–F(21) ⁱⁱ	90.4(2)
F(2)–Ta(1)–F(1) ^I	90.6(1)	F(21)–Ta(2)–F(22) ⁱⁱ	179.4(1)
F(3)–Ta(1)–F(1)	89.4(1)	F(21)–Ta(2)–F(22)	90.3(1)
F(1) ^I –Ta(1)–F(1)	178.8(2)	F(22) ⁱⁱ –Ta(2)–F(22)	89.1(2)
F(2)–Ta(1)–F(4)	89.3(1)	F(22)–Ta(2)–F(23) ⁱⁱ	89.9(1)
F(3)–Ta(1)–F(4)	90.7(1)	F(21)–Ta(2)–F(23)	90.2(1)
F(1)–Ta(1)–F(4)	89.4(1)	F(21) ⁱⁱ –Ta(2)–F(23)	89.7(1)
F(1)–Ta(1)–F(4) ^I	90.6(1)	F(22)–Ta(2)–F(23)	90.2(1)
F(4)–Ta(1)–F(4) ^I	178.6(2)	F(23) ⁱⁱ –Ta(2)–F(23)	179.9(2)
F(31)–Ta(3)–F(32)	178.1(2)	F(32)–Ta(3)–F(36)	90.3(2)
F(31)–Ta(3)–F(33)	89.3(2)	F(33)–Ta(3)–F(34)	179.6(2)

Table 3. continued

Bond angles			
F(31)–Ta(3)–F(34)	91.1(2)	F(33)–Ta(3)–F(35)	89.9(1)
F(31)–Ta(3)–F(35)	90.3(2)	F(33)–Ta(3)–F(36)	91.8(2)
F(31)–Ta(3)–F(36)	89.4(2)	F(34)–Ta(3)–F(35)	90.1(1)
F(32)–Ta(3)–F(33)	88.8(2)	F(34)–Ta(3)–F(36)	88.2(1)
F(32)–Ta(3)–F(34)	90.8(2)	F(36)–Ta(3)–F(35)	178.2(2)
F(32)–Ta(3)–F(35)	90.1(2)		

Symmetry transformations used to generate equivalent atoms: *i* $-x+1, y, -z+1/2$; *ii* $-x+1, y, -z+3/2$.

Table 4. Torsion angles (°) in complexes 1–4

Angle	1	2			
O(1)–C(2)–C(3)–O(4)	55.1(3)	55.1(4)			
C(2)–C(3)–O(4)–C(5)	74.8(3)	74.5(4)			
C(3)–O(4)–C(5)–C(6)	–178.1(2)	–178.0(3)			
O(4)–C(5)–C(6)–O(7)	63.2(2)	63.4(3)			
C(5)–C(6)–O(7)–C(8)	171.4(2)	171.5(3)			
C(6)–O(7)–C(8)–C(9)	–177.0(2)	–177.3(3)			
O(7)–C(8)–C(9)–O(10)	–62.3(2)	–62.0(3)			
C(8)–C(9)–O(10)–C(11)	169.2(2)	168.7(3)			
C(9)–O(10)–C(11)–C(12)	–177.8(2)	–177.7(3)			
O(10)–C(11)–C(12)–O(13)	61.1(2)	60.7(3)			
C(11)–C(12)–O(13)–C(14)	173.6(2)	174.2(3)			
C(12)–O(13)–C(14)–C(15)	161.9(2)	162.3(3)			
O(13)–C(14)–C(15)–O(16)	62.5(2)	62.6(4)			
C(14)–C(15)–O(16)–C(17)	171.8(2)	171.7(3)			
C(15)–O(16)–C(17)–C(18)	–178.4(2)	–178.8(3)			
O(16)–C(17)–C(18)–C(19)	–7.0(3)	–6.7(4)			
C(17)–C(18)–C(19)–C(20)	–68.8(3)	–69.3(4)			
C(18)–C(19)–C(20)–O(1)	5.5(3)	5.8(4)			
C(19)–C(20)–O(1)–C(2)	–101.7(2)	–101.5(3)			
C(20)–O(1)–C(2)–C(3)	166.4(2)	166.6(3)			
Angle	3	4	4a	4b	4c
O(1)–C(2)–C(3)–O(4)	64.7(2)	–63.7(4)	–64.7(4)	–67.4(4)	–70.6(4)
C(2)–C(3)–O(4)–C(5)	168.9(2)	–174.6(3)	–175.7(3)	179.2(4)	179.6(3)
C(3)–O(4)–C(5)–C(6)	165.6(2)	–175.8(3)	–171.7(3)	–175.7(4)	–173.9(4)
O(4)–C(5)–C(6)–O(7)	–69.9(3)	65.8(5)	68.0(5)	64.1(5)	63.8(5)
C(5)–C(6)–O(7)–C(8)	–179.2(2)	–176.8(3)	–174.7(3)	–170.1(4)	–170.3(4)
C(6)–O(7)–C(8)–C(9)	–78.5(3)	90.9(5)	85.4(4)	174.5(4)	173.0(4)
O(7)–C(8)–C(9)–O(10)	–67.3(3)	69.1(5)	68.0(5)	–67.6(4)	–66.7(5)
C(8)–C(9)–O(10)–C(11)	178.9(2)	173.4(4)	177.4(3)	–170.2(4)	–172.2(4)
C(9)–O(10)–C(11)–C(12)	170.4(2)	–172.2(3)	–169.2(3)	176.4(4)	179.0(4)
O(10)–C(11)–C(12)–O(13)	67.4(3)	–63.9(4)	–64.4(4)	65.9(5)	68.8(5)
C(11)–C(12)–O(13)–C(14)	–163.3(2)	158.2(3)	157.4(3)	75.4(5)	77.1(5)
C(12)–O(13)–C(14)–C(15)	165.4(2)	–163.1(4)	–165.1(4)	–163.2(4)	–168.6(4)
O(13)–C(14)–C(15)–O(16)	–1.2(3)	2.1(5)	1.8(6)	6.0(5)	7.4(6)
C(14)–C(15)–O(16)–C(17)	120.1(2)	–99.3(4)	–95.9(4)	–82.9(5)	–81.7(5)
C(15)–O(16)–C(17)–C(18)	174.5(2)	–179.8(3)	174.1(3)	172.8(4)	167.3(4)
O(16)–C(17)–C(18)–O(1)	0.1(3)	–1.1(5)	–2.2(5)	–4.3(5)	–5.6(5)
C(17)–C(18)–O(1)–C(2)	170.0(2)	–173.2(3)	–176.0(3)	179.8(3)	177.3(3)
C(18)–O(1)–C(2)–C(3)	–177.0(2)	176.0(3)	177.3(3)	178.3(3)	179.8(3)

from 1.867(2) up to 1.891(2) Å and with the F–Nb–F valent angles between *cis*-fluorine atoms being in the range 87.9(1)–91.8(1)° and between *trans*-fluorine atoms being in the range 176.7(1)–179.8(2)°. The geometry of the NbF₆[–] anion is in a close concern with that found in 3-chloro-1,3,4,2,5-thiadiselenadiazolium hexafluoronio-

bium [3] and in *bis*(pyrazine)dicopper *bis*(hexafluoronio-*bis*(piperazine) solvate [4].

The TaF₆[–] anions in the complexes **2** and **4** also adopt the usual octahedral geometry with Ta–F distances ranging from 1.859(3) up to 1.895(2) Å and with the F–Ta–F valent angles between *cis*-fluorine atoms

being in the range $87.9(1)$ – $91.9(1)^\circ$ and between *trans*-fluorine atoms being in the range $176.8(1)$ – $180.0(1)^\circ$. This geometry is in a close concern with that found in catena-[(μ -chloro)-*bis*(μ -fluoro)tetrafluoro-hexamethyltantalum] ditin [5] and in methyltriphenylphosphonium hexafluorotantalate [6].

The ORTEP view of complex **1** is shown in Figure 1. In the complex cation $[\text{BP20C6} \cdot \text{H}_3\text{O}]^+$, the oxygen atom of oxonium ion is disordered over two positions, O(1w) and O(1wa) with the common hydrogen atoms, the both images being of the pyramidal geometry. The major component, O(1w) deviates at $-0.212(3)$ Å, while the minor component, O(1wa) deviates at $0.703(6)$ Å from the mean plane of six oxygen atoms [$-0.215(5)$ and $0.69(1)$ in complex **2**, correspondingly]. Further, only major position of the disordered oxonium ion will be discussed. The details of hydrogen-bonding geometry in **1**–**4** are summarized in Supplementary Table 2S. Three $\text{O}_{(1w)} \cdots \text{O}_{\text{crown}}$ distances for the hydrogen bonds range from $2.504(3)$ to $2.589(3)$ Å, while three other $\text{O}_{(1w)} \cdots \text{O}_{\text{crown}}$ separations are longer and equal to $2.615(3)$ [O(4)], $2.859(3)$ [O(10)] and $3.061(3)$ Å [O(16)] [$2.618(4)$ (O4), $2.864(4)$ (O10) and $3.060(4)$ Å (O16) in complex **2**]. It is reasonable that an “aromatic” oxygen atom O(16), associated with the biphenyl moiety, appears to be shielded for the interaction with the oxonium ion. On the other hand, the size of the crown ether ring is sufficient for the displacement of oxonium cation and accumulation of all of its hydrogen atoms.

The benzene rings of the BP20C6 molecule are arranged with the twist angle between their mean planes equal to $69.4(1)^\circ$ [$69.1(1)^\circ$ in **2**], this value being close to that one found in the complex of BP20C6 with amidosulfuric acid, $65.9(2)^\circ$ and $69.7(2)^\circ$ in two independent formula units, and a slightly higher than in a pure BP20C6 itself [$63.8(1)^\circ$] [9]. The conformation of

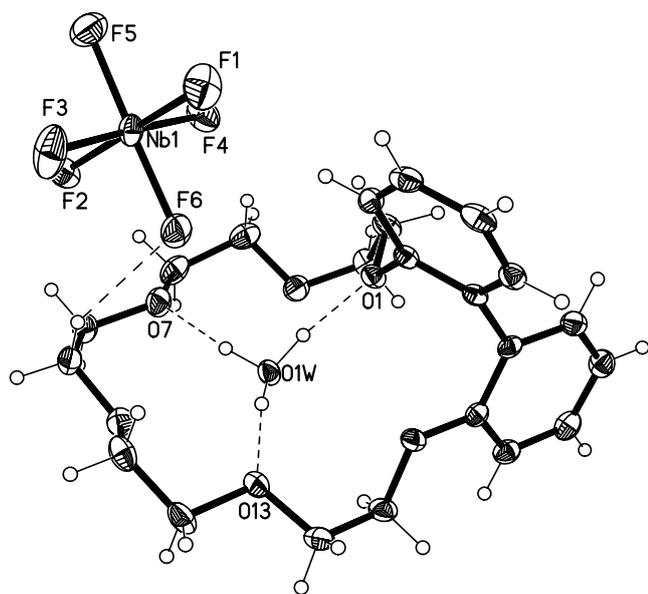


Figure 1. ORTEP drawing of **1** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level.

BP20C6 molecule is described by six *gauche*-torsion angles along five Csp^3 – Csp^3 and one Csp^2 – Csp^2 bonds, two *cis*-torsion angles along two Csp^2 – Csp^2 bonds that belong to the aromatic rings, and ten *anti*- and two *gauche*-C–O angles, and differs from the crown conformation in its complex with amidosulfuric acid by two C–O bonds in *gauche*-conformation.

The supramolecular architecture in **1** is sustained by weak C–H \cdots O and C–H \cdots F interactions, which combine the components into 3D network (Figure 2).

The ORTEP view for complex **3** is shown in Figure 3. The asymmetric unit of **3** comprises one [1.5]DB18C6 crown molecule and one O(1w) water molecule, both located in general positions, O(2w) oxonium cation, and NbF_6^- anion, both located in special positions, on the two-fold axis. The pyramidal geometry of the oxonium cation conflicts with the two-fold axis symmetry, so oxonium cation appears to be disordered. Water molecule O(1w) deviates at $1.499(2)$ Å from the mean plane of six crown oxygen atoms, which are coplanar within 0.403 Å, and donates both of its hydrogen atoms for two bifurcated $\text{OH} \cdots \text{O}$ hydrogen bonds with the “aliphatic” and “aromatic” crown oxygens, O \cdots O separations being in the range $2.859(3)$ – $3.014(3)$ Å. Acting as H-acceptor, this water molecule donates one of its lone pairs for the $\text{OH} \cdots \text{O}$ hydrogen bond with the oxonium hydrogen, O \cdots O separation being $2.438(3)$ Å, by which, in its turn, oxonium cation bridges two related by the two-fold axis ([1.5]DB18C6 \cdot H $_2$ O) units. The third hydrogen atom of oxonium cation alternately interacts with O(10)

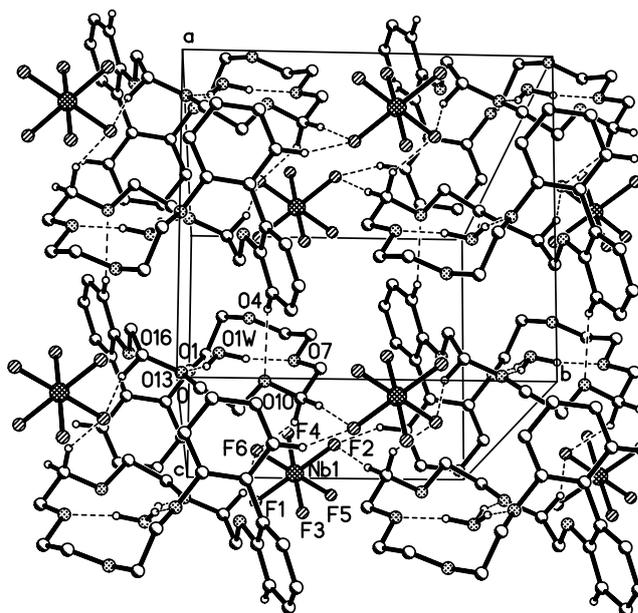


Figure 2. Fragment of crystal packing for **1**. Only hydrogens involved in hydrogen bonds are shown. Along *a* direction the inversion-related macrocycles are linked by $\text{CH} \cdots \text{O}$ hydrogen bonds, $\text{C}(25)\text{--H}(25\text{A}) \cdots \text{O}(10)(-x, -y + 1, -z)$ $3.131(3)$, $\text{H} \cdots \text{O}$ 2.42 Å, CHO angle 133.0° , while along *b* direction the NbF_6^- anions are bridging the neighboring macrocycles *via* weak $\text{CH} \cdots \text{F}$ hydrogen bonds into 3D network, C \cdots F contacts being in the range $3.185(3)$ – $3.462(3)$, $\text{H} \cdots \text{F}$ 2.48 – 2.54 Å, CHF angles 128 – 168° .

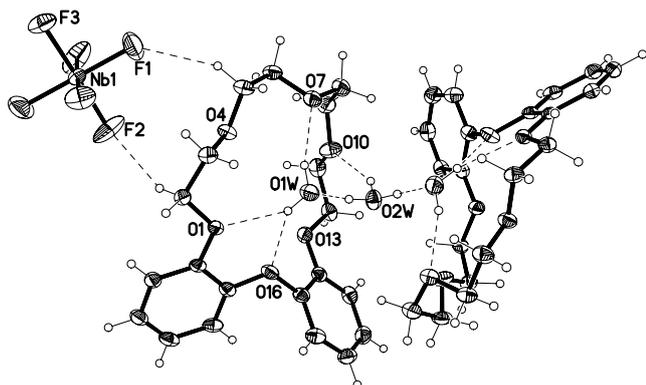


Figure 3. ORTEP drawing of **3** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level. Only major position for oxonium ion (O2w) is shown.

crown oxygens of two related by the two-fold axis crown molecules, $O_{\text{oxonium}} \cdots O(10)_{\text{crown}}$ separation being 2.935(2) Å. The three-membered $O1w \cdots O2w \cdots O1w(-x, y, -z + 1/2)$ cluster of the alternating water \cdots oxonium \cdots water entities of the composition $H_7O_3^+$ is closed in the cage of two crown molecules.

The benzene rings of the [1.5]DB18C6 molecule are arranged with the twist angle between their mean planes equal to 66.1(1)° (for comparison, the same angle is equal to 69.2(5)° in the [1.5]DB18C6 complex with dithiouracil and 87.5(1)° in the [1.5]DB18C6 molecule itself [9, 10]). The macrocyclic 18-membered skeleton is described by four *gauche*-Csp³-Csp³ and two *cis*-Csp²-Csp² torsion angles, eleven *anti*- and one *gauche*-C-O torsion angles. The specific feature of complex **3** (as in the above-mentioned complex with dithiouracil), is that two [1.5]DB18C6 molecules in the same conformation formulate a supramolecular capsule with the charged $(H_7O_3)^+$ unit inside.

Figure 4 reveals how NbF_6^- anion *via* four C-H \cdots F hydrogen bonds bridges the neighboring related by the two-fold axis 5-membered cations, $[(1.5]DB18C6)_2 \cdot H_7O_3^+$ into chains propagated along *c* direction in the unit cell.

In the asymmetric unit of complex **4** (Figure 5) four [1.5]DB18C6 molecules (depicted by the numerical indexes, and indexes *a*, *b* and *c*, four water molecules, O(1w), O(1wa), O(1wb), and O(1wc), two oxonium ions, O(2w) and O(21w), and one TaF_6^- anion occupy the general positions, while two other TaF_6^- anions reside on the two-fold axis. In contrary to complex **3**, the O(2w) and O(21w) H_3O^+ oxonium cations occupy general positions without distortion of their pyramidal geometry. That results in two 5-membered associates, each composed of $H_7O_3^+$ cations enclosed inside the cage of two different crown molecules (in pairs: molecule *a* – molecule *b*; molecule *c* – molecule with numerical indexes). The organization of these associates is very close to **3**, the shortest are four $O_{\text{water}} \cdots O_{\text{oxonium}}$ distances which are in the range 2.424(5)–2.521(4) Å, the next in length are two $O_{\text{oxonium}} \cdots O_{\text{crown}}$ distances that adopt the values of 2.615(4) and 2.636(4) Å, and the

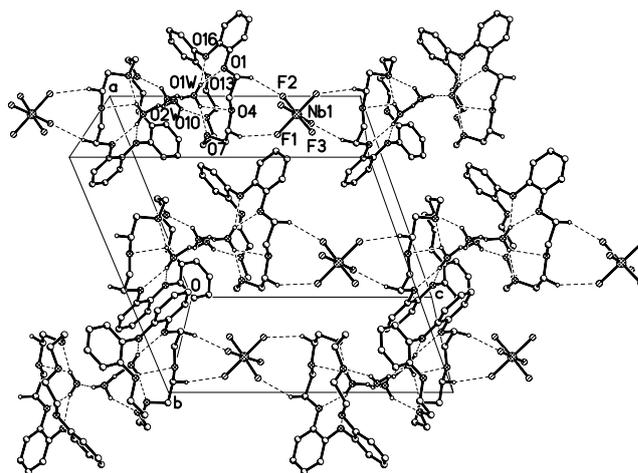


Figure 4. Fragment of crystal packing for **3**. Only hydrogens involved in hydrogen bonds are shown. Along *c* direction the related by two-fold axis units are linked by $CH \cdots F$ hydrogen bonds in the chains, C(2)–H(2B) \cdots F(2) 3.296(3), H \cdots F 2.43 Å, CHF angle 146°, and C(5)–H(5B) \cdots F(1) 3.432(4), H \cdots F 2.55 Å, CHF angle 149°.

longest are $O_{\text{water}} \cdots O_{\text{crown}}$ distances which range from 2.712(4) to 3.036(4) Å. However, the main distinctive feature is that two these capsules occupy general positions in the asymmetric unit. It results in the different $O_{\text{water}} \cdots O_{\text{oxonium}}$ distances in the three-membered water clusters, equal to 2.521(5) and 2.438(5) Å in the chain $O(1w) \cdots O(21w) \cdots O(1wc)$, and 2.509(5) and 2.428(5) Å in the chain $O(1wa) \cdots O(2w) \cdots O(1wb)$. Each of the oxonium cations have only one contact with the crown oxygen, $O(21w) \cdots O(10)_{\text{crown}}$ being 2.614(4) Å, and $O(2w) \cdots O(10A)_{\text{crown}}$ being 2.635(4) Å in two 5-membered capsules, correspondingly. As a sequence of the different mode of hydrogen bonding, both of these two capsules combine two crown molecules in different conformations, one of which being rather close to that one found in **3**. In each pair the conformations of two molecules differ only by C(6)–O(7)–C(8)–C(9) angle, which adopts the values of 85.4(4) and 174.5(4)° in the first pair, and 90.9(5) and 173.0(4)° in the second pair, the same torsion angle is equal to 78.5(3)° in complex **3** (Table 4).

The bridging TaF_6^- anion [defined by Ta(3) atom], occupies the general position, and fulfills the double function, *via* F(31) and F(35) atoms it participates in the short C–H \cdots F contacts with two crown molecules that belong to one capsule, C(23) \cdots F(31) 3.291(6), H \cdots F 2.36 Å, CHF angle 166°, C(8c) \cdots F(35) 3.492(6), H \cdots F 2.52 Å, CHF angle 166°, and *via* F(32) atom it bridges two independent capsules, C(24a) \cdots F(32) 3.345(6), H \cdots F 2.57 Å, CHF angle 138°. The crystal packing for **4** keeps the main property typical for such previously studied crystals, built on the macrocycle – fluoride-containing anion (GeF_6^{2-} , SiF_6^{2-} , SiF_5^- etc), and water: the crystal is built as a napoleon, with the alternative organic (macrocycle) and inorganic (anions) rows in the 3D network (Figure 6).

Thus, the list of the 18-membered hexadentate crown ethers capable to dispose effectively H_3O^+ oxonium

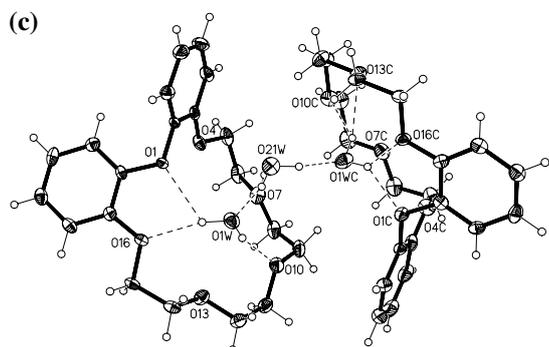
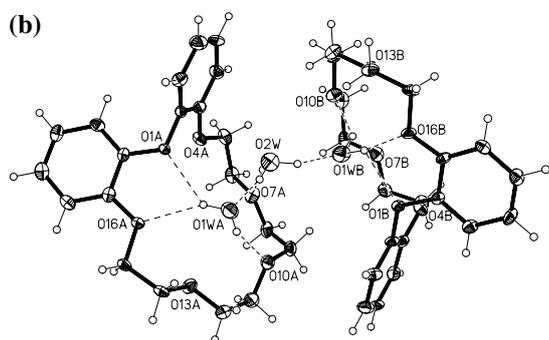
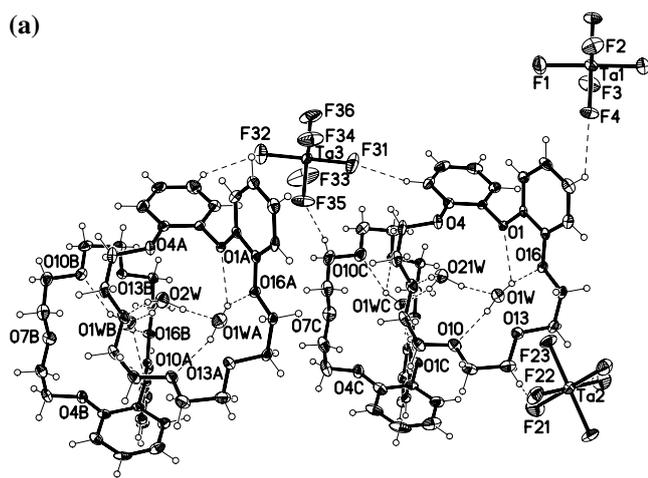


Figure 5. ORTEP drawing of **4** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level. (a) General view of the asymmetric unit with the shortest CH...F distances shown by dashed lines; (b–c) two crystallographically independent 5-membered supramolecular capsules in the projection on the best plane.

cation can be supplemented by the 20-membered hexadentate crown ether, BP20C6 (L^1), containing biphenyl fragment, as complexes **1** and **2** demonstrate the suitable fit between the BP20C6 macrocycle cavity and oxonium ion.

In contrary, the presence of the diphenyloxide fragment in the 18-membered hexadentate crown ether [1.5]DB18C6 (L^2) in complexes **3** and **4** is a decisive factor for the arrangement of the $H_7O_3^+$ entity within the cage formed by two crown molecules with the formation of the closed capsule with the only very weak interactions with the NbF_6^- and TaF_6^- anions. So, complexes **3** and **4** complete the scanty list of the crown ethers capable to incorporate $H_7O_3^+$ oxonium cations.

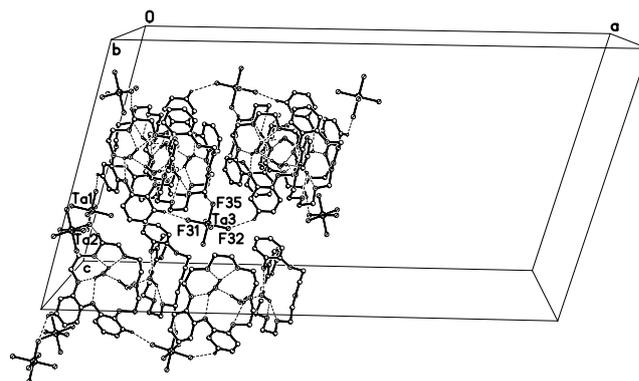


Figure 6. Fragment of crystal packing for **4**. Only hydrogens involved in hydrogen bonds are shown.

Conclusion

The interaction of Nb_2O_5 and Ta_2O_5 oxides with the hydrofluoric acid in the presence of biphenyl-20-crown-6, BP20C6 and [1.5]dibenzo-18-crown-6, [1.5]DB18C6 yield the complexes of the composition $[BP20C6 \cdot (H_3O)] [MeF_6]$ and $[2[1.5]DB18C6 \cdot (H_7O_3)MeF_6]$ ($Me = Ta, Nb$). According to the X-ray data, in the first two isostructural adducts the H_3O^+ oxonium cation centers the crown cavity through a near-ideal “tripod” arrangement of $OH \cdots O$ hydrogen bonding to alternate crown oxygen atoms. In the case of the rare complexes $[2[1.5]DB18C6 \cdot (H_7O_3)MeF_6]$ the $H_7O_3^+$ oxonium cation is enclosed inside the cage formed by two crown ethers. Complexes **3** and **4** represent a bright example of supramolecular isomerism (i.e., the existence of more than one hydrogen-bonding network for the similar building blocks) [20].

It is necessary to note that in the studied conditions the complexes of crown ethers with less symmetrical and carrying more negative charge (in comparison with NbF_6^- and TaF_6^-) oxofluoride anions are not formed, since the last ones are present in the reaction solutions Me_2O_5 ($Me = Nb, Ta$) – $HF - H_2O$. Evidently, this fact demonstrates a tendency to stabilize the oxonium complexes of crown ethers in preference to the monoanions (Table 1).

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, deposition numbers CCDC 290090 (**1**), CCDC 290088 (**2**), CCDC 290089 (**3**), CCDC 290087 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

1. A.G. Babkin, V.G. Maiorov, and A.I. Nikolaev: Extraction of niobium, tantalum and other elements from fluoride-containing solutions (Russ.) L., Nauka 224 (1988).
2. V.K. Bel'skii and B.M. Bulychev: *Uspekhi khimii (Russ.)* **68**, 136 (1999).
3. A. Haas, J. Kasproski, K. Angermund, P. Betz, C. Kruger, Y.-H. Tsay, and S. Werner: *Chem. Ber.* **124**, 1895 (1991).
4. P. Halasyamani, K.R. Heier, M.J. Willis, C.L. Stern, and K.R. Poeppelmeier: *Z. Anorg. Allg. Chem.* **622**, 479 (1996).
5. O.I. Guzyr, M. Schormann, J. Schimkowiak, H.W. Roesky, C. Lehmann, M.G. Walawalkar, R. Murugavel, H.-G. Schmidt, and M. Noltemeyer: *Organometallics* **18**, 832 (1999).
6. M.A. McLoughlin, N.L. Keder, and W.C. Kaska: *Acta Crystallogr.* **C48**, 1098 (1992).
7. V.V. Yakshin: *Russ. Koord. Khim.* **28**, 742 (2000).
8. Ed.V. Ganin: *Russ. Khim. Geterocycl. Soed.* 1571 (1997).
9. S.A. Kotlyar, M.S. Fonari, E.V. Ganin, Yu.A. Simonov, G. Bocelli, O.V. Shishkin, S.V. Shishkina, V.V. Tkachuk, R.Ya. Grygorash, and G.L. Kamalov: *J. Incl. Phenom.* **52**, 75 (2005).
10. Ed.V. Ganin, M.S. Fonari, Yu.A. Simonov, G. Bocelli, S.S. Basok, V.V. Tkachuk, S.A. Kotlyar, and G.L. Kamalov: *J. Incl. Phenom.* **52**, 63 (2005).
11. F.N. Allen: *Acta Crystallogr.* **B58**, 380 (2002).
12. (a) S. Nagayama and S. Kobayashi: *J. Am. Chem. Soc.* **122**, 11531 (2000); (b) C.B. Knobler, E.F. Maverick, K.N. Trueblood, R.C. Helgeson, and D.J. Cram: *Acta Crystallogr.* **C42**, 156 (1986); (c) H.L. Ngo and Wenbin Lin: *J. Am. Chem. Soc.* **124**, 14298 (2002); (d) A.M. Costero, C. Andreu, E. Monrabal, A. Tortajada, L.E. Ochando, and J.M. Amigo: *Supramol.Chem.* **9**, 211 (1998).
13. (a) I. Goldberg: *J. Am. Chem. Soc.* **102**, 4106 (1980); (b) D.J. Cram, R.A.G. de Graafe, C.B. Knobler, D.S. Lingenfelter, E.F. Maverick, and K.N. Trueblood: *Acta Crystallogr.* **B55**, 432 (1999).
14. M. Calleja, K. Johnson, W.J. Belcher, and J.W. Steed: *Inorg. Chem.* **40**, 4978 (2001) (and references therein).
15. (a) B.M. Bulychev and V.K. Bel'sky: *Zh. Neorg. Khim. (Russ.) (Russ. J. Inorg. Chem.)* **40**, 1834 (1995); (b) H. Feinberg, I. Columbus, S. Cohen, M. Rabinovitz, H. Selig, and G. Shoham: *Polyhedron* **12**, 1811 (1993); (c) L.J. Barbour, L.R. MacGillivray, and J.L. Atwood: *J. Chem. Cryst.* **26**, 59 (1996); (d) B. Neumuller, M. Plate, and K. Dehnicke: *Z. Kristallogr.* **209**, 92 (1994); (e) V.S. Sergienko, L. Kh. Minacheva, N.Kh. Ashurova, M.A. Porai-Koshits, K.G. Yakubov, and V.G. Sakharova: *Russ. J. Inorg. Chem.* **36**, 381 (1991); (f) V.S. Sergienko, L.Kh. Minacheva, G.G. Sadikov, N.Kh. Ashurova, V.V. Minin, K.G. Yakubov, and V.M. Sherbakov: *Russ. J. Inorg. Chem.* **37**, 346 (1992); (g) J.L. Atwood, S.G. Bott, P.C. Junk, and M.T. May: *J. Coord. Chem.* **37**, 89 (1996); (i) H. Feinberg, I. Columbus, S. Cohen, M. Rabinovitz, H. Selig, and G. Shoham: *Polyhedron* **12**, 2913, (1993); (j) M. Calleja, K. Johnson, W.J. Belcher, and J.W. Steed: *Inorg. Chem.* **40**, 4978 (2001); (k) P.C. Junk and J.L. Atwood: *J. Chem. Cryst.* **24**, 247 (1994) (l) R. Chenevert, D. Chamberland, M. Simard, and F. Brisse: *Can. J. Chem.* **68**, 797 (1990); (m) J.L. Atwood, S.G. Bott, P.C. Junk, and M.T. May: *J. Organomet. Chem.* **487**, 7 (1995); (n) J.L. Atwood, S.G. Bott, C.M. Means, A.W. Coleman, Hongming Zhang, and M.T. May: *Inorg. Chem.* **29**, 467 (1990); (o) P.C. Junk, L.R. MacGillivray, M.T. May, K.D. Robinson, and J.L. Atwood: *Inorg. Chem.* **34**, 5395 (1995); (p) S.A. El Khalik, M.El Essawi, I. Dombrowski, and K.-F. Tebbe: *Z. Naturforsch., Teil B* **54**, 136 (1999); (q) J.L. Atwood, P.C. Junk, M.T. May, and K.D. Robinson: *J. Chem. Cryst.* **24**, 243 (1994); (r) Yu.A. Simonov, N.F. Krasnova, A.A. Dvorkin, V.V. Yakshin, V.M. Abashkin, B.N. Laskorin: *Dokl. Akad. Nauk SSSR (Russ.) (Proc. Natl. Acad. Sci. USSR)* **272**, 1129 (1983); (s) V.O. Gel'mbol'dt, E.V. Ganin, L.V. Ostapchuk, A.A. Ennan, Yu.A. Simonov, V.Kh. Kravtsov, M.S. Fonari, and J. Lipkowski: *Russ. J. Inorg. Chem.* **44**, 1139 (1999); (t) V.O. Gelmboldt, E.V. Ganin, Yu.A. Simonov, J. Lipkowski, M.S. Fonari, and V.Kh. Kravtsov: *Russ. J. Inorg. Chem.* **40**, 594 (1995); (u) J.-P. Behr, P. Dumas, and D. Moras: *J. Am. Chem. Soc.* **104**, 4540 (1982); (v) S.P. Petrosyants, A.M. Shpirt, and A.B. Ilyukhin: *Russ. J. Inorg. Chem.* **45**, 954 (2000); (w) J.L. Atwood and P.C. Junk: *J. Coord. Chem.* **51**, 379 (2000); (x) P.C. Junk and J.L. Atwood: *J. Chem. Soc. Dalton Trans.* **4393** (1997).
16. R. Hooft: *Collect*, Nonius, Delft, Netherlands (1998).
17. Z. Otwinowski and W. Minor: In C.W. Carter and R.M. Sweet (eds.), *Methods in Enzymology, Macromolecular Crystallography, Part A*, Academic Press, London (1996), pp. 276–307.
18. G.M. Sheldrick: *SHELXS97 and SHELXL97, Programs for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).
19. K. Nakamoto: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley-Interscience, NY (1986).
20. G.R. Desiraju: *Science* **278**, 404 (1997).