

*Review Article*

# Inclusion Compounds: the Products of the Interaction of Silicon, Germanium and Boron Fluorides with Crown Ethers

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**Abstract.** This review deals with the problem of the interaction of Si(IV), Ge(IV) and B(III) fluorides with crown ethers and their aza analogues. The crystallographic structures have been determined of the stable products obtained by the interaction of  $\text{H}_2\text{SiF}_6$  solution with the following crown ethers: 18-crown-6 (18C6), monoaza-18C6 (MA18C6), 1,10-diaza-18C6 (DA18C6) and 1,7-diaza-15C5 (DA15C5). The complexes obtained are stabilized by a system of H-bonds of the O—H···O, N—H···O, N—H···F and O—H···F types. For  $\text{H}_2\text{GeF}_6$  the adducts obtained are similar to those obtained using  $\text{H}_2\text{SiF}_6$ . The crystal structures of three new boron fluoride-containing complexes with 18-membered crown ethers are also described. During macrocycle complexation the guest entities undergo chemical transformations which are stabilized by creation of the H-bond system. The results of vibrational and NMR spectra are also discussed.

**Key words:** Molecular recognition, crystalline inclusion complexes, X-ray crystal structures, H-bonding, crown ethers.

## 1. Introduction

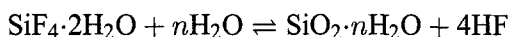
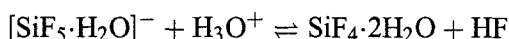
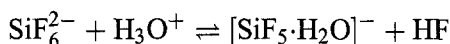
Crown ethers find widespread use for the stabilization of unstable or intermediate products in the form of host–guest (H–G) type complexes. Systems containing the fluorocomplexes of *p*-elements as guests deserve special consideration as they are distinguished by a high reactivity and inclination to undergo hydrolytic conversions in aqueous solutions or in moist air [1]. It has been reported [2] that 18-crown-6 (18C6) can increase the stability to hydrolysis of organofluorosilicon-containing

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pentacoordinated anions in the salt-like form,  $(K.18C6)[R_nSiF_{5-n}]$  ( $n = 1-3$ ). Such compounds have found some use in the preparative synthesis of penta- and hexacoordinated organofluosilicates [3]. The stabilization of  $[BF_3 \cdot H_2O]$  (which melts at  $6.0^\circ C$  and partly decomposes with loss of  $BF_3$  at  $20^\circ C$  [4]) by complexation with 18-crown-6 has also been reported [5]. These reports stimulated us to examine the complexation peculiarities for Si(IV), Ge(IV) and B(III)-containing fluoride compounds with crown ethers.

The main tasks of the investigation include the clarification of the possible ways in which fluorocomplexes (mainly aquafluorocomplexes) of the above mentioned elements are stabilized in the form of host-guest compounds and determination of specific structural features of the complexes. It has previously [1] been shown that aqueous solutions of siliconhydrofluoric acid ( $H_2SiF_6$ -SHFA) with the fluorine number  $\varphi$  (the ratio of fluorine to silicon atoms) close to 6 undergo the following hydrolytic equilibria:



$^{19}F$  NMR studies [6] showed that in the SHFA solutions with  $\varphi = 5$  fluorine is present as the following species: 30–40%  $SiF_6^{2-}$ ; 60–70%  $[SiF_5 \cdot H_2O]^-$  and 5%  $[SiF_4 \cdot 2H_2O]$ . The presence of  $[SiF_5 \cdot H_2O]^-$  in the SHFA solutions has been disputed [7–9], where the potentiometric data were interpreted on the assumption that these solutions contain only the anion,  $SiF_6^{2-}$ .

Complexes obtained from solutions of SHFA - L (where L = 18C6, giving complex number **(I)**, 15C5 **(II)** [10], monoaza-18-crown-6 – MA18C6 **(III)**, 1,10-diaza-18-crown-6 – DA18C6 **(IV)** [11] and 1,7-diaza-15-crown-5 – DA15C5 **(V)** [12]) have been characterized by the methods of X-ray analysis (complexes **(I)**, **(III)**–**(V)**) and vibrational spectroscopy. Crystals of **(II)** suitable for X-ray investigation could not be prepared.

## 2. Discussion

### 2.1. SILICON(IV)- AND GERMANIUM(IV)-CONTAINING MOLECULAR COMPLEXES

#### 2.1.1. Silicon-Containing Complexes – Overall System of Interaction

Complex **(I)** has been obtained and structurally characterized as a product of the interaction of silicon tetrafluoride with a hexane solution of 18C6 exposed to atmospheric moisture [13]. Complex **(I)** is regarded as a typical complex of the second coordination sphere, where direct interaction of the central atom with the macrocycle electron donor atoms is absent.

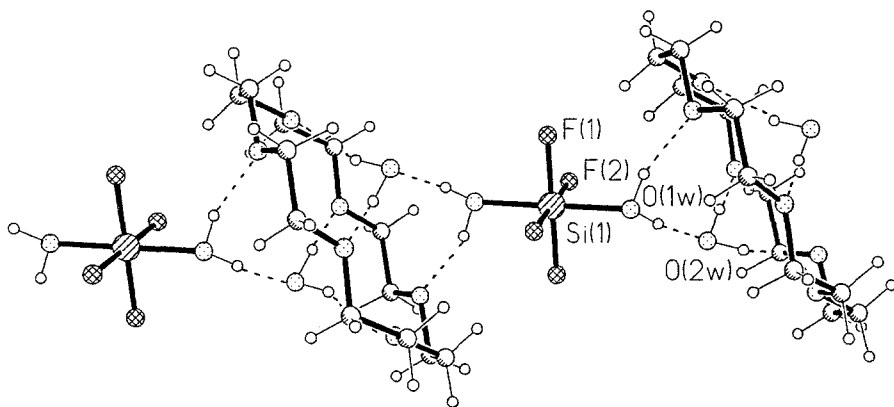


Figure 1. The chain fragment in complex (I).

A portion of the crystal structure of (I) is shown in Figure 1. It may be considered as a polymeric structure formed by the [*trans*-SiF<sub>4</sub>·2H<sub>2</sub>O], 18C6 and water entities in the ratio 1:2:2. Water molecule O(2W), forming H-bonds with the crown ether, [O(2W)···O(7) = 2.870(2), O(2W)···O(4b) = 2.853(2) Å], behaves as a go-between to bind an inorganic complex to the crown ether which, in turn, serves as a H-acceptor with the participation of all six O-atoms in the H-bond system. Coordinated to the inorganic moiety the O(1W) water molecule forms one H-bond with the crown ether, while the second H-atom takes part in a O(1W)···O(2W) H-bond with a O···O distance of 2.599(3) Å.

Changing the binding sites in a crown host can strongly influence its binding power and affect its guest selectivity. The additional bonding valence of nitrogen (in comparison with oxygen) allows many interesting structural variations. For N-containing macrocycles the opportunities for interaction are essentially expanded due to use of NH-host donor groups. In the aza crown ethers described here, MA18C6, DA18C6 and DA15C5, one or two ether oxygen atoms are replaced by the >NH structural element. Being more basic than an ether oxygen, the amine group can easily be protonated by strong acids. In turn, protonated macrocycles are able to extract the negatively-charged species from the equilibrium mixture. The structures of complexes (III) and (IV) are shown in Figures 2 and 3 respectively. They are built of macrocyclic cations protonated at the nitrogen atoms [MA18C6H·H<sub>2</sub>O]<sup>+</sup> in (III), [DA18C6H<sub>2</sub>]<sup>2+</sup> in (IV), [SiF<sub>5</sub>·H<sub>2</sub>O]<sup>-</sup> anions and water molecules.

In (III) three water molecules play different roles in the complex architecture: the O(1W) molecule is coordinated to the silicon atom and enters the inorganic anionic entity; the external O(2W) molecule fills the voids in the crystal space and participates in the creation of the chain structure and the O(3W) molecule is centered in the macrocyclic cavity. The protonated nitrogen atom serves as a suitable binding site for the water molecule lone pair. Thus, the water entity, (O3W), enters deeper into the macrocyclic cavity in comparison with (I), forming the nest-type com-

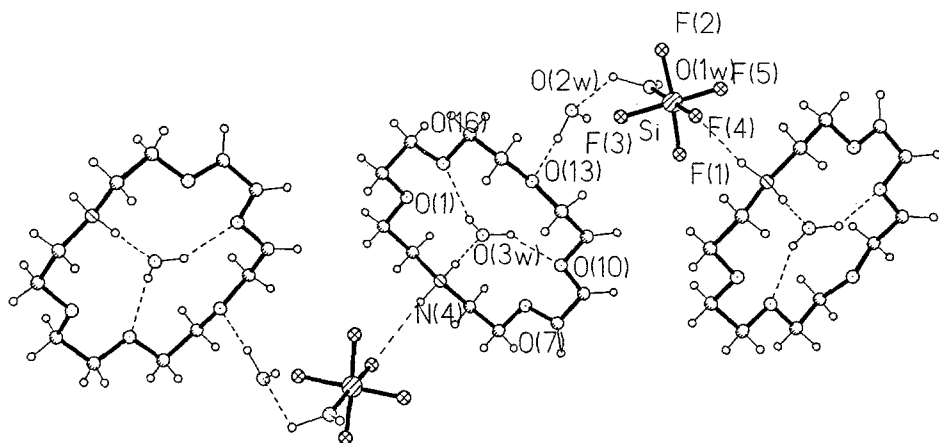


Figure 2. View of the chain motif in complex (III).

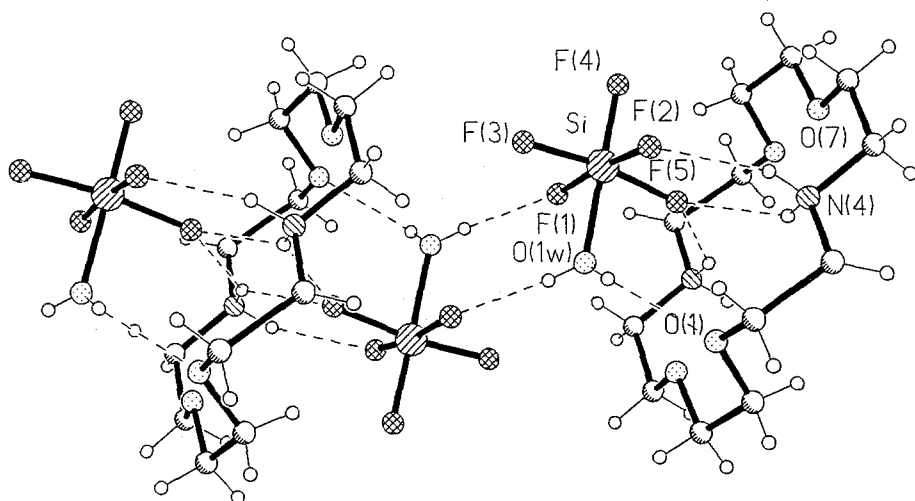
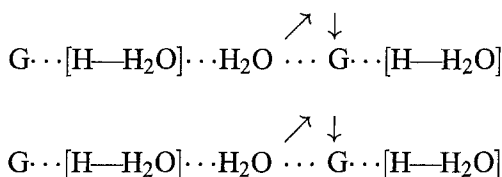


Figure 3. The chain architecture in complex (IV).

plex,  $[\text{MA18C6H}\cdot\text{H}_2\text{O}]^+$ , stabilized by two  $\text{OH}\cdots\text{O}$  [ $\text{O}(1\text{W})\cdots\text{O}(10) = 2.81(1)$ ,  $\text{O}(1\text{W})\cdots\text{O}(16) = 2.82(1)$  Å] and one  $\text{NH}\cdots\text{O}$  [ $\text{O}(1\text{W})\cdots\text{N}(4) = 2.70(1)$  Å] H-bonds in a trigonal manner with every second heteroatom of the ring (the deviation of  $\text{O}(3\text{W})$  from the mean plane of the six heteroatoms is 0.029 Å). The additional proton at the nitrogen atom is involved in the H-bonding as well as the water molecules and the fluorine atom of the  $[\text{SiF}_5\cdot\text{H}_2\text{O}]^-$  entity [ $\text{F}(4)\cdots\text{N}(4) = 2.84(1)$  Å] and decreases the number of H-bonds between the solvated water molecule and the crown host to one [ $\text{O}(2\text{W})\cdots\text{O}(13) = 2.82(1)$  Å] instead of two in (I). Unlike (I), where two similar guest entities approach from both sides to the crown ether possessing the inversion center, in (III) the single-charged  $[\text{MA18C6H}\cdot\text{H}_2\text{O}]^+$  entity has a different environment because of the engagement of the  $\text{H}_2\text{O}$  and F atoms in

OH<sub>water</sub> ··· O<sub>crown</sub> and NH<sub>crown</sub> ··· F contacts. The crystal structure organization for (III) can be described schematically by the following layer structure:

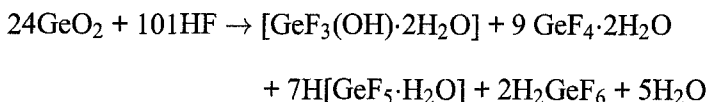


In the case of the dication [DA18C6H<sub>2</sub>]<sup>2+</sup> in complex (IV), only one type of water molecule, coordinated to the [SiF<sub>5</sub>·H<sub>2</sub>O]<sup>-</sup> entity to ensure a hexacoordinated silicon-containing anion, remains in the complex. However, its role is somewhat different. The guest [SiF<sub>5</sub>·H<sub>2</sub>O]<sup>-</sup> entity serves as a double-bridge, with OH ··· F guest-guest contacts being responsible for this function and they join two symmetrically dependent crown molecules, [O(1W) ··· F(1b) = 2.680(4) Å]. These contacts unite the complexes in the chain with the composition G-H-G-G-H-G-. Host-guest interactions are saturated by four NH ··· F and two OH ··· O contacts [O(1W) ··· O(1) = 2.829(5) Å], the N ··· F distances being 2.922(5)–2.971(5) Å.

The structure of (V) (Figure 4) is built from the [DA15C5H<sub>2</sub>]<sup>2+</sup> cations and SiF<sub>6</sub><sup>2-</sup> anions joined in the crystal by a H-bond system. The SiF<sub>6</sub><sup>2-</sup> anion is bound to three symmetrically dependent macrocyclic molecules by means of four H-bonds of the NH ··· F type. The [DA15C5H<sub>2</sub>]<sup>2+</sup> macrocyclic cation has a boat conformation with the essential deviation of the N(7) (1.50 Å) and N(13) (1.46 Å) atoms from the plane defined by the O(1), O(4), C(8) and C(11) atoms. The F(1) atom deviates by 2.53 Å from the same plane. Such a ring conformation provides its chelating H-bonding with the F(1) atom with distances of 2.787 Å and 2.823 Å. Two other H-atoms of the macrocycle aminogroups are responsible for the H-bonding with the symmetrically dependent SiF<sub>6</sub><sup>2-</sup> anions. Thus three out of six fluorine atoms of the SiF<sub>6</sub><sup>2-</sup> anion are involved in H-bonds. Taking into account the H-bond system as a whole, (V) represents a chain directed along the *y* axis in the crystal.

### 2.1.2. Germanium-Containing Complexes

It is interesting to note the structural similarity of the interaction products in the solutions SFHA—L and GeO<sub>2</sub>—HF—L (L = 18C6, DA18C6) [14]. The crystalline complexes [(*trans*-GeF<sub>4</sub>·2H<sub>2</sub>O)·18C6·2H<sub>2</sub>O] (VI) and [(DA18C6H<sub>2</sub>)(GeF<sub>5</sub>·H<sub>2</sub>O)<sub>2</sub>] (VII) appear to be the structural analogues of complexes (I) and (IV). <sup>19</sup>F NMR data [15] indicate that dissolution of GeO<sub>2</sub> in hydrofluoric acid is accompanied by the formation of a number of germanium-containing fluoride compounds. For the ratio HF:GeO<sub>2</sub> = 4.2 the following equilibrium exists:



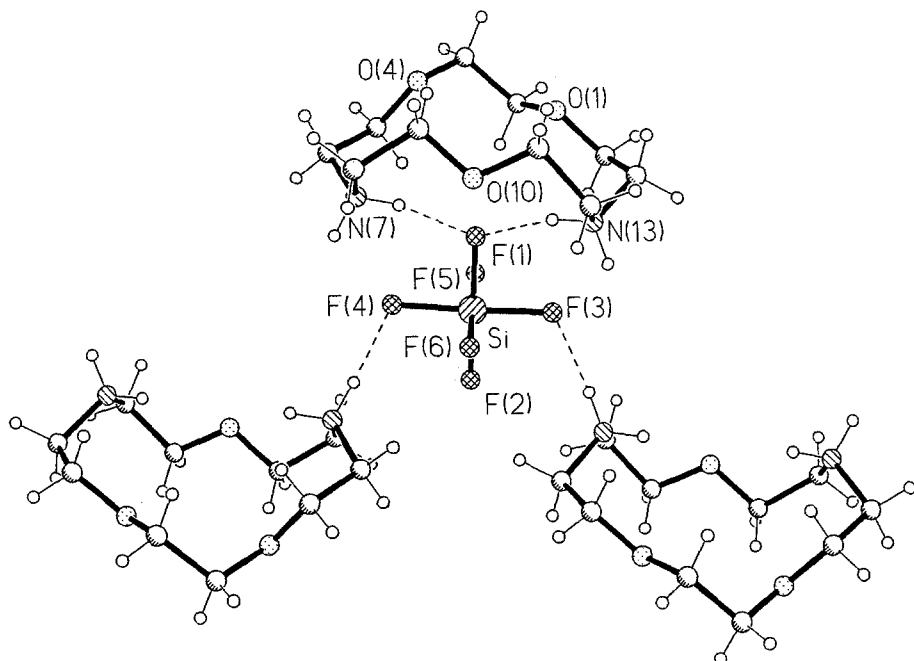


Figure 4. The chain structure organization in complex (V).

In contrast to  $[trans\text{-SiF}_5 \cdot 2\text{H}_2\text{O}]$  the germanium complex exists in solution as an equilibrium mixture of *cis-trans* isomers (*cis:trans*=3) [15]. Selective stabilization of the  $[trans\text{-GeF}_4 \cdot 2\text{H}_2\text{O}]$  moiety in (VI) can be considered as the first example of the stereospecific isolation of an octahedral fluorocomplex of a *p*-element from a mixture of *cis*- and *trans*-isomers in the form of a host-guest compound. The difference in H-bond distribution in isostructural complexes based on germanium and silicon is determined by the greater Ge—F distances in comparison to Si—F distances.

We would like to stress that the complexes  $[trans\text{-SiF}_4 \cdot 2\text{H}_2\text{O}]$ ,  $[trans\text{-GeF}_4 \cdot 2\text{H}_2\text{O}]$ ,  $[\text{SiF}_5 \cdot \text{H}_2\text{O}]^-$  and  $[\text{GeF}_5 \cdot \text{H}_2\text{O}]^-$  are stabilized in the solid phase and have been structurally characterized in the form of the compounds (I), (III), (IV), (VI), (VII) for the first time.

It might be expected that alteration of the crown ether in the SHFA–L systems will result in the selective stabilization of one of the coexisting species in the SHFA solutions by forming the corresponding host-guest complexes. What factor is responsible for the selective complexation of each complex with the crown ether? In [10] it was assumed that in every case it could be the aspiration to the high structural organization of H-G complexes provided by the maximum possible number of H-bonds between H and G which stabilize the complexes. Thus, for example, the selective separation of  $[trans\text{-SiF}_4 \cdot 2\text{H}_2\text{O}]$  (i.e. the form with the least equilibrium concentration in the initial aqueous solution) is achieved by the creation

of the stabilized system of H-bonds of the  $\text{OH} \cdots \text{X}$  type where all six O-atoms of 18C6 participate in the form of H-acceptors. Similarly the stabilization of the  $\text{SiF}_6^{2-}$  and  $[\text{SiF}_5 \cdot \text{H}_2\text{O}]^-$  moieties is possible only in the form of the organic salts.

### 2.1.3. Macrocycle Conformations in Si- and Ge-Containing Complexes

The macrocycle conformations in **(I)** and **(VI)** correspond to  $D_{3d}$  symmetry as deduced from vibrational spectroscopic data. Bands in the vibrational spectrum of **(I)** at 1085, 980, 853, 836, 530  $\text{cm}^{-1}$  (IR) and 864, 550  $\text{cm}^{-1}$  (Raman) are indicative of  $\text{OCH}_2\text{CH}_2\text{O}$  fragments in an *aga* conformation [16]. The great similarity of the vibrational spectra of **(I)** and **(II)** in the Si—F vibration regions ( $\nu(\text{SiF})$  about 775, 715 (IR), 650, 430  $\text{cm}^{-1}$  (Raman);  $\delta(\text{SiF}_2)$  about 440, 420 (IR), 370  $\text{cm}^{-1}$  (Raman)) allows us to assume that the [*trans*- $\text{SiF}_4 \cdot 2\text{H}_2\text{O}$ ] units also exist in **(II)**. The spectral data show the existence in the macrocyclic ring of  $\text{OCH}_2\text{CH}_2\text{O}$  units in *aga* and *agg* conformations. The macrocycle conformation in **(III)** is described by the sequence of six *aga* fragments (crown-like type); in **(IV)** it is a biangular conformation with the following set of torsion angles:  $ag + a$ ,  $g + g + a$ ,  $ag - a$ ,  $ag - a$ ,  $g - g - a$ ,  $ag + a$ . A similar conformation for the  $[\text{DA18C6H}_2]^{2+}$  dication was found in the compound  $[(\text{DA18C6H}_2)(\text{SCN})_2]$  [17]. The spectral characteristics for **(III)** and **(IV)** for conformational-sensitive bands of valent-deformational (1000–800  $\text{cm}^{-1}$ ) and deformational (600–500  $\text{cm}^{-1}$ ) modes of the macrocycle vibrations agree with their structure peculiarities. Thus the position of the bands for  $\text{OCH}_2\text{CH}_2\text{O}$  in the IR spectrum of **(III)** at 978, 855 and 832  $\text{cm}^{-1}$  practically coincide with the band positions in the spectrum of **(I)** [10] where the macrocycle is built of six *aga* fragments.

### 2.1.4. Structure of Inorganic Complexes

In the centrosymmetric octahedral [*trans*- $\text{SiF}_4 \cdot 2\text{H}_2\text{O}$ ] moiety of **(I)** Si—F(1), Si—F(2) and Si—O bond distances are equal to 1.655(1), 1.658(1) and 1.841(2) Å respectively. The average Si—O and Si—F bond distances in the aquapentafluorosilica anion in **(III)** and **(IV)** are equal to 1.880(6) and 1.663(5) Å and are close to those found for [*trans*- $\text{SiF}_4 \cdot 2\text{H}_2\text{O}$ ] in **(I)** [10]. The Si—F bond distance redistribution in **(III)** and **(IV)** is caused by the fluorine atoms participating as acceptors in H-bonds. Thus, in **(III)** the longest Si—F bonds [1.662(8) and 1.679(8) Å] are observed for the fluorine atoms [F(3) and F(4)] participating in H-bonds. In **(IV)** the longest bond [Si—F(1) = 1.702(2) Å] corresponds to the shortest H-bond distance  $\text{O}(1\text{W}) \cdots \text{F}(1)$  [ $\text{O} \cdots \text{F} = 2.680(4)$  Å]. The fluoroligands involved in H-bonding result in an electron density redistribution in the Si—F bonds. The  $\text{SiF}_6^{2-}$  anion in **(V)** has a distorted octahedral structure with Si—F distances in the range 1.663–1.713 Å. In the literature there is extremely limited information about hexacoordinated germanium(IV) complexes. Moreover, data about aquafluoro complexes are completely lacking, because they possess low stability, as do the

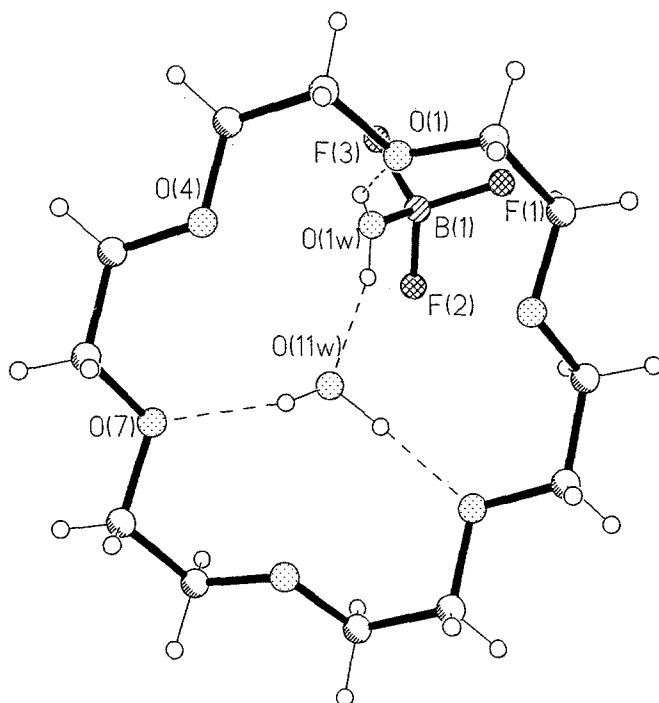


Figure 5a. View of complex (VIII) in the plane of the crown O-atoms (the second guest entity is omitted for clarity).

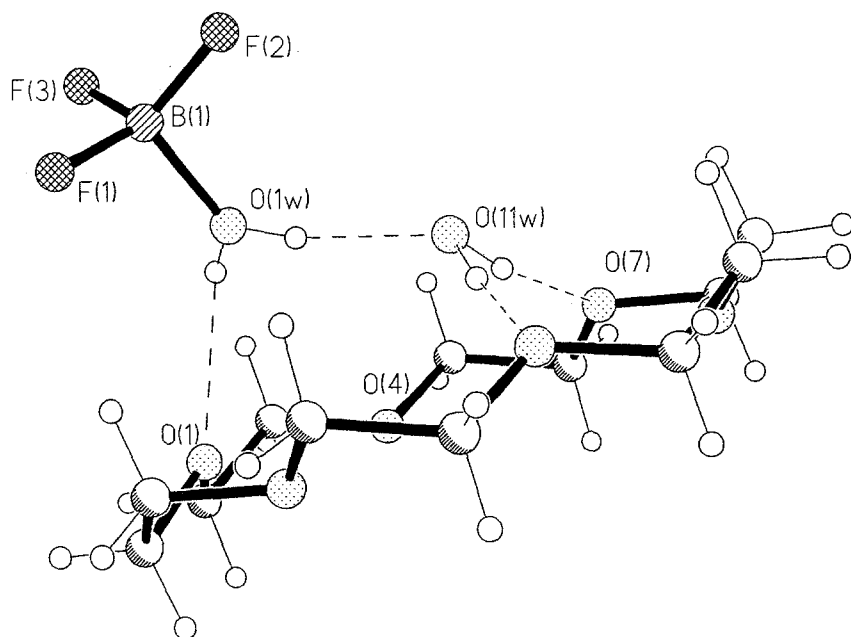


Figure 5b. View of the guest perching mode in complex (VIII).



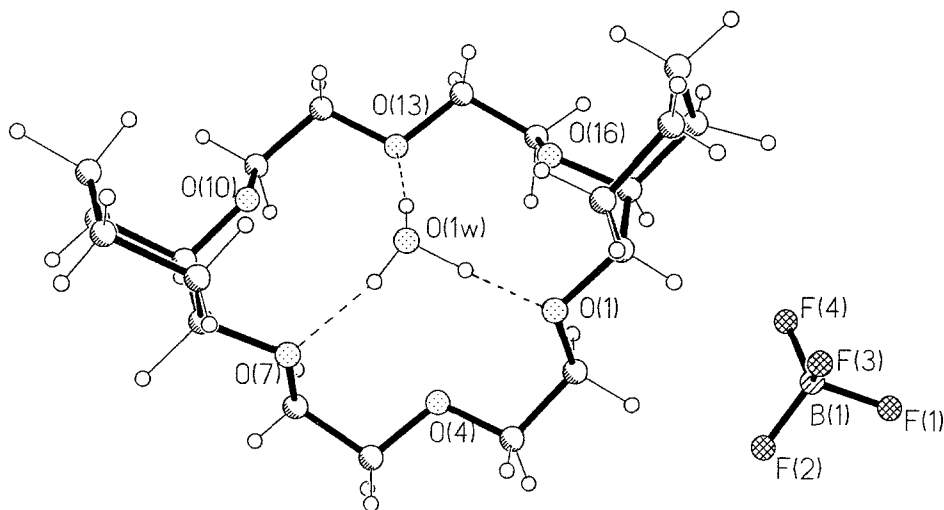


Figure 6a. View of complex (IX) in the plane of the crown O-atoms.

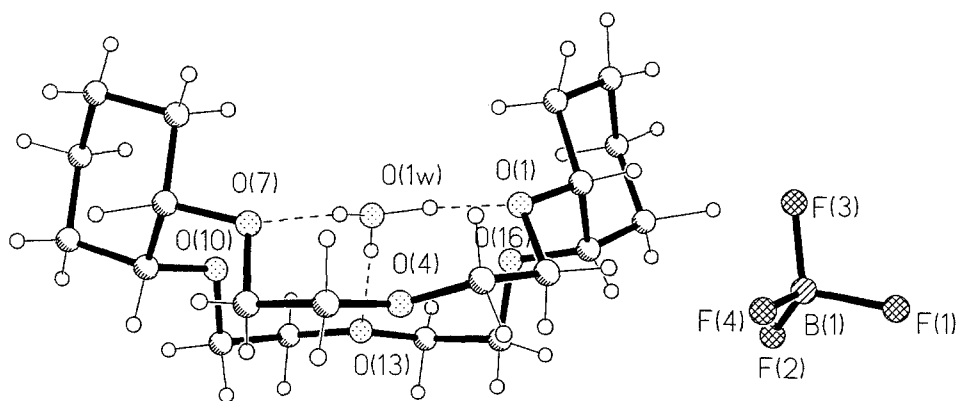


Figure 6b. Proximal arrangement of  $[\text{DCH-6A}\cdot\text{H}_3\text{O}]^+$  in complex (IX).

appropriate silicon complexes. In the  $[\text{GeF}_5\cdot\text{H}_2\text{O}]^-$  entity an octahedral polyhedron structure is achieved. The metal octahedron is slightly extended in the direction of the water molecule. In complex (VI) Ge—F distances vary within the range of 1.738(2)–1.799(2) Å, and the shortest distance is observed for the bond located in a *trans*-position to a water molecule [Ge—O(H<sub>2</sub>O) distance = 1.966(3) Å]. The metal coordination polyhedron has approximate  $C_{4v}$  symmetry. For germanium-containing complexes we do not observe a dependence of the M—F distance on the number and type of H-bonds in which the fluorine atom participates. For the  $[\text{trans-GeF}_4\cdot 2\text{H}_2\text{O}]$  entity Ge—F distances are 1.763(2) and 1.764(2) Å, Ge—H<sub>2</sub>O = 1.927(2) Å. The polyhedron symmetry is close to  $D_{4h}$ .

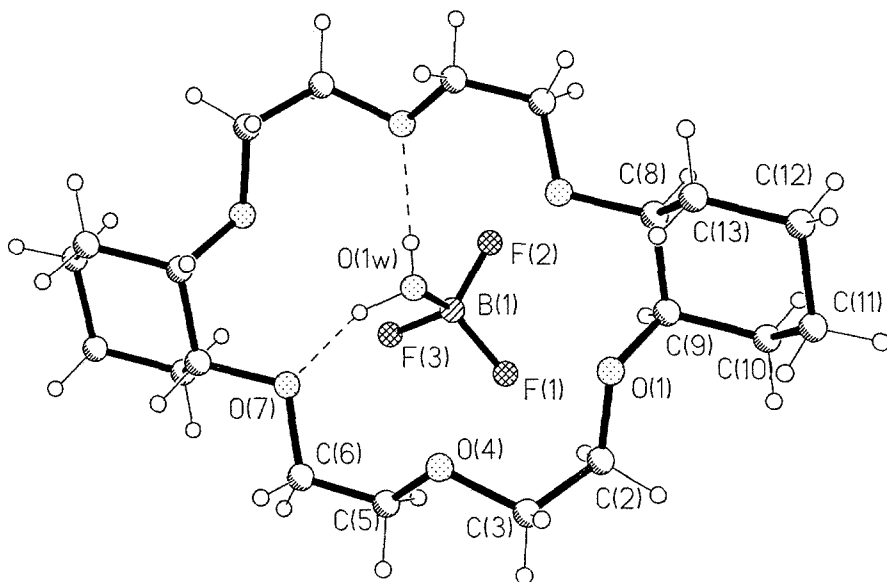


Figure 7a. View of complex (X) in the plane of the crown O-atoms (the second guest entity is omitted for clarity).

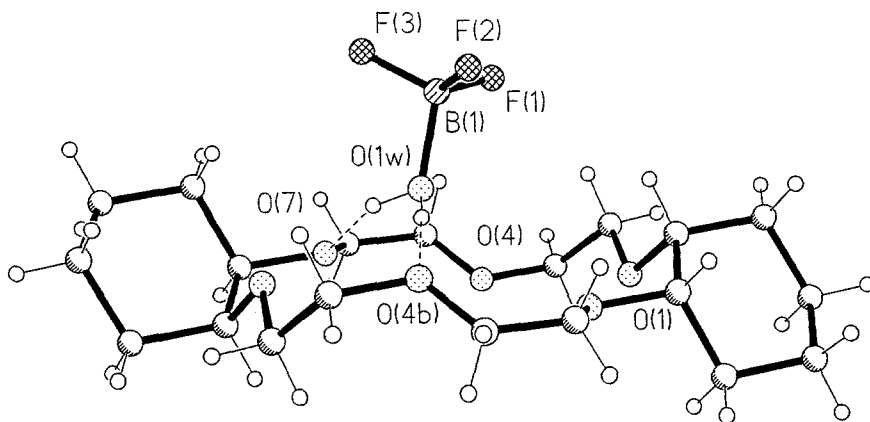


Figure 7b. Guest perching position in complex (X).

Summarizing the results obtained for the  $\text{H}_2\text{SiF}_6$  ( $\text{H}_2\text{GeF}_6$ )–crown ether system, one may conclude that the final product obtained depends on the crown ether used and the acidity of the initial solution. All the products are shown schematically below.

Guest	Host	Complex obtained	H : G : H <sub>2</sub> O
	18C6	[18C6· <i>trans</i> -SiF <sub>4</sub> ·2H <sub>2</sub> O(H <sub>2</sub> O) <sub>2</sub> ]	1 : 1 : 4
	18C6	[18C6· <i>trans</i> -GeF <sub>4</sub> ·2H <sub>2</sub> O(H <sub>2</sub> O) <sub>2</sub> ]	1 : 1 : 4
H <sub>2</sub> SiF <sub>6</sub> (solution)	MA18C6	[MA18C6H·H <sub>2</sub> O][SiF <sub>5</sub> ·H <sub>2</sub> O]·H <sub>2</sub> O	1 : 1 : 3
or H <sub>2</sub> GeF <sub>6</sub> (solution)	DA18C6	[DA18C6H <sub>2</sub> ·(SiF <sub>5</sub> ·H <sub>2</sub> O) <sub>2</sub> ]	1 : 1 : 2
	DA18C6	[DA18C6H <sub>2</sub> ·(GeF <sub>5</sub> ·H <sub>2</sub> O) <sub>2</sub> ]	1 : 1 : 2
	DA15C5	[DA15C5H <sub>2</sub> ·(SiF <sub>6</sub> )]	1 : 1

## 2.2. BORON-CONTAINING COMPLEXES

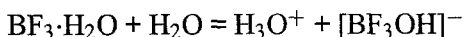
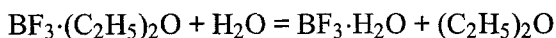
Despite being one of the strongest Lewis acids, BF<sub>3</sub> forms rather unstable adducts with water. Nevertheless, its mono- [H<sub>2</sub>O·BF<sub>3</sub>] and dihydrates [(H<sub>2</sub>O)<sub>2</sub>·BF<sub>3</sub>] [18, 19] are known in the solid state. Macrocycles serve to stabilize the hydrated BF<sub>3</sub> moieties. BF<sub>3</sub>–crown ether complexes appear to be rather versatile systems and can include guests as neutral or charged entities [4,20,21]. In addition to [BF<sub>3</sub>·H<sub>2</sub>O·18C6] [4] and [(HBF<sub>4</sub>·H<sub>2</sub>O)<sub>2</sub>·18C6] [21] three new complexes [(BF<sub>3</sub>·H<sub>2</sub>O)<sub>2</sub>·18C6·2H<sub>2</sub>O] (**VIII**) [22], [DCH—6A·H<sub>3</sub>O][BF<sub>4</sub>] (**IX**, DCH-6A-*cis-syn-cis* isomer of dicyclohexano-18C6) [23] [DCH—6B·(BF<sub>3</sub>·H<sub>2</sub>O)<sub>2</sub>] (**X**, DCH-6B-*cis-anti-cis* isomer of dicyclohexano-18C6) [24] have been obtained and characterized by X-ray crystallography. As previously reported [4] we used the simplest way to prepare complexes by heating the mixture containing BF<sub>3</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O and the crown ether in the presence of moist air. The structure of (**VIII**) has a molecular character. Only van der Waals contacts are revealed (Figure 5) between the individual associates of (**VIII**), possessing a center of symmetry. In each associate of (**VIII**) the BF<sub>3</sub>·H<sub>2</sub>O inorganic entity, 18C6 and water molecules are united by the H-bond system involving all the O-atoms (D<sub>3d</sub> crown ether symmetry). The guest entity, BF<sub>3</sub>·H<sub>2</sub>O, interacts with the crown ether in two ways: directly through the O(1) atom [O(1W)···O(1) = 2.637 Å], or through a bridging solvate water molecule. The O(1W) water molecule coordinated to boron and the solvated O(11W) water molecules are joined by a strong H-bond [O···O = 2.480 Å]. In turn, the solvated water molecule is joined to the O(4) and O(7) crown atoms by H-bonds with O···O distances of 2.824 and 2.833 Å, respectively.

Note that in addition to the stoichiometric distinctions, the related compounds, [BF<sub>3</sub>·H<sub>2</sub>O·18C6] [4] and (**VIII**) have different structural organizations. First, the character of the H–G interactions is different. In the complex [BF<sub>3</sub>·H<sub>2</sub>O·18C6] both H-atoms belonging to the coordinated water molecule are involved in the direct contacts with the crown ether while in complex (**VIII**) only one of the H atoms is involved. In addition, the crown ether structural function becomes essentially different. Thus, in the [BF<sub>3</sub>·H<sub>2</sub>O·18C6] associate only two out of the six crown ether oxygen atoms are engaged in host–guest interactions; in (**VIII**) all six O atoms participate in these contacts. Thus, in the system BF<sub>3</sub>—H<sub>2</sub>O—18C6 there

are at least two different complexes distinguished by their self-organization and, as a consequence, complexes with different stoichiometries have been isolated.

The ionic structure of **(IX)** consists (Figure 6) of the complicated cations,  $[\text{DCH}-6\text{A}\cdot\text{H}_3\text{O}]^+$  and  $[\text{BF}_4]^-$  anions bound by electrostatic interactions. The structure might be considered as a distorted NaCl-like type, where the voids in the crystal space of the bulky  $[\text{DCH}-6\text{A}\cdot\text{H}_3\text{O}]^+$  cations are occupied by the  $[\text{BF}_4]^-$  anions. The  $[\text{DCH}-6\text{A}\cdot\text{H}_3\text{O}]^+$  cation itself is a typical perching complex (Figure 6b) stabilized by three  $\text{OH}\cdots\text{O}$  H-bonds between the hydronium ion and alternate crown O-atoms. The  $\text{O}\cdots\text{O}$  ( $\text{H}_3\text{O}^+\cdots\text{O}_{\text{cr}}$ ) distances are in the range 2.624(6)–2.650(6) Å. Three other  $\text{O}\cdots\text{O}$  distances corresponding to electrostatic interactions are in the range 2.856(6)–2.893(6) Å. The  $\text{H}_3\text{O}^+$  entity lies at 0.85 Å above the macrocyclic plane defined by the six O-atoms approaching it from the side shielded by the bulky substituents giving a proximal complex. In terms of its geometrical parameters, the cation in **(IX)** is very similar to that found in the structure  $[\text{DCH}-6\text{A}\cdot\text{H}_3\text{O}][\text{ClO}_4]$  [25].

In **(X)** (Figure 7) the H-bond system is close to that described in [4] except that the complex host-guest stoichiometry is 1 : 2 in **(X)** compared with 1 : 1 in [4]. The  $\text{O}(\text{O1W})\cdots\text{O}_{\text{crown}}$  distances are in the range 2.589(4)–2.639(4) Å, with the water entity deviating from the mean plane of the ring heteroatoms. In [26] the possible ways of  $[\text{BF}_4]^-$  ion formation in the reaction mixture were proposed:



Numerous  $\text{O}(\text{H})\cdots\text{F}$  contacts described in [18, 19] and resulting in the hydrogen-bonded three dimensional network in  $[\text{BF}_3\cdot 2\text{H}_2\text{O}]$  are replaced in **(VIII)–(X)** by  $\text{O}(\text{H}_2\text{O})\cdots\text{O}_{\text{cr}}$  interactions with the simplification of the molecular structure giving the individual complexes with different host : guest : water stoichiometries: 1 : 2 : 4 for **(VIII)**, 1 : 1 : 1 (provisionally) for **(IX)**, 1 : 2 : 2 for **(X)** and 1 : 1 : 1 in [4].

The inorganic complex  $\text{BF}_3\cdot\text{H}_2\text{O}$  has a distorted tetrahedral structure with the distances  $\text{B}-\text{O} = 1.510(3)$  and  $\text{B}-\text{F} = 1.367(4)$ – $1.379(5)$  Å, the angles at the B atom are in the range 105.8(8)–117.1(8)°. In the vibrational spectra of **(VIII)** the  $\nu(\text{BO})$  vibration was identified at 741(IR) and 747  $\text{cm}^{-1}$  (Raman),  $\nu_s(\text{BF}_3)$  at 905 (IR) and 901  $\text{cm}^{-1}$  (Raman),  $\delta(\text{BF}_3)$  at 505 (IR) and 508, 531  $\text{cm}^{-1}$  (Raman),  $\rho(\text{BF}_3)$  about 370  $\text{cm}^{-1}$  (Raman). The  $[\text{BF}_4]^-$  anion has a tetrahedral structure with  $\text{B}-\text{F}$  distances in the range 1.291(1)–1.408(1) Å, and  $\text{F}-\text{B}-\text{F}$  angles in the range 105.7(8)–113.6(9)°.

Thus, the interaction of silicon(IV), germanium(IV), and boron(III) fluorocomplexes with crown ethers in solution results in the formation of stable H–G type crystalline complexes. In the case of the first two compounds the H–G composition is defined to a great extent by the nature of the crown ether. O-containing crown

ethers are able to stabilize neutral molecular aquafluorocomplexes as guests while aza crown ethers protonated in acidic media bind anionic fluorocomplexes. The main structural organizing role in the H—G compounds described here belongs to the systems of intermolecular H-bonds of GuestH $\cdots$ Host and HostH $\cdots$ Guest types.

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