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Review

Supramolecular compounds of fluorocomplexes of *p*-elements with crown and azacrown ethers: Synthesis, transformations and crystal structures

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Dedicated to the memory of
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ABSTRACT

The review covers systematic publications on various aspects of supramolecular aggregates formed by boron(III), silicon(IV), germanium(IV) or tin(IV) fluorocomplexes with macrocyclic ligands. The syntheses, structural features, spectral characteristics, thermo-chemical conversions of these compounds, as well as the selectivity problems in these complex systems composed of inorganic fluorocomplexes and macrocyclic ligands are discussed.

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Contents

1. Introduction

Nowadays crown and azacrown ethers as well as their analogs manifest themselves as effective stabilizers for various unstable and highly reactive compounds in the form of supramolecular complexes of the ‘guest–host’ type [1,2]. Of particular interest and concern are the fluoro-complexes prone to hydrolytic transformations in aqueous solutions or in moist air, thus giving rise to the labile compounds, aqua and hydroxofluorocomplexes as the products of substitution of fluoroligands [3,4]. The macrocyclic ligands have proven to be suitable for stabilization in the form of crystalline complexes the products of hydrolytic transformations of fluorocomplexes for a series of *p*-elements that allowed to shed light on the structure of these ‘guests’ as well as on the structural organization and properties of the resulting supramolecular

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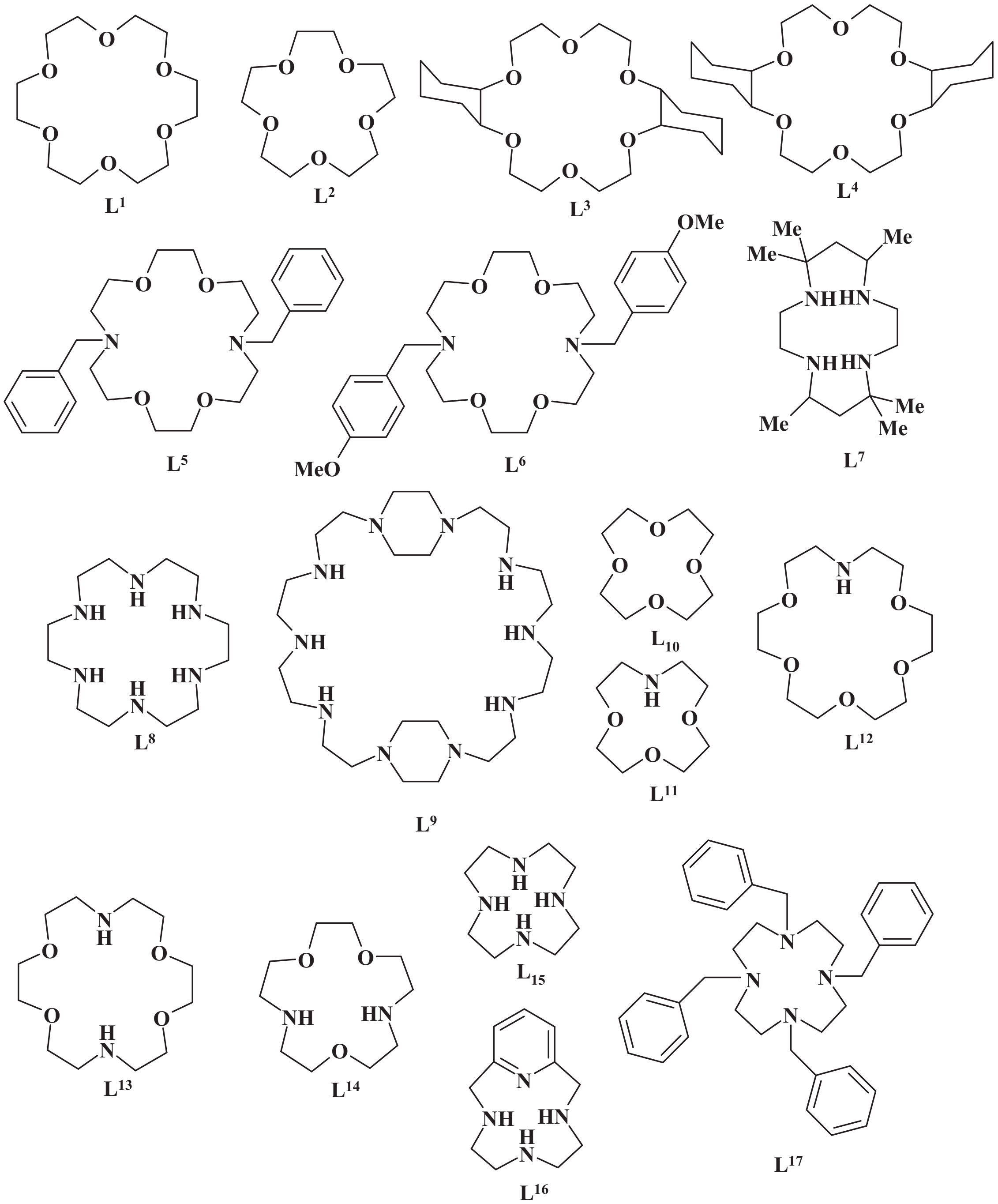
complexes. One should be emphasized that before our studies, many of the discussed herein fluorocomplexes, in particular aquafluorocomplexes with the general formula $[MF_{6-n}(H_2O)_n]^{-2+n}$ (M = Si, Ge, n = 1, 2; M = Sn, n = 1) were known only as solutions of the corresponding complex fluoroacids, while the information about their stereochemistry was based primarily on spectroscopic data (mainly ^{19}F NMR) [5,6]. The early reviews in this field were focused on different aspects of the chemistry of halide complexes of p- and d-elements with macrocyclic ligands which predominantly were the classic crown ethers (CE) [7–12], and oxonium salts were mainly considered as stabilizable systems [10].

This review is aimed to generalize our recent results in the field of stabilization of fluorocomplexes of the 13–14 group p-block elements in the form of supramolecular compounds with crown ethers and aza cycles with an emphasis on structure and properties of these compounds. The schematic representation of macrocyclic molecules used in our research is given in Scheme 1.

2. Structure of fluorocomplexes

2.1. Boron(III) fluorocomplexes

Atwood et al. demonstrated stabilization of the unstable aqua complex $BF_3{\cdot}H_2O$ and the monohydrate of non-ionized form of tetrafluoroboronic acid $HBF_4{\cdot}H_2O$ in the form of compounds $[(BF_3{\cdot}H_2O){\cdot}L^1]$ (**I**) and $[(HBF_4{\cdot}H_2O)_2{\cdot}L^1]$ (L^1 = 18-crown-6, 18C6) [13,14]. Complex **I** was obtained by heating a mixture of $AgBF_4$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and L^1 in aqueous toluene, whereas attempts of



Scheme 1. Schematic representation of macrocyclic molecules used in our research.

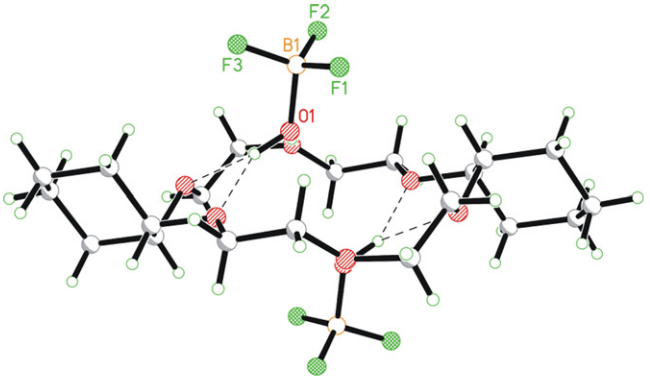


Fig. 1. Structure **IV** stabilized by OH·O hydrogen bonds.

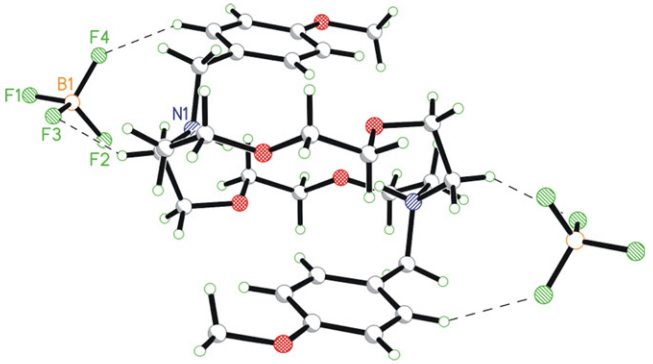


Fig. 2. Structure of **VII**.

direct synthesis through the interaction of $BF_3{\cdot}H_2O$ with L^1 in toluene were unsuccessful. These findings stimulated our studies in this field. Using the simple general procedure based on interaction of $BF_3{\cdot}OEt_2$ with CEs in unprotected from moisture atmosphere molecular complexes with the compositions $[(BF_3{\cdot}H_2O){\cdot}2L^2]$ (**II**) [15], $[(BF_3{\cdot}H_2O)_2{\cdot}L^1{\cdot}2H_2O]$ (**III**) [16], and $[(BF_3{\cdot}H_2O)_2{\cdot}L^3]$ (**IV**) [17] (L^2 = 15C5; L^3 = *cis-anti-cis*-dicyclohexano-18C6) were obtained. In the case of *cis-syn-cis*-dicyclohexano-18C6 (L^4) the interaction product represents ionic complex $[(H_3O{\cdot}L^4)BF_4]$ (**V**) [18]. According to the single crystal X-ray data, the components in the complexes **I**–**IV** as well as those of the complex macrocyclic cation in **V** are linked by the integrated system of OH···O hydrogen bonds, where the CE oxygen atoms act as H-acceptors (six, four or three oxygen atoms from L^1, L^3 and L^4, respectively). The structure of complex **IV** is shown in Fig. 1.

Complex **III** was also synthesized through interaction of HBF_4 with L^1 in the solvent mixture CH_2Cl_2/CCl_4, and its crystal structure was reported in [19]. For the ionic complex $[(H_3O{\cdot}L^1)BF_4]$ whose structure was also reported in [19], the synthetic procedure as well as IR and Raman spectra were published earlier [20]. The recently documented molecular complex $[(BF_3{\cdot}H_2O){\cdot}2Ph_3PO]$ with the non-macrocyclic ligand Ph_3PO is stabilized by two strong H-bonds of the P=O···H–O–H···O=P type (O···O distances range 2.488(6)–2.499(7) Å) [21]. The selected parameters of H-bonds and thermal characteristics of boron fluorocomplexes with CEs are summarized in Table 1. According to the thermogravimetric data [15–18], the thermochemical transformations can be described as consecutive stages including melting and subsequent decomposition with complete isolation of the components in the gas phase:

$$[(BF_3{\cdot}H_2O)_n{\cdot}mL]_{(s)} \rightarrow [(BF_3{\cdot}H_2O)_n{\cdot}mL]_{(l)} \rightarrow nBF_{3(g)} + nH_2O_{(g)} + mL_{(g)}, \quad (1)$$

$$[(H_3O \cdot L)BF_4]_{(s)} \rightarrow [(H_3O \cdot L)BF_4]_{(l)} \rightarrow BF_{3(g)} + H_2O_{(g)} + HF_{(g)} + L_{(g)} \quad (2)$$

The stability of complexes **I**–**V** is significantly higher compared to their inorganic guest components: for example, compound $BF_3{\cdot}H_2O$ melts at 6.0 °C and partially decomposes at 20 °C [22], while $(H_3O)BF_4$ melts with decomposition at 52 °C [23]. The studied compounds are characterized by the very similar thermal stability, and in the row of molecular complexes the relatively higher melting and decomposition temperatures has compound $[(BF_3{\cdot}H_2O)_2{\cdot}L^3]$ (**IV**) (Table 1), whose structure is stabilized by the strongest H-bonds (O···O distances are in the range 2.589–2.642 Å). According to the ^{19}F and ^{11}B NMR data [24], in acetone solution complexes **III** and **IV** are subjected to partial solvolysis following the solvolysis scheme (3):

$$[(BF_3{\cdot}H_2O)_2{\cdot}L{\cdot}nH_2O] + Me_2CO \rightarrow BF_3{\cdot}Me_2CO + (H_3O)[BF_3OH] + L + nH_2O \quad L = L^1, n = 2; L = L^3, n = 0 \quad (3)$$

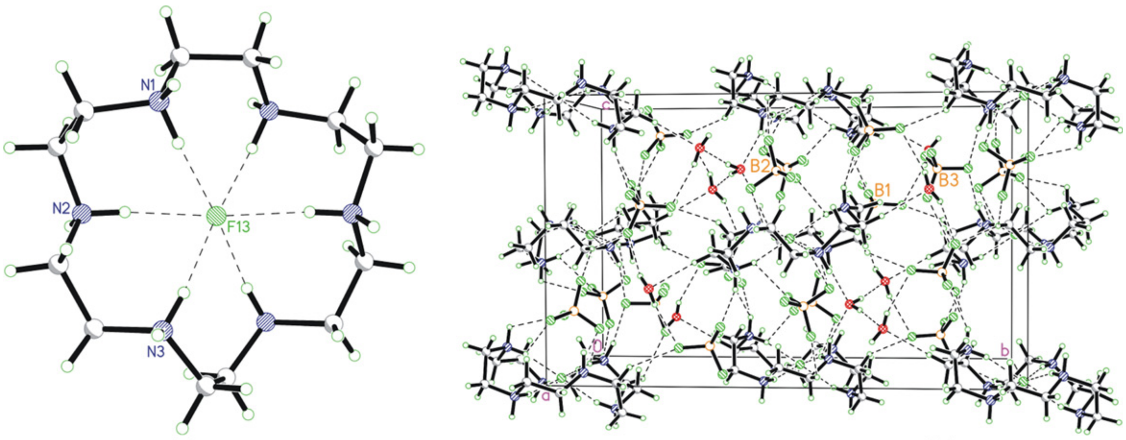
Probably, crown ethers, which reveal stronger H-acceptor properties compared to acetone [25] can stimulate the formation of the ionized form $(H_3O)[BF_3OH]$.

The azacrown ethers and azacycles whose macrocyclic frameworks contain NH-groups, easily protonated in the acidic medium, manifest themselves as efficient receptors capable to fix either the naked halide anions [26,27], or the complex $[AF_n]^-$ fluoroanions *via* combination of electrostatic interaction $>NH_2^+AF_n^-$ and H-bonding of NH···F type. The products of interaction of $BF_3{\cdot}OEt_2$ with azacrown ethers in methanol or ethanol solutions represent exclusively ionic tetrafluoroborate complexes. Compounds $[(L^5H_2)(BF_4)_2]{\cdot}H_2O$ (**VI**) [28] and $[(L^6H_2)(BF_4)_2]$ (**VII**) [29] (Fig. 2) include the dications of two lariat ethers, *N*,*N′*-dibenzyl-1,10-diaza-18C6 (L^5) and *N*,*N′*-4-methoxydibenzyl-1,10-diaza-18C6 (L^6) with the mixed donor (NH^+), acceptor (–O–) functions. Both macrocyclic dications obey C_i-symmetry with *endo*-oriented NH-groups that participate in intramolecular NH···O hydrogen bonds, and the benzyl arms being arranged above and below the macrocyclic cavity in folded conformation. The ionic species are linked only *via* weak CH···F interactions, which in the case of **VI**

Table 1
H-bond and thermal characteristics of boron fluorocomplexes with crown ethers.

Complex	Number of H-bonds[a]	Distance D···A, Å	mp, °C	t_{decomp}, °C	Reference
$[(BF_3{\cdot}H_2O){\cdot}L^1]$	2	2.76, 2.80	72[b]	–	[13]
$[(BF_3{\cdot}H_2O){\cdot}2L^2]$	–	–	110–150	185	[15]
$[(BF_3{\cdot}H_2O)_2{\cdot}L^1{\cdot}2H_2O]$	6	2.65–2.85	60–75	145–190	[16,19]
$[(BF_3{\cdot}H_2O)_2{\cdot}L^3]$	4	2.589–2.642	140–155	172–200	[17]
$[(H_3O{\cdot}L^1)BF_4]$	3	2.68–2.73	140–143[a]	–	[19]
$[(H_3O{\cdot}L^4)BF_4]$	3	2.624–2.650	90–130	175–220	[18]

[a] The separations with D(donor)–H···A(acceptor) < 2.6 Å and angle DHA > 120° were taken in consideration.
[b] Visual data.



(a) (b)

Fig. 3. Structure of **IX**: (a) view of complex cation $[L^8H_6(F)]^{5+}$ stabilized by six NH···F hydrogen bond and (b) crystal packing.

provide the formation of channels occupied by the H-bonded water molecules.

The reported in [30] complex $[(L^7H_2)(BF_4)_2]\cdot H_2O$ (**VIII**) (L^7 = *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has the perching structure with two $[BF_4]^-$ anions arranged above and below the average plane of the 14-membered macrocyclic dication. The symmetry of the dication is close to C_2. According to [30], thermolysis of complex **VIII** is accompanied by the effects of dehydration (50–80 °C), melting (225–240 °C) and decomposition (270–311 °C) following the schemes (4)–(6):

$$[(L^7H_2)(BF_4)_2]\cdot H_2O_{(s)} \rightarrow [(L^7H_2)(BF_4)_2]_{(s)} + H_2O_{(g)}, \quad (4)$$

$$[(L^7H_2)(BF_4)_2]_{(s)} \rightarrow [(L^7H_2)(BF_4)_2]_{(l)}, \quad (5)$$

$$[(L^7H_2)(BF_4)_2]_{(l)} \rightarrow L^7{}_{(l)} + 2HF_{(g)} + BF_{3(g)}. \quad (6)$$

Compared to the oxonium complex $[(H_3O\cdot L^4)BF_4]$ (**V**) the essentially higher thermal stability of **VIII** has its origin in the different H-acceptor capabilities of the heteroatoms in macrocycles L^4 and L^7, as well as in the contribution to the general complex stability in **VIII** made by the system of host–guest H-bonds absent in **V**. Recently we reported the first example of the mixed-anionic complex of hexaaza-18C6 (L^8) with the composition $[L^8H_6(F)(BF_4)_5]\cdot 3H_2O$ (**IX**), where the fluoride perfectly centers the hexaazonia macrocyclic cavity that obeys the C_2-symmetry [31]. In the complex cation $[L^8H_6(F)]^{5+}$ (Fig. 3a) each $>NH_2^+$ group is involved in single NH···F H-bond with fluoride (the average distance N···F 2.793(3) Å, the angle N–H···F 164°), whereas the $[BF_4]^-$ anions and water molecules participate in the NH···F, NH···O and OH···F H-bonds giving rise to the 3D-supramolecular architecture with the alternation of organic and inorganic regions in the crystal solid (Fig. 3b).

In complex $[(L^9H_{10})(BF_4)_{10}]\cdot 10H_2O$ (**X**) the 30-membered macrocycle with two piperazine rings incorporated in the macrocyclic skeleton, decaazatricyclo[28.2.2.213.16]tetratriacontane (L^9) acts as decaazonia cation, linking the $[BF_4]^-$ anions and water molecules *via* an extensive network of intermolecular H-bonds of NH···F, NH···O, OH···F and OH···O types (Fig. 4) [32]. Water molecules compete with the $[BF_4]^-$ anions for the place in the second coordination sphere of the macrocycle, acting as bridges between the macrocycle and the $[BF_4]^-$ anions or between the anions.

2.2. Silicon(IV) fluorocomplexes

Structural and spectroscopic studies of host–guest compounds, the products of interaction of fluorosilicic acid with crown and azacrown ethers provided important arguments in discussion of composition of the silicon fluorocomplexes in aqueous solutions of fluorosilicic acid and acid solutions of its salts [6,33]. One should be emphasized, that according to the data summarized in [3], the solutions of fluorosilicic acid represent an equilibrium multi-component system comprising the $[SiF_6]^{2-}$ anions and the products of their hydrolytic transformations, as it follows from Eqs. (7)–(9):

$$[SiF_6]^{2-} + H_3O^+ \rightleftarrows [SiF_5(H_2O)]^- + HF, \quad (7)$$

$$[SiF_5\cdot H_2O]^- + H_3O^+ \rightleftarrows SiF_4\cdot 2H_2O + HF, \quad (8)$$

$$SiF_4\cdot 2H_2O + nH_2O \rightleftarrows SiO_2\cdot nH_2O + 4HF. \quad (9)$$

It is known, that equilibrium (7) dominates at the atomic ratio $\varphi = \Sigma F/\Sigma Si \approx 6$. An alternative point of view, the most comprehensively sounded in the survey [34], considers the $[SiF_6]^{2-}$ anions

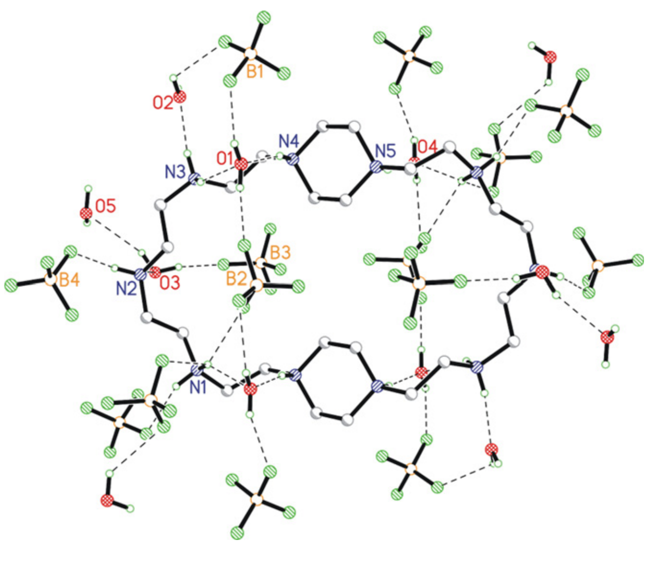


Fig. 4. The closest environment of deca-cation $[(L^9H_{10})]^{10+}$ in **X**. C-bound H-atoms are omitted for clarity.

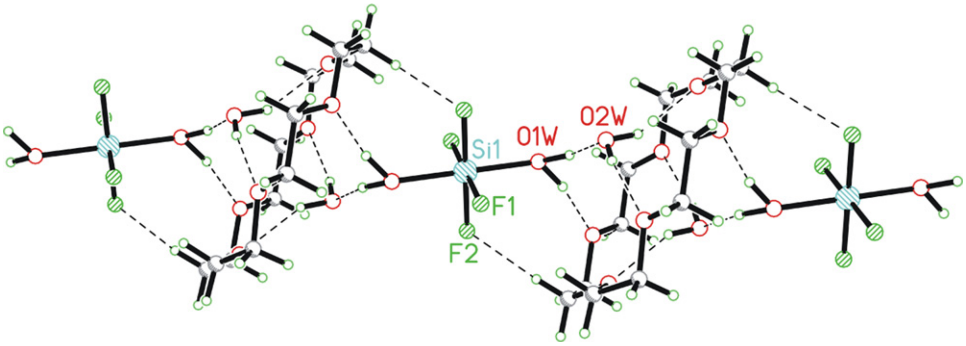


Fig. 5. Fragment of polymeric chain in **XI**.

as dominant species in solutions of fluorosilicic acid with relatively low acidity, and the possibility for SiF_4 accumulation in strongly acidic solutions, while the contribution of aquafluorosilicate anion in the equilibrium processes is excluded. The specific behavior of fluorosilicic acid in reactions with classic crown ethers has been elucidated. The products of interaction of fluorosilicic acid with L^1, L^2, and 12C4 (L^{10}) represent molecular complexes with the compositions [(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot L^1 \cdot 2H_2O$] (**XI**), [(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot L^2 \cdot H_2O$] (**XII**) and [(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot 2L^{10}$] (**XIII**), whose structures were studied by vibration spectroscopy and X-ray analysis [35,36]. Complex **XI** (Fig. 5) was primarily identified in the solid state as the product of interaction of SiF_4 with the hexane solution of L^1 in unprotected from moisture atmosphere [37]. In the chain structure water molecules fulfill the bridging functions, linking the *trans*-$SiF_4{\cdot}2H_2O$ complexes and macrocycle L^1.

The identical spectral characteristics allowed us to assign the similar structures to **XII** and **XIII,** as the pronounced similarities exist in the long-wavelength region in the IR spectra for **X**–**XII**, where the bands corresponding to ν(SiF) and $\delta(SiF_2)$ vibrations of inorganic 'guest' (Table 2) definitely indicate in favor of its *trans*-configuration [35,36]. Splitting into two components the band assigned to the doubly degenerate vibrations ν(SiF) of the E_u-type can be attributed to the crystal lattice forces. The physico-chemical characteristics of silicon fluorocomplexes with crown ethers are summarized in Table 3. As far as it follows from the thermogravimetric and differential scanning calorimetry (DSC) data [35,36], the thermolysis of complexes is accompanied by melting, followed by decomposition according to schemes (10) and (11):

$$[(SiF_4{\cdot}2H_2O){\cdot}nL{\cdot}mH_2O]_{(s)} \rightarrow [(SiF_4{\cdot}2H_2O){\cdot}nL{\cdot}mH_2O]_{(l)} \rightarrow SiF_{4(g)} + (m+2)H_2O_{(g)} + nL_{(l)}, \quad (10)$$

$$[(H_3O \cdot L^4)SiF_5]_{(s)} \rightarrow SiF_{4(g)} + H_2O_{(g)} + HF_{(g)} + L^4{}_{(g)}. \quad (11)$$

The characteristic curve of DSC (Fig. 6) demonstrates the thermochemical conversion of compound **XII** which is accompanied by endothermic effects. Note that the experimentally determined value of the mass loss that accompanied the decomposition of complex **XII** with the release in the gas phase

Table 2
IR data for silicon(IV) fluorocomplexes as the 'guests' in the supramolecular compounds with crown and azacrown ethers.

Complex	Guest	Guest symmetry	ν(SiF)	$\delta(SiF_n)$	Reference
XI	*trans*-[$SiF_4{\cdot}2H_2O$]	D_{4h}	775 v.s. (E_u) 715 sh (E_u)	440 v.s. (A_{2u}) 415 sh (E_u)	[35]
XII	*trans*-[$SiF_4{\cdot}2H_2O$]	D_{4h}	765 s (E_u) 715 sh (E_u)	445 s (A_{2u}) 420 sh (E_u)	[35]
XIII	*trans*-[$SiF_4{\cdot}2H_2O$]	D_{4h}	772 m (E_u) 728 sh (E_u)	468 m (A_{2u})	[36]
XIV	$[SiF_5]^-$	D_{3h}	875 s br ($\acute{E}$) 785 sh (A_2'') 745 sh (A_2'')	478 s ($A''{}_2$) 445 s (A_2'')	[42]
XIX	$[SiF_6]^{2-}$	C_{2V}	765 s (A_{2u}) 720 s (E_u) 680 s (E_u)	482 v.s. (A_{2u}) 473 s (E_u) 452 sh (E_u)	[51]

Note: m = medium; s = strong; v.s. = very strong; sh = shoulder; br = broad.

Table 3
H-bond and thermal characteristics of silicon fluorocomplexes with crown ethers.

Complex	Number of H-bonds[a]	Distance D···A, Å	mp, °C	t_{decomp}, °C	Reference
[(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot L^1 \cdot 2H_2O$]	4	2.599–2.870	40–90	110–120	[35]
[(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot L^2 \cdot H_2O$]	–	–	50–80	90–120	[35]
[(*trans*-$SiF_4{\cdot}2H_2O$)$\cdot 2L^{10}$]	–	–	35–40	128	[36]
[$(H_3O{\cdot}L^4)SiF_5$]	3	2.615–2.882	70–100	145	[42]
$(NH_4{\cdot}L^1)_2[SiF_6]{\cdot}4H_2O$	8	2.797–3.057	>70	–	[45]

[a] The separations with D(donor)–H···A(acceptor) < 2.6 Å and angle DHA > 120° were taken in consideration.

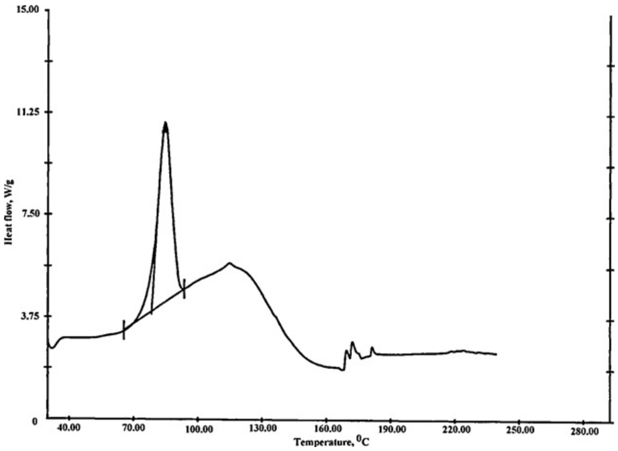


Fig. 6. DSC curve for **XII**.

of one mole of SiF_4 and four moles of H_2O (Δm_{found} = 42.5%) agrees well with the calculated value ($\Delta m_{calc.}$ = 39.9%).

Although the structural data for the complexes based on 15C5 (L^2) and 12C4 (L^{10}) are absent, the tendency of their melting points increase in order $[(trans\text{-}SiF_4{\cdot}2H_2O){\cdot}2L^{10}] < [(trans\text{-}SiF_4{\cdot}2H_2O){\cdot}L^2{\cdot}H_2O] < [(trans\text{-}SiF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ indicates in favor of the increased efficacy of hydrogen bonding in this row as the number of the potential H-bond acceptors increases from 12C4 to 18C6 [38]. The pentafluorosilicate anion $[SiF_5]^-$, which can be considered as a product of dehydration of $[SiF_5(H_2O)]^-$, is less symmetrical compared to $[SiF_6]^{2-}$ (D_{3h}, and O_h symmetries, respectively), and it is usually stabilized in the form of salts with large tetraalkylammonium [39] or metal cations [40,41], whereas the oxonium salt $(H_3O)SiF_5$ remains unknown in the individual state so far. We managed to isolate and study by single crystal X-ray diffraction complex with the composition $[(H_3O{\cdot}L^4)SiF_5]$ (**XIV**) which represents the product of interaction of H_2SiF_6–HF with L^4 in methanol solution [42]. In **XIV** (Fig. 7), which is structurally similar to the tetrafluoroborate analog $[(H_3O{\cdot}L^4)BF_4]$, the cation–anion interactions are of predominantly electrostatic origin. The IR spectroscopic characteristics of $[SiF_5]^-$ in complex **XIV** (Table 2) are typical for pentafluorosilicates with the trigonal-bipyramidal geometry of the anion (symmetry D_{3h}) [43].

In line with the concepts sounded in [4], the rate-limiting step for hydrolysis of hexafluorosilicate anion according to scheme (7) is the loss of the first fluoride anion with the formation of $[SiF_5]^-$ following the dissociative S_N1-mechanism. In this concern, the formation of complex **XIV** in the reaction system H_2SiF_6–HF–L^4 may, in some extent, be considered as an example of the crown ether's stabilizing effect on the $(H_3O)SiF_5$ ionic pair being unstable intermediate in the hydrolytic conversion of the hexafluorosilicate anion. According to the ^{19}F and ^{29}Si NMR data [24], complex **XIV** is not subjected to solvolysis with the conservation of the $[SiF_5]^-$ anion in acetone solution, whereas in aqueous environment, according to [41], the hydrolysis occurs in accordance with scheme (12):

$$[(H_3O \cdot L^4)SiF_5] + H_2O \rightarrow L^4 + SiO_2 + 5HF. \qquad (12)$$

It has been proven [44] that interaction of ionic complex **XIV** with 18C6 (L^1) in the presence of air moisture results in the above discussed molecular compound $[(trans\text{-}SiF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ (**XI**) with the yield of 73% in accordance with scheme (13):

$$[(H_3O \cdot L^4)SiF_5] + L^1 + 3H_2O \rightarrow [(trans{-}SiF_4{\cdot}2H_2O) \cdot L^1{\cdot}2H_2O] + L^4 + HF. \qquad (13)$$

The given conversion accompanied by the transformation of the 'guest' fragments, illustrates the decisive influence of the macrocyclic ligand on composition and structure of the labile fluorocomplexes and their 'host–guest' complexes with crown ethers. To the best of our knowledge the oxonium–CE–hexafluorosilicate complex is unknown so far. At the same time the crystalline complex $(NH_4{\cdot}L^1)_2[SiF_6]{\cdot}4H_2O$ (**XV**) was obtained from the system $SiF_4{\cdot}2NH_3$–L^1–H_2O and its crystal structure was reported in [45]. In **XV** three hydrogen atoms of ammonium cation are involved in NH···O H-bonds with O-atoms of macrocycle (N···O distances 2.923(5)–2.940(5) Å); while the fourth hydrogen atom is involved in the NH···F H-bond with $[SiF_6]^{2-}$ anion (N···F 2.797(6) Å) (Fig. 8).

It is interesting that complex **XV** was obtained under conditions very similar to those used for the synthesis of $[(BF_3{\cdot}NH_3){\cdot}L^1]$ [46]. The difference in the final products obtained from the systems $SiF_4{\cdot}2NH_3$–L^1–H_2O and $BF_3{\cdot}NH_3$–L^1–H_2O reflects the hydrolytic stability of complex $BF_3{\cdot}NH_3$ (it can be recrystallized from warm water solution) contrary to silicon analog subjected to hydrolysis in accordance with scheme (14) [47]:

$$3(SiF_4{\cdot}2NH_3) + 2H_2O \rightarrow 2(NH_4)_2SiF_6 + SiO_2 + 2NH_3. \qquad (14)$$

Thus, instead of the expected molecular complex between the $SiF_4{\cdot}2NH_3$ adduct and L^1 the ionic compound **XV** was obtained. It is evident that the presence of CE in the reaction system $SiF_4{\cdot}2NH_3$–L^1–H_2O stimulates equilibrium (14) due to efficient binding of tripod ammonium cation. Attempts to obtain complex **XIV** by

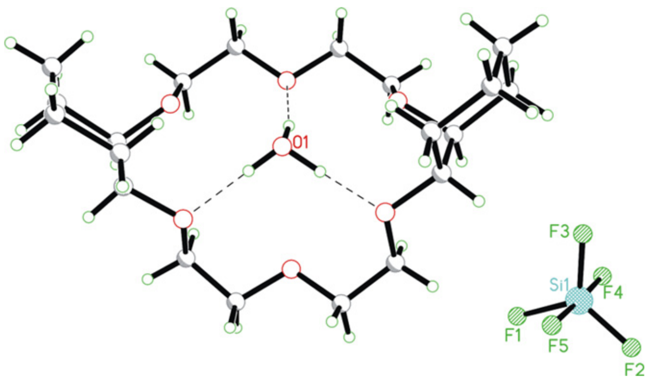


Fig. 7. Structure of **XIV**.

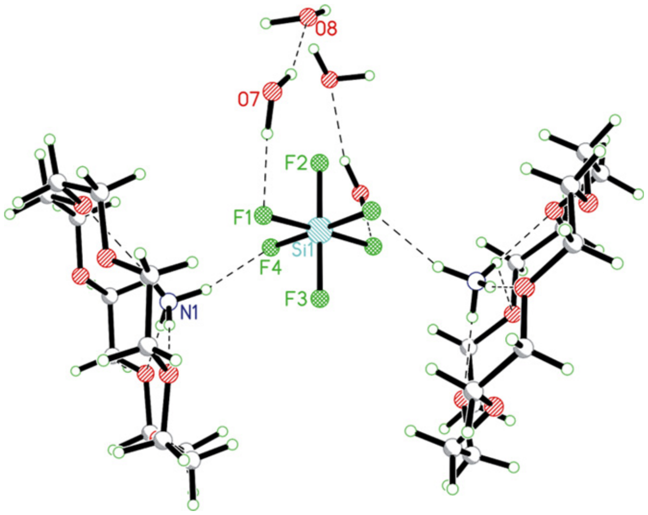


Fig. 8. Structure of **XV**.

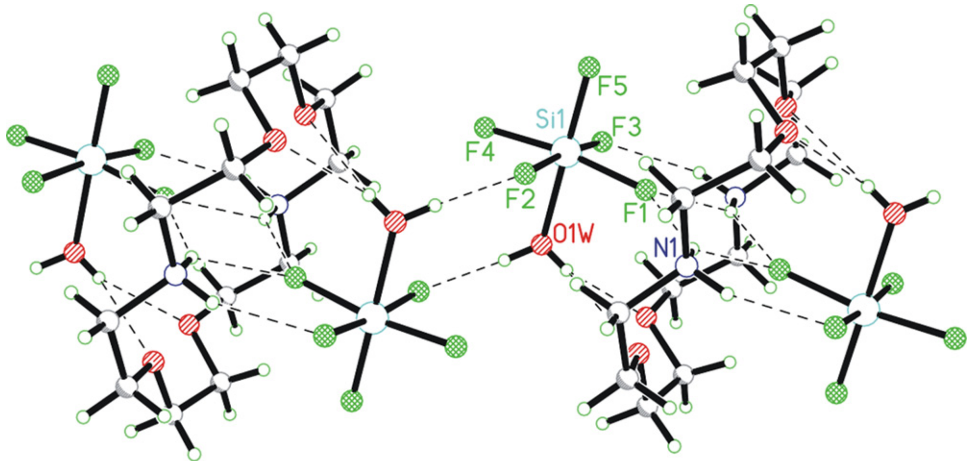


Fig. 9. Polymeric chain in **XVIII**. Two $[SiF_5(H_2O)]^-$ anions are associated in centrosymmetric dimers *via* a pair of OH···F hydrogen bonds.

direct synthesis in the system $(NH_4)_2SiF_6$–L^1–H_2O were unsuccessful [45]. Unexpectedly, interaction of fluorosilicic acid with monoaza-12C4 (L^{11}), monoaza-18C6 (L^{12}), and 1,10-diaza-18C6 (L^{13}) afforded the crystalline complexes with the compositions $(L^{11}H)_2[SiF_5(H_2O)]_2 \cdot 3H_2O$ (**XVI**), $(L^{12}H \cdot H_2O)[SiF_5(H_2O) \cdot H_2O]$ (**XVII**) and $(L^{13}H_2)[SiF_5(H_2O)]_2$ (**XVIII**), whose structures were studied by single crystal X-ray diffraction and vibration spectroscopy [48,49]. The octahedral anion $[SiF_5(H_2O)]^-$ discovered in structures **XVI**–**XVIII** is stabilized by the systems of NH···F, NH···O, OH···F, and OH···O H-bonds (Figs. 9 and 10).

These findings [48,49] show structural evidence in favor of the aquapentafluorosilicate anion existence in solutions of fluorosilicic acid. Currently the only three above mentioned azacrown ethers in their cationic forms are documented to stabilize the $[SiF_5(H_2O)]^-$ anion in the form of crystalline complexes of the 'host–guest' type. The ^{19}F NMR data [48] indicate that dissolution of **XV** in acetonitrile is accompanied by disproportionation of the $[SiF_5(H_2O)]^-$ anion followed by hydrolytic destruction of diaquatetrafluorocomplex, schemes (15) and (16):

$$2[SiF_5(H_2O)]^- \rightarrow [SiF_6]^{2-} + cis-,trans-[SiF_4(H_2O)_2], \qquad (15)$$

$$cis\text{-},trans\text{-}[SiF_4(H_2O)_2] + H_2O \rightarrow SiO_2 \cdot H_2O + 4HF. \qquad (16)$$

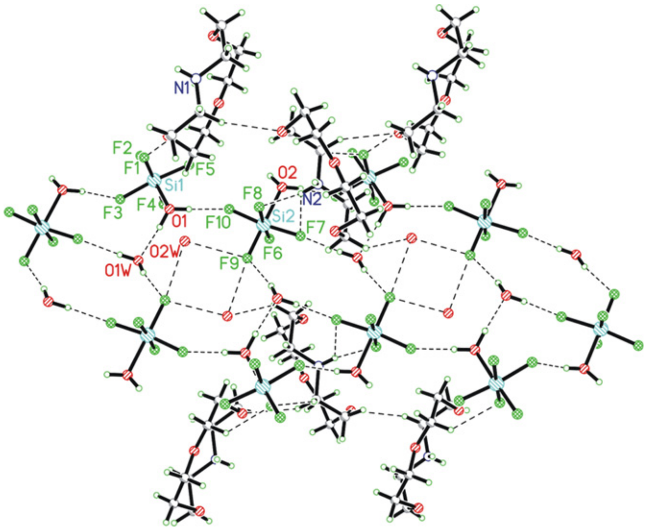


Fig. 10. Fragment of crystal packing in **XVI**. The $[SiF_5(H_2O)]^-$ anions are associated in the layer through OH···F and OH···O hydrogen bonds.

The easiness of transformations (15) and (16) is explained as follows. The labile anion $[SiF_5(H_2O)]^-$, formed by the weak Lewis acid $[SiF_5]^-$ and the weak Lewis base (H_2O), when dissolved in the absence of the stabilizing effect of interionic H-bonds is transformed into two species, the more stable $[SiF_6]^{2-}$ anion and the neutral complex $[SiF_4(H_2O)_2]$. The latter, being a strong Bronsted acid [50], is relatively stable only in strong acidic solutions and is hydrolyzed easily when the acidity of the reaction medium is decreasing.

On the contrary to L^{11}–L^{13}, 1,7-diaza-15C5 (L^{14}) forms the hexafluorosilicate complex with the composition $[(L^{14}H_2)SiF_6]$ (**XIX**) [51], where participation of three from six fluoroligands in strong NH···F H-bonds (N···F 2.722(3)–2.823(2) Å) affords the anion's symmetry decrease to C_{2v} (Fig. 11). The corresponding decrease of symmetry reflects a more complicated IR spectrum (Table 2) compared with the expected one for the isolated anion (point group O_h, the two vibrations are active in the IR spectrum [43]). It should be emphasized that interaction of fluorosilicic acid with aminopodands L, being acyclic analogs of azacrown ethers and containing the structural fragments –NH–$(CH_2)_2$–O–$(CH_2)_2$–NH– and –NH–$(CH_2)_2$–O–$(CH_2)_2$–O–$(CH_2)_2$–NH– results in the corresponding hexafluorosilicates with the general formula $(LH_2)SiF_6$ [52].

In its turn, interaction of fluorosilicic acid with tetraazacycles, the twelve-membered 1,4,7,10-tetraazacyclododecane (L^{15}), 1,4,7,10-tetraaza-2,6-pyridinophane[12] (L^{16}), and the fourteen-membered *meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^7) afforded the hydrated hexafluorosilicates

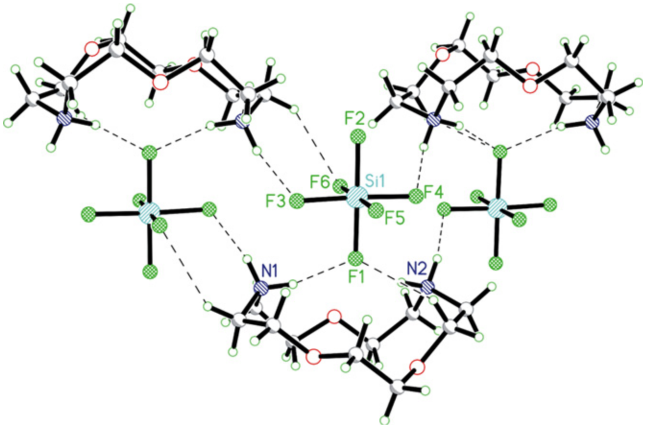


Fig. 11. Fragment of polymeric tape in **XIX** stabilized by NH···F interactions.

$(L^{15}H_4)_2(SiF_6)_4{\cdot}7H_2O$ (**XX**) [53], $(L^{16}H_3)_2(SiF_6)_3{\cdot}4H_2O$ (**XXI**) [54], and $(L^7H_4)(SiF_6)_2{\cdot}4H_2O$ (**XXII**) [55]. The intriguing feature of **XX** is the formation of linear five-membered water cluster fixed by strong H-bonds ($O\cdots O$ 2.806(7)–2.834(6) Å). In general, the interionic interactions of the $NH\cdots F$ type dominate in structures **XX**–**XXII**, and for the hexafluorosilicate anion the symmetry deviation from the ideal octahedral one is dictated by its closest environment and an involvement of all or part of the fluoroligands in H-bonds of different strength. Interaction of fluorosilicic acid with 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (L^{17}) also resulted in the complex hydrate $(L^{17}H_3)(F)(SiF_6){\cdot}4H_2O$ (**XXIII**), however, of a mixed-anionic composition [56]. In the crystal structure **XXIII** the macrocyclic trication $[L^{17}H_3]^{3+}$ encapsulates the fluoride inside the cavity and holds it through three strong $NH\cdots F$ hydrogen bonds ($N\cdots F$ 2.507(2)–2.647(2) Å) (Fig. 12). Being involved in these interactions the macrocyclic cation undergoes a substantial change of its conformation compared with the free ligand. One might be noted, that very few examples of $[F]^-$, $[SiF_6]^{2-}$ mixed anionic complexes of macrocyclic ligands are known so far and they incorporate either the 18-membered azacryptandes containing aromatic moieties [57–59], or oxa, azacryptandes [60]. Compound **XXIII** is the first example of the crystalline metal-free complex of L^{17}.

2.3. Germanium(IV) and tin(IV) fluorocomplexes

According to the ^{19}F NMR data [61,62], solutions $GeO_2–HF–H_2O$ and $SnF_4–HF–H_2O$ represent equilibrium mixtures of fluorocomplexes $[MF_6]^{2-}$, $[MF_5(H_2O)]^-$, and *cis*-,*trans*-$[MF_4(H_2O)_2]$ (M = Ge, Sn). For the system $GeO_2–HF–H_2O$ the possibility of trifluorocomplex $[GeF_3(H_2O)_2(OH)]$ was also discussed. In particular, for solution $GeO_2–HF–H_2O$ with the ratio $HF/GeO_2 = 4.2$ the equilibrium between the forms is expressed by equation (17):

$$24GeO_2 + 101HF \rightarrow [GeF_3(H_2O)_2(OH)] + 9[GeF_4(H_2O)_2] + 7H[GeF_5(H_2O)] + H_2GeF_6 + 5H_2O \qquad (17)$$

where the ratio of isomers *cis*-$[GeF_4(H_2O)_2]$/*trans*-$[GeF_4(H_2O)_2]$ = 3 [61], being close to the statistical value of 4.

The stabilization and spectroscopic evidence for the $[GeF_5(H_2O)]^-$ anion in the form of solid salts with bulky tetraalkylammonium cations, $(R_4N)[GeF_5(H_2O)]$ ($R = C_3H_7$, C_4H_9) was documented [63]. Similar to the silicon(IV) fluorocomplexes, for a long time the spectral data remained the only source of information about the stereochemistry of mixed-ligand germanium(IV) and tin(IV) aquafluorocomplexes. In line with the results documented in [35,49], interaction of $GeO_2–HF–H_2O$ solution with 18C6 (L^1) and 1,10-diaza-18C6 (L^{13}) resulted in complexes with the compositions $[(trans\text{-}GeF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ (**XXIV**) and $(L^{13}H_2)[GeF_5(H_2O)]_2$ (**XXV**) [64]. In its turn, complex $[(trans\text{-}SnF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ (**XXVI**) was obtained as a product of interaction of $SnF_4–HF–H_2O$ solution with L^1 [65]. According to the X-ray data, compounds $[(trans\text{-}MF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ (M = Si, Ge, Sn) and $(L^{13}H_2)[MF_5(H_2O)]_2$ (M = Si, Ge) form two series of isostructural complexes, and until now compound $[(trans\text{-}SnF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ represents the unique 'host–guest' supramolecular aggregate between tin(IV) aquafluorocomplex and crown ether. In the series of structures $[(trans\text{-}MF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$ (M = Si, Ge, Sn) a slight increase in the unit cell dimensions proportional to an increase of the effective radius of the central atom was observed. As it was noted in [64], the structural feature of complex **XXV** is the non-equivalence of the Ge–F bond lengths in the fragment $[GeF_5(H_2O)]^-$: the Ge–F bond in *trans*-position to the $Ge–O(H_2O)$ bond is shorter than the four equatorial Ge–F bonds being 1.738(2) and 1.761(2) against 1.799(2) Å, respectively. This bond length difference, namely, *trans*-strengthening and *cis*-weakening of the Ge–F bonds relative to the $Ge–O(H_2O)$ bond with a more covalent ligand, may reflect the effects of static inter-ligand influence typical for the complexes with the non-transition elements of the first halves of the periods [66,67].

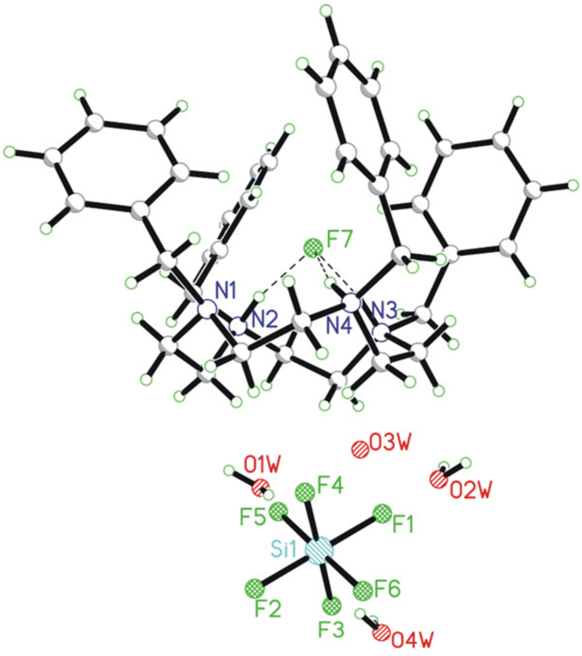


Fig. 12. Structure of **XXIII**.

The product of interaction of the $GeO_2–HF–H_2O$ solution with the fourteen-membered tetraazamacrocycle L^7, represents a hydrated hexafluorogermanate complex with the composition $(L^7H_4)(GeF_6)_2{\cdot}4H_2O$ (**XXVII**) which crystallizes in two different space groups, triclinic (sp. gr. $P{-}1$) [55] and monoclinic (sp. gr. $P2_1/c$) [68] ones, thus representing example of true polymorphs. The geometric characteristics of the $[GeF_6]^{2-}$ anions in two structures are very close. In particular, the Ge–F bond lengths are in the range 1.732(5)–1.802(4) and 1.746(1)–1.825(1) Å for the triclinic and monoclinic forms, respectively. These two compounds possess the same immediate environment of the macrocyclic cation $[L^7H_4]^{4+}$ (that obeys C_i-symmetry) and only differ by the organization of H-bonds. The reason for crystallization of two polymorphs of **XXVII** may originate from the different synthetic conditions: the reaction mixtures were kept at a room temperature in [55], while at 100 °C in [68], followed by the cooling and spontaneous evaporation at room temperature. One might also be noted that the triclinic forms of **XXVII** and its silicon analog $(L^7H_4)_2(SiF_6)_4{\cdot}4H_2O$ (**XXII**) [55] are isostructural. An attempt to synthesize the germanium analog of complex $(L^{16}H_3)_2(SiF_6)_3{\cdot}4H_2O$ (L^{16} = 1,4,7,10-tetraaza-2,6-pyridinofan [12]) by interaction in the system $GeO_2–HF–H_2O–L^{16}$ was unsuccessful. The interaction of L^{16} with solution $GeO_2–HF–H_2O–HNO_3$ resulted in complex $[(L^{16}H_3)_2(GeF_6)(NO_3)_4]$ (**XXVIII**), being the double salt whose structure is stabilized by the system of $NH\cdots F$, $NH\cdots O$, and $NH\cdots N$ H-bonds [54].

3. Conclusions

In conclusion, it should be emphasized that competition in aqueous medium between water, fluoride and macrocyclic ligand for the place in the coordination environment of the 13 or 14 *p*-group element always gives advantage to the formers (H_2O, F^-) because of their stronger electron-donating properties and the steric preferences. The macrocycles act as outer ligands being linked with the first coordination sphere of the inorganic complexes through intermolecular (interionic) hydrogen bonds [69]. The systems of intermolecular H-bonds are the main driving forces and structure-directing factors in the chemistry of these compounds, and an obvious relationship between the structure of the macrocyclic ligands and the nature of the stabilized labile fluorocomplexes is documented. The rather evident conclusion sounds that the protonated in the acidic media azacrown ethers and azamacrocycles stabilize the anionic forms of fluorocomplexes, and in the systems involving boron(III) fluorocomplexes the only stabilized form is the tetrafluoroborate anion (no examples of stabilization by macrocycles such anions as $[BF_{4-n}(OH)_n]^-$ being the hydrolyzed products of $[BF_4]^-$ [4] have been reported so far). The silicon(IV) and germanium(IV) fluorocomplexes demonstrate the differentiating effect of the macrocyclic ligand: the protonated azacrown ethers, depending on the structure, bind either pentafluoroanions, $[SiF_5(H_2O)]^-$ (monoaza-12C4 [48], monoaza-18C6, 1,10-diaza-18C6 [49]) and $[GeF_5(H_2O)]^-$ (1,10-diaza-18C6 [64]) or hexafluoroanions, while the protonated forms of tetraazamacrocycles bind exclusively $[SiF_6]^{2-}$ and $[GeF_6]^{2-}$ anions. It might not be excluded that the specific capability of protonated forms of azacrown ethers to stabilize the anion $[SiF_5(H_2O)]^-$ in the complexes **XVI–XVIII** is provided by the H-acceptor properties of O-donor ligands being absent in azacycles.

The most pronounced selectivity in the systems inorganic fluorocomplexes—macrocyclic ligand demonstrate classic crown ethers. In [70] attention was focused on the spatial conveniences of the 18-membered crown ethers as crucial factor that determines the final product of their interaction with the equilibrium mixture of molecular and ionic forms of fluorocomplexes. The centrosymmetric crown ethers with the equally sterically shielded sides selectively elicit from solutions the neutral adducts such as $BF_3{\cdot}H_2O$ with the aid of 18C6 [16] and *cis-anti-cis*-dicyclohexano-18C6 [17], *trans*-$MF_4{\cdot}2H_2O$ (M = Si, Ge, Sn) with the aid of 18C6 again [35,64,65], while the *cis-syn-cis*-dicyclohexano-18C6 (L^4) with the sterically non-equivalent sides, binds the single-charged anionic complexes $[BF_4]^-$ and $[SiF_5]^-$ in the form of oxonium salts, $[(H_3O{\cdot}L^4)BF_4]$ [18] and $[(H_3O{\cdot}L^4)SiF_5]$ [42]. The specific feature of *cis-syn-cis*-dicyclohexano-18C6 to form the oxonium salts of single charged anions $[BF_4]^-$, $[SiF_5]^-$ and $[ClO_4]^-$ is explained by the capability of the bulky macrocyclic cation $[H_3O{\cdot}L^4]^+$ to generate stable structural motifs in the form of zigzag channels, which assemble the single-charged anions as the guests. The crystal structure of complex $[(H_3O{\cdot}L^4)ClO_4]$ was reported in [71].

One more interesting aspect of the above given results is the stereoselective interaction of 18C6 (L^1) with an equilibrium mixture of geometric isomers $MF_4{\cdot}2H_2O$ (M = Ge, Sn), resulting in the selective binding of *trans*-isomers in the form of compounds $[(trans\text{-}MF_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$. One should be emphasized that although tin(IV) aquachloride complex $SnCl_4{\cdot}2H_2O$ forms with L^1 the product of the same composition $[(cis\text{-}SnCl_4{\cdot}2H_2O){\cdot}L^1{\cdot}2H_2O]$, it differs by the stereochemistry of inorganic complex being $[(cis\text{-}SnCl_4{\cdot}2H_2O)]$ [72], whereas 15C5 (L^2) forms the complex with *trans*-isomer with the composition $[(trans\text{-}SnCl_4{\cdot}2H_2O){\cdot}L^2]$ [73].

The collected data demonstrate selective complexation of fluoride compounds of 13–14 group elements with macrocyclic ligands, and reveal that the bulky macrocycles with the multiple sets of H-donor and H-acceptor binding sites, give origin to strong and branched intermolecular H-bonds as a main stabilizing factor which made possible the identification of unique supramolecular compounds of fluorocomplexes of *p*-elements in the solid state.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.12.014.

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