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Stabilization of Germanium(IV) Aquafluorocompounds in Host–Guest Type Complexes with Crown Ethers. Synthesis, Crystal Structure and IR Spectra of the Complexes $[(GeF_5{\cdot}H_2O)_2{\cdot}(H_2\text{-}1,10\text{-Diaza-}18\text{-Crown-}6)]$ and $[(trans\text{-}GeF_4{\cdot}2H_2O){\cdot}18\text{-Crown-}6{\cdot}2H_2O]$

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Abstract. Stable products have been obtained from the interaction of GeO_2–HF solution with 18-membered crown ethers, 1,10-diaza-18-crown-6 and 18-crown 6. Complexes were characterized by X-ray analysis and IR spectroscopy. Both Ge(IV) aquafluorocompounds are isostructural with their Si analogues. It was established that in the host–guest type complexes the germanium moiety as a central atom has been stabilized in the form of octahedral complexes. The host–guest interaction occurs by means of $O—H(W)\cdots O_{cr}$, $OH\cdots F$ and $N—H\cdots F$ hydrogen bonds.

Key words. 18-Membered crown ethers, host–guest complex structure, H-bonds, stabilization of germanium aquafluorocomplexes.

Supplementary Data relevant to this paper have been deposited with the British Library as Supplementary Publication No. 82203 (15 pages) and include: the list of F_{obs}, F_{cal}, tables of U_{ij} and fractional atomic coordinates for hydrogen atoms.

1. Introduction

Specific complexing properties of crown ethers and their analogues have found wide application in various areas of chemistry and in technological processes and

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continue to be widely studied [1–3]. The ability of crown ethers to stabilize unstable compounds in host–guest complexes is important from a synthetic viewpoint. Interesting objects for stabilization in the capacity of 'guest' components in such systems are fluorocompounds which are susceptible to hydrolysis in solution or in moist air. In particular, it has been reported [4] that the 18-crown-6 molecule can increase the stability to hydrolysis of pentacoordinated organofluorosilicon anions in the form of salts with the composition $(K{\cdot}18\text{-crown-6})[R_nSiF_{5-n}]$ (n = 1–3). This property has been used in the synthesis of organofluorosilicates [5–9] and an interesting example has been given of the stabilization of a low stability compound $[BF_3{\cdot}H_2O]$ in the form of the molecular complex $[(BF_3{\cdot}H_2O){\cdot}18\text{-crown-6}]$ which occurs due to H-bonds with crown ether O-atoms [10].

We have managed to isolate and structurally characterize the complex with the distinctive composition $[(BF_3{\cdot}H_2O)_2{\cdot}18\text{-crown-6}{\cdot}2H_2O]$ [11], together with some other complexes including Lewis acids such as $[(\textit{trans}\text{-}SiF_4{\cdot}2H_2O){\cdot}18\text{-crown-6}{\cdot}2H_2O]$ [12, 13], $[(SiF_5{\cdot}H_2O){\cdot}H_2O{\cdot}(H\text{-monoaza-18-crown-6}{\cdot}H_2O)]$ and $[(SiF_5{\cdot}H_2O)_2{\cdot}(H_2\text{-1,10-diaza-18-crown-6})]$ [14]. The last three compounds are the products of the interaction of the appropriate crown ethers with a solution of silicon hydrofluoric acid, which, according to ^{19}F-NMR spectral data [15], consists of an equilibrum mixture of SiF_6^{2-}, $[SiF_5{\cdot}H_2O]^-$ and $[\textit{trans}\text{-}SiF_4{\cdot}2H_2O]$ fluorocomplexes. The structures of complexes stabilized in the form of host–guest type silicon aquafluorocompounds $[\textit{trans}\text{-}SiF_4{\cdot}2H_2O]$ and $[SiF_5{\cdot}H_2O]^-$ have been established previously [12, 14] by X-ray analysis for the first time.

The present work continues [11–14] the search for stabilization of aquafluorocomplexes containing p-elements in the form of host–guest complexes on the basis of the crown ethers and is devoted to the synthesis, crystal structure and IR spectra of two new complexes: $[(GeF_5{\cdot}H_2O)_2{\cdot}(H_2\text{-1,10-diaza-18-crown-6})]$ (**I**) and $[(\textit{trans}\text{-}GeF_4{\cdot}2H_2O){\cdot}18\text{-crown-6}{\cdot}2H_2O]$ (**II**).

2. Experimental

2.1. SYNTHESIS OF COMPLEXES I AND II

2.1.a. *Synthesis of* $[(GeF_5{\cdot}H_2O)_2{\cdot}(H_2\text{-1,10-diaza-18-crown-6})]$ (**I**)

A solution of GeO_2–HF (3 mL) was added to a solution of 1,10-diaza-18-crown-6 (1 g, 0.0038 mol) in 10 mL of methanol and the mixture was evaporated on a water bath. Crystals of the complex, suitable for X-ray investigation, were obtained by recrystallization from water. Colourless transparent crystals of (**I**) soluble in water, insoluble in methanol, benzene, hexane; m.p. >230 °C. *Anal. found* (%) C 22.56, H 5.15, N 4.54, F 30.01. *Calcd.* for $C_{12}H_{32}N_2O_2F_{10}Ge_2$, C 22.68, H 5.08, N 4.41, F 29.89.

2.1.b. *Synthesis of [(trans-$GeF_4{\cdot}2H_2O$)·18-crown-6·$2H_2O$]* (**II**)

Hydrofluoric acid (100 mL, 40% solution) was added to germanium dioxide (3g, 0.0287 mol) placed in a Teflon vessel and the mixture was heated on a water bath until the GeO_2 dissolved, followed by evaporation to a volume of 10 mL. The solution of GeO_2–HF (1.5 mL) was added to an 18-crown-6 solution (1g, 0.0038 mol) in 5 mL methanol and left to evaporate at room temperature. Crystals of the complex, suitable for X-ray analysis, were obtained by recrystallization from a methanol : benzene = 1 : 1 mixture by spontaneous evaporation of the solvents. Colourless transparent crystals (**II**) soluble in methanol, ethanol, acetone, water, insoluble in benzene, hexane; m.p. 198–199 °C (with decomposition). *Anal. found* (%) C 33.98, H 7.73, F 18.37; *Calcd.* for $C_{12}H_{32}F_4O_{10}Ge$, C 34.24, H 7.66, F 18.05.

IR absorption spectra were recorded on a Specord 75 IR spectrophotometer (range 4000–400 cm^{-1}, samples as suspensions in Nujol mulls, between KRS-5 plates).

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

The main crystallographic data are given in Table I. The data were collected on a KM-4 (KUMA) diffractometer using MoK_α-radiation by the $\theta/2\theta$ scan technique. Absorption correction was not applied to the intensity data in the data reduction process. The structures were solved by the heavy atom method using the package of programs SHELXS-86 and SHELXL-93 [16, 17] and were refined by the least squares method using an anisotropic approach for non-hydrogen atoms and an isotropic one for H. During refinement the experimental weighting scheme was used. The final values of R-factors, R_1 and wR_2 are given in Table I. Tables IIa and IIb contain the final atomic coordinates for (**I**) and (**II**), respectively. In the process of structure determination and refinement it was established that both complexes are isostructural with appropriate products of the interaction of H_2SiF_6 solution with 1,10-diaza-18-crown-6 and 18-crown-6 having the compositions [($SiF_5{\cdot}H_2O)_2{\cdot}H_2$-1,10-diaza-18-crown-6] (**I***) and [(*trans*-$SiF_4{\cdot}2H_2O$)·18-crown-6·$2H_2O$] (**II***). The complexes (**II**) and (**II***) belong to the same crystallographic space group. However, due to a different choice of the triclinic unit cells in (**I**) and (**I***) the crystal axes of (**I**) have to be transformed ($\mathbf{a}' = \mathbf{b} + \mathbf{c}$; $\mathbf{b}' = \mathbf{b}$; $\mathbf{c}' = -\mathbf{a}$) to obtain an isostructural unit cell with (**I***). Tables IIIa and IIIb contain the main geometrical parameters of complexes (**I**) and (**II**) respectively, and Table IV the torsion angles in their macrocyclic frameworks.

Table I. Crystal data and summary of intensity data collection and structure refinement for complexes **I** and **II**.

Compound	I	II
Formula	$C_{12}H_{32}F_{10}Ge_2N_2O_6$	$C_{12}H_{32}F_4GeO_{10}$
Formula weight	317.79	242.48
Temperature, K	293(2)	293(2)
Wavelength, Å	0.71069	0.71069
Crytal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a, Å	8.242(7)	9.687(2)
b, Å	8.928(1)	7.771(1)
c, Å	9.171(2)	13.344(3)
α, deg.	115.91(2)	90
β, deg.	105.81(5)	96.33(3)
γ, deg.	91.04(4)	90
V, Å^3	576.7(5)	998.4(3)
Z	1	4
D (calc), g/cm^3	1.830	1.613
μ, mm^{-1}	2.717	1.616
$F(000)$	320	504
Crystal size, mm	0.22 × 0.48 × 0.75	0.25 × 0.35 × 0.60
θ range, deg.	2.57–35.07	2.47–35.07
h range	−13 to 2	0 to 15
k range	−13 to 13	0 to 12
l range	−13 to 13	−21 to 21
Reflections collected	3453	3201
Independent reflections	3315	3064
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.136	1.073
$R(hkl)$ $[I > 2\sigma(I)]$, R_1	0.0502	0.0594
wR_2	0.1176	0.1392
Largest diff. peak, e/Å^3	1.628	3.317
Largest diff. hole, e/Å^3	−1.411	−1.592

3. Discussion

3.1. OVERALL SYSTEM OF HOST–GUEST INTERACTIONS IN (I) AND (II)

Both (**I**) and (**II**) are referred to as typical complexes of the second coordination sphere [18], where direct metal interaction with the macrocycle electron donor atoms is absent. In (**I**) the opportunities for interaction are essentially expanded due to the use of NH–host donor groups. Figure 1 shows the ORTEP diagram of complex (**I**), which is built up from monoanions $[GeF_5{\cdot}H_2O]^-$ and doubly-charged

Table IIa. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times$ 10^3) for complex **I**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ge	1940(1)	1251(1)	3035(1)	29(1)
F(1)	730(2)	781(2)	4154(2)	34(1)
F(2)	56(2)	1720(2)	1872(2)	41(1)
F(3)	3720(2)	532(3)	4021(3)	51(1)
F(4)	2991(3)	1432(3)	1672(3)	53(1)
F(5)	2637(3)	3339(3)	4580(3)	59(1)
O(1W)	1196(5)	−1126(3)	1316(3)	48(1)
N(1)	−2875(3)	776(3)	3846(3)	34(1)
C(2)	−2842(5)	2649(4)	4508(5)	42(1)
C(3)	−2566(5)	3528(5)	6401(5)	48(1)
O(4)	−986(3)	3379(3)	7402(3)	45(1)
C(5)	459(6)	4285(4)	7403(5)	53(1)
C(6)	2021(6)	4138(5)	8610(5)	58(1)
O(7)	2061(3)	2417(3)	8122(3)	49(1)
C(8)	3689(4)	1994(5)	8664(4)	48(1)
C(9)	3497(4)	154(5)	8048(4)	40(1)

Table IIb. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for complex **II**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ge	−5000	0	0	22(1)
F(1)	−5570(2)	247(3)	1202(1)	37(1)
F(2)	−5001(2)	2253(2)	−157(1)	37(1)
O(1W)	−3100(2)	122(3)	601(2)	30(1)
O(2W)	1240(3)	−1647(4)	322(2)	40(1)
O(1)	164(3)	−180(3)	2039(2)	38(1)
C(2)	−753(3)	−1232(5)	2527(2)	38(1)
C(3)	−910(3)	−2937(5)	2010(2)	38(1)
O(4)	−1637(2)	−2705(3)	1029(2)	36(1)
C(5)	−1791(4)	−4257(4)	451(3)	38(1)
C(6)	−2170(2)	−3832(4)	−626(3)	38(1)
O(7)	−1086(2)	−2880(3)	−1005(2)	35(1)
C(8)	−1416(4)	−2467(5)	−2042(2)	41(1)
C(9)	255(4)	1531(5)	2434(3)	42(1)

Table IIIa. Bond lengths (Å) and angles (°) for complex **I**.

Ge—F(1)	1.772(2)	C(2)—C(3)	1.506(5)
Ge—F(2)	1.799(2)	C(3)—O(4)	1.421(5)
Ge—F(3)	1.789(2)	O(4)—C(5)	1.427(5)
Ge—F(5)	1.738(2)	C(5)—C(6)	1.503(6)
Ge—F(4)	1.761(2)	C(6)—O(7)	1.404(4)
Ge—O(1W)	1.966(3)	O(7)—C(8)	1.418(5)
N(1)—C(2)	1.505(4)	C(8)—C(9)	1.474(5)
N(1)—C(9)^1	1.486(4)		
F(1)—Ge—F(2)	89.4(1)	F(4)—Ge—F(5)	94.2(1)
F(1)—Ge—F(3)	89.6(1)	F(4)—Ge—O(1W)	85.9(1)
F(1)—Ge—F(4)	171.7(9)	F(5)—Ge—O(1W)	178.7(1)
F(1)—Ge—F(5)	94.0(1)	C(2)—N(1)—C(9)^1	112.5(2)
F(1)—Ge—O(1W)	86.0(1)	N(1)—C(2)—C(3)	111.7(3)
F(2)—Ge—F(3)	173.3(1)	O(4)—C(3)—C(2)	114.3(3)
F(2)—Ge—F(4)	88.6(1)	C(3)—O(4)—C(5)	113.4(3)
F(2)—Ge—F(5)	93.6(1)	O(4)—C(5)—C(6)	108.0(3)
F(2)—Ge—O(1W)	87.7(1)	O(7)—C(6)—C(5)	107.9(3)
F(3)—Ge—F(4)	91.6(1)	C(6)—O(7)—C(8)	115.6(3)
F(3)—Ge—F(5)	93.0(1)	O(7)—C(8)—C(9)	108.3(3)
F(3)—Ge—O(1W)	85.7(1)	C(8)—C(9)—N(1)^1	111.5(3)

Symmetry transformations used to generate equivalent atoms:
^{1} $-x, -y, 1 - z$.

organic cations (H$_2$-1,10-diaza-18-crown-6)$^{2+}$in the ratio 2 : 1. Anion and cation interact (Table V) via N—H· · ·F and O—H· · ·OH bonds with host NH$_2$ groups and the water molecule acting as H-bond donors. The latter forms the H bond O(1W)—H· · ·O(4) of length 2.760 Å. Both hydrogen atoms of the aminogroups form donor–acceptor contacts, which can be considered as H bonds (Table V). The host is connected to two guest entities by two bifurcated N(1)—H· · ·F(1) H-bonds. One may consider such joining as the chelating of the guest by two host NH$_2$-groups placed in the 1,10-positions of the ring. The second H atom of the NH$_2$ group participates in the N(1)—H· · ·F(3) H bond. Thus each guest anion is bound to the host by four H bonds. Between themselves the anions are joined by strong O—H· · ·F(2) (2.622 Å) hydrogen bonds (Figure 2). All the H bonds mentioned above are responsible for chain formation, having the composition —H—G—G—H—G—G—H— and directed along the z axis in the unit cell. The chains related by translation along x are joined by the N(1)—H· · ·F(3) H bond and a three-dimensional network of H-bonded structural units is formed. The distinction between H bond distribution in isostructural complexes on the basis of germanium (**I**) and silicon (**I***) atoms is defined by the increased Ge—F distances in comparison with Si—F.

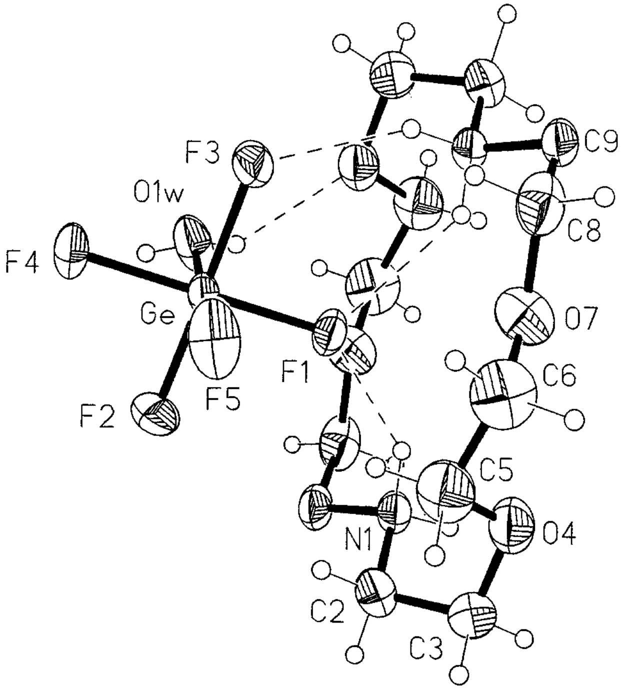

Figure 1. ORTEP view of complex (**I**) (the second guest entity is omitted) with the H bond description and atomic numbering scheme.

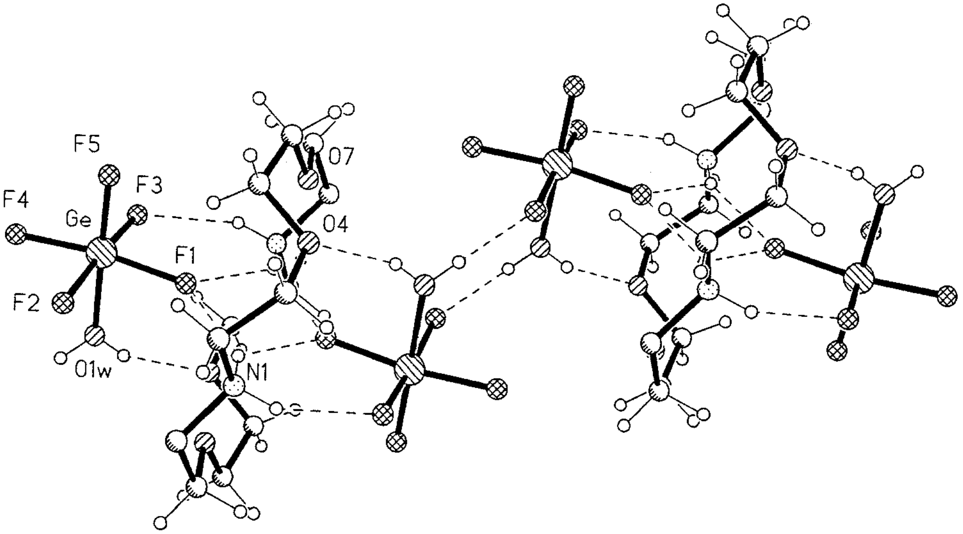

Figure 2. Fragment of the chain motif in complex (**I**).

Table IIIb. Bond lengths (Å) and angles (°) for complex **II**.

Ge—F(1)	1.763(2)	O(4)—C(5)	1.430(4)
Ge—F(2)	1.764(2)	C(5)—C(6)	1.481(5)
Ge—O(1W)	1.927(2)	C(6)—O(7)	1.422(4)
O(1)—C(2)	1.417(4)	O(7)—C(8)	1.421(4)
C(2)—C(3)	1.494(5)	C(8)—C(9)^{2}	1.482(5)
C(3)—O(4)	1.428(4)	C(9)—O(1)	1.429(4)
F(1)—Ge—F(2)	90.2(1)	O(4)—C(3)—C(2)	109.0(3)
F(1)—Ge—F(2)^{1}	89.8(1)	C(3)—O(4)—C(5)	113.5(3)
F(1)—Ge—O(1W)	89.8(1)	O(4)—C(5)—C(6)	109.6(3)
F(1)—Ge—O(1W)^{1}	90.2(1)	O(7)—C(6)—C(5)	110.3(3)
F(2)—Ge—O(1W)^{1}	90.7(1)	C(8)—O(7)—C(6)	111.6(3)
F(2)—Ge—O(1W)	89.3(1)	O(7)—C(8)—C(9)^{2}	110.9(3)
C(2)—O(1)—C(9)	112.6(2)	O(1)—C(9)—C(8)^{2}	110.2(3)
O(1)—C(2)—C(3)	109.7(3)		

Symmetry transformations used to generate equivalent atoms:
^{1} $1 - x, -y, -z$.
^{2} $-x, -y, -z$.

Table IV. Selected torsion angles for complexes **I** and **II**.

Complex I		Complex II	
O(9)^{1}—N(1)—C(2)—C(3)	168.2(3)	C(9)—O(1)—C(2)—C(3)	174.2(3)
N(1)—C(2)—C(3)—O(4)	61.9(4)	O(1)—C(2)—C(3)—O(4)	−68.0(3)
C(2)—C(3)—O(4)—C(5)	69.1(4)	C(2)—C(3)—O(4)—C(5)	177.5(3)
C(3)—O(4)—C(5)—C(6)	175.6(3)	C(3)—O(4)—C(5)—C(6)	−163.6(3)
O(4)—C(5)—C(6)—O(7)	54.3(4)	O(4)—C(5)—C(6)—O(7)	63.0(3)
C(5)—C(6)—O(7)—C(8)	157.5(3)	C(5)—C(6)—O(7)—C(8)	179.5(3)
C(6)—O(7)—C(8)—C(9)	179.9(3)	C(6)—O(7)—C(8)—C(9)^{2}	−178.0(3)
O(7)—C(8)—C(9)—N(1)^{1}	62.3(3)	O(7)—C(8)—C(9)^{2}—O(1)^{2}	−72.1(3)
C(8)—C(9)—N(1)^{1}—C(2)^{1}	174.1(3)	C(8)^{2}—C(9)—O(1)—C(2)	169.1(3)

Symmetry transformations used to generate equivalent atoms:
^{1} $-x, -y, 1 - z$.
^{2} $-x, -y, -z$.

Additionally in crystals, numerous C—H···F interactions take place with C···F and H(C)···F distances in the ranges 3.16–3.39 and 2.32–2.62 Å, respectively. They are formed by the fluorine atoms (F(2), F(4), F(5)) which are not involved partially or completely in NH···F or OH···F hydrogen bonds.

For complex (**II**) a polymer-like structure, including neutral guest entities [*trans*-$GeF_4 \cdot 2H_2O$], water and 18-crown-6 molecules is attained. In the complex the ratio of the components is 1 : 2 : 1 (Figure 3). The interaction between an inorganic com-

Table V. The possible H-bonds in the compounds **I** and **II**.

Donor D	Acceptor A	Distance, Å D—A, A	Symmetry code for A	Distance, Å H···A	Angle (°)
Complex **I**					
N(1)	F(1)	2.907	x, y, z	2.12	145
N(1)	F(1)	2.995	$-x, -y, 1 - z$	2.32	138
N(1)	F(3)	2.896	$-x, -y, 1 - z$	2.10	147
N(1)	F(3)	2.864	$-1 + x, y, z$	2.21	130
O(1W)	O(4)	2.760	$-x, -y, 1 - z$	2.15	145
O(1W)	F(2)	2.622	$-x, -y, -z$	1.84	170
Complex **II**					
O(1W)	O(2W)	2.580	$-x, -y, -z$	1.63	161
O(1W)	O(4)	2.643	x, y, z	1.68	168
O(2W)	O(1)	2.857	x, y, z	2.12	169
O(2W)	O(7)	2.872	x, y, z	2.04	153

plex and the crown ether molecule is achieved by the coordination to the germanium moiety water molecule O(1W) and through the bridging water molecule O(2W) (Table V). The latter one is bound by H bonds with crown ether oxygen atoms O(1) and O(7) (Figure 4). Between themselves the water molecules interact by a strong O(1W)···O(2W) H bond. The fluorine atoms of the neutral inorganic complex [*trans*-$GeF_4 \cdot 2H_2O$] do not participate in H bonds. The axis of the polymeric chain is directed along a spaceous [111] cell diagonal. In general the character of the host–guest interaction completely coincides with that found in the appropriate silicon complex [12–14].

3.2. STRUCTURES OF INORGANIC COMPLEXES

There is extremely limited information in the literature about hexacoordinated germanium(IV) complexes. Moreover, data about its aquafluorocomplexes are completely absent, because, like the appropriate silicon complexes, they possess low stability. In the known germanium compounds, [$GeF_4 \cdot$2,2′-Bipy] [19], K_2[*cis*-$Ge(C_2O_4)_2F_2] \cdot 2H_2O$ [20] and K_2[*cis*$(CF_3)_2 \cdot GeF_4$] [21] the metal polyhedron appears essentially distorted due to participation in the coordination of chelating bidentate ligands such as bipyridine and oxalate ion. The coordinated CF_3 groups in K_2[*cis*$(CF_3)_2 \cdot GeF_4$] [21] also cause distortions. It was shown [19–21] that Ge—F distances vary in the range 1.757—1.833 Å. In $[GeF_5 \cdot H_2O]^-$, as in [*trans*-$GeF_4 \cdot 2H_2O$] moieties, a practically undistorted corner octahedral structure is realized. The metal octahedron is slightly extended in the direction of the water molecule tops. In complex (**I**) Ge—F distances vary within the range of 1.738–1.799 Å, and the shortest distance is observed for the bond to the F atom located *trans*

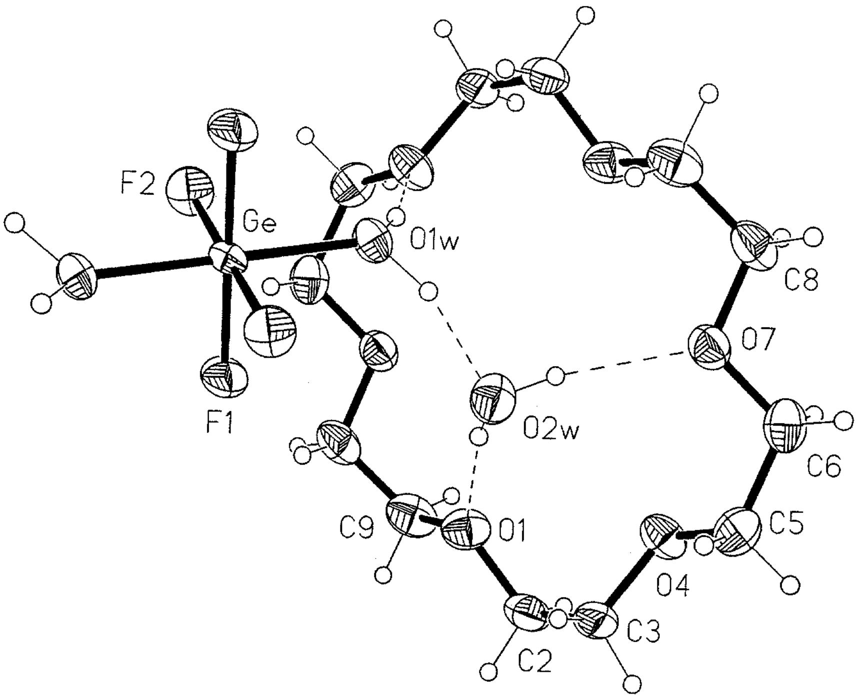

Figure 3. ORTEP view of complex (**II**) (the second guest entity is omitted) with the H-bond description and atomic numbering scheme.

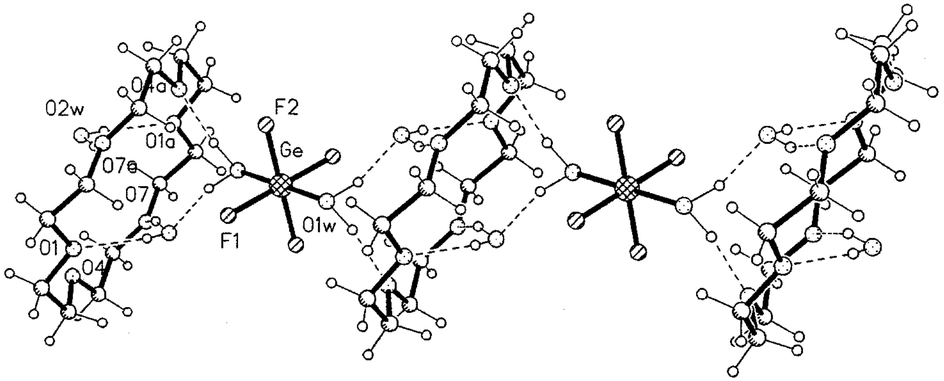

Figure 4. Fragment of the chain motif in complex (**II**).

to a water molecule (Ge—O(H_2O) distance —1.966 Å). The metal coordination polyhedron has approximate C_{4v} symmetry. For germanium-containing complexes we do not observe a dependence of the Me—F distance on the number and types of H bonds in which fluorine atoms participate. For the [*trans*-$GeF_4 \cdot 2H_2O$]

entity Ge—F distances are 1.763 and 1.764 Å, while Ge—H_2O is 1.927 Å. The polyhedron symmetry is close to D_{4h}.

3.3. MACROCYCLE CONFORMATION AND GEOMETRY

The conformation of the H_2-1,10-diaza-18-crown-6 entity is described by a sequence of torsion angles $ag + g + ag + aag + aag - g - ag - aag - a$ (Table IV). The same conformation for the diaza-18-crown-6 entity is found in a number of its complexes e.g. with $CuCl_2$ [22], $CuBr_2$ [23], thiourea [24] etc. [25]. This indicates, that angular $g + g + (g - g-)$ fragments are formed at C(3) and the atom symmetrically related to it. The transannular distances N(1)· · ·N(1)*, O (4)· · ·O(4)* and O(7)· · ·O(7)* are equal to 5.118, 6.284 and 5.498 Å, respectively. The macrocycle O atoms are coplanar, while the N(1) and N(1)* atoms deviate from this plane by +0.282 Å. The geometrical characteristics of the crown ether molecule are: C—C = 1.505, C—O = 1.418, C—N = 1.495 Å, bond angles: CCO = 109.6, CCN = 111.6, COC = 114.5 and CNC = 112.5° (Table IIIa) and do not differ from those found in other complexes [22–25]. The 18-crown-6 entity in **(II)** has a typical crown-like form (D_{3d} symmetry) with the oxyethylene moieties containing a sequence of $ag+/-a$ of bonds. The average distances and bond angles have the values: C—C = 1.486, C—O = 1.424 Å, CCO = 110.0 and COC = 112.6°.

3.4. IR SPECTROSCOPIC CHARACTERISTICS OF (I) AND (II)

A very strong band at 1075 cm^{-1} observed in the spectrum of **(II)** is assigned to the asymmetric stretching mode ν_{as} (COC) of the OCCO sections in the *aga* conformation [26, 27], in agreement with the X-ray data. The presence in the spectrum of **(II)** of vibrational bands of the OCCO units (1000–800 cm^{-1}), and the bending band of average intensity at 845 and 830 cm^{-1} are also characteristic of the *aga* conformation. The X-ray data of **(I)** indicate two OCCO and two NCCO units in *aga* conformations and two NCCO units in *agg* conformations. A reduction of the crown ether symmetry during complexation results in an appreciable complication of the IR spectrum of **(I)** in comparison with the spectrum of free diaza-18-crown-6 in the region of 1165–800 cm^{-1}. Thus, in the spectrum of **(I)**, in addition to the bands at 967, 830, 820 cm^{-1} and 950, 870 cm^{-1}, attributed to the OCCO and NCCO unit vibrations in *aga* conformations [26–28], bands also appear at 1017, 918, 850 cm^{-1}, which arise from the presence in the macrocyclic framework of two NCCO units in *agg* conformations. The change of conformational state of the diaza-18-crown-6 entity during complexation is also indicated by the intensity changes of the following vibration bands ν_{as} (CNC), ν_{as} (COC), ν (CC), the most intense in the spectrum of **(II)** being the bands at 1135 and 1108 cm^{-1}, while the most intense bands in the spectrum of diaza-18-crown-6 are those at 1118 and 1085 cm^{-1}. Taking into account the data from [29], the ν (GeF) vibrations of the 'guest' fragment of [*trans*-$GeF_4 \cdot 2H_2O$] in the IR spectrum of **(II)** are identified at

630 and 585 cm^{-1}, and the splitting is expected on the basis of X-ray data (D_{4h} symmetry coordination polyhedron *trans*-$GeF_4{\cdot}2H_2O$) the singlet band of the E_u type vibration being split into two components due to the effects of the crystal environment. In turn the ν (GeF) vibrations in the spectrum of (**I**) (coordination polyhedron $GeF_5{\cdot}H_2O$ with $C_{4\nu}$ symmetry) are observed at 630, 582 and 560 cm^{-1}; the latter probably contains contributions of the skeletal bending mode of a macrocycle $-\delta$(CCO) and δ(CNC). We note an essential similarity of the ν (GeF) bands in the IR spectra of (**I**) and the $(R_4N)[GeF_5{\cdot}H_2O]$ complexes investigated earlier [30] which contain the same anionic fragment $[GeF_5{\cdot}H_2O]^-$.

4. Conclusion

Interaction in GeO_2–HF–L solutions (L = 1,10-diaza-18-crown-6, 18-crown-6) results in the formation of host guest type complexes (**I**) and (**II**), respectively. Complexes (**I**) and (**II**) are structural analogues of the related complexes containing $[SiF_5{\cdot}H_2O]^-$ and [*trans*-$SiF_4{\cdot}2H_2O$] moieties as the guests [12–14].

According to ^{19}F-NMR data [30] when GeO_2 is dissolved in hydrofluoric acid a number of germanium-containing fluorocomplexes are formed. In particular, for the ratio $HF/GeO_2 = 4.2$ the authors [30] give the following equilibrium:

$$24GeO_2 + 101HF = [GeF_3(OH){\cdot}2H_2O] + 9GeF_4{\cdot}2H_2O + 7H[GeF_5{\cdot}H_2O] + 2H_2GeF_6 + 5H_2O,$$

the stability of $[GeF_4{\cdot}2H_2O]$, and especially of $[GeF_5{\cdot}H_2O]^-$, being due to the presence of excess of HF. In contrast to the silicon diaquatetrafluorocomplex, possessing a *trans*-configuration [15], the $[GeF_4{\cdot}2H_2O]$ complex exists in solutions as an equilibrum mixture of geometrical isomers with a *cis* : *trans* ratio of ~3 [30].

Complexation with 18-crown-6 causes the selective stabilization of the [*trans*-$GeF_4{\cdot}2H_2O$] moiety in (**II**), and it appears to be the first example of 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.

In summary we emphasize, that the stabilization of 'guest' fragments [*trans*-$GeF_4{\cdot}2H_2O$] and $[GeF_5{\cdot}H_2O]^-$ in complexes (**I**) and (**II**) is provided by the systems of intermolecular H bonds of the OH···O, NH···F and OH···F type.

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References

1. M. Hiraoka: *Crown Compounds, Their Characteristics and Applications,* Kodansha Amsterdam–Oxford–New York, p. 25 (1982).

2. F. Vögtle and E. Weber (eds.): *Host–Guest Complex Chemistry of Macrocycles. Synthesis, Structures, Applications*, Springer-Verlag, Berlin, p. 421 (1985).
3. H.M. Colquhoun, J.F. Stoddart, and D.J. Williams: *Angew. Chem. Int. Ed. Engl.* **25**, 487 (1986).
4. R. Damrauer and S.E. Danahey: *Organometallics* **5**, 1490 (1986).
5. R. Damrauer, O'Connell, S.E. Danahey, and R. Simon: *Organometallics* **8**, 116 (1989).
6. F.H. Carre, R.J.P. Corriu, C. Guerin, B.J.L. Henner, and W.W.C. Wong Chi Man: *J. Organomet. Chem.* **347**, C1 (1988).
7. S.E. Johnson, R.O. Day, and R.R. Holmes: *Inorg. Chem.* **28**, 3182 (1989).
8. S.E. Johnson, J.S. Payne, R.O. Day, J.M. Holmes, and R.R. Holmes: *Inorg Chem.* **28**, 3190 (1989).
9. K. Tamao, T. Hayashi, Y. Ito, and M. Shiro: *Organometallics* **11**, 2099 (1992).
10. S.G. Bott, A. Alvanipour, and J.L. Atwood: *J. Incl. Phenom.* **10**, 153 (1991).
11. Yu.A. Simonov, V.O. Gelmboldt, Ed.V. Ganin, A.A. Dvorkin, M.S. Fonari, L.V. Ostapchuk, and J. Lipkowski: *Koord. Khim. (Russ.)* **21**, 760 (1995).
12. Yu.A. Simonov, Ed.V. Ganin, A.A. Dvorkin, M.S. Fonari, V.O. Gelmboldt, and A.A. Ennan: *Supramol. Chem.* **3**, 185 (1994).
13. V.O. Gelmboldt, Ed.V. Ganin, Yu.A. Simonov, L.V. Ostapchuk, M.S. Fonari, J. Lipkowski, A.A. Dvorkin, and A.A. Ennan: *Koord. Khim.* (Russ). **21**, 183 (1995).
14. V.O. Gelmboldt, Yu.A. Simonov, Ed.V. Ganin, M.S. Fonari, V.Ch. Kravtsov, A.A. Dvorkin, L.V. Ostapchuk, and A.A. Ennan: *Koord. Khim.* (Russ.) **22**, 21 (1996).
15. Yu.A. Buslaev and S.P. Petrosyants: *Koord. Khim.* (Russ.) **5**, 21 (1979); *Chem. Abstr.* **90**, 161427t (1979).
16. G.M. Sheldrick: SHELXS-86. *Program for the Solution of Crystal Structures*, Göttingen, Germany (1986).
17. G.M. Sheldrick: SHELXL-93. *Program for Crystal Structure Refinement*, Univ. Göttingen, Germany (1993).
18. E. Weber, in: S. Pata and Z. Rappoport (eds.), *Crown Ethers and Analogs*, Wiley and Sons, New York, pp. 305–357 (1989).
19. A.D. Adley, P.H. Bird, A.R. Frazer, and M. Onyszchuk: *Inorg. Chem.* **11**, 1402 (1972).
20. R.L. Davidovich, S.B. Ivanov, V.S. Sergienko, and A.N. Levin: *VIIth All-Union Symposium on Inorganic Chemistry of Fluorides*, Abstracts. Moscow. Nauka, p. 124 (1987).
21. D.J. Brauer, H. Burger, and R. Eujen: *Angew. Chem.* **92**, 859 (1980).
22. M. Herceg and R. Weiss: *Acta Crystallogr.* **B29**(5), 1088 (1973).
23. M. Herceg and R. Weiss: *Rev. Chim. Min.* **10**, 509 (1973).
24. G. Weber: *Acta Crystallogr.* **B38**(10), 2712 (1982).
25. A.P. Chehlov: *Izvestia AN SSSR, Seria Khimia* (Russ.) **2**, 500 (1991).
26. O.A. Raevsky, S.V. Trepalin, V.E. Zubareva, and D.G. Batir: *Koord. Khim.* (Russ.) **12**, 723 (1986).
27. A.Yu. Tsivadze, A.A. Varnek, and V.E. Khutorsky: *Coordination Compounds of Metals with Crown-Ligands*. (Russ.) Moscow: Nauka (1991).
28. L.Ch. Minacheva, N.B. Generalova, I.K. Kireeva, V.G. Saharava, A.Yu. Tsivadze, and M.A. Porai-Koshiz: *Zh. Neorg. Khim.* **38**, 1166 (1993).
29. I. Wharf and M. Onyszchuk: *Can. J. Chem.* **48**, 2250 (1970).
30. Yu.A. Buslaev, S.P. Petrosyants, and V.P. Tarasov: *Zh. Struct. Khim.* (Russ.) **10**, 411 (1969); *Chem. Abstr.* **71**, 54278f (1969).