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Stabilization of silicon tetrafluoride by crown ether complexation. Crystal and molecular structure of the host:guest complex 1:1:2 between trans-tetrafluoro-bis(aqua) silicon, 18-crown-6 and water

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The product of the interaction of silicon tetrafluoride with a solution of 18-crown-6 in hexane has been obtained. The composition and structure of the compound [(*trans*-$SiF_4.2H_2O$).18C6.$2H_2O$] (complex I) have been determined by X-ray methods. The compound (I) is monoclinic, space group $P2_1/a$, $a=15.484(5)$, $b=9.651(3)$, $c=7.795(2)$ Å, $\gamma=121.45(3)°$, $Z=2$ for the composition $C_{12}H_{32}F_4O_{10}Si$. In the crystal of (I) the polymer-like structure is realized where water and [*trans*-$SiF_4.2H_2O$] moieties are connected with the host and between each other by the system of O-H...O hydrogen bonds. O(H)...O distances are in the limits 2.60(1)–2.91(1) Å. It was proved that in the process of crown ether complexation the hydratation of SiF_4 occurred with the formation of a *trans*-octahedral [$SiF_4.2H_2O$] moiety, Si-F and Si-O distances are equal to 1.658(7) and 1.853(9) Å, respectively. Between the individual chains there are only van der Waals interactions.

INTRODUCTION

The intensive development of host-guest complex chemistry with crown ethers is stimulated by their high selectivity in the reactions with both metal cations of groups 1–3 of the periodic table and inorganic complexes with neutral organic molecules.[1–3] These compounds have a wide spectrum of applied application in the processes of metal extraction, separation and concentration, analytical practice, and catalysis. In host-guest chemistry the problem of the interaction between the components in different phases with the final crystalline adduct is of independent interest. Besides, recently liquid clathrates have been prepared from trialkylaluminium or trimethylgallium compounds.[4] The synthesis of indium-based liquid clathrates as well as a crystal structure of the parent complex have also been determined.[5]

Crown ethers are known to be of particular interest in the stabilization of numerous harmful or otherwise unobtainable or uncharacterizable species through either primary[6] or secondary sphere coordination.[1] Thus, in ref. 7 the stabilization of one of the strongest Lewis acids, BF_3 in the form of its rather unstable hydrate, [$H_2O.BF_3$] as the 1:1:1 complex with 18-crown-6 was prepared. Here BF_3 is covalently bonded to the oxygen atom of the water molecule which in turn is hydrogen bonded to 18-crown-6. Until now there has been no report of crown ether complexes with the strong Lewis acid SiF_4,[8] the main component of the remaining gases of a number of chemical and metallurgical industries. Moreover, in the literature there are no examples of X-ray structural identification of silicon tetrafluoride complexes with O-donor molecules.[8]

In this paper the results of the synthesis, composition and structure determination for the new complex [*trans*-($SiF_4.2H_2O$).18C6.$2H_2O$] are given.

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EXPERIMENTAL

Synthesis of complex I

18-Crown-6 (7.9 g, 0.03 mol) was dissolved in 400 mL of hexane and was barbatated by silicon tetrafluoride till the cessation of sediment formation. The product was separated by filtration. Crystals of the complex suitable for X-ray crystallography were obtained by the recrystallization of a 0.1 g sample from 50 mL mixture of acetone and hexane in the ratio 1:1. Colourless, transparent crystals are soluble in acetone, unsoluble in chloroform or hexane, m.p. 91–92 °C. IR (Specord-75IR, oil)ν, cm^{-1}: 3430 (OH), 2935, 2910, 2870 (CH), 1145, 1122, 1095 (COC), 775, 702 (SiF). Mass-spectrum (Varian MAT 112), m/z (I in %): 265 (M+H crown ether, 0.7), 134(24), 90(100), 89(24), 88(47), 86(30), 74(57), 73(26), 60(37), 59(39). Analysis: found, % for $C_{12}H_{32}F_4O_{10}Si$: Si, 6.51; F, 17.69. Calcd. Si, 6.38; F, 17.25.

In accordance with thermogravimetric analysis (derivatograf OD-102 Paulic-Paulic-Erdei system), the complex decomposition occurs in the temperature interval 40–140 °C and is followed by the endothermic effect.

X-ray data collection, structure determination and refinement

Because the quality of the crystals was rather poor and the complex was quite unstable and decomposed quickly during the experiment, the experimental data were obtained from two samples. The intensity data collection was made on four-circle automatic RED-4 diffractometer equipped with a M-6000 computer, graphite monochromator, and MoK$_\alpha$-radiation was used. The intensities were corrected for Lp and background effects but not for absorption. Data in the range $2 < 2\theta < 46°$ were collected by $\theta/2\theta$ scans with $(\sin\theta/\lambda)_{max} = 0.53$ Å^{-1}.

Table 1 Crystallographic data for I

Formula	$C_{12}H_{32}F_4O_{10}Si$
Crystal system	monoclinic
Space group	$P2_1/a$
Cell constants	
a, Å	15.484(5)
b, Å	9.651(3)
c, Å	7.795(2)
γ (deg)	121.45(3)
Cell volume, Å^3	994(1)
D_{calc}(g cm^{-3})	1.579(2)
μ(cm^{-1})	2.88
Radiation	MoK$_\alpha$(λ=0.71069)
Diffractometer	RED-4
Reflections	
measured	742
unique	737
R(hkl)	0.076

Table 2 Atomic fractional parameters ($\times 10^4$) and B_{eq} for I

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Si	5000	5000	0	1.8(2)
F(1)	5154(5)	5141(9)	2096(8)	3.0(3)
F(2)	3856(4)	3334(8)	230(9)	3.1(3)
O(1)	6016(6)	−82(10)	−2893(11)	3.2(4)
C(2)	7058(9)	624(17)	−2489(18)	3.4(6)
C(3)	7460(10)	2251(17)	−1558(17)	3.8(6)
O(4)	7060(6)	1919(9)	182(11)	2.9(3)
C(5)	7547(8)	3298(14)	1207(17)	2.8(5)
C(6)	7052(9)	2939(17)	2931(18)	3.5(6)
O(7)	6030(6)	2667(10)	2691(10)	2.9(4)
C(8)	5469(10)	2286(15)	4285(16)	3.1(6)
C(9)	5624(9)	−1560(15)	−3819(16)	3.1(6)
OW	5576(5)	3734(10)	−119(10)	2.5(3)
OW1	4647(6)	918(10)	−1640(11)	3.2(4)

Table 3 Bond distances (Å) and endocyclic and torsion angles (deg) in I

Atoms	*Distance*	*Atoms*	*Angle*
18-crown-6			
O(1)-C(2)	1.42(2)	C(2)-O(1)-C(9)	112.1(10)
O(1)-C(9)	1.42(2)	O(1)-C(2)-C(3)	110.3(12)
C(2)-C(3)	1.53(2)	C(2)-C(3)-O(4)	108.4(12)
C(3)-O(4)	1.45(2)	C(3)-O(4)-C(5)	111.6(10)
O(4)-C(5)	1.39(2)	O(4)-C(5)-C(6)	109.7(11)
C(5)-C(6)	1.49(2)	C(5)-C(6)-O(7)	107.4(11)
C(6)-O(7)	1.47(2)	C(6)-O(7)-C(8)	112.4(10)
O(7)-C(8)	1.45(2)	O(7)-C(8)-C(9)*	106.9(11)
C(8)-C(9)	1.50(2)	O(1)-C(9)-C(8)	112.2(11)
		C(9)-O(1)-C(2)-C(3)	−177.5
		O(1)-C(2)-C(3)-O(4)	−73.0
		C(2)-C(3)-O(4)-C(5)	−167.9
		C(3)-O(4)-C(5)-C(6)	−175.1
		O(4)-C(5)-C(6)-O(7)	67.8
		C(5)-C(6)-O(7)-C(8)	−179.3
		C(6)-O(7)-C(8)-C(9)*	163.2
		O(7)-C(8)-C(9)*-O(1)*	−62.6
		C(2)-O(1)-C(9)-C(8)*	178.3
[*trans*-$SiF_4.2H_2O$]			
Si-F(1)	1.647(6)	F(1)-Si-F(2)	90.4(4)
Si-F(2)	1.668(7)	F(1)-Si-OW	90.2(4)
Si-OW	1.853(9)	F(2)-Si-OW	90.2(4)

* Denote the atoms connected with the basic ones by symmetry 1-x, -y, -z.

The structure was solved by direct methods using CSD complex[10] and refined by the block-diagonal least-squares approach. Non-hydrogen atoms were treated isotropically. Macrocyclic H-atoms were placed in calculated positions (C-H 1.05 Å) with isotropic B = 5.0 Å^2. Water hydrogen atoms were located from difference Fourier maps. Convergence was achieved with R = 0.076 and goodness-of-fit 2.53, residual extrema in final difference map 0.43, −0.38 (e/Å^3). X-ray data are given in Table 1, final positional atomic parameters in Table 2, bond distances, endocyclic and torsion angles in Table 3.

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RESULTS AND DISCUSSION

Unlike hydrogen bonded crystalline complexes between crown compounds and NH- or OH-acidic uncharged organic molecules, complexes involving OH-acidic molecules or water are rather rare in the literature.[1-3] Ordinally, water molecule behaves as a go-between to bind a second guest to the crown (ternary complex), this being an organic molecule (as a rule, phenol or dicarbonic acid derivatives) or a transition metal complex.[11] As a rule, *trans*-aqua ligands are invariably hydrogen bonded to the macrocyclic ring faces, to give linear polymeric chains of alternating guests and 18-crown-6 molecules.

Structure of the host-guest complex [(trans-$SiF_4.2H_2O$).18C6.$2H_2O$]

In Fig 1 the fragment of the polymeric chain of compound (I) is shown. Being centrosymmetric, the complex has a host:guest ratio 1:1:2. The guest entities are arranged in a similar manner on both sides of the centrosymmetric host molecule. Two oxygen atoms connected by the inversion center and non-coordinated to the guest entity water molecules (OW1 and OW1*) as H-donors are connected by O-H ... O hydrogen bonds with O(1) and O(4)* of the 18-crown-6. O-H ... O distances are: OW1 ... O(1) = 2.91 Å and OW1 ... O(4)* = 2.86 Å (O(4)* is related to O(4) by the symmetry operation (1-x, -y, -z). Besides these bonds OW1 takes part in more weak hydrogen bonds with the parameters: OW1 ... 07*, 3.15(1); H(1W1) ... 07*, 2.35(1) Å; OW1-H(1W1) ... O7*, 130°. The hydrogen bond associated with H(1W1) may be considered as a bifurcated one.

The characteristics of O-H ... O hydrogen bonds for (I) are given in Table 4. They are similar to those found for water molecules coordinated by the crown ethers (as a rule 18-crown-6). For comparison $O_{water} ... O_{crown}$ distances are: [18C6.2(HO)Ph(NO_2).$2H_2O$], 2.847, 2.933 Å;[12] [18C6.$(CH)_2(COOH)_2.2H_2O$], 2.863, 2.917 Å;[13] and [18C6.$(CH_2)_2(COOH)_2$], 2.819, 2.910 Å.[14] In turn, the same water molecule as H-acceptor by its lone pair takes part in $O_{water} ... O_{guest}$ contacts with water molecules (OW) bonding to the [*trans*-$SiF_4.2H_2O$] entity. The distance OW ... OW1 is 2.60 Å. The general regularity of increasing $O_w ... O_{crown}$ distances in comparison with $O_w ... O_{guest}$ distances is keeping here (in the complexes mentioned above the

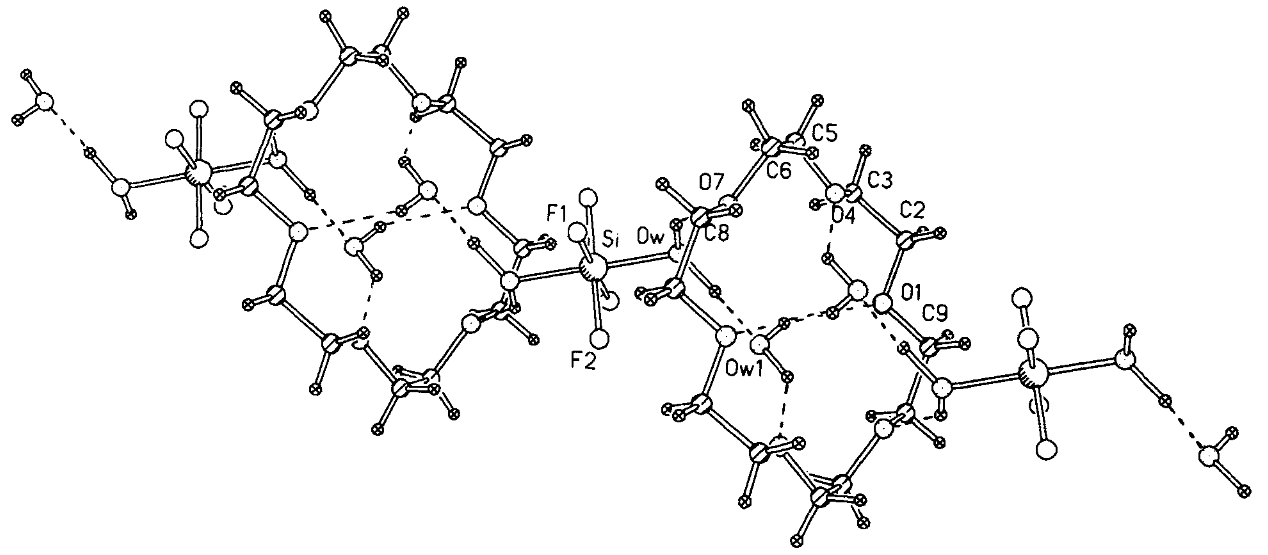

Figure 1 The fragment of the polymeric chain for I with hydrogen bonds shown by dashed lines.

Table 4 Geometric parameters of hydrogen bonds in I

O ... O, Å		*H ... O, Å*		*O ... H-O, deg.*	
OW1 ... O(1)	2.91(1)	H(1W1) ... O(1)	2.23(1)	OW1-H(1W1) ... O(1)	150
OW1 ... O(4)*	2.86(1)	H(2W1) ... O(4)*	1.93(1)	OW1-H(2W1) ... O(4)*	142
OW ... OW1	2.60(1)	H(1W) ... OW1	1.53(1)	OW-H(1W) ... OW1	156
OW ... O(7)	2.66(1)	H(2W) ... O(7)	1.82(1)	OW-H(2W) ... O(7)	137

O(7)* is connected with the one in Table 2 by (1-x, -y, -z).

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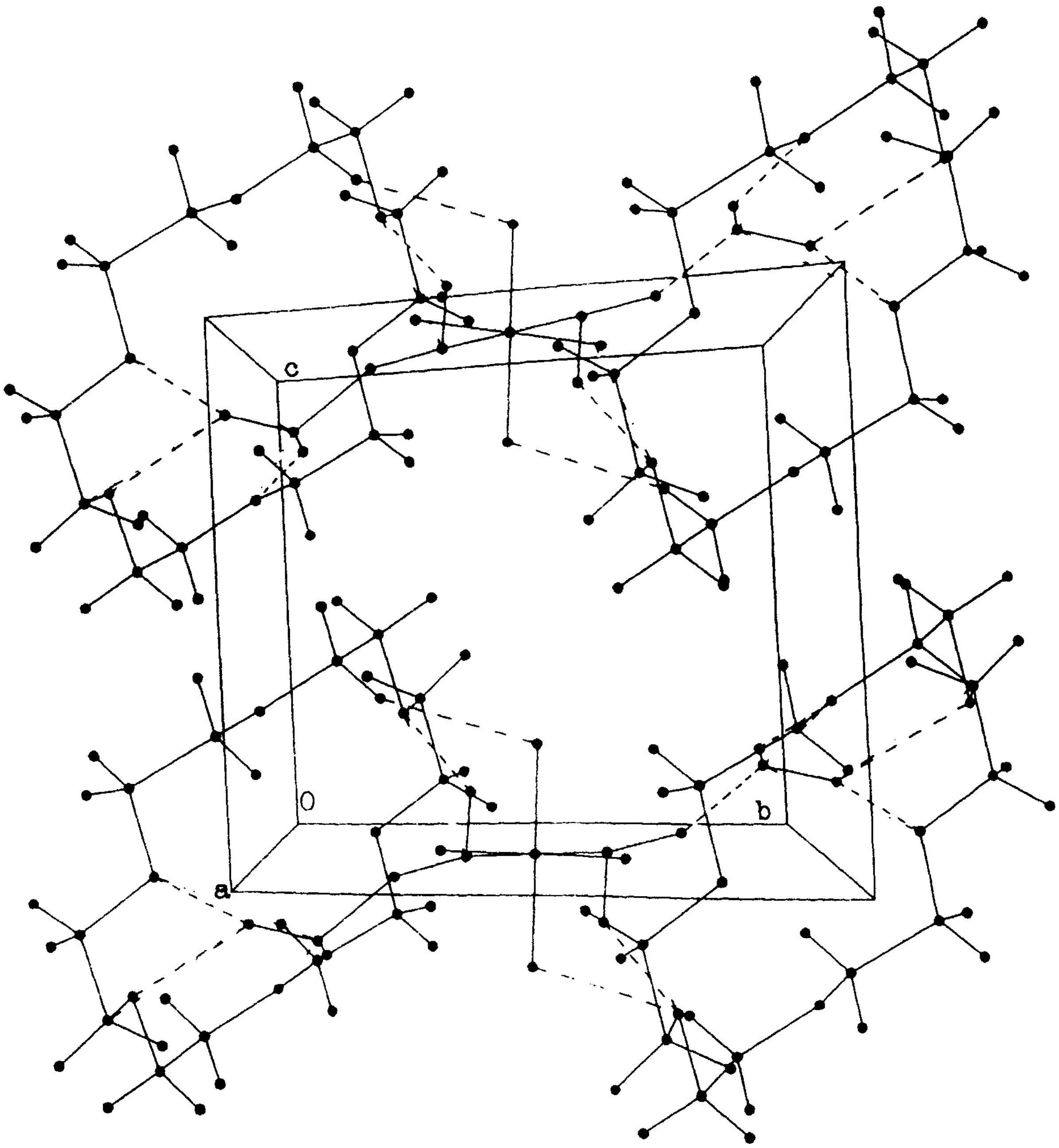

Figure 2 The crystal packing of I.

proper $O_w...O_{guest}$ distances are 2.552,[12] 2.536,[13] 2.657 Å.[14]) Besides the $O_{water}...O_{guest}$ contact, the guest moiety participates in direct guest... host contacts, OW ... O7 = 2.66 Å. So, the water molecule coordinated to the SiF_4 moiety behaves as a single bridge between host molecules. The complex is rather similar to $[SnCl_4.2H_2O.18C6].2H_2O$,[15] Although the H_2O molecules within the octahedral $[SnCl_4.2H_2O]$ units are *cis*- to each other, they still support a hydrogen bonded polymeric structure by involving non-coordinated H_2O molecules bound to each face of the 18C6 ring as in our case. O-atoms of independent water molecules taking part in complexation are at distances 2.61 Å (OW) and 1.71 Å (OW1) from the average plane of the crown ether heteroatoms. Besides O ... O contacts in the structure short F ... CH_2 host-guest distances were found (Fig 2): F(1) ... C(9)* 3.29(2) (*, 1-x, -y, -z), F(2) ... C(3)** (**, −0.5+x, y, −0.5-z), and F(2) ... C(6)*** (***, −0.5+x, y, 0.5-z).

18-crown-6 geometry

The 18-crown-6 molecule displays its normal geometry. C-C and C-O distances average 1.51 and 1.43 Å, and the C-O-C and C-C-O angles, 112.0 and 109.2°. The

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centrosymmetric host molecule has the pseudo-D_{3d} conformation with the torsion angles within the limits: O-C-C-O, (62.6–73.0°) and C-O-C-C, 163.2–175.1°. Macrocyclic heteroatoms are coplanar to within 0.24 Å. They form a rather regular hexagon with the distances between the neighbouring heteroatoms in the range 2.83(1)–2.97(1) Å and between transanular O-atoms, 5.46(1)–6.09(1) Å.

Structure of the [trans-$SiF_4.2H_2O$] entity

In the literature there are no data about structures of O-containing hexacoordinated SiF_4 complexes. In the centrosymmetric octahedron the Si-F distances are 1.649 to 1.667 Å, and the Si-O(H_2O), 1.855 Å (Table 4). The deviations of the F-Si-F and H_2O-Si-F angles from 90° do not exceed experimental accuracy (Table 3). The distances are similar to those in [SiF_4.2Py], where Si-F and Si-N are 1.64 and 1.93 Å, respectively. Undoubtedly the interesting chemical aspect of this investigation is the structural identification. [*Trans*-$SiF_4.2H_2O$] is an acid base product in which the water appears because the reaction was not protected from the atmosphere. During the complexation the tetrahedral SiF_4 molecule is transformed into the planar fragment of the octahedral complex [$SiF_4.2H_2O$]. The existence of this complex had been postulated[15–16] in connection with the discussion of the reasons for the solubility of silicon dioxide in silicon hydrofluoric acid and strong acidic solutions of hexafluorosilicates:

$$2SiF_6^{2-} + 4H_3O^+ + SiO_2 \rightarrow 3[SiF_4.2H_2O]$$

^{19}F NMR for water and water-alcohol solutions of $SiF_4.2H_2O$ have been obtained[17,18] and interpreted on the basis of a trans structure. This proposal is now confirmed by the X-ray structural analysis. Obviously, the stabilization of this complex is due to the intermolecular OH ... O hydrogen bonds. It is interesting to note that the structure of the [$SiF_4.2H_2O$] moiety may be considered as a model of a hexacoordinated intermediate or a transition state in the nucleophilic substitution reactions at the tetrahedral silicon center and in the racemization of optically active halosilanes in the process of nucleophilic activation.

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