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Structure of the 18-Crown-6 Complex with Ammonium Hexafluorosilicate and Water *

MARINA S. FONARI†, VICTOR CH. KRAVTSOV and YURII A. SIMONOV
Institute of Applied Physics, Academy of Sciences of Moldova, MD 2028, Academy str. 5, Chisinau, Moldova

EDWARD V. GANIN and VLADIMIR O. GELMBOLDT
Physico-Chemical Institute of Environmental and Human Protection, Odessa State University, Odessa, 27000 Ukraine

JANUSZ LIPKOWSKI
Institute of Physical Chemistry, Polish Academy of Sciences, PL 01-224 Warszawa, Poland

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Abstract

The crystalline host–guest type complex $[(\text{18-crown-6}\cdot NH_4)_2][SiF_6]\cdot 4H_2O$ has been obtained as the result of the interaction of $SiF_4\cdot 2NH_3$ with 18-crown-6 (18C6) in an aqueous medium. Crystal data: monoclinic, space group $C2/c$, $a = 26.541(2)$, $b = 8.363(2)$, $c = 20.469(2)$ Å, $\beta = 122.43(1)°$ and $Z = 4$. The final R-value is 0.070 for 3253 reflections with $I \geq 2\sigma(I)$. The crystals consist of the complex $[NH_4\cdot 18C6]^+$ cations, $[SiF_6]^{2-}$ anions and water molecules. The ammonium cation is hydrogen bonded by three of its H-atoms to the crown ether oxygen atoms with N(1) $\cdots$O separations 2.923(5)–2.940(5) Å and by the fourth H-atom to the fluorine atom of the hexafluorosilicate anion, the N(1)$\cdots$F(4) distance being 2.797(6) Å. The conformation of the macrocycle and the hydrogen-bond geometry in the complex cation closely resemble those in related adducts between 18-crown-6 and ammonium salts. All crystal components are connected via a system of hydrogen bonds into a ribbon along the *b* axis in the unit cell.

Introduction

In the course of our previous work it has been proved [1–2] that both tetrafluorosilane in moist air or an aqueous solution of fluorosilicic acid interact with 18-crown-6 (18C6) yielding the crystalline product: $[(trans\text{-}SiF_4\cdot 2H_2O)\cdot 18C6\cdot 2H_2O]$. In accord with X-ray data, the compound can be formulated as the 'host–guest' complex, where the components are linked by OH$\cdots$O hydrogen bonds. The *trans*-$SiF_4\cdot 2H_2O$ molecules and bridging water molecules approach from both sides to the centrosymmetric crown molecule and form a hydrogen-bonded chain where inorganic complexes and crown molecules alternate. In a similar way the 18C6 molecule forms crystalline adducts with transition-metal ammines. In the case of *trans*-$[PtCl_2PMe_3)(NH_3)]$ guest [3] where a 2:1 crystalline adduct is formed between the neutral transition-metal ammine and 18-crown-6, all six of the oxygen atoms are hydrogen bonded in approximately trigonal fashions, the two NH_3 molecules drawing near from opposite faces of the crown. In turn, transition-metal complexes both neutral, e.g., *trans*-$[PtCl_2(NH_3)_2]$ and charged, e.g., $[Cu(NH_3)_4(H_2O)]^{2+}$ [4], which carry two *trans*-related NH_3 molecules, build crystalline hydrogen-bonded polymers with a 1:1 ratio in which the inorganic complex and the crown ether alternate. In the same fashion the complexes between ammonia and electron-deficient BX_3 compound molecules are also bound with crown ethers through hydrogen bonding. The neutral 1:1 addition compounds with the compositions $[BF_3\cdot NH_3\cdot 18C6]$ and $[BH_3\cdot NH_3\cdot 18C6]$ have been also described [5]. On the other hand, several crystal structures of 18-crown and ammonium salt complexes have been reported [6–7]. To date, all have been found to have 1:1 stoichiometry and to involve hydrogen bonding of the ammonium centre to oxygen atoms of the crown ether ring, which invariably adopts an all-*gauche* conformation with pseudo D_{3d} symmetry.

The present investigation reports on the preparation and structural characterisation of the crystalline product obtained in the system $SiF_4\cdot 2NH_3 - 18C6 - H_2O$. The X-ray structure analysis determines unequivocally the formula of the title compound as $[(\text{18-crown-6}\cdot NH_4)_2][SiF_6]\cdot 4H_2O$.

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[*] **Supplementary Data** relevant to this article have been deposited with the British Library as Supplementary Publication No. 82274 (10 pages) and include: the list of F_{obs} and F_{calc}, tables of anisotropic displacement parameters for non-hydrogen atoms and fractional atomic coordinates for non-hydrogen and hydrogen atoms.

[†] Author for correspondence.

Experimental

Synthesis

$SiF_4 \cdot 2NH_3$ (1 mmole) was added to a solution of 18C6 (1 mmole) in water (7 mL) and the solution stirred for 3 hours at 20 °C. The mixture was allowed to stand at room temperature for 48 hours, after which the white crystalline solid was filtered off, washed with water and dried *in vacuo.* Crystallisation from ether yielded the desired product in 69% yield, m.p. > 70 °C (with decomposition).

Colourless transparent crystals, soluble in water and methanol; insoluble in ether and hexane. *Anal. calcd.* for $C_{24}H_{64}F_6N_2O_{16}Si$: F 14.64 Si 3.61. *Found:* F 14.63 Si 3.47.

Crystal data

Crystallographic measurements were performed on a KUMA diffractometer using graphite monochromatized Cu-K_α radiation ($\lambda = 1.54178$ Å). Lattice parameters were obtained from least-squares refinement of 25 reflections in the θ range $11.3 < 0 < 18.7°$. Single crystal intensity data were collected using a ω-2θ mode. The intensities of 3 reflections were checked every 100 measurements to monitor crystal stability and showed no decay during data collection. The data were corrected for Lp effects but not absorption. The structure was solved by direct methods using SHELXS86 [8] and refined anisotropically for non-hydrogen atoms and isotropically for H-atoms using SHELXL97 [9]. Positions for hydrogens bonded to carbons were calculated based on a known atom geometry with C–H distances of 0.96 Å. These hydrogens were allowed to ride on their neighboring carbons during the refinement. Their thermal parameters were assigned the value of 1.2 times the initial equivalent isotropic thermal parameters of their neighboring carbons and were not refined. The ammonium H-atoms were located on difference Fourier synthesis and refined isotropically with restraints to maintain the geometry derived from the difference map.

Special attention has been paid to the refinement of two water molecules. The oxygen atoms of these molecules show high thermal motion and essential anisotropy. U_{eq} adopts the values 0.272(6) and 0.243(4) Å^2 and their displacement parameters are in the range 0.078–0.622 and 0.087–0.509 for O(1w) and O(2w) respectively. An attempt was made to split the oxygen atoms locations into two positions, however the corresponding refinement did not improve the R-factor and showed again the high anisotropy for both locations. So the anisotropic refinement of non-split atoms has been used for the final model. The refinement of s.o.f. for these two oxygen atoms led to the values 1.00(2) in the both cases. Among the 15 highest peaks on the difference Fourier map four peaks have been found in positions suitable for possible H-atoms. Although these positions in the structure could not be located with a high degree of certainty, the interatomic H$\cdots$O and H$\cdots$F distances correspond to the H-bonding. These peaks have been included in the refinement model as the H-atoms of water molecules with some obvious constraints on O–H bond lengths and HOH angles. The thermal parameters were assigned the values of 1.5 times the initial equivalent isotropic thermal parameters of their neighboring oxygen atoms.

Table 1. Crystal data and summary of intensity data collection and structure refinement for $[(\text{18-crown-6.NH}_4)_2][SiF_6].4H_2O$

Compound	$[(\text{18-crown-6.NH}_4)_2][SiF_6].4H_2O$
Empirical formula	$C_{24}H_{64}F_6N_2O_{16}Si$
Formula weight	778.86
Temperature, K	293(2)
Wavelength Å	1.54178
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a, Å	26.541(2)
b, Å	8.363(2)
c, Å	20.469(2)
β, deg.	122.43(1)
Cell volume, Å^3	3834.8(1)
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.349
μ, mm^{-1}	1.394
F(000)	1672
Crystal dimensions, mm	$0.15 \times 0.20 \times 0.70$
θ range for data collection, deg.	3.95 to 75.19
Limiting indices	$-28 < h < 0$, $0 < k < 10$, $-21 < l < 22$
Reflections collected/unique	3336/3253 [R(int) = 0.0158]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3253/20/251
Goodness-of-fit on F^2	1.013
Final R indices $[I > 2\sigma(I)]$	R1=0.0699, wR2=0.2135
R indices (all data)	R1=0.1516, wR2=0.2554
Largest diff. peak and hole e Å^{-3}	0.382 and −0.405

The crystal data, the details of data collection and refinement are summarized in Table 1. Bond lengths and angles are listed in Table 2.

Discussion of results

The structure of the complex ammonium cation $[NH_4 \cdot 18C6]^+$ with numbering scheme is depicted in Figure 1. An upper triangle of alternating crown O atoms forms N–H$\cdots$O hydrogen bonds with N(1)$\cdots$O distances falling in the range 2.923(5)–2.940(5) Å (Table 3). The N$^+\cdots$O distances to three other O atoms are also short and indicative of strong dipolar attractions being in the range 3.059(7)–3.138(7) Å. The N atom is displaced by 1.122 (7) Å from the best plane of all six crown O atoms. The ammonium ion-crown ether molecule host–guest complex organization is very close to two related ammonium complexes, $[NH_4 \cdot 18C6] \cdot Cl \cdot 2H_2O$ [6] and $[NH_4 \cdot 18C6] \cdot Br \cdot 2H_2O$ [7]. In the former complex N$\cdots$O contacts nearest to the ammonium ion average 2.887(4) Å, the remainder being 3.058(5) Å and the ammonium ion itself is 0.99 Å from the mean plane of all six O-atoms. In the latter complex N$\cdots$O contacts nearest to the

Table 2. Bond distances (Å) and angles (deg) for $[(18\text{-crown-}6\cdot NH_4)_2][SiF_6]\cdot 4H_2O$

Atoms	Distance	Atoms	Angle
O(1)–C(2)	1.401(7)	C(2)–O(1)–C(18)	112.1(4)
O(1)–C(18)	1.429(6)	O(1)–C(2)–C(3)	108.9(5)
C(2)–C(3)	1.471(8)	O(4)–C(3)–C(2)	110.8(4)
C(3)–O(4)	1.419(5)	C(5)–O(4)–C(3)	111.9(4)
O(4)–C(5)	1.414(6)	O(4)–C(5)–C(6)	110.0(4)
C(5)–C(6)	1.481(7)	O(7)–C(6)–C(5)	108.7(4)
C(6)–O(7)	1.437(6)	C(8)–O(7)–C(6)	112.4(4)
O(7)–C(8)	1.388(5)	O(7)–C(8)–C(9)	110.3(4)
C(8)–C(9)	1.490(7)	O(10)–C(9)–C(8)	108.4(4)
C(9)–O(10)	1.427(5)	C(11)–O(10)–C(9)	113.8(4)
O(10)–C(11)	1.375(6)	O(10)–C(11)–C(12)	109.5(4)
C(11)–(12)	1.489(7)	O(13)–C(12)–C(11)	109.6(4)
C(12)–O(13)	1.417(6)	C(12)–O(13)–C(14)	113.5(4)
O(13)–C(14)	1.428(5)	O(13)–C(14)–C(15)	108.6(4)
C(14)–C(15)	1.476(7)	O(16)–C(15)–C(14)	111.2(4)
C(15)–C(16)	1.411(6)	C(17)–C(16)–C(15)	112.4(4)
O(16)–C(17)	1.386(6)	O(16)–C(17)–C(18)	109.7(5)
C(17)–C(18)	1.488(8)	O(16)–C(18)–C(17)	109.1(4)
Si(1)–F(3)	1.626(7)	F(3)–Si(1)–F(1)	89.11(19)
Si(1)–F(1)	1.636(4)	F(1)–Si(1)–F(1)^i	178.2(4)
Si(1)–F(2)	1.645(5)	F(3)–Si(1)–F(2)	180.00(4)
Si(1)–F(4)	1.686(4)	F(1)–Si(1)–F(2)	90.89(18)
		F(3)–Si(1)–F(4)	90.39(17)
		F(1)–Si(1)–F(4)	88.0(2)
		F(2)–Si(1)–F(4)	89.61(17)
		F(4)6i–Si(1)–F(4)	179.2(3)

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

ammonium ion average 2.871 Å, the remainder 3.064 Å, and the ammonium ion is 1.00 Å from the mean plane of all six O-atoms.

Among the 18-membered crown ethers – NH_4^+ host–guest complexes where the ring framework remains the same, the NH_4^+-crown interaction is a strong function of the nature of the substituents on the ring which control the electron-pair donicity as well as the flexibility of the macrocyclic molecules [10]. The presence of two cyclohexyl groups allow the pumping of electrons into the crown ring and thus increases the basicity of the oxygen atoms, while the flexibility of the macrocycle remains approximately the same as for 18C6. Thus, a higher stability is expected for the NH_4^+ – DC18C6 (where DC18C6 is dicyclohexano-18-crown-6) complex compared to the other 18-crowns used. The complexes of *cis-syn-cis-* and *cis-anti-cis*-DC18C6 with ammonium and its alkyl derivatives were generated and studied in the gas phase using Fourier transform ion cyclotron resonance mass spectrometry [11]. Both the experiments and the calculations indicated that the *cis-syn-cis*-isomer has a higher ammonium cation affinity than the *cis-anti-cis*-isomer. The authors [11] proposed that the *cis-syn-cis-* isomer bound the ammonium cation preferentially on the face of the macroring enclosed by the cyclohexano units. We carried out the crystal structure investigation for the ammonium iodide complex with the *cis-syn-cis-* isomer of dicyclohexano-18-crown-6 (DC18C6), having the composition $[NH_4\cdot DC18C6]_2\cdot 2I\cdot 2H_2O$ [12]. The X-ray data confirmed the above mentioned suggestions and showed that the ammonium ion occupies the proximal position at the cyclohexyl groups hindered side of the crown molecule. The shortest N$\cdots$O distances are 2.889(5), 2.881(5), 2.890(5) the remainder being 2.952(5)–3.056(5) Å. The effect of substitution of two benzogroups on the 18C6 ring is a marked lowering of the stability of the ammonium complex. It is noteworthy that the introduction of two electron-withdrawing groups reduces the donicity of the oxygen atoms in the ring and hence reduces the cation-crown interaction. On the other hand, DB18C6 is a more rigid molecule than 18C6, so that the existence of two bulky benzogroups on the ring of 18C6 prevents the macrocycle from finding the optimum configuration for NH_4^+ binding.

Figure 2 shows a fragment of the crystal packing. The fourth NH_4^+ hydrogen protrudes upward from the center and is approximately perpendicular to the plane of the oxygens of the crown ether. It is pointing towards the fluorine of the hexafluorosilicate counterion, the N(1)$\cdots$F(4) separation being 2.797(6) Å. The hexafluorosilicate anion resides on the two fold axis and bridges two symmetry related $[NH_4\cdot 18C6]^+$ complex cations in the neutral associate with a 1:2 ratio and C_2 symmetry. The dihedral angle between the best planes of the two crown molecules in this sandwich is 50.2°. Some other examples of crown complexes are known from the literature [13–14] where the fourth ammonium H-atom is responsible for the intermolecular cation-anion hydrogen bonds and as the result, for the supramolecular host–guest assembly.

Two water molecules O(1w) and O(2w) cooperate in the complex and couple *via* a O–H$\cdots$O hydrogen bond [O(1w)$\cdots$O(2w) distance 2.91(2) Å] (Figure 2, Table 3). The O(1w) water molecule provides one of its hydrogen atoms while the O(2w) water molecule donates its lone pair for this interaction. Moreover, each water molecule is involved in the OH$\cdots$F hydrogen bonds with hexafluorosilicate anions [O(1w)$\cdots$F(1) = 2.935(9) Å and O(2w)$\cdots$F(3)(x, $y-1$, z) = 2.82(1) Å]. Thus, hexafluorosilicate anions and water molecules combine in an alternate fashion in the inorganic chain. The second O(2w) water molecule is weakly connected via its hydrogen with crown oxygen, O(2w)$\cdots$O(l3) = 3.057(7) Å. As can be seen from Figure 2, a ribbon-like structure is built of the inorganic chain encapsulated between two successive rows of complex crown cations. The ribbon is propagated along the *b* axis in the unit cell. The crown ether and water molecules, ammonium cations and hexafluorosilicate anions, are all brought together by the diverse system of N–H$\cdots$F, O–H$\cdots$F and O–H$\cdots$O hydrogen bonds. There are no intermolecular contacts shorter than the sum of van der Waals radii between the ribbons in the crystal.

The structures of the above mentioned compounds $[NH_4\cdot 18C6][Cl\ \text{or}\ Br]\cdot 2H_2O$ [6–7] show that one of the water molecules bridges the successive chloride (or bromide) anions, also constitute an inorganic chain hidden between two rows of crown molecules. In the complex

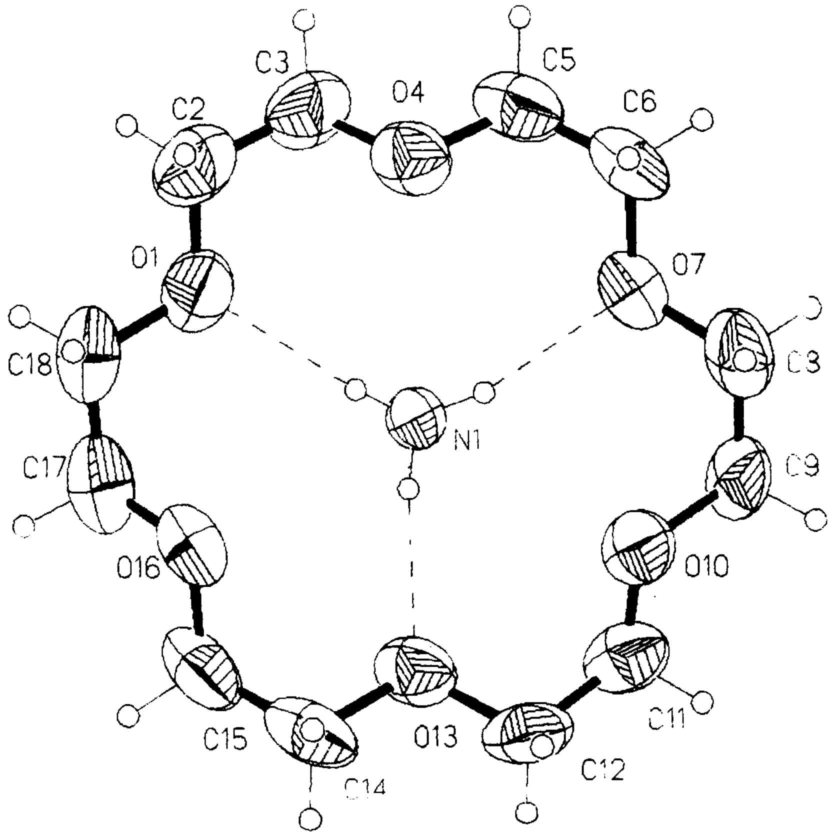

Figure 1. The view of the complex $[NH_4.18C6]^+$ cation with the atom labelling and hydrogen bonds as dotted lines. The thermal ellipsoids are given with the 50% probability.

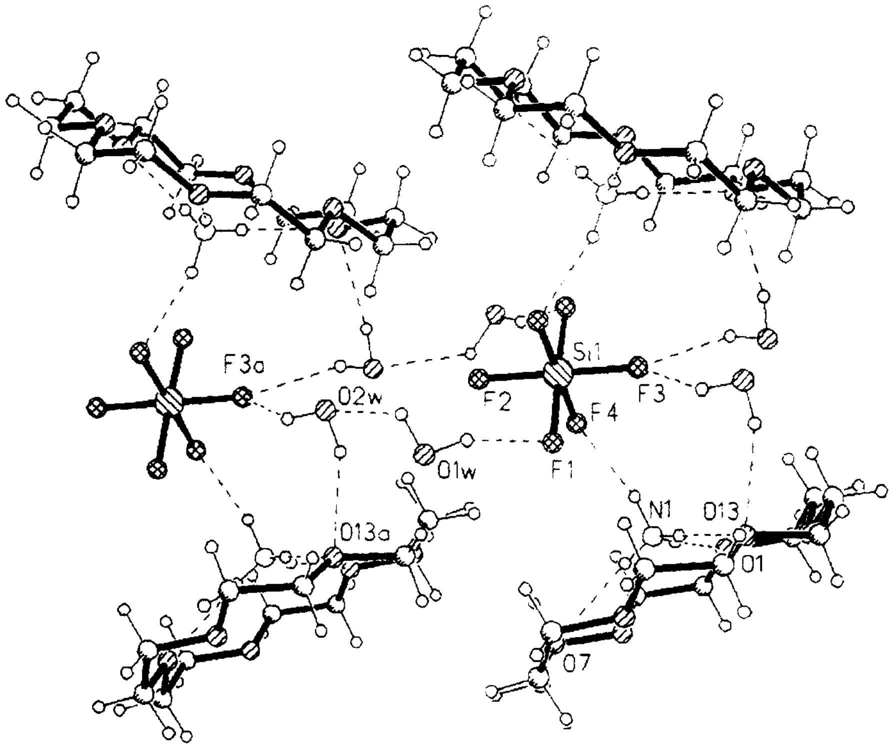

Figure 2. Packing diagram for the complex $[(18\text{-crown-}6.NH_4)_2][SiF_6].4H_2O$.

Table 3. Hydrogen bonds (Å and deg.) for $[(18\text{-crown-}6.NH_4)_2][SiF_6].4H_2O$

D–H···A	D(D–H) Å	d(H···A) Å	d(D···A) Å	< (DHA), deg
N(1)–H(1N1)···O(1)	0.82(3)	2.11(3)	2.924(5)	169(4)
N(1)–H(2N1)···O(7)	0.86(4)	2.10(4)	2.940(5)	167(5)
N(1)–H(4N1)···O(13)	0.83(4)	2.10(4)	2.923(5)	172(5)
N(1)–H(3N1)···F(4)	0.89(3)	1.93(3)	2.797(5)	163(4)
O(1w)–H(1w1)···O(2w)	0.96(2)	2.02(2)	2.91(2)	153(6)
O(1w)–H(2w1)···F(1)	0.96(3)	2.01(2)	2.935(9)	163(9)
O(2w)–H(1w2)···$F(3)^{ii}$	0.96(1)	2.01(2)	2.82(1)	141(3)
O(2w)–H(2w2)···$O(13)^{ii}$	1.00(3)	2.08(1)	3.057(8)	166(9)

Symmetry transformations used to generate equivalent atoms: $ii\ x, y-1, z$.

$[NH_4I\cdot DC18C6\cdot H_2O]_2$ [8], water acts as the bridge between ammonium and iodide ions, with both charged and neutral moieties being fully encapsulated between two crown molecules. The analysis of O–H···O and O–H···F values shows that the link is weak when it connects 18C6 and water (O···O value 3.057(7) Å) and is stronger when it connects the fluorine atom of the SiF_6^{2-} anion and water [O···O values 2.82(1) and 2.935(9) Å].

For the crown molecule the observed bond lengths (average O–C = 1.411(6) C–1.483(7) Å) and angles (average O–C–C = 109.5(4) and C–O–C = 112.7(4)°) fall in the commonly found ranges [15]. The preferred and the most common conformations about C–C and C–O bonds in the crown molecule are *gauche*- (*g*) and *anti*- (*a*) respectively. In the complex the crown molecule exhibits an approximate D_{3d} symmetry with all O–C–C–O torsion angles being *gauche*-, with the values 66.1(6)–67.8(5)° and alternating in sign, and the C–C–O–C torsion angles *anti*-, 173.7(4)–179.5(5)°. The hexafluorosilicate anion has a geometry of a distorted octahedron with the Si–F distances 1.625(7)–1.685(4) Å and F–Si–F angles close to 90° and 180 degrees. As previously mentioned [1–2], the longest S–F(4) distance corresponds to the strongest NH···F hydrogen bond.

It should be noted that the title complex has been obtained under conditions very similar to those used for the preparation of $[(BF_3\cdot NH_3)\cdot 18C6]$ [5]. The differences observed for the final products in the systems $SiF_4\cdot 2NH_3$–18C6–H_2O and $BF_3\cdot NH_3$–18C6–H_2O reflect the higher stability to hydrolysis of the compound $BF_3\cdot H_2O$ (recrystallisation from warm solution) in contrast to its silicon analogue, for which the hydrolysis is described by the scheme below [16]:

$$3(SiF_4\cdot 2NH_3) + 2H_2O = 2(NH_4)_2SiF_6 + SiO_2 + 2NH_3.$$

So instead of the expected complex binding with the neutral molecule we have obtained the associate uniting both the neutral and charged species. The presence of the crown ether in the system $SiF_4\cdot 2NH_3$–18C6–H_2O stimulates the development of (1) due to the efficient tripodal binding of the ammonium cations. Attempts to obtain the final complex by the forward synthesis in the system $(NH_4)_2SiF_6$–18C6–H_2O failed.

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