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Layered polyhydrate 18-crown-6·$C_3H_7NH_3F$·10H_2O

Konstantin A. Udachin*[a] and Janusz Lipkowski[b]

[a] *Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 3832 355 960; e-mail: kuku@che.nsk.su*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, 01 224 Warsaw, Poland. Fax: +4822 325 276; e-mail: klatrat@alfa.ichf.edu.pl*

New polyhydrate 18-crown-6·$C_3H_7NH_3F$·10H_2O which melts incongruently at −0.8 °C has been found in the 18-crown-6–$C_3H_7NH_3F$–H_2O system; a single crystal X-ray structure of this layered hydrate is reported, in which layers of water molecules and fluoride anions are made up of tetra-, penta- and heptagons and also contain vacant polyhedral cavities; the crown ether complexes with cations $C_3H_7NH_3{}^+$ are situated between water–fluoride layers and do not form hydrogen bonds with the molecules of the layers.

Among numerous framework water structures there are quite a few in which water forms cavities. This is typical of gas hydrates[1,2] and many similar clathrate compounds of peralkylammonium salts and their analogues.[2,3] However, it was only recently that we found a channel structure hydrate with vacant polyhedral cavities.[4] Therefore, a layered hydrate with polyhedral cavities of molecular size is not common and of particular interest. We found it while studying the hydrate formation of crown ethers and complexes. This paper discusses the layered polyhydrate found in 18-crown-6–$C_3H_7NH_3F$–H_2O.

Figure 1 shows a section of the tertiary system 18-crown-6–$C_3H_7NH_3F$–H_2O with a constant molar ratio of 18-crown-6 and $C_3H_7NH_3F$ of 1:1 and variable water content. It is seen from the figure that in the studied interval of the phase diagram a hydrate forms of composition 18-crown-6·$C_3H_7NH_3F$·10H_2O which melts incongruently at −0.8 °C. The hydrate crystals exist in equilibrium with an aqueous solution in a very narrow temperature and concentration range. At −0.8 °C the hydrate melts, forming a solution of composition 18-crown-6·$C_3H_7NH_3F$·12.8H_2O and a hydrate containing less water than the initial one. Analysis of the hydrate crystals for water content by Fischer's technique[5] gave the composition 18-crown-6·$C_3H_7NH_3F$·10.05(6)H_2O (in brackets we give the standard deviation for five independent measurements). Using the phase diagram data, we grew single crystals of this hydrate, from water solutions, of composition 18-crown-6·$C_3H_7NH_3F$·12H_2O at −5 °C. Under these conditions the solid and liquid phases were present in approximately the same proportions, which favoured the growth and selection of single crystals. The solutions were rapidly cooled until crystallization began; the temperature was then increased to −5 °C. The solution with crystals was then kept at this temperature for several days; the temperature was regularly increased to above the melting point of the crystals for several minutes which resulted in the melting of some crystals. Subsequently the temperature was decreased to −5 °C. The single crystals obtained in this way had clear-cut faces and looked like needles with square cross-sections.

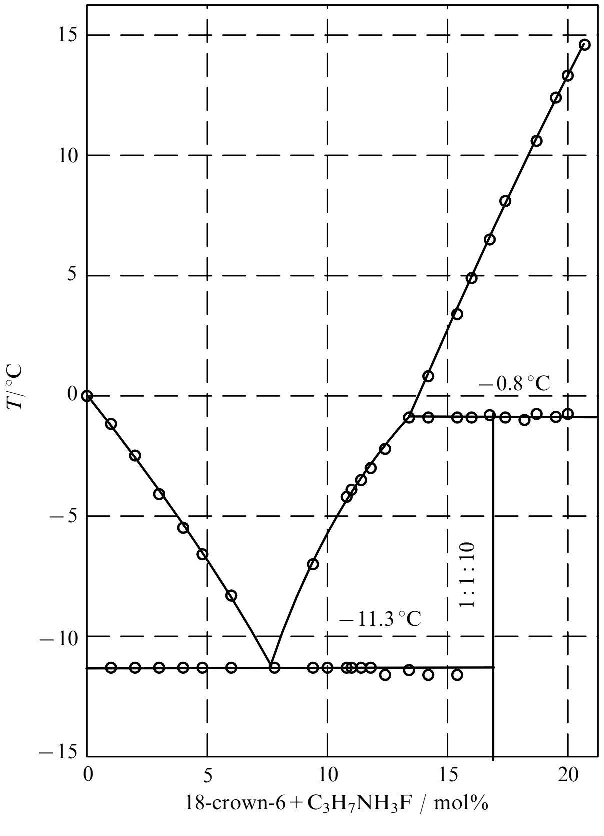

Figure 1 Section of the tertiary system 18-crown-6–$C_3H_7NH_3F$–H_2O with constant molar ratio of 18-crown-6 to $C_3H_7NH_3F$ of 1 : 1 and variable water content.

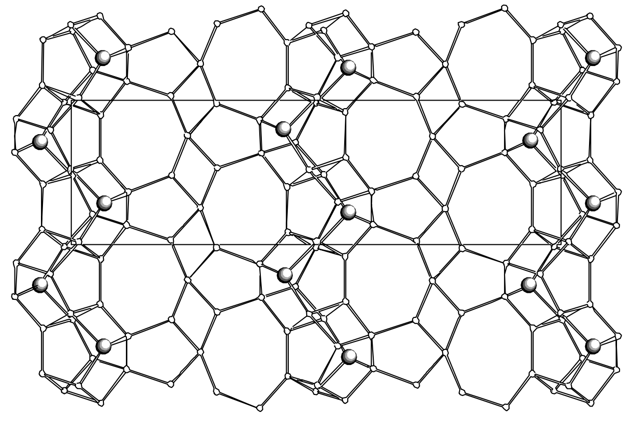

Figure 2 Water–fluoride layer of the 18-crown-6·$C_3H_7NH_3F$·$10H_2O$ hydrate with cavities 4^45^4 as viewed approximately along the *z* axis (hydrogen atoms are omitted; fluoride ions are marked as large balls).

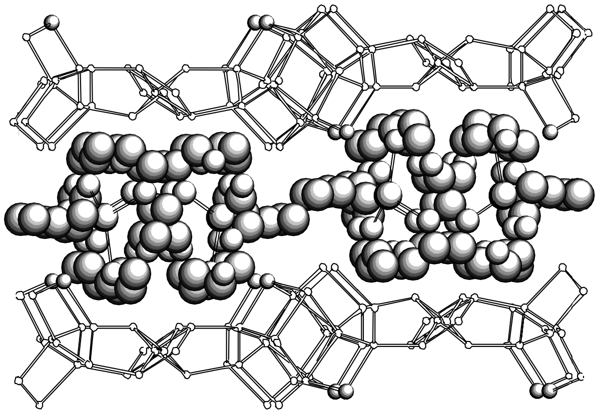

Figure 3 Plot of the arrangement of the crown ether complexes and water–fluoride layers in the 18-crown-6·$C_3H_7NH_3F$·$10H_2O$ hydrate, viewed approximately along the *y* axis (hydrogen atoms are omitted; fluoride ions in the water–anion layers are marked as large balls).

A single crystal of the hydrate ($0.2 \times 0.2 \times 0.8$ mm) was placed in a thin-walled glass capillary and analysed by X-ray crystallography. We carried out this analysis on a Cad-4 diffractometer, using CuKα radiation and a graphite monochromator. The unit cell of the studied polyhydrate has the following parameters: $a = 8.408(2)$, $b = 24.446(5)$, $c = 28.566(6)$ Å, ($T = -100\,^\circ$C), the space group is *Pbca*, $Z = 8$, $\rho_{calc} = 1.185$ g cm^{-3}. Solvation and refinement of the structure was carried out with the help of the programs SHELX-86 and SHELX-93.[6,7] For 1200 [$I > 4\sigma(I)$] observed reflections the structure was refined to $R = 0.11$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the crown ether and the cation $C_3H_7NH_3{}^+$ were placed in calculated positions and those associated with the H_2O molecules were located on a difference Fourier map.

The polyhydrate 18-crown-6·$C_3H_7NH_3F$·$10H_2O$ is a layered structure. Water molecules and fluoride anions connect with each other *via* hydrogen bonds, forming tetra-, penta- and heptagons which in turn make up layers (Figure 2). Crown ether complexes with the cation $C_3H_7NH_3{}^+$ located between the water – fluoride layers are not connected with them through hydrogen bonds (Figure 3). The shortest distance $O \cdots O_w$ is equal to 3.97 A, and with $C \cdots O_w$, it is 3.35 A. Crown ether molecules form hydrogen bonds between the atoms O-1, O-7 and O-13 and the NH_3 group of the cation $C_3H_7NH_3{}^+$ (the lengths of the $N \cdots O$ bonds are 2.84–2.88 A) while the remaining oxygen atoms O-4, O-10 and O-16 of the crown ether are not involved in the formation of hydrogen bonds. In this case the crown ether assumes the D_{3d} conformation.

Water molecules and fluoride ions build a water–fluoride layer in which the fluoride anions are statistically disordered and are at a distance of 4.53 A from the nitrogen atom of the $C_3H_7NH_3{}^+$cation. The lengths of the hydrogen bonds $O_w \cdots O_w$ vary from 2.52 to 2.90 A, and the angles $O_w \cdots O_w \cdots O_w$ between the hydrogen bonds in the water–fluoride framework vary from 78.3 to 141.4°. Thus, the requirements of the tetrahedral arrangement of the hydrogen bonds in water molecules are not met sufficiently. This and the presence of the vacant cavities account for the relatively low melting point of the polyhydrate 18-crown-6·$C_3H_7NH_3F$·$10H_2O$.

The water–fluoride layer is not monomolecular. It has the polyhedral cavities 4^45^4 previously observed in the hydrates *tert*-$C_4H_9NH_2$·$9.75H_2O$[8] and (*iso*-C_5H_{11})$_4$NF·$27H_2O$.[9] The descriptor 4^45^4 means that the cavity is a polyhedra, constructed from four quadrilaterals and four pentagons. As is the case with other polyhydrates the cavities we found in the polyhydrate are vacant. The free inner diameter of this type of cavity is rather short (3.10 A), and they can accommodate only small molecules such as He. Earlier, by the example of cubic structure II clathrate hydrates, we showed that He atoms were able to stabilize clathrate structures, acting as auxiliary components.[10] The cavity 4^45^4 is more suitable for the inclusion of He molecules since it fits the size of He guest molecule better.

In conclusion it should be mentioned that this is the first time that a layered polyhydrate with polyhedral cavities has been found.

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