Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1995, **5(6)**, 237–238

Mendeleev Communications

Polyhydrate 1,10-Diaza-18-crown-6·8.25H_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 355960; e-mail: kuku@che.nsk.su*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, 01 224 Warsaw, Poland. Fax: +48 22 325276; e-mail: klatrat@alfa.ichf.edu.pl*

The phase diagram of the system 1,10-diaza-18-crown-6–H_2O has been studied; polyhydrate 1,10-diaza-18-crown-6·8.25H_2O, which melts incongruently at 16.0 °C, has been found in this system. Each cavity of the three-dimensional framework made of water molecules accommodates four molecules of crown ether; the hydrate has the following crystallographic parameters: a = 18.848(2), c = 13.159(2) Å ($T = -100$ °C), space group $P4_2/n$ and Z = 8.

Crystals of crown ether complexes, obtained from solutions containing water, are often hydrates. As a rule in these hydrates there are from one to two water molecules per one crown ether molecule.[1,2] Water is included in the crown ether cavity either as an ion H_3O^+ [3,4] or as an individual molecule.[5,6] Water can be present as a molecule outside the crown ether cavity, forming a hydrogen bond with the ligand,[7] or as chains of water molecules connected by hydrogen bonds.[8] Clearly, the amount of water in such hydrates is not sufficient for the construction of water frameworks, which is why the formation of clathrate hydrates does not occur. Only one polyhydrate of the crown ether 1,10-diaza-18-crown-6 with glycylglycine having a layered structure has so far been observed.[9] However, no one has ever observed polyhydrates of crown ethers. We decided to study the phase diagram of the system 1,10-diaza-18-crown-6–H_2O in the hope of finding hydrates of the clathrate type.

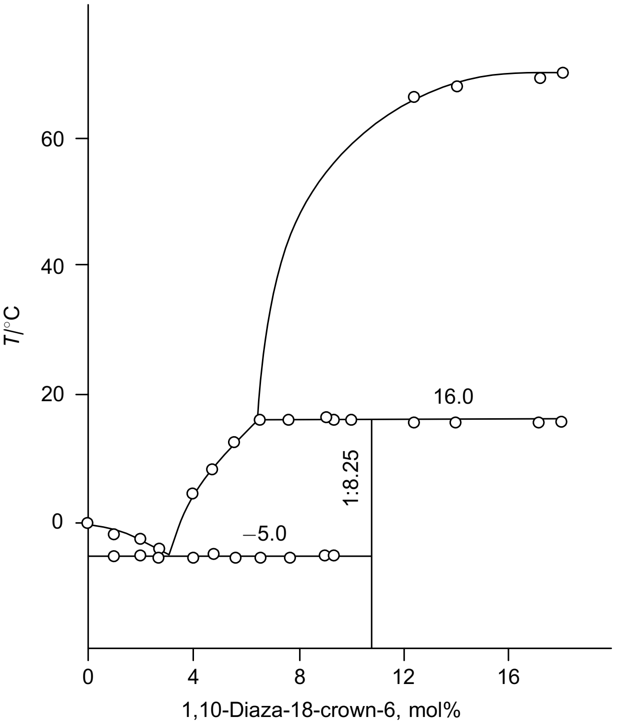

Figure 1 Phase diagram for the system 1,10-diaza-18-crown-6–H_2O.

The phase diagram was studied using the differential thermal analysis (DTA) technique and the hydrate 1,10-diaza-18-crown-6·8.25H_2O melting incongruently at 16 °C was obtained. At this temperature the hydrate decomposes reversibly into the solid dihydrate 1,10-diaza-18-crown-6·2H_2O and an aqueous solution of composition 1,10-diaza-18-crown-6·14.4H_2O (Figure 1). The hydrate exists over a very narrow temperature and concentration range: from −5 to 16 °C and from 3.2 to 10 mol% of crown ether, respectively. Using the phase diagram data we grew single crystals of this hydrate from water solutions containing 7 mol% of 1,10-diaza-18-crown-6 at 0 °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. After a day transparent well-edged rectangular prisms of the hydrate 1,10-diaza-18-crown-6·8.25H_2O had formed from the solution. Analysis of the hydrate for water content by Fisher's technique resulted in the composition 1,10-diaza-18-crown-6·8.27(4)H_2O (in parentheses we give the standard deviation for six independent measurements). The hydrate

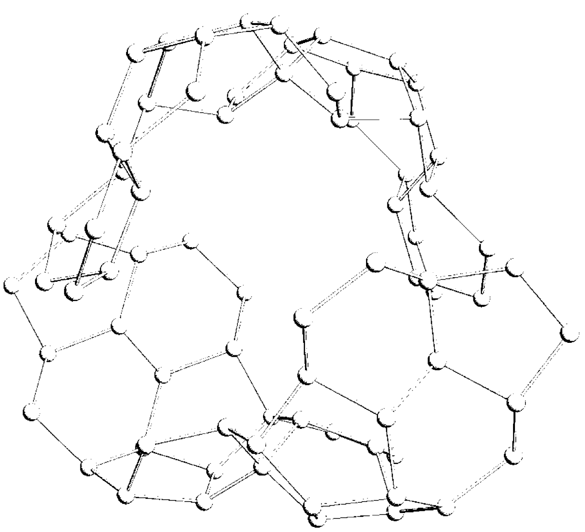

Figure 2 Cavity in the water framework of the hydrate 1,10-diaza-18-crown-6·8.25H$_2$O as viewed approximately along the *x* axis. (Hydrogen atoms are omitted).

single crystal was placed into a thin-wall glass capillary and analysed by the X-ray technique. We carried out the experiment on a Cad-4 diffractometer, using CuK$_\alpha$ radiation and a graphite monochromator. The unit cell of the hydrate studied had the following parameters: $a = 18.848(2)$, $c = 13.159(2)$ A ($T = -100\,^\circ$C), space group $P4_2/n$ and $Z = 8$. Solvation and refinement of the structure was carried out with the help of the programs SHELXS86 and SHELXS76.[10,11] For 2485 [$I > 3\sigma(I)$] observed (4909 total) reflections the structure was refined to $R = 0.053$ ($R_w = 0.048$). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the crown ether were placed in calculated positions and those associated with the H$_2$O molecules were located on a difference Fourier map.

The compound we studied is a polyhydrate which can be classified with the clathrates. The crown ether polyhydrate is similar to the hydrates of amines in that it has directed (hydrogen) bonds between the guest and the host molecules.[12,13] The latter were named by Jeffrey[14] semi-clathrates to distinguish them from the classic gas hydrates[15] in which between the guest and the host molecules there is only van der Waals interaction. The host in the hydrate 1,10-diaza-18-crown-6·8.25H$_2$O forms a three-dimensional framework made up of pentagons and hexagons which in their turn consist of water molecules connected with hydrogen bonds. In this framework it is possible to distinguish cavities (Figure 2) each of which accommodates four crown ether molecules (Figure 3). The crown ether atoms N$_1$, O$_7$, N$_{10}$ and O$_{13}$ form hydrogen bonds with the water framework. These bonds (N...O$_w$ and O...O$_w$) are from 2.75 to 2.81 Å long, and the lengths of the hydrogen bonds in the water framework (O$_w$...O$_w$) are from 2.70 to 2.85 Å. The crown ether molecules do not take water into their cavities, but simultaneously interact with several water framework molecules. Thus, the crown ether molecule in the polyhydrate is a ring with a vacant cavity 2.8 Å in diameter rather than an ellipse with two methylene groups turned inward[16] as is the case with the free crown ether. All the oxygen and nitrogen atoms of the crown molecule are planar to 0.23 Å, and the oxygen atom of the water molecule nearest to the plane is 2.63 Å from the plane.

The water framework consists of pentagons and hexagons and has no square or heptagonal fragments. Thus, conditions are created for a favourable arrangement of the hydrogen bonds of the water molecules. The size of the angles between the hydrogen bonds (O$_w$...O$_w$) in the water framework varies from 99 to 120°. This explains the relatively high melting point of the hydrate, which would be still higher if the crystallization field of the hydrate were not overlapped by the crystallization field of the crown ether dihydrate.

Figure 3 Cavity filled with four crown ether molecules as viewed approximately along the *z* axis. (Hydrogen atoms are omitted).

In conclusion, it should be mentioned that the polyhydrate we found is the first clathrate with a crown ether as a guest that has ever been observed.

This work was partially supported by the International Science Foundation and the Russian Government (grant nos. NPZ000, NPZ300).

References

1 M. Dobler, J. D. Dunitz and P. Seiler, *Acta Crystallogr., Sect. B*, 1974, **30**, 2741.

2 O. Nagano, *Acta Crystallogr., Sect. B*, 1979, **35**, 465.

3 J. L. Atwood, P. C. Junk, M. T. May and K. D. Robinson, *J. Chem. Cryst.*, 1994, **24**, 243.

4 P. C. Junk and J. L. Atwood, *J. Chem. Cryst.*, 1994, **24**, 247.

5 I. Goldberg, *Acta Crystallogr., Sect. B*, 1978, **34**, 3387.

6 G. R. Newkome, H. C. R. Taylor, F. R. Fronczek, T. J. Delord, D. K. Kohli and F. Vogtle, *J. Am. Chem. Soc.*, 1981, **103**, 7376.

7 G. R. Newkome, F. R. Fronczek and D. K. Kohli, *Acta Crystallogr., Sect. B*, 1981, **37**, 2114.

8 J. L. Atwood, S. G. Bott, K. D. Robinson, E. J. Bishop and M. T. May, *J. Crystallogr. Spectr. Res.*, 1991, **21**, 459.

9 J. Lipkowski, O. V. Kulikov and W. Zielenkiewicz, *Supramolecular Chem.*, 1992, **1**, 73.

10 G. M. Sheldrick, *SHELXS86,* in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krueger and R. Goddard, Oxford University Press, 1985, p. 175.

11 G. M. Sheldrick, *SHELXS76, Program for Crystal Structure Determination*, University of Cambridge, England, 1976.

12 R. K. McMullan, T. H. Jordan and G. A. Jeffrey, *J. Chem. Phys.*, 1967, **47**, 1218.

13 C. S. Brickenkamp and D. Panke, *J. Chem. Phys.*, 1973, **58**, 5284.

14 G. A. Jeffrey, *Acc. Chem. Res.*, 1969, **2**, 344.

15 G. A. Jeffrey, in *Inclusion Compounds*, London, Acad. Press, 1984, vol. 1, p. 135.

16 E. Maverick, P. Seiler, W. B. Schweizer and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1980, **36**, 615.

Received: Moscow, 2nd June 1995
Cambridge, 25th July 1995; Com. 5/03646A