

Communications to the Editor

18-Crown-6 and Water: Crystal Structure of a Binary Hydrate^{1,2}

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18-Crown-6 is the prototype synthetic macrocyclic polyether and a prominent compound in supramolecular chemistry. It combines with a large variety of substances to form binary, ternary, and more intricately composed ionic and molecular complexes, and many of these have already been characterized by their crystal structure. Nevertheless, the present investigation is the first of this kind done on a *binary hydrate*, 18-crown-6·6H₂O. It lends itself to relevant comparisons with further experimental and computational studies of real and model states of the hydrated but otherwise uncomplexed crown molecule.

Evidence of a solid hydrate of 18-crown-6 was first obtained by Raman spectroscopy, followed by thermal analysis of the whole underlying binary system.³ Formation of the hydrate was confirmed in this laboratory (mp 24.6 °C), and the composition was found by crystal structure analysis⁴ to be that of a hexahydrate. The hydrogen-bonded formula unit around an inversion center of the space group is shown in Figure 1, and a larger part of the structure is shown in Figure 2.

The conformation of the macrocycle in the hydrate is fundamentally different from that of the solid crown ether by itself⁵ and has close to *D*_{3d} symmetry.⁶ This is in agreement with the Raman work referred to above. *D*_{3d} conformation of the hydrated crown ether has also been found by Raman spectroscopy⁷ and X-ray diffraction⁸ of aqueous solutions as well as by Monte Carlo and molecular dynamics simulations^{9,10} of the free molecule in an aqueous model environment.

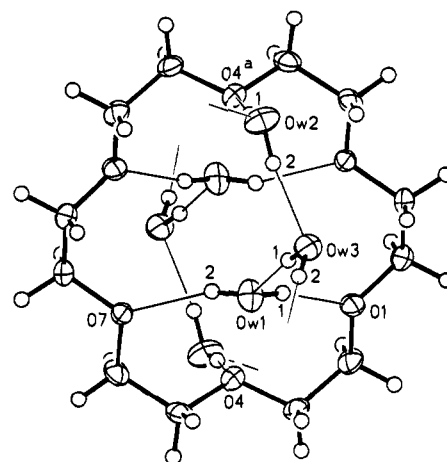


Figure 1. Atoms of one hydrogen-bonded formula unit, situated around a crystallographic inversion center. 50% ellipsoids are shown for the non-hydrogen atoms.

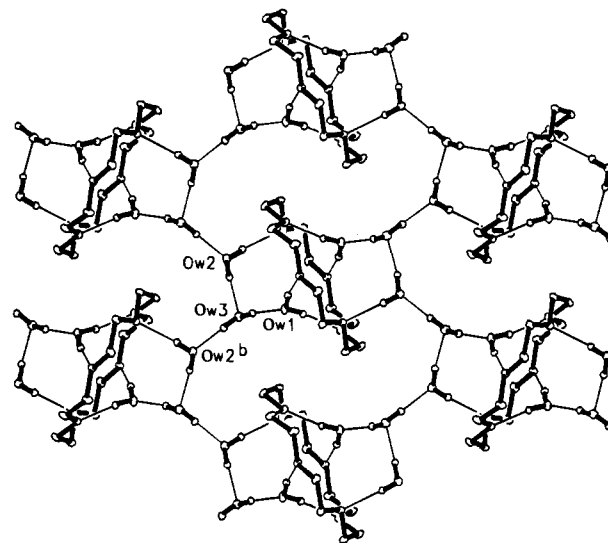


Figure 2. Hydrogen-bonded layer parallel (101). H atoms of crown molecules are omitted for clarity.

Another topical point for comparison is the geometry of hydration. In the hexahydrate, water molecule Ow1 donates a hydrogen bond each to crown ether atoms O1 and O7,¹¹ while water molecule Ow2 makes such a bond to the remaining independent ring O atom O4. This arrangement corresponds to what was found in one of the Monte Carlo simulations⁹ and was seen as an identical hydration¹⁰ in the crystal structure¹² of the *ternary* hexahydrate 18-crown-6·2H₃PO₄·6H₂O. However, in contrast to those patterns, Ow2 donates its second hydro-

(1) Dedicated to Dr. Richard K. McMullan on the occasion of his retirement from the Brookhaven National Laboratory.

(2) This is paper 12 of the series Hydrates of Weak and Strong Bases. For Paper 11, see: Mootz, D.; Rütter, H.; Wiskemann, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1509–1513.

(3) Matsuura, H.; Fukuhara, K.; Ikeda, K.; Tachikake, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1814–1816.

(4) Crystal growth from the melt in a thin-walled glass capillary (diameter = 0.3 mm), using a miniature zone-melting technique.¹³ Monoclinic, space group *P*2₁/*n*, *a* = 7.431(5) Å, *b* = 8.083(6) Å, *c* = 17.02(1) Å, β = 94.97(5)°, *V* = 1018(1) Å³ at –150 °C, *Z* = 2, *d*(calcd) = 1.40 mg mm^{–3}; Siemens-Stoe AED 2 diffractometer, graphite-monochromated Mo K α radiation (λ = 0.71073 Å), μ = 0.11 mm^{–1}, 2 θ (max) = 65°, 2366 independent reflections with $|F_o| \geq 4\sigma_F$; direct methods, 181 refined parameters, weighting by $w = 1/(\sigma_F^2 + 10^{-4}|F_o|^2)$, final *R*(*F*) = 0.043; computer program SHELXTL PLUS.¹⁴

(5) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta Crystallogr.* **1980**, *B36*, 615–620.

(6) Bond lengths and angles: C–O and C–C, 1.421–1.429 and 1.495–1.502 Å; C–O–C and C–C–O, 110.8–113.0 and 108.6–110.0°; esd = 0.002 Å and 0.1°. Dihedral angles (between –179.9 and 180.0°, absolute values): C–C–O–C and O–C–C–O, 167.5–178.8 and 68.6–73.3°.

(7) Fukuhara, K.; Ikeda, K.; Matsuura, H. *Spectrochim. Acta* **1994**, *50A*, 1619–1628 and references therein.

(8) Ozutsumi, K.; Natsuhara, M.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2807–2818.

(9) Ranghino, G.; Romano, S.; Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1985**, *107*, 7873–7877.

(10) Wipff, G.; Troxler, L. In *Computational Approaches in Supramolecular Chemistry*; Wipff, G., Ed.; Kluwer Acad. Publ.: The Netherlands, 1994; pp 319–348 and references therein.

(11) The intramolecular distance O1···O7, bridged by the water molecule Ow1, is distinctly shorter than the other two distances between second-nearest O atoms around the ring (4.639 Å vs 5.128 and 5.016 Å for O4···O1^a and O7···O4^a, esd = 0.002 Å). This appears to be a major factor for the small deviation of the ring from ideal *D*_{3d} symmetry.

(12) Norlander, E. H.; Burns, J. H. *Inorg. Chim. Acta* **1986**, *115*, 31–36. Another case in point is the crystal structure of the also *ternary* hexahydrate 18-crown-6-hydroquinone·6H₂O: Belamri, B.; Bavoux, C.; Thozet, A. *J. Inclusion Phenom.* **1990**, *8*, 383–388.

(13) Brodalla, D.; Mootz, D.; Boese, R.; Osswald, W. *J. Appl. Crystallogr.* **1985**, *18*, 316–319.

(14) SHELXTL PLUS, Structure Determination System, Revision 4.21/V; Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1990.

gen bond not to Ow1 but to the remaining independent water molecule Ow3, which then donates to Ow1 and to another Ow2.

The last-mentioned hydrogen bond links the centrosymmetrical formula unit of Figure 1 with neighboring ones in the layer of Figure 2, unlimited along the *a*- and *c*-axis directions. The overall distances of the hydrogen bonds are 2.710–2.752 Å between water molecules and 2.862–2.891 Å between a water molecule and a crown ether O atom (esd = 0.003 Å).

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Note Added in Proof: A reviewer drew our attention to a study of polyhydrates of crown ethers by K. A. Udachin and J. Lipkowski, presented as a poster at a recent conference (8th

International Symposium on Molecular Recognition and Inclusion, Ottawa, ON, Canada, July 31–August 5, 1994). The short abstract contains, among others, a figure without H atoms showing the structures of a hexa- and a dodecahydrate of 18-crown-6. No crystallographic and geometric data are given, but the hexahydrate may well be the same as the one dealt with above.

Supplementary Material Available: Tables with atomic parameters and interatomic distances and angles for the title compound (4 pages); listings of observed and calculated structure factors for the title compound (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.