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THE X-RAY CRYSTAL STRUCTURE OF A 1:1 COMPLEX BETWEEN 1,3 1',3':4,6:4',6'-TETRA-O-METHYLENE--2,2':5,5'-BIS-O-OXYDIETHYLENEDI-D-MANNITOL AND WATER

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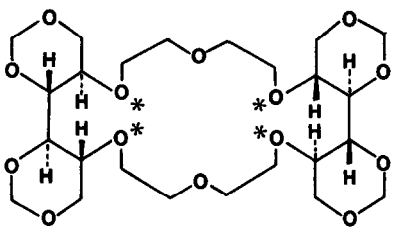
In the crystalline complex referred to in the title, the host molecule DD-1 has crystallographic C_2 symmetry with the hydrogen bonded guest water molecule straddling the two-fold axis.

Previously, we have reported on the preparation of the 22-crown-6 derivative DD-1 which incorporates *two* 1,3 4,6-di-*O*-methylene-D-mannitol residues into its constitution and commented on the extremely weak complexes it forms with RNH_3^+ ions in solution.[1] In view of recently acquired knowledge on the solid[2] and solution[3] state structures of some 1 1 complexes between organic cations of this type and 20-crown-6 derivatives incorporating either *one* 1,3.4,6-di-*O*-methylene-D-mannitol residue or *one* 1,3:4,6-di-*O*-benzylidene-D-mannitol residue, it is tempting to suggest that this observation reflects the reduced basicity[2,4] of the four macrocyclic oxygen atoms (O^*) directly bonded to the 1,3-dioxan rings in DD-1. Thus, it came as a surprise to us to learn that when DD-1 is recrystallised from 95% aqueous ethanol, a crystalline 1 1 complex with water can be isolated. Moreover, the *X*-ray structural analysis (Figure 1) of this complex reveals that in the crystalline state DD-1 adopts a conformation with C_2 symmetry and is hydrogen bonded through two of its O^* atoms to the C_2-symmetrically-located water molecule. It is also significant that DD-1 forms (O—H····O) hydrogen bonds with a water molecule whose oxygen atom does not act as an electron donor atom towards an electrophilic group somewhere else in the structure. In previously discussed[5-7] crystalline complexes between crown ethers and water molecules, *X*-ray crystallography has revealed that interactions involving the oxygen atom of the water molecule with electropositive centres possibly enhance the ability of the water molecule to form (O—H····O) hydrogen bonds to the crown ethers. This is the situation, for example,[5] in the case of (*i*) [Ba(picrate)$_2$.dibenzo-24-crown-8.H_2O],[6a] (*ii*) [monoaza-18-crown-6.HCl.H_2O],[6b] (*iii*) [3,3'-1,1'-(bi-2-naphthol).21-crown-5.H_2O],[6c] (*iv*) (*S*)-$PhCHMeNH_3ClO_4$.bis-(1,4 3,6-dianhydro-D-mannitolo)-30-crown-10.H_2O],[6d] and (*v*) [$(LiI)_2$.18,18'-spirobi-(19-crown-6).$4H_2O$].[6e] The nature and the orientation of the binding of the water molecule in the crystalline [DD-1.H_2O] complex suggests that DD-1 might be an ideal chiral host molecule for adduct formation[7] to transition and post-transition metal complexes containing aqua ligands.[8]

We are grateful to Dr. D.A Laidler for preparing the sample of DD-1 from which hydrated single crystals suitable for *X*-ray crystallography were obtained. Since this communication was submitted, an interesting publication[9] describing the 'encircling of water by crown compounds' has come to our attention.



DD-1

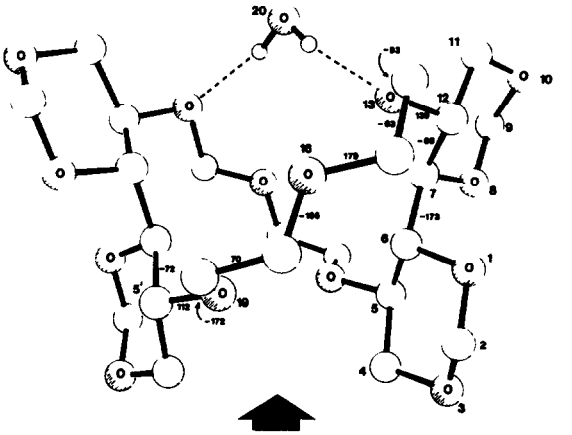


Figure 1. The *X*-ray crystal structure of DD-1. Crystals of DD-1-H_2O obtained from 95% aqueous ethanol are orthorhombic, space group $C222_1$, a = 9.917(1), b = 15.223(2), c = 18.678(4) Å, U = 2820 Å^3, Z = 4. Of the 1092 independent reflections ($\theta \leq 58^\circ$) measured on a diffractometer using Cu-K_α radiation, 30 were classified as unobserved. The structure was solved by direct methods and refined anisotropically to give a current R = 0.032. The molecule has crystallographic C_2 symmetry with the water molecule straddling the two-fold axis. The position of the water hydrogen atom was clearly resolved in a difference electron density map and was refined isotropically. Bond lengths (Å) in the polyether chains of DD-1 1.411(4), C(15)-O(16) to 1.423(3), O(19)-C(5') and 1.476(5), C(14)-C(15) to 1.527(4), C(7)-C(12) Bond angles (°) at O atoms 113.2(3), O(16) to 116 4(2), O(13). Torsional angles (°) (O-C-C-O and C-C-O-C) associated with the 22-membered ring are shown beside the relevant C-C and C-O bonds in the structure. Angle (°) between the mean planes of the dioxan rings (1/6) - (7/12), 77. Hydrogen bond distances, R[O·····O]Å, R[H· ·O]Å, angles (θ_O and θ_H°) between COC planes and (a) OO vector and (b) HO vector, O—H··· O angle (°) at the H atom [O(13) - O(20)], 2 82 [H—O(13)], 1.96, (a) 26.3, (b) 22.8, H, 163.

References and Footnotes

1. D.A. Laidler and J.F. Stoddart, *Tetrahedron Lett.*, 1979, 453.
2. S.E. Fuller, J F Stoddart, and D.J. Williams, to be published.
3. S.E. Fuller, B.E. Mann, and J.F. Stoddart, to be published.
4. T W. Bell, *J. Amer. Chem. Soc.*, 1981, 103, 1163.
5. For a review, see F. Vögtle, H. Sieger, and W M. Muller in Topics in Current Chemistry. Host Guest Complex Chemistry I (ed. F. Vögtle), Springer Verlag, Berlin, 1981, p. 107.
6. (a) D L. Hughes and J.N. Wingfield, *J.C.S. Chem. Comm.*, 1977, 804, (b) G.W. Gokel and B J. Garcia, *Tetrahedron Lett.*, 1977, 317, (c) I. Goldberg, *Acta Cryst.*, 1978, B34, 3387, (d) J C. Metcalfe, J.F. Stoddart, G. Jones, T.H. Crawshaw, E. Gavuzzo, and D.J. Williams, *J.C.S. Chem. Comm.*, 1981, 432, (e) M Czugler and E. Weber, *J.C.S. Chem. Comm.*, 1981, 472.
7. H M. Colquhoun and J.F. Stoddart, *J.C.S. Chem. Comm.*, 1981, 612, and references therein
8. A. Knöchel, J. Klimes, J. Oehler, and G. Rudolph, *Inorg. Nucl. Chem. Lett.*, 1975, 11, 787, A. Knöchel, J. Kopf, J Oehler, G. Rudolph, *Inorg. Nucl. Chem. Lett.*, 1978, 14, 61, P.G. Eller and R.A. Penneman, *Inorg. Chem.*, 1976, 15, 2439, P. Charpin, R.M. Costes, G. Folcher, P. Plurien, A. Navaza, and C. de Rango, *Inorg. Nucl. Chem. Lett.*, 1977, 13, 341, G. Bombieri, G. de Paoli, A. Cassol, and A. Immitzi, *Inorg. Chim. Acta*, 1976, 18, L23, *J. Inorg. Nucl. Chem.*, 1978, 40, 799, T B. Vance, E.M Holt, C.C. Pierpont, and S.L. Holt, *Acta Cryst.*, 1980, 36B, 150, T.B. Vance, E.M. Holt, D.L. Varie, and S.L. Holt, *Acta Cryst.*, 1980, 36B, 153
9. G.R. Newkome, H.C R. Taylor, F.R Fronczek, T.J. Delord, D.K. Kohli, and F. Vögtle, *J. Amer. Chem. Soc.*, 1981, 103, 7376.

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