

Crystal Structure of the 1 : 1 : 6 Complex between 18-crown-6, Hydroquinone and Water

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Abstract. Hydroquinone forms a 1 : 1 : 6 complex with 18-crown-6 and water. Crystals of this complex are monoclinic, space group $P2_1/a$ with $a = 14.289(1)$, $b = 7.972(1)$, $c = 11.596(1)$ Å, $\beta = 97.72(1)^\circ$, $Z = 2$, $D_c = 1.22$ g cm⁻³. The hydroquinone and crown ether molecules lie on centres of symmetry with the crown in the D_{3d} conformation. The water molecules act as a bridge between hydroquinone and the crown ether. The structure consists of molecules linked by a 3-dimensional network of hydrogen bonds: the hydroquinone and two water molecules lie roughly in the (001) plane; the crown ether and four water molecules form bipyramidal structures which are stacked in layers alternating with the previous planes.

Key words. crown ether, hydroquinone, complexation, crystal structures, hydrogen bonding.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. Sup 82080 (16 pages).

1. Introduction

In order to obtain molecules of phenols in various surroundings and to study the variations of their reactivity with the modifications of their environment, we have complexed some of them with 18-crown-6 and published the corresponding crystal structures [1–3].

A variety of complexes between 18-crown-6 (as host) and small neutral molecules (as guest) has been synthesized and among them are compounds in which the guest has one or two phenolic functional groups [4–7]. The participation of water molecules is a striking feature in these compounds: a hydrogen bond links the phenolic hydrogen with the oxygen of the water molecule and the hydrogens of the water molecule are bonded with the crown ether; thus the water molecule bridges the host and the guest.

Herein we present another complex in which the guest molecule has two phenolic groups. A specific feature of this compound is the high number of water molecules compared with the number of host and guest molecules. Trying to correlate this feature with characteristics of the structure is one purpose of this work.

2. Experimental

The complex was obtained by dissolution in acetone of 18-crown-6 and hydroquinone in stoichiometric amounts and slow evaporation of the solution at room temperature. The resulting crystals are colorless thin plates.

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The crystal suitable for the X-ray experiment was a fragment of dimensions $0.1 \times 0.1 \times 0.2$ mm cut from a larger crystal and sealed in a glass capillary. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator. Crystal data are: $\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot \text{C}_6\text{H}_6\text{O}_2 \cdot 6 \text{H}_2\text{O}$, formula weight: 482.52, monoclinic, $P2_1/a$, $a = 14.289(1)$, $b = 7.972(1)$, $c = 11.596(1) \text{ \AA}$, $\beta = 97.72(1)^\circ$, $Z = 2$, $D_c = 1.22 \text{ g cm}^{-3}$, $\mu = 8.11 \text{ cm}^{-1}$, $T = 295 \text{ K}$, lattice parameters from least squares fit with 25 reflections. Two standard reflections were measured, one every 60 min to monitor the intensity and one every 100 reflections to control the orientation of the crystal. 2515 reflections measured $1 < \theta < 73^\circ$, 2262 reflections observed with $I > 3\sigma(I)$. Data reduction included Lorentz and polarisation corrections but no absorption effect.

The structure was solved by direct methods and refined by full matrix least squares based upon F with unit weight using SHELX [8]. Non-hydrogen atoms were refined anisotropically, H atoms were located in a difference Fourier map and refined isotropically. The residual electron density was within -0.07 and $+0.08 e \text{ \AA}^{-3}$. $(\Delta/\sigma)_{av} = 0.02$. $R = 0.067$ for the 2262 observed reflections. The goodness of fit was 0.61. Table I gives the final atomic coordinates and B_{eq} . (numbering scheme in Figure 1), for non hydrogen atoms.

3. Discussion

The asymmetric unit of the title compound contains half a crown ether, half a hydroquinone and three water molecules, the crown ether and the hydroquinone molecules each residing around a centre of inversion. Bond distances, angles and torsion angles are given in Table II.

Distances and angles in the hydroquinone molecule are similar to those found when it is uncomplexed [9] except for the O(10)—C(10) distance which is $1.373(3) \text{ \AA}$ in this compound and $1.393(2) \text{ \AA}$ in the uncomplexed molecule.

The shortening of the C—O bond in a phenol when it participates in a complex with 18-crown-6 has been observed for other molecules: 2-isopropyl-3-methyl phenol ($1.374(3)$ and $1.403(3) \text{ \AA}$) [10, 3]; 2,4-dinitrophenol ($1.330(4)$ and $1.343(5) \text{ \AA}$) [5, 11, 12]; 3,5-dichlorophenol ($1.35(2)$ and $1.371(6) \text{ \AA}$) [1, 13]. It may be due to the modification of the environment of the phenolic group and the variations of the strength of the hydrogen bonds, and it has often been correlated with the pK values [12].

The 18-crown-6 molecule exhibits an approximate D_{3d} symmetry which is often observed when it is complexed. Average distances (C—O: $1.42(1) \text{ \AA}$; C—C: $1.48(2) \text{ \AA}$) and angles (C—O—C: $113(1)^\circ$; C—C—O: $109.6(5)^\circ$) are also similar to those found in other 18-crown-6 complexes.

Three water molecules W_1 , W_2 and W_3 participate in the compound and their geometry corresponds to the expected values.

Figure 2 represents a view of the crystal structure drawn by PLUTO [14]. It can be described as planes of hydroquinone and W_1 water molecules connected with alternating layers of 18-crown-6, W_2 and W_3 water molecules.

The hydroquinone molecule belongs approximately to the (001) plane (angle of 14° between its mean plane and (001)). The water molecule W_1 is at a short distance

Table I. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with esd.s in parentheses
$$B_{\text{eq}} = 4/3 \sum_i \beta_{ij} a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
O(1)	4590(1)	2321(2)	2953(1)	4.53(5)
C(2)	3609(2)	2276(4)	2581(3)	5.46(9)
C(3)	3293(2)	489(5)	2398(2)	5.69(9)
O(4)	3350(1)	-323(2)	3495(1)	4.48(4)
C(5)	3097(2)	-2074(4)	3380(3)	5.58(9)
C(6)	3097(2)	-2832(4)	4542(3)	5.48(9)
O(7)	4031(1)	-3008(2)	5098(2)	4.51(5)
C(8)	4069(2)	-3834(4)	6203(4)	5.55(9)
C(9)	5057(2)	-3950(3)	6750(3)	5.38(10)
O(10)	3381(1)	-3247(2)	10290(2)	5.32(6)
C(10)	4178(2)	-4137(3)	10139(2)	3.70(6)
C(20)	4142(2)	-5819(3)	9818(2)	3.90(7)
C(60)	5037(2)	-3330(3)	10311(2)	4.10(7)
O(100)	3102(2)	1(2)	9381(2)	5.85(6)
O(200)	4211(2)	1663(3)	5478(2)	4.91(5)
O(300)	4103(2)	154(3)	7575(2)	7.35(8)

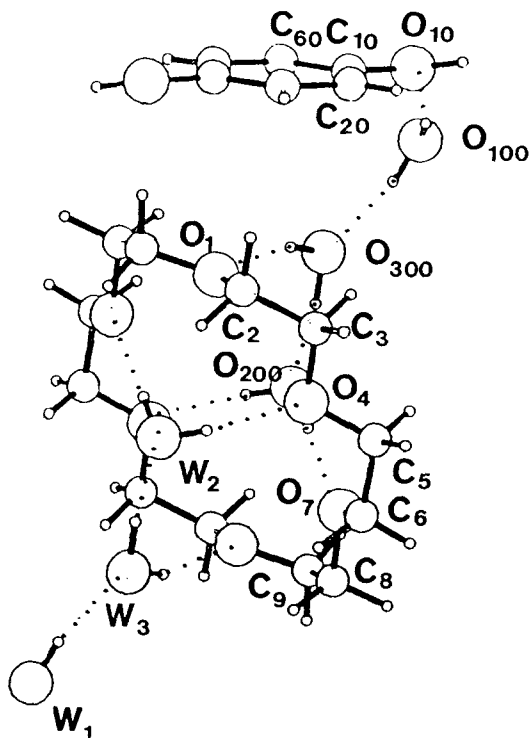


Fig. 1. Numbering scheme.

Table II. Bond distances (Å) angles (deg) and torsion angles (deg)

Atoms	Distance	Atoms	Distance
O(10)—C(10)	1.373(3)	O(4)—C(5)	1.443(3)
C(10)—C(20)	1.391(3)	C(5)—C(6)	1.477(5)
C(10)—C(60)	1.376(3)	C(6)—O(7)	1.408(3)
C(20)—C(60)	1.381(4)	O(7)—C(8)	1.435(4)
O(1)—C(2)	1.410(3)	C(8)—C(9)	1.471(5)
C(2)—C(3)	1.501(5)	C(9)—O(1)	1.419(3)
C(3)—O(4)	1.419(3)		

Atoms	Angles	Atoms	Angles
O(10)—C(10)—C(20)	122.1(3)	C(3)—C(4)—C(5)	112.0(2)
O(10)—C(10)—C(60)	118.6(2)	O(4)—C(5)—C(6)	110.0(2)
C(20)—C(10)—C(60)	119.3(3)	C(5)—C(6)—O(7)	110.1(3)
C(10)—C(20)—C(60)	120.1(2)	C(6)—O(7)—C(8)	112.0(2)
C(10)—C(60)—C(20)	120.6(2)	O(7)—C(8)—C(9)	109.5(3)
O(1)—C(2)—C(3)	109.6(3)	C(8)—C(9)—O(1)	109.6(2)
C(2)—C(3)—O(4)	109.1(2)	C(9)—O(1)—C(2)	113.8(2)

Atoms	Angles
O(1)—C(2)—C(3)—O(4)	69.8(3)
C(2)—C(3)—O(4)—C(5)	-177.3(3)
C(3)—O(4)—C(5)—C(6)	-175.8(3)
O(4)—C(5)—C(6)—O(7)	-71.9(3)
C(5)—C(6)—O(7)—C(8)	-176.5(3)
C(6)—O(7)—C(8)—C(9)	-178.9(3)
O(7)—C(8)—C(9)—O(1)	69.8(3)
C(8)—C(9)—O(1)—C(2)	-171.2(2)
C(9)—O(1)—C(2)—C(3)	174.6(2)

Table III. Geometry of the hydrogen bonds

Connected molecules	Donor O—H	Acceptor O	Distance O...O(Å)	Distance H...O(Å)	Angle O—H...O(°)
C ₆ H ₆ O ₂ -W ₁	O(10)—H(10)	O(100)	2.61	1.68	164
C ₆ H ₆ O ₂ -W ₁	O(100)—H(102)	O(10)	2.80	2.00	164
18-crown-6-W ₂	O(200)—H(201)	O(7)	2.89	2.02	167
18-crown-6-W ₂	O(200)—H(202)	O(4)	2.92	1.98	178
18-crown-6-W ₃	O(300)—H(301)	O(1)	2.84	1.85	156
W ₂ -W ₃	O(300)—H(302)	O(200)	2.74	1.74	179
W ₁ -W ₃	O(100)—H(101)	O(300)	2.69	1.81	168

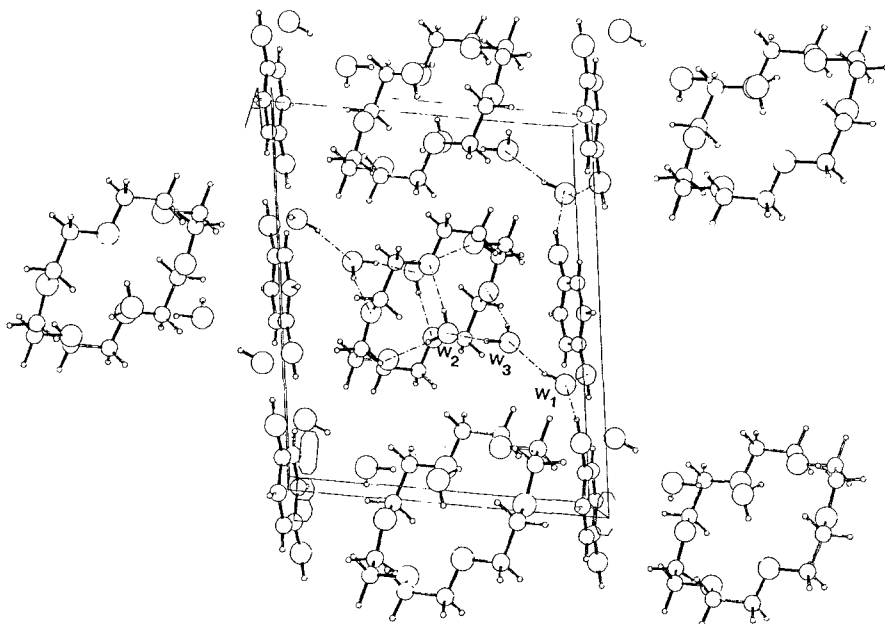


Fig. 2. View of the crystal structure drawn by PLUTO.

(0.21 Å) from this plane. These two molecules are linked by hydrogen bonds which form a 2-dimensional network roughly in the (001) plane; their geometry is described in Table III.

The crown ether molecule, the W_2 and W_3 water molecules and their symmetry related form constitute a bipyramidal structure in which 18-crown-6 is the base, W_3 the top, and W_2 bridges the two previous molecules. These molecules are linked by hydrogen bonds; the bonding scheme is described in Table III. These assemblies are stacked and form layers parallel to the (001) plane.

The planes alternate with the layers; both are connected by hydrogen bonds between W_1 and W_3 . Thus the hydrogen bonds form a three dimensional network.

Bonding between guest and 18-crown-6 via water molecules leads to the stabilization of the structure [15]. In other similar compounds, one molecule of water bridges the host and the guest molecule; but in the title compound three water molecules are connected to each other and thus involved in the bonding of hydroquinone with 18-crown-6.

The analysis of the values describing the geometry of hydrogen bonds shows that the link is weak when it connects 18-crown-6 and water ($O\cdots O$ values within 2.84 and 2.92 Å) and strong when it connects the phenolic hydrogen of the guest and water ($O\cdots O = 2.61$ Å). The same situation is observed in the other compounds [2-7].

A 3-dimensional network of hydrogen bonded molecules is rather unusual for such compounds. Most often they exhibit the formation of supramolecular entities separated from the neighbouring ones by van der Waals contacts. An example

similar to the title compound is the 1 : 5 adduct of 18-crown-6 with urea [16] where layers of urea molecules (three out of five) are linked via other urea molecules (two out of five) with layers of 18-crown-6 molecules.

The usual stoichiometry (1 host, 1 guest, 1 water or 1 host, 2 guest, 2 water) leads mostly to supramolecular entities. On the contrary the common feature of structures with 3-dimensional networks of bonds is the high number of guest or water molecules compared with the number of 18-crown-6 molecules e.g. the 1 : 4 adduct of 18-crown-6 with methyl 4-aminobenzoate [17] and the 1 : 2 : 6 adduct of 18-crown-6 with phosphoric acid and water [18].

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