A 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)–2,4-Dinitrophenol–Water (1:2:2) Complex, $C_{12}H_{24}O_6.2C_6H_4N_2O_5.2H_2O$

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Abstract. $M_r = 668.6$, triclinic, $P\bar{1}$, $a = 8.064$ (2), $b = 13.139$ (3), $c = 7.682$ (1) Å, $\alpha = 98.53$ (1), $\beta = 94.93$ (1), $\gamma = 99.73$ (2)°, $V = 788.2$ (3) Å^3, $Z = 1$, $D_x = 1.408$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 1.07$ mm^{-1}, $F(000) = 352$, $T = 293$ K. Final $R = 0.049$, for 1621 observed reflexions. The 18-crown-6 host molecule is situated on an inversion center and has pseudo-symmetry approximating D_{3d}. Two inversion-related water molecules each act as hydrogen-bond donors to two crown ether O atoms. Each water molecule accepts a hydrogen bond from the hydroxyl group of a guest 2,4-dinitrophenol molecule. Binding between host and guest is thus effected by bridging water molecules.

Introduction. There is considerable interest in the nature of host–guest interactions involving neutral organic molecules. The changes in conformation associated with weak intermolecular interactions such as those involving 'acidic' methyl or methylene groups (Goldberg, 1975; Bandy, Truter & Vögtle, 1981; Knochel, Kopf, Oehler & Rudolph, 1978; Watson, Galloy, Grossie, Vögtle & Müller, 1983) and the intervention of water molecules to form ternary complexes (Grossie, Watson, Vögtle & Müller, 1982) are of importance in model studies. As a continuation of these investigations we have studied the properties of the title ternary complex.

Experimental. Crystals sensitive to both X-rays and atmospheric water; best data set obtained from cube 0.27 × 0.22 × 0.25 mm cut from large crystal and coated with silicone grease. Lattice parameters by least-squares refinement of angular data for 15 reflexions with $5.6 < \theta < 13.3°$. 2147 independent reflexions

$[(\sin\theta/\lambda)_{max} = 0.546$ Å^{-1}; h,k,l range: 8, ±13, ±8] collected on a Syntex $P2_1$ four-circle diffractometer using Cu $K\alpha$ radiation, $\theta:2\theta$ scan mode with variable speed, range 3.91–29.30° min^{-1}. Intensity of check reflexion (001) decreased by 20% during 41 h data-collection period; intensities treated by point-to-point scaling based on check-reflexion intensities measured after every 15 reflexions. After Lp corrections, 1621 reflexions with $I > 3\sigma(I)$; absorption ignored. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Isotropic, followed by anisotropic blocked-matrix refinement for non-H atoms using XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Phenolic and hydrate H atoms located in difference Fourier syntheses and positions refined; all other H atoms included at calculated positions and constrained (C−H 1.08 Å) with fixed isotropic U in the range 0.050–0.075 Å^2. 217 parameters refined; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ (derived from counting statistics). $(\Delta/\sigma)_{max}$ in final cycle 0.30, $(\Delta/\sigma)_{av}$ 0.05; $R = 0.049$, $R_w = 0.061$, $S = 2.803$, no peaks higher than 0.18 e Å^{-3} in final difference synthesis.

Discussion. Table 1 gives the final atomic coordinates and U values and Table 2 lists bond lengths, angles and hydrogen-bond data.† The molecular complex is illustrated in Fig. 1. The macrocyclic ring has a conformation approximating D_{3d} symmetry; bond

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† Lists of H-atom coordinates, anisotropic thermal parameters, dihedral angles, equations of least-squares planes, non-bonded distances and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38998 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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lengths, bond angles and torsion angles agree with those reported for 18-crown-6 in related complexes (Grossie et al., 1982; Caira, Watson, Vögtle & Müller, 1984). The nitro groups and the aromatic ring of the guest 2,4-dinitrophenol are each planar within experimental error. Deviations from hexagonal symmetry in the benzene ring are similar to those observed in uncomplexed 2,4-dinitrophenol (Iwasaki & Kawano, 1977), but there are significant differences in bond lengths and angles in the region of the o-substituents (Table 3). In uncomplexed 2,4-dinitrophenol, the hydroxyl group is involved in a bifurcated hydrogen-bonding scheme, the principal O—H···O(nitro) bond being intramolecular. In the present case, the hydroxyl group participates in an intermolecular O—H···O(water) hydrogen bond only. The N(18)—O(19) bond length is about 5σ shorter than the mean of the other three N—O distances, the difference being the same as that observed in m-dinitrobenzene (Trotter & Williston, 1966). The bond lengths have not, however, been corrected for torsional oscillations of the —NO$_2$ groups about the C—N bonds, a characteristic feature of nitroaromatics (Trueblood, Goldish & Donohue, 1961; Trotter & Williston, 1966). Such motion is implied by the relatively high thermal parameters obtained for the O atoms in question.

The hydrogen bond O(11)—H(11)···O(10) is strong and almost linear while those between atom O(10) and the host atoms O(1) and O(7) are somewhat weaker (Table 2). Atom O(4) is only 3·056 (4) Å from hydrate atom O(10) and it appears to be involved in a strong interaction with phenyl atom H(17^i) [O(4)···H(17^i) 2·31 (4), O(4)···C(17^i) 3·281 (6) Å].

This structure is another example of a substrate (guest) molecule which binds to host sites through the mediation of water molecules. In 18-crown-6–4,4'-biphenyldiol.(H$_2$O)$_2$ (Grossie et al., 1982), a very similar hydrogen-bonding scheme occurs. It differs essentially in that the widely separated —OH groups in the 4,4'-biphenyldiol guest permit bridging of two macrocyclic ligands via hydrogen bonding to water molecules, whereas here the ternary complex is discrete.
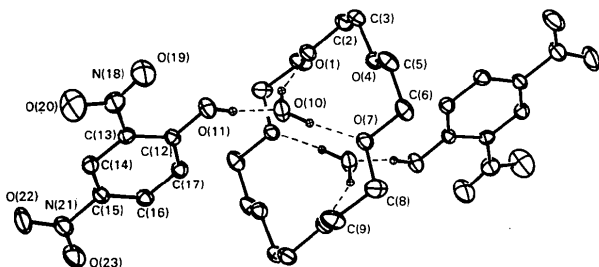

Fig. 1. *ORTEP* plot (Johnson, 1971) of the title complex. Thermal ellipsoids are drawn at the 20% probability level. For clarity, only the phenolic and hydrate H atoms are drawn, their numbering following that of their parent atoms. Principal hydrogen bonding is indicated by dashed lines.

Table 1. *Fractional atomic coordinates (non-H × 10^4, H × 10^3) and isotropic thermal parameters (Å^2 × 10^3) with e.s.d.'s in parentheses*

	x	y	z	$U_{eq}*/U_{iso}$
O(1)	583 (3)	1302 (2)	3312 (3)	61 (1)
C(2)	1737 (5)	2269 (3)	3437 (4)	70 (2)
C(3)	3319 (4)	2066 (3)	2692 (5)	67 (2)
O(4)	2921 (2)	1710 (2)	845 (3)	56 (1)
C(5)	4339 (4)	1479 (3)	−2 (5)	67 (2)
C(6)	3770 (4)	1037 (3)	−1892 (5)	69 (2)
O(7)	2670 (3)	56 (2)	−2000 (3)	58 (1)
C(8)	2177 (4)	−453 (3)	−3753 (5)	79 (2)
C(9)	1026 (5)	−1474 (3)	−3771 (5)	81 (2)
O(10)	1339 (4)	−541 (2)	1089 (4)	73 (2)
O(11)	2311 (3)	−2151 (2)	2019 (3)	64 (1)
C(12)	1126 (4)	−2998 (2)	1952 (4)	48 (2)
C(13)	1516 (4)	−3887 (2)	2598 (4)	50 (2)
C(14)	289 (4)	−4755 (2)	2597 (4)	56 (2)
C(15)	−1339 (4)	−4746 (2)	1922 (4)	54 (2)
C(16)	−1782 (4)	−3900 (2)	1238 (4)	54 (2)
C(17)	−548 (4)	−3032 (2)	1277 (4)	52 (2)
N(18)	3255 (4)	−3936 (3)	3283 (4)	77 (2)
O(19)	4349 (4)	−3207 (3)	3446 (5)	133 (2)
O(20)	3487 (4)	−4759 (3)	3699 (6)	153 (3)
N(21)	−2632 (4)	−5686 (2)	1872 (4)	76 (2)
O(22)	−2255 (4)	−6384 (2)	2620 (5)	112 (2)
O(23)	−4004 (4)	−5733 (2)	1064 (4)	109 (2)
H(10A)	107 (5)	−21 (3)	176 (5)	66
H(10B)	168 (4)	−40 (3)	19 (4)	66
H(11)	190 (4)	−163 (2)	164 (4)	55

* $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma]$.

Table 2. *Bond lengths (Å), bond angles (°) and hydrogen-bond data with e.s.d.'s in parentheses*

O(1)—C(2)	1·428 (4)	C(15)—C(16)	1·384 (4)
C(2)—C(3)	1·490 (5)	C(16)—C(17)	1·376 (4)
C(3)—O(4)	1·417 (4)	C(17)—C(12)	1·395 (5)
O(4)—C(5)	1·418 (4)	C(13)—N(18)	1·470 (5)
C(5)—C(6)	1·484 (5)	C(15)—N(21)	1·469 (4)
C(6)—O(7)	1·423 (4)	C(12)—O(11)	1·330 (4)
O(7)—C(8)	1·404 (4)	N(18)—O(19)	1·171 (5)
C(8)—C(9)	1·494 (5)	N(18)—O(20)	1·211 (6)
C(9)—O(1^i)	1·419 (5)	N(21)—O(22)	1·218 (5)
		N(21)—O(23)	1·209 (4)
C(12)—C(13)	1·407 (4)	O(11)—H(11)	0·88 (3)
C(13)—C(14)	1·378 (4)	O(10)—H(10A)	0·70 (4)
C(14)—C(15)	1·372 (5)	O(10)—H(10B)	0·80 (3)

C(9^i)—O(1)—C(2)	111·1 (3)	C(16)—C(17)—C(12)	121·6 (3)
O(1)—C(2)—C(3)	109·4 (3)	O(11)—C(12)—C(13)	120·8 (3)
C(2)—C(3)—O(4)	108·1 (2)	O(11)—C(12)—C(17)	121·6 (3)
C(3)—O(4)—C(5)	113·0 (2)	C(12)—C(13)—N(18)	121·5 (3)
O(4)—C(5)—C(6)	108·9 (3)	C(14)—C(13)—N(18)	117·1 (3)
C(5)—C(6)—O(7)	109·1 (3)	C(14)—C(15)—N(21)	118·3 (3)
C(6)—O(7)—C(8)	112·6 (3)	C(16)—C(15)—N(21)	119·4 (3)
O(7)—C(8)—C(9)	109·9 (3)	C(13)—N(18)—O(19)	121·3 (4)
C(8)—C(9)—O(1^i)	110·3 (3)	C(13)—N(18)—O(20)	116·7 (3)
		O(19)—N(18)—O(20)	122·0 (4)
C(17)—C(12)—C(13)	117·6 (3)	C(15)—N(21)—O(22)	118·3 (3)
C(12)—C(13)—C(14)	121·5 (3)	C(15)—N(21)—O(23)	118·2 (3)
C(13)—C(14)—C(15)	118·5 (3)	O(22)—N(21)—O(23)	123·5 (3)
C(14)—C(15)—C(16)	122·3 (3)	C(12)—O(11)—H(11)	112 (2)
C(15)—C(16)—C(17)	118·5 (3)	H(10A)—O(10)—H(10B)	128 (4)

O(11)···O(10)	2·552 (4) Å	O(11)—H(11)···O(10)	173 (4)°
H(11)···O(10)	1·67 (3)		
O(10)···O(1)	2·933 (4)	O(10)—H(10A)···O(1)	159 (4)
H(10A)···O(1)	2·27 (4)		
O(10)···O(7)	2·847 (4)	O(10)—H(10B)···O(7)	176 (4)
H(10B)···O(7)	2·05 (3)		

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Comparison of selected distances (Å), angles (°) and torsion angles (°) in complexed and uncomplexed 2,4-dinitrophenol*

Atomic nomenclature used is that of the present work.

	Title complex	2,4-Dinitrophenol (Iwasaki & Kawano, 1977)
N(18)–O(19)	1·171 (5)	1·240 (6)
O(11)···O(19)	2·596 (5)	2·615 (6)
O(11)–C(12)–C(13)	120·8 (3)	125·6 (4)
C(13)–N(18)–O(19)	121·3 (4)	117·9 (4)
C(13)–N(18)–O(20)	116·7 (3)	119·0 (4)
C(12)–C(13)–N(18)–O(19)	6·2 (5)	1·9 (5)
C(16)–C(15)–N(21)–O(23)	7·7 (5)	−5·2 (4)
C(13)–C(12)–O(11)–H(11)	−176 (2)	−12 (3)

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Structures of 2-Cyano-3-(4-diethylaminophenyl)thioacrylamide, C₁₄H₁₇N₃S, and 6-Amino-3,5-dicyano-3,4-dihydro-2,4-bis(3-methoxyphenyl)-2*H*-thiapyran-3-carbothioamide* Ethanol Solvate (1:1), C₂₂H₂₀N₄O₂S₂.C₂H₆O

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Abstract. C₁₄H₁₇N₃S: $M_r = 259·4$, monoclinic, $P2_1/n$, $a = 10·7555$ (11), $b = 12·3646$ (13), $c = 10·8680$ (10) Å, $\beta = 104·254$ (7)°, $U = 1400·8$ (2) Å³, $Z = 4$, $D_m = 1·24$, $D_x = 1·230$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1·54178$ Å, $\mu = 1·83$ mm⁻¹, $F(000) = 552$, $T = 291$ (2) K, final $R = 0·083$ for 1866 observed reflections. The aryl and thioamide groups occupy *trans* positions across the alkene double bond, whilst the diene fragment C=C—C=S has an *s-trans* geometry. The stereochemical consequences of conjugation in this molecule are successive twists of 8·3 and 18·9° about the single bonds linking aryl and alkene, and alkene and

* IUPAC name: 6-amino-3,5-dicyano-3,4-dihydro-2,4-bis(3-methoxyphenyl)-2*H*-thiin-3-carbothioamide.
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