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Structure of a Hydrogen-bonded Lattice Compound between Phosphoric Acid and 18-Crown-6: $H_3PO_4 \cdot 0.5(C_{12}H_{24}O_6) \cdot 3H_2O$

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Abstract

Phosphoric acid and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been shown to form a hydrated lattice compound held together by hydrogen bonds. Its crystal structure at 297 K was determined by X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$, with $a = 8.494(2)$, $b = 10.701(3)$, $c = 15.210(5)$ Å, $\beta = 104.41(2)^\circ$ and $Z = 4$. The phosphoric acid molecules form hydrogen-bonded dimers, which are linked by intermediate water molecules to crown ether rings through a series of hydrogen bonds. Each crown ether molecule receives a hydrogen bond to each of its six oxygen atoms, and in this symmetrical arrangement adopts the pseudo-D_{3d} conformation often found in crown ether–cation complexes instead of the elongated shape it has in the uncomplexed state.

Introduction

Crown ethers have received much attention because of their potential for selectively complexing various ions and molecules. Bonding between the crown ether and its adduct is generally one of three kinds: (1) coordination of a cation by the O atoms of the crown, (2) hydrogen bond donation from a 'guest' molecule directly to the ether O atoms, or (3) indirect linkage of ions or molecules to the crown through the formation of hydrogen bonds involving intermediate water molecules. Structures of many examples of each type have been determined.

Of special interest here is the conformation adopted by the 18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane) molecule in its various modes of complexation. It has been calculated by molecular mechanics [1, 2] that the structure exhibited by the uncomplexed 18-crown-6 molecule [3] is of the lowest energy; but that certain other conformations are only a little higher, and sufficient energetic gains are made on complexation to stabilize these shapes in complexes.

The conformation of the crown can be described by its sequence of 18 torsion angles [4], beginning with C–C–O–C. In the uncomplexed ether the ring is elongated and has the sequence $(aaa)(g^-g^+a)$-$(ag^-a)(aaa)(g^+g^-a)(ag^+a)$ with symmetry C_i (a = *anti*; g = *gauche*). In the case of complexation through H bonding the ring converts to one of two configurations in most cases[§]. One is the somewhat more circular ring having the sequence $(ag^-a)_2$-$(g^-g^-a)(ag^+a)_2(g^+g^+a)$, also centrosymmetric and designated C_i' (ref. 1); the other has $[(ag^+a)(ag^-a)]_3$ and is circular, with approximately D_{3d} symmetry. Examples of complexes having these two kinds of crown structures are given in Table I. Analysis of the structure of $H_3PO_4 \cdot 0.5$(18-crown-6)$\cdot 3H_2O$ affords the opportunity to examine the conformation of the ring under the influence of a set of symmetrically disposed H bonds, one to each of its six O atoms.

The structure determination described here also provides a new, precise measurement of the H_3PO_4 molecule. Previous studies included the structure of pure H_3PO_4 [24], without determination of the H atom positions, and of $H_3PO_4 \cdot 0.5H_2O$ [25] in which only part of the protons were located. A precise determination of H atom sites in the H_3PO_4-urea addition compound was made by neutron diffraction [26], and in that compound one acid proton is partially ionized.

Experimental

Preparation of the Compound

The title compound precipitated as colorless crystals from concentrated H_3PO_4 solutions in which we were attempting to complex certain metal ions, *viz.* Fe(III), U(IV), with 18-crown-6 (Aldrich Chem.

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[§] One possible exception is in the structure of $Co(H_2O)_6$-$CoCl_4 \cdot$18-crown-6$\cdot C_3H_6O$ in which one ring contains a pair of *ggg* torsion angles [5]. However, disorder in some atomic positions makes this somewhat uncertain.

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TABLE I. Symmetries of the 18-Crown-6 Molecules in Hydrogen-bonded Complexes

	Bonding type	Reference
$[(ag^{+}a)(ag^{-}a)]_3$[a], pseudo D_{3d}		
NH_4Br•18-crown-6•$2H_2O$	direct H bonds	6
Benzylammonium•18-crown-6•NCS	direct H bonds	2
$(Malononitrile)_2$•18-crown-6	direct H bonds	7
$(Nitromethane)_2$•18-crown-6	direct H bonds	8
Dimethylacetylene dicarboxylate•18-crown-6	direct H bonds	9
$(Dimethylsulfone)_2$•18-crown-6	direct H bonds	10
$Mn(NO_3)_2 \cdot 6H_2O$•18-crown-6	intermediate H_2O	11
$Mn(ClO_4)_2 \cdot 6H_2O$•18-crown-6	intermediate H_2O	12
$Gd(NO_3)_3 \cdot 3H_2O$•18-crown-6	intermediate H_2O	13
$UO_2(NO_3)_2 \cdot 4H_2O$•18-crown-6	intermediate H_2O	14
$U(SCN)_4 \cdot 7H_2O$•18-crown-6•$(C_6H_{12}O)$	intermediate H_2O	15
$SnCl_4 \cdot 4H_2O$•18-crown-6•$CHCl_3$	intermediate H_2O	16
$H_3PO_4 \cdot 3H_2O \cdot 0.5$(18-crown-6)	intermediate H_2O	this work
$(ag^{+}a)_2(g^{+}g^{+}a)(ag^{-}a)_2(g^{-}g^{-}a)$, C_i'		
$(Benzenesulfonamide)_2$•18-crown-6	direct H bonds	17
(Guanidinium $nitrate)_2$•18-crown-6	direct H bonds	18
$(Urea)_5$•18-crown-6	direct H bonds	19
$(2,4\text{-Dinitroaniline})_2$•18-crown-6	direct H bonds	20
$(4\text{-Nitro-1,2-benzenediamine})_2$•18-crown-6	direct H bonds	21
$UO_2(NO_3)_2 \cdot 2H_2O$•18-crown-6	intermediate H_2O	22
$[(CH_3)_2SnCl_2 \cdot H_2O]_2$•18-crown-6	intermediate H_2O	23

[a]Sequence of torsion angles; see text.

TABLE II. Crystal Parameters and Experimental Conditions

$H_3PO_4 \cdot 0.5(C_{12}H_{24}O_6) \cdot 3H_2O$	
Formula weight	284.13
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.494(2)
b (Å)	10.701(3)
c (Å)	15.210(5)
β (°)	104.41(2)
V (Å^3)	1339(2)
Z	4
$F(000)$	608
D_c (g cm^{-3})	1.41
D_m (g cm^{-3})	1.38(2)
Melting point (°C)	59(6)
Crystal dimensions (mm)	0.22 × 0.46 × 0.17
Radiation	Mo Kα (0.7107 Å)
Filter	Nb
μ(Mo Kα) (cm^{-1})	2.5
Temperature (°C)	24
Scan mode	$\omega-2\theta$
Background	10 s at ends of scan
Number of reflections $>3\sigma$	1423
Number of parameters varied	218
$R(F)$	0.044
R_w	0.091
σ_1	1.88

Co.). Subsequently it was found that the addition of water to a mixture of conc. H_3PO_4 and 18-crown-6 yielded crystals of the same morphology, and X-ray precession photographs proved these crystals to be the same as those obtained earlier from solutions.

The measured density, 1.38(2) g cm^{-3}, in conjunction with the unit-cell dimensions (Table II) suggested the stoichiometry $H_3PO_4 \cdot 0.5(C_{12}H_{24}O_6) \cdot 3H_2O$. Other evidence indicating the correctness of this stoichiometry came from the titration against NaOH of a known weight of crystals dissolved in H_2O. This indicated 36 wt.% H_3PO_4 and the calculated value was 34 wt.%. This stoichiometry was verified from the crystal structure analysis.

A complex of H_3PO_4, H_2O, and dicyclohexano-18-crown-6 (mixture of isomers) was prepared in similar fashion. Its crystals are triclinic, but the stoichiometry has not been determined. Sulfuric acid and 18-crown-6 did not yield any crystals.

X-ray Diffraction

X-ray precession photographs showed that the lattice of $H_3PO_4 \cdot 0.5$(18-crown-6)$\cdot 3H_2O$ is monoclinic and the systematic absences are $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; these are indicative of space group $P2_1/c$. A prismatic crystal, approximately 0.22 × 0.46 × 0.17 mm, was sealed in a thinwalled glass capillary and mounted on a computer-controlled Picker four-circle diffractometer. Twelve reflections were carefully centered and used to refine the lattice parameters by the method of least-squares. A total of 1423 unique reflections greater than 3σ, of type $+h$, $+k$, $\pm l$, were measured out to $(\sin\theta)/\lambda \approx 0.60$. The radiation used was Mo Kα (Nb filtered) and the diffractometer operated in the ω–2θ scanning mode. A standard reflection, $(1, 5, -6)$, was measured every 26th reflection. The crystal moved slightly in the capillary during the data collection and its alignment had to be adjusted four times. The standard deviation of the intensity of the standard reflection during the data collection was approximately 3.6% of the mean value. Crystal parameters and experimental conditions are listed in Table II.

Structure Determination and Refinement

The intensities were corrected* for absorption, Lorentz and polarization effects, and normalized through interpolation between measurements of the standard reflection, yielding a set of observed structure factors squared, F_o^2.

The phosphate groups were found from Harker vectors in a Patterson map and are in general positions. A subsequent Fourier map revealed the position of the crown ether ring and the oxygen atoms of the water molecules, which are also in general positions. Some of the hydrogen atoms could be identified from Fourier maps and the positions of the rest were calculated based on their known configuration in the ether and on a hydrogen-bonding scheme deduced from O···O distances.

This approximate structure, including the H atoms, was refined by the method of least-squares. The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$ in which F_c is the calculated structure factor and the weight, w, is estimated to be $1/[\sigma_c^2 + (0.03\,F_o^2)^2]$, where σ_c^2 is based on counting statistics. Scattering factors for the atoms were taken from the International Tables [27]. The 218 parameters which were varied consisted of a scale factor, an extinction parameter, 114 positional parameters including those of H atoms, and the 102 anisotropic thermal parameters for all nonhydrogen atoms. The isotropic temperature factors of the H atoms of the ether were fixed at estimated values based upon the average thermal parameters of the C atom to which they were attached. Other H-atom thermal parameters were fixed at $B = 6.0$. It was found that the observed values of the stronger reflections were too small, *i.e.*, F_o^2/F_c^2 was smaller than 0.90 for about 3% of the reflections. An isotropic correction for extinction [28] was applied to the data and its value refined in the least-squares treatment. The smallest correction factor applied to F_c^2 was 0.46.

The agreement index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for the refined structure was 0.044 and the weighted agreement index, $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^4|]^{1/2}$, was 0.091. The standard deviation of an observation of unit weight, $\sigma_1 = [\Sigma w(|F_o^2| - |F_c^2|)^2/(m - n)]^{1/2}$ (m = number of observed reflections, n = number of parameters) was 1.88. The atomic coordinates are listed in Table III. Bond lengths and angles are listed in Table IV and the H-bond geometries are in Table V**.

TABLE III. Atomic Fractional Coordinates and their Standard Deviations

	Atom	$10^4\,x$	$10^4\,y$	$10^4\,z$
PO_4	P	4628(2)	5535(1)	3638(1)
	O(1)	3925(4)	6296(3)	4308(2)
	O(2)	5397(4)	6469(3)	3101(2)
	O(3)	5844(3)	4610(3)	4106(2)
	O(4)	3137(4)	4948(3)	2980(2)
Crown ether	O(5)	840(4)	−1609(3)	3819(2)
	O(6)	1596(4)	1021(3)	3832(2)
	O(7)	1409(4)	2583(3)	5318(2)
Water	O(8)	3532(4)	4173(3)	1475(2)
	O(9)	3533(5)	7484(3)	1749(2)
	O(10)	1396(4)	9076(3)	5631(2)
	C(1)	1288(8)	−962(5)	3108(4)
	C(2)	2435(7)	60(6)	3500(4)
	C(3)	2592(6)	2082(5)	4125(4)
	C(4)	1648(7)	3029(5)	4483(4)
	C(5)	403(7)	3364(4)	5704(4)
	C(6)	56(7)	2715(5)	6489(4)
	Atom	$10^3\,x$	$10^3\,y$	$10^3\,z$
$-CH_2-$	H(1)[a]	28(8)	−59(6)	267(4)
	H(2)	188(7)	−152(6)	279(4)
	H(3)	292(7)	46(6)	303(4)
	H(4)	324(8)	−27(6)	404(4)
	H(5)	308(6)	236(5)	362(4)
	H(6)	365(7)	184(5)	461(4)
	H(7)	49(7)	316(5)	408(4)
	H(8)	224(7)	382(5)	460(4)
	H(9)	−67(7)	353(5)	515(4)
	H(10)	93(6)	418(5)	592(4)
	H(11)	−60(7)	321(5)	678(4)
	H(12)	115(6)	250(5)	697(4)
H_3PO_4	H(13)	390(7)	590(5)	486(4)
	H(14)	473(7)	688(5)	259(4)
	H(15)	329(7)	461(5)	248(4)

(continued overleaf)

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*The calculations in this work employed the following Oak Ridge computer programs: data reduction and absorption corrections with ORDATLIB (Ellison, *et al.*); Fourier syntheses with ORFFP (Levy); least squares with ORXFLS-4 (Busing, *et al.*); bond lengths and angles with ORFFE-4 (Busing, *et al.*); and drawings with ORTEP-II (Johnson).

**See also 'Supplementary Material'.

TABLE III *(continued)*

	Atom	10^3x	10^3y	10^3z
Water	H(16)	286(7)	467(6)	111(4)
	H(17)	333(7)	348(6)	130(4)
	H(18)	379(7)	813(6)	147(4)
	H(19)	292(7)	699(6)	141(4)
	H(20)	132(7)	881(5)	509(4)
	H(21)	41(7)	908(5)	576(4)

[a]H(1) to H(12) are attached in pairs to C(1) to C(6).

TABLE IV. Interatomic Distances (Å) and Angles (°)

Atoms	Distance	Atoms	Angle
P–O(1)	1.536(3)	O(1)–P–O(4)	104.8(2)
P–O(2)	1.535(3)	O(2)–P–O(4)	108.0(2)
P–O(3)	1.479(3)	O(2)–P–O(1)	107.2(2)
P–O(4)	1.539(3)	O(3)–P–O(4)	113.7(2)
C(6)–O(5)	1.422(5)	O(3)–P–O(1)	112.0(2)
O(5)–C(1)	1.414(5)	O(3)–P–O(2)	110.7(2)
C(1)–C(2)	1.487(7)	P–O(1)–H(13)	116(4)
C(2)–O(6)	1.415(8)	P–O(2)–H(14)	120(4)
O(6)–C(3)	1.420(5)	P–O(4)–H(15)	117(4)
C(3)–C(4)	1.478(7)	H(16)–O(8)–H(17)	107(6)
C(4)–O(7)	1.419(5)	H(18)–O(9)–H(19)	113(5)
O(7)–C(5)	1.422(5)	H(20)–O(10)–H(21)	111(5)
C(5)–C(6)	1.473(7)	C(6)–O(5)–C(1)	112.3(4)
		O(5)–C(1)–C(2)	109.2(4)
		C(1)–C(2)–O(6)	109.8(4)
		C(2)–O(6)–C(3)	112.3(4)
		O(6)–C(3)–C(4)	109.2(4)
		C(3)–C(4)–O(1)	108.1(4)
		C(4)–O(7)–C(5)	114.0(4)
		O(7)–C(5)–C(6)	108.6(4)
		C(5)–C(6)–O(5)	108.9(4)

Results and Discussion

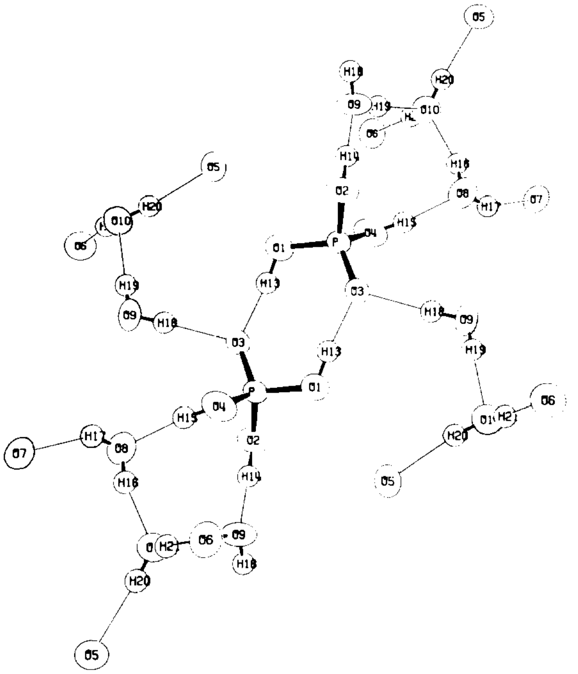

Fig. 1. Details of the hydrogen bonding network. Atoms O(5), O(6) and O(7) belong to crown ether molecules not shown entirely.

The crystal structure of $H_3PO_4\cdot0.5$(18-crown-6)$\cdot3H_2O$ contains pseudotetrahedral H_3PO_4 molecules joined into centrosymmetric dimers by H bonds involving an acidic proton from each. The other two protons on each H_3PO_4 form H bonds to the O atoms of water molecules. These H_2O molecules, in turn, are H bonded directly or through other H_2O molecules to crown-ether rings. The dimers and their environment are shown in Fig. 1.

The H bonds donated by the phosphoric acid are shorter (2.51–2.56 Å) than those donated by the water molecules (2.70–2.88 Å). The O–H distances appear to be short, an artifact usually observed in X-ray determinations of this type. The O(8)–H(17)···O(7) bond is the longest (weakest) H bond in the structure, but the well determined O(8)···O(7) distance indicates that it is not as weak as the bond angle and O(8)–H(17), H(17)···O(7) distances

TABLE V. Hydrogen Bond Geometries

	Distances (Å)			Angles (°)
	O···O	O–H	H···O	O–H···O
O(1)–H(13)···O(3)	2.560(4)	0.94(6)	1.63(6)	169(5)
O(2)–H(14)···O(9)	2.509(4)	0.95(6)	1.56(6)	175(6)
O(4)–H(15)···O(8)	2.534(5)	0.88(6)	1.66(6)	171(6)
O(8)–H(16)···O(10)	2.700(4)	0.88(6)	1.85(6)	164(6)
O(8)–H(17)···O(7)	2.881(4)	0.79(6)	2.23(6)	140(6)
O(9)–H(18)···O(3)	2.737(4)	0.86(6)	1.88(6)	174(6)
O(9)–H(19)···O(10)	2.728(4)	0.83(6)	1.90(6)	177(6)
O(10)–H(20)···O(5)	2.776(4)	0.86(6)	1.92(6)	171(6)
O(10)–H(21)···O(6)	2.859(4)	0.91(6)	1.96(6)	174(6)

imply. Clearly, the accuracy of the H(17) position is low, as is the case for the H atoms in general. However, their positions have been determined with sufficient precision to establish with certainty which oxygen donates and which oxygen receives each proton.

H-bonded dimers are also observed in solid H_3PO_4 where, in addition, other H bonds link the molecules into infinite sheets. The length of the bridging H bond observed here, 2.56 Å, is in good agreement with the corresponding bond in solid H_3PO_4 (2.53 Å). The dimer is slightly skewed; the P atoms deviate by ±0.111(2) Å from the best plane through the P, O(1) and O(3) atoms of the two H_3PO_4 molecules, the O(1) atoms deviate by ±0.088(2) Å and the O(3) atoms by ±0.095(2) Å. The phosphate tetrahedron is slightly distorted with O–P–O angles varying from 104.8(2) to 113.7(2)° (Table IV). The phosphoryl oxygen was easily identified, because the P–O(3) bond length is clearly shorter than the three other P–O distances, which are identical within the limits of the standard deviation, as is also the case in solid H_3PO_4. These bond lengths in Table IV are in good agreement with those reported for $(NH_2)_2CO \cdot H_3PO_4$ [26] and found in other neutron diffraction studies, e.g. $CaHPO_4 \cdot 2H_2O$ [29], $N_2H_5H_2PO_4$ [30], $N_2H_6(H_2PO_4)_2$ [31] and $KH_5(PO_4)_2$ [32].

The crown-ether rings in the title compound are positioned about crystallographic centers of symmetry. In addition they have a pseudo-D_{3d} symmetry in which the O atoms are alternately up and down in relation to the best plane through them; O(5) is 0.21 Å up, O(6) is 0.21 Å down and O(7) is 0.20 Å up. The three remaining O atoms, O(5)′, O(6)′ and O(7)′ are related to the former by inversion through the crystallographic center of symmetry. The torsion angles are shown in Fig. 2. All C–O bonds are *anti* and all C–C bonds are *gauche*; this gives the sequence $[(ag^+a)(ag^-a)]_3$ characteristic of the pseudo-D_{3d} configuration. The C–O bonds average 1.42 Å and the C–C bonds 1.48 Å while the C–C–O angles average 109.0° and the C–O–C angles 112.9°. These values agree well with previously determined 18-crown-6 structures.

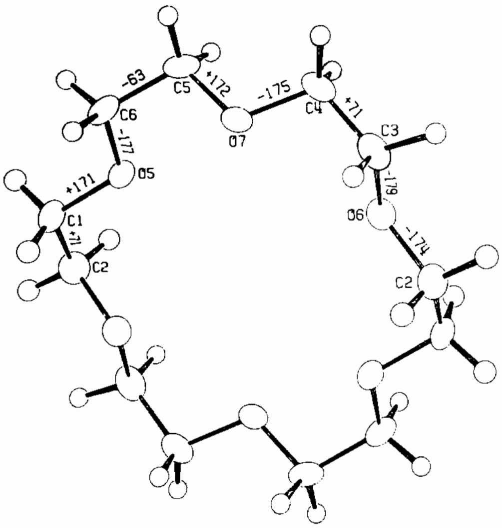

Fig. 2. The centrosymmetric 18-crown-6 ether ring with its torsion angles. Carbon and oxygen atoms are represented by their 20% probability thermal ellipsoids; hydrogen atoms by 10% probability.

Each O atom in the crown ether receives one H bond from a water molecule (Fig. 3). The water containing O(10) straddles the ring and is H bonded to ether oxygens O(5) and O(6)′ while that containing O(8) is H bonded to water O(10) and ether O(7). The same kind of H bonding network links the remaining three O atoms of the ring with two

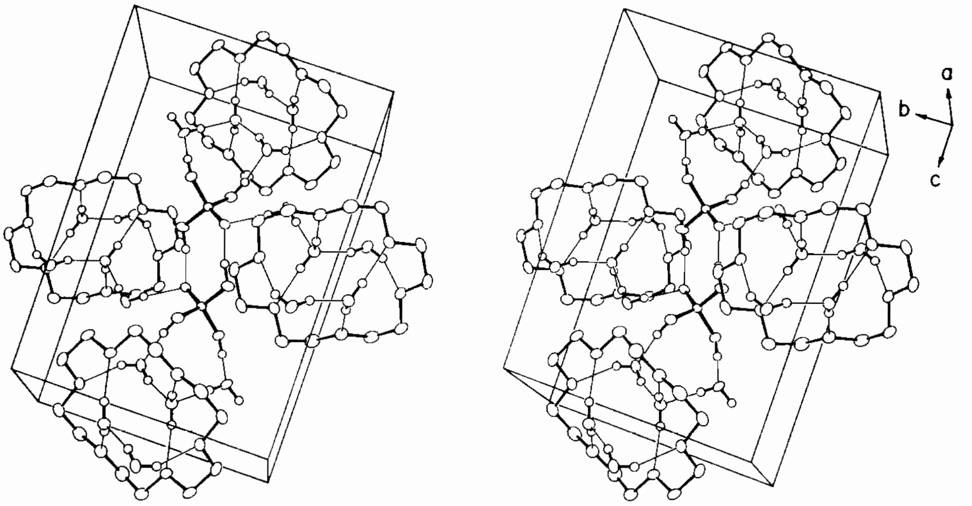

Fig. 3. A stereoscopic drawing of a portion of the unit cell contents showing the linkage between H_3PO_4 and 18-crown-6 molecules.

H_2O molecules on the opposite side of the ether plane. Every crown ether is linked to four H_3PO_4 molecules via H-bonded H_2O molecules. The hexagon of O atoms, compared to an ideal D_{3d} conformation, is slightly pinched at O(5)–O(6)′ and O(5)′–O(6) in order to facilitate the H bonding to the H_2O molecule containing O(10). As a result, the diagonals O(5)–O(5)′ and O(6)–O(6)′ are slightly shortened; they are 5.418(4) Å and 5.436(4) Å, respectively, while O(7)–O(7)′ is elongated, 5.681(4) Å. Among the known structures (Table I) the one having the closest resemblance in the disposition of H-bonds is that of $SnCl_4 \cdot 4H_2O \cdot 18\text{-crown-6} \cdot CHCl_3$; there also the ring has pseudo-D_{3d} symmetry [16].

In complexes with spherical ions (e.g. K^+, Ca^{2+}) [33] and species with circularly disposed H-atom donors (e.g. NH_4^+) [6] the 18-crown-6 ring usually has the pseudo-D_{3d} configuration, while the more elongated C_i' shape is adopted when it is attached to adduct molecules whose bonding centers are less symmetrically arrayed. As for ions or molecules H bonded to the crown through intermediate H_2O molecules, an insufficient number of structures with H atoms located have been determined to generalize reliably. There is, however, a balance achieved between the number of H bonds which can be formed for a given configuration and the increase in internal energy of the crown ether as it adopts either the C_i' or D_{3d} symmetry. In the case of $H_3PO_4 \cdot 0.5(18\text{-crown-6}) \cdot 3H_2O$ the symmetrical array of six H-bond donors acting on the crown from both sides favors the more circular geometry for the ring and the pseudo-D_{3d} symmetry results.

Supplementary Material

Thermal parameters for all atoms and a listing of F_o and F_c values are available from author J.H.B. on request.

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