

## A potassium–18-crown-6 salt of a cyclic *myo*-inositol phosphate

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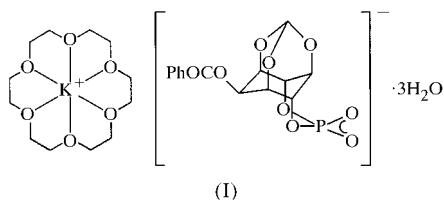
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The six-membered phosphorinane ring in (1,4,7,10,13,16-hexaoxacyclooctadecane)potassium 2-*O*-benzoyl-1,3,5-*O*-methylidyne-*myo*-inositol 4,6-cyclophosphate trihydrate,  $[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)](\text{C}_{14}\text{H}_{12}\text{O}_9\text{P})\cdot 3\text{H}_2\text{O}$ , has a boat rather than a chair conformation. The  $\text{K}^+$  ion is eight-coordinate and is connected to one of the phosphate O atoms, one of the O atoms of the *myo*-inositol residue and the six O atoms of the crown ether.

### Comment

Inositol phosphates have attracted the attention of a large number of chemists as a result of the role of some of these compounds as secondary messengers in signal transduction (Potter & Lampe, 1995). Our interest lies mainly in cyclic phosphorus compounds (Kumara Swamy *et al.*, 1998; Muthiah & Kumara Swamy, 1999) and in this connection we felt that various cyclic phosphates could be generated from suitably protected inositol derivatives. It should be noted that, despite so much interest in inositol phosphates, few cyclic derivatives have been structurally characterized, although the crystal structures of two cyclic phosphates derived from inositol have been reported recently (Dietrich *et al.*, 1999; Neidle *et al.*, 1998). In the present paper, we report the structure of a cyclic inositol phosphate as a trihydrate of its potassium–18-crown-6 salt, *viz.*  $[\text{K}(\text{18-crown-6})]^+[\text{myo-C}_6\text{H}_6\text{-2-}\{\text{OC}(\text{O})\text{Ph}\}\text{-1,3,5-}(\text{O}_3\text{CH})\text{-}\{\text{O}_2\text{P}(\text{O})\text{O}\}]^-\cdot 3\text{H}_2\text{O}$ , (I).



An ellipsoid plot of (I), excluding the O atoms of the water molecules, is shown in Fig. 1. Apart from the six O atoms of the crown ether, potassium is coordinated to O2 of the inositol residue and to O7 of the phosphate residue in the neighbouring cell along *b*, leading to a chain structure (Fig. 2).

The  $\text{K}-\text{O}^{\text{i}}$  distance [2.771 (4) Å] is the shortest of all the  $\text{K}-\text{O}$  distances in this compound [symmetry code: (i)  $x, y-1, z$ ]. The  $\text{P}-\text{O}$  bond distances involving the inositol residue

[ $\text{P}-\text{O}1$  1.608 (3) Å and  $\text{P}-\text{O}5$  1.627 (3) Å] are normal but longer than the mean value of 1.580 (2) Å found by Neidle *et al.* (1998) in  $\text{C}_6\text{H}_6(\text{OH})_3[\text{O}_3\text{P}(\text{O})]$ , (II).

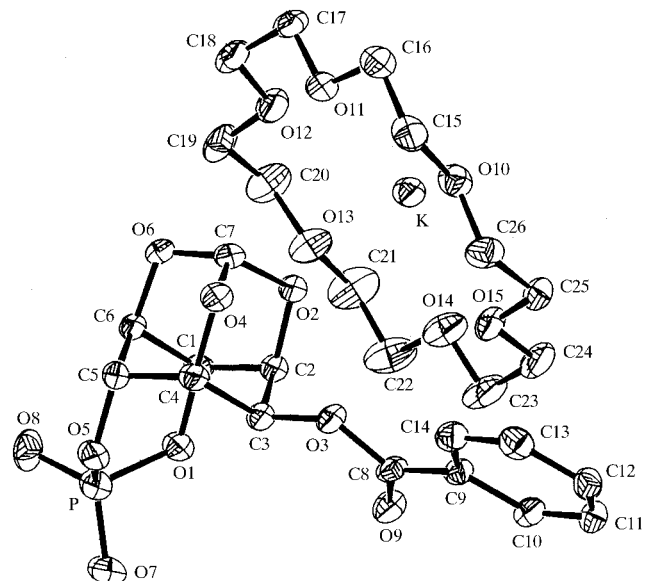


Figure 1

The molecular structure of (I) showing the atom-numbering scheme. Atoms are represented by 25% probability displacement ellipsoids. Water O atoms and all H atoms have been omitted for clarity, as have all  $\text{K}-\text{O}$  bonds.

Interestingly, in (I), the six-membered 1,3,2-dioxaphosphorinane ring adopts a boat conformation (Fig. 3), with P and C6 (respectively the prow and stern of the boat) on the same side at distances of 0.608 and 0.675 Å, respectively, from the mean plane through C1, C5, O1 and O5 (the maximum deviation from this mean plane is 0.004 Å). This is different from the situation found in (II), where all three six-membered 1,3,2-dioxaphosphorinane rings have chair conformations (Neidle *et al.*, 1998). It should also be noted that a chair conformation is normally found for 1,3,2-dioxaphosphorinane rings containing tri- or tetracoordinate phosphorus (Maryanoff *et al.*, 1979). A boat conformation is found mainly for pentacoordinate phosphorus in which the 1,3,2-dioxaphosphorinane ring bridges one apical and one equatorial site of a trigonal-bipyramidal arrangement (Said *et al.*, 1997). However, in these compounds, an apical O atom and the C atom opposite it lie at the prow and stern of the boat. It is likely that in (I), steric interactions involving the phosphorus and the C3 H atom are greater in the alternative chair conformation.

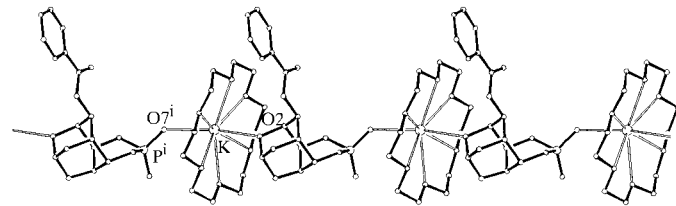
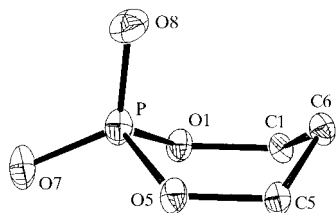


Figure 2

A diagram showing the eight-coordination at potassium and the chain structure. Water O atoms have been omitted. [Symmetry code: (i)  $x, y-1, z$ ].

In (I), there are hydrogen-bonding interactions involving O7, O8, O9 and the water O atoms. While O7 is within hydrogen-bonding distance of O16A and O16B of a second molecule, atom O8 has intermolecular hydrogen-bonded contacts to O17A, O17B and O18A. The carbonyl O9 atom is rather weakly hydrogen bonded to O16B, judging by the long



**Figure 3**

A diagram showing the boat conformation of the six-membered 1,3,2-dioxaphosphorinane ring.

O...O distance of 3.033 (9) Å. Since it was not possible to locate or fix the water H atoms, no discussion of this aspect of the structure is possible.

## Experimental

The crude phosphate (0.070 g, 0.20 mmol), prepared by adding  $\text{PCl}_3$  to 2-*O*-benzoyl-*myo*-inositol 1,3,5-orthoformate (Ozaki *et al.*, 1994) followed by oxidation and hydrolysis ( $\text{I}_2/\text{water}$ ), was added to a mixture of 18-crown-6 (0.061 g, 0.23 mmol) and KF (0.022 g, 0.38 mmol) in tetrahydrofuran (5 ml). The mixture was refluxed for 2 h, stirred overnight, then filtered to remove undissolved KF and left to crystallize. Needle-shaped crystals of (I) were obtained. M.p. 377–379 K.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , p.p.m.):  $\delta$  2.40 (*br s*, *ca* 6H,  $\text{H}_2\text{O}$ ), 3.65 (*s*, 24H,  $\text{CH}_2$  of 18-crown-6), 4.55–4.58 (*m*, 2H, CH), 4.85–4.91 (*m*, 2H, CH), 5.50–5.55 (*m*, 2H, CH), 5.81–5.83 (*m*, 1H, CH), 7.35–7.65 (*m*, 3H, Ar-H), 8.11–8.60 (*m*, 2H, Ar-H);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , p.p.m.):  $\delta$  –11.1.

### Crystal data

$[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)](\text{C}_{14}\text{H}_{12}\text{O}_9\text{P})\cdot 3\text{H}_2\text{O}$   
 $M_r = 712.67$   
 Monoclinic,  $P2_1/c$   
 $a = 17.146$  (2) Å  
 $b = 10.9380$  (16) Å  
 $c = 18.965$  (9) Å  
 $\beta = 109.96$  (2)°  
 $V = 3343.1$  (18) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.416$  Mg m<sup>–3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 9.5$ – $12.0^\circ$   
 $\mu = 0.28$  mm<sup>–1</sup>  
 $T = 293$  (2) K  
 Block cut from needle, colourless  
 $0.30 \times 0.30 \times 0.20$  mm

### Data collection

Enraf–Nonius MACH3 diffractometer  
 Profile data from  $\omega$  scans  
 5867 measured reflections  
 5867 independent reflections  
 2662 reflections with  $I > 2\sigma(I)$   
 $\theta_{\text{max}} = 25.0^\circ$

$h = 0 \rightarrow 20$   
 $k = 0 \rightarrow 12$   
 $l = -22 \rightarrow 21$   
 3 standard reflections  
 frequency: 90 min  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.059$   
 $wR(F^2) = 0.198$   
 $S = 1.04$   
 5867 reflections  
 416 parameters  
 H-atom treatment: see below

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 3.92P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.53$  e Å<sup>–3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>–3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0019 (5)

**Table 1**

Selected geometric parameters (Å, °).

K–O2	2.896 (3)	K–O14	2.823 (4)
K–O7 <sup>i</sup>	2.771 (4)	K–O15	2.913 (4)
K–O10	2.808 (4)	P–O1	1.608 (3)
K–O11	2.979 (3)	P–O5	1.627 (3)
K–O12	2.818 (4)	P–O7	1.472 (4)
K–O13	2.830 (4)	P–O8	1.476 (4)
O1–P–O5	101.31 (17)	O5–P–O7	106.7 (2)
O1–P–O7	107.57 (19)	O5–P–O8	110.2 (2)
O1–P–O8	109.2 (2)	O7–P–O8	120.2 (2)

Symmetry code: (i)  $x, y - 1, z$ .

**Table 2**

Hydrogen-bonding O...O distances (Å).

O16A...O7 <sup>i</sup>	2.600 (14)	O17B...O8 <sup>ii</sup>	2.880 (13)
O16B...O7 <sup>i</sup>	2.883 (9)	O18A...O8 <sup>i</sup>	2.726 (15)
O16B...O9 <sup>i</sup>	3.033 (9)	O16B...O17B	2.603 (15)
O17A...O8 <sup>ii</sup>	2.668 (10)		

Symmetry codes: (i)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $1 - x, 1 - y, -z$ .

H atoms were placed geometrically and refined using a riding model with C–H distances constrained to 0.93–0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . There were three positionally disordered lattice water molecules (O16A/O16B, O17A/O17B and O18A/O18B) and these O atoms were refined isotropically using free variable restraints with the total occupancy for each pair of disordered O-atom positions set to unity. H atoms on these O atoms could not be located and so were not included in the refinement model.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SDP* (Frenz, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1456). Services for accessing these data are described at the back of the journal.

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