

(18-Crown-6)-bis(tetrahydrofuran)potassium iodide

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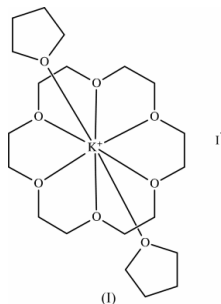
Key indicators

Single-crystal X-ray study
T = 160 K
Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
R factor = 0.037
wR factor = 0.081
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)(\text{C}_4\text{H}_8\text{O})_2]\text{I}$, has iodide anions on crystallographic twofold rotation axes and cations in general positions. The coordination of potassium is distorted hexagonal bipyramidal, with an 18-crown-6 ligand as an equatorial belt and two axial tetrahydrofuran ligands. Distortion is marked, consisting mainly of a significant bending of the axial arrangement $[\text{O}-\text{K}-\text{O} = 148.53 (13)^\circ]$ and a shortening of the two equatorial $\text{K}-\text{O}$ bonds closest to the axial O atoms. This conformation is unprecedented in the previous reports of this cation, with almost thirty different occurrences in nearly twenty crystal structures.

Comment

The title compound, (I), was obtained as an unexpected product of an attempted reaction to exchange Li for K in an 18-crown-6 complex of potassium with an amide ligand (see *Experimental*), when the lithium complex could not be obtained by direct reaction with the ligands (Liddle *et al.*, 2004). A lithium amide complex probably remained in solution, while the title compound crystallized as a consequence of the excellent size match of 18-crown-6 for K^+ .



There are two crystallographically distinct sites for the iodide anions in (I), both on twofold rotation axes, while the potassium-centred complex cation lies in a general position (Fig. 1). The potassium ion is eight-coordinate, the geometry being that of a distorted hexagonal bipyramid. The crown ether ligand forms an equatorial belt, with two tetrahydrofuran (THF) molecules as axial ligands.

A search of the Cambridge Structural Database (Version 5.24 of November 2002, together with three updates; Allen, 2002) finds 28 occurrences of this cation in 19 different crystal structures. The anions range from simple AlCl_4^- to polynuclear complex anions. Several of the structures contain some disorder, often of coordinated or uncoordinated THF molecules. Despite these variations and the limitations on precision because of disorder, there is a remarkable degree of similarity in the geometry of the cations, all of which have the

Received 18 November 2003

Accepted 20 November 2003

Online 29 November 2003

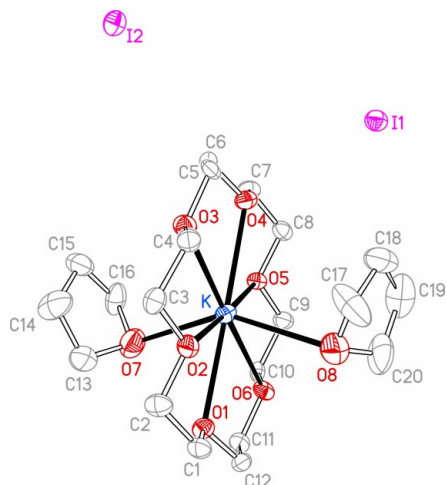


Figure 1
The molecular structure of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids for non-H atoms.

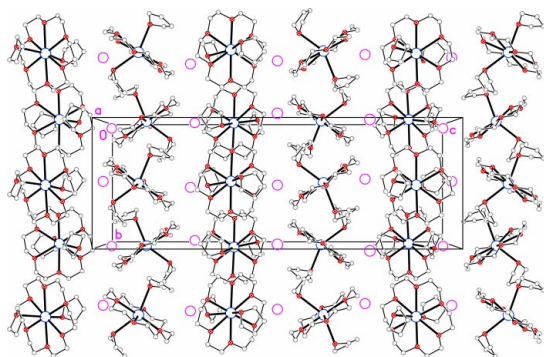


Figure 2
The crystal packing of (I), viewed along the *a* axis, showing the alternating layers of cations and anions.

same overall hexagonal bipyramidal framework as the title compound. The equatorially bound crown ether is a constant feature, and the angle between the axially coordinated THF molecules is usually close to 180° (exactly linear for those complexes that are crystallographically centrosymmetric), with deviations of up to 15° in two instances, but otherwise under 10° . In three-quarters of the cations, the K—O bond lengths to the axial THF ligands are shorter than those with the crown ether, and in the others they are approximately the same. Equatorial K—O bond lengths range from 2.704 to 2.894 Å, with a mean of 2.799 Å, and axial K—O(THF) bond lengths range from 2.546 to 2.912 Å, with a mean of 2.720 Å. The mean O—K—O angle for the axial ligands is 177.7° .

The cation in the title compound, which is fully ordered, deviates markedly from this pattern. The interaxial bond angle is only $148.53(13)^\circ$, and the axial bonds are longer than all the equatorial bonds (Table 1). The significant non-linearity of the axial linkage correlates with an asymmetry of the binding of the crown ether, with two equatorial K—O bonds significantly shorter than the others, these two being closest to the axial O atoms. The origin of this unsymmetrical arrangement is not obvious and it is an unexplained curiosity; there are no particularly short intermolecular contacts, the packing being essentially driven by a combination of electrostatic and van

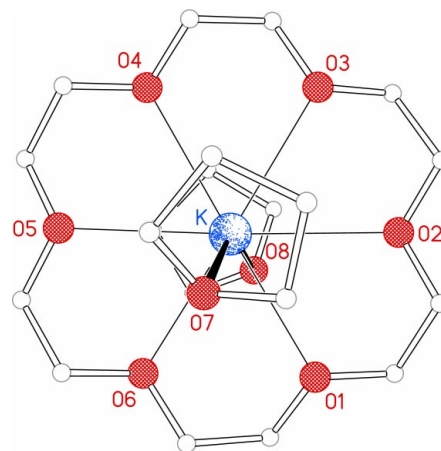


Figure 3
The cation of (I), viewed along the axial direction of the hexagonal bipyramid, showing the eclipsed orientation of the THF ligands.

der Waals forces. The cations are arranged in layers and the anions are sandwiched between them (Fig. 2).

The cation in this structure is unique among its reported salts in another respect also. In the vast majority of the previously reported structures, the THF ligands are oriented away from the crown ether, lying approximately along the axial directions. In the few cases where there is any significant tilt of the THF rings towards the equatorial belt, they lie in directly opposite directions, either approximately or (for strictly centrosymmetric cases) exactly. In the title compound, the two THF ligands both have an envelope conformation, with the O atom as the flap angle, the fold tilting the ring markedly towards the equatorial belt. In projection along the axial direction, the two THF rings almost eclipse one another, as shown clearly in Fig. 3.

Experimental

A solution of (18-crown-6) K_2 (PhN-2- C_5H_4N) $_2$ (Liddle *et al.*, 2004) (0.95 g, 1.48 mmol) in THF (50 ml) was added to LiI (0.2 g, 1.49 mmol) to give a turbid yellow solution, which was stirred for one day. The solution was filtered and concentrated. Storage at 278 K yielded crystals of (I) suitable for X-ray crystallography. 1H -NMR ($CDCl_3$): δ 1.79 (THF), 3.63 (18-crown-6), 3.68 (THF).

Crystal data

$[K(C_{12}H_{24}O_6)(C_4H_8O)_2]I$
 $M_r = 574.52$
Tetragonal, $P4_12_12$
 $a = 12.2645(15)$ Å
 $c = 34.372(6)$ Å
 $V = 5170.2(13)$ Å 3
 $Z = 8$
 $D_x = 1.476$ Mg m $^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 6732 reflections
 $\theta = 2.8$ – 28.6°
 $\mu = 1.44$ mm $^{-1}$
 $T = 160(2)$ K
Square antiprism, colourless
 $0.66 \times 0.62 \times 0.54$ mm

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{min} = 0.29$, $T_{max} = 0.46$
26 143 measured reflections

4570 independent reflections
4051 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.050$
 $\theta_{max} = 25.0^\circ$
 $h = -13 \rightarrow 14$
 $k = -13 \rightarrow 14$
 $l = -40 \rightarrow 39$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.081$	$\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$
$S = 1.10$	Extinction correction: <i>SHELXTL97</i>
4570 reflections	Extinction coefficient: 0.00029 (6)
273 parameters	Absolute structure: Flack (1983);
H-atom parameters constrained	1862 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 5.4555P]$	Flack parameter = 0.00 (3)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (\AA , $^\circ$).

K—O1	2.758 (3)	K—O5	2.844 (3)
K—O2	2.825 (3)	K—O6	2.772 (3)
K—O3	2.835 (3)	K—O7	2.866 (4)
K—O4	2.834 (3)	K—O8	2.876 (5)
O1—K—O2	60.56 (9)	O4—K—O5	59.06 (9)
O1—K—O6	63.21 (10)	O5—K—O6	60.71 (9)
O2—K—O3	59.26 (9)	O7—K—O8	148.53 (13)
O3—K—O4	60.80 (10)		
O1—C1—C2—O2	−64.9 (5)	O4—C7—C8—O5	64.1 (5)
O2—C3—C4—O3	65.6 (5)	O5—C9—C10—O6	−65.6 (5)
O3—C5—C6—O4	−68.9 (4)	O6—C11—C12—O1	69.8 (4)

H atoms were positioned geometrically and treated as riding [C—H = 0.99 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The displacement parameters of the O and C atoms of the THF ligands, together with some irregularity in the internal geometry of these ligands, suggest possible disorder, but resolution of this into alternative atom positions could not be achieved.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank the EPSRC for financial support.

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