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Isolated pentaiodide anions in [K(18-crown-6)]I_5

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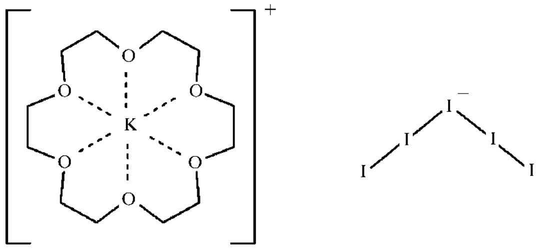
(1,4,7,10,13,16-Hexaoxacyclooctadecane-κ^6O)potassium pentaiodide, $[K(C_{12}H_{24}O_6)]I_5$, obtained by slow evaporation of an ethanol solution of KI, 18-crown-6 and I_2, contains [K(18-crown-6)]$^+$ cations (C_i symmetry) and I_5^- anions (C_2 symmetry), which are arranged in alternating layers parallel to (001). In contrast to the well known tendency of I_5^- ions to form chains and nets, the I_5^- units in the title compound are isolated.

Comment

Polyiodide anions are synthesized by the addition of elemental iodine to I^- ions and can be incorporated into crystalline solids in the presence of suitable cations. They show considerable diversity in I—I bond lengths, covering the whole range between a strongly covalent bond and the sum of the van der Waals radii of two I atoms. However, the bond lengths are never uniform. As a consequence, the structural diversity of polyiodide ions is remarkably great (Svensson & Kloo, 2003). To date, no systematic procedure for the synthesis and crystallization of iodine-rich polyiodides is known, and this remains an ultimate goal of our work. We wish to take account of the structures and compositions of polyiodide matrices by variation of the shape, charge and size of the corresponding cations. In previous work, we showed that bulky low-charge cations of the general formula $[M(\text{crown-ether})]^{x+}$ (where M is an element of group 1 or 2, crown-ether is benzo-18-crown-6, benzo-15-crown-5 or dibenzo-18-crown-6, and x = 1 or 2) positively influence the stability of polyiodides in the solid state (Tebbe & Dombrowski, 1999; Pantenburg & Tebbe, 2001, 2002; Pantenburg *et al.*, 2002).

In the series of polyiodides with the cation (18-crown-6)potassium, [K(18-crown-6)]I_x, only the triiodide (x = 3) has been structurally characterized (Sievert *et al.*, 1996) and represents the first member of the series with $x = 2n + 1$. In this paper, the second representative, [K(18-crown-6)]I_5 (n = 2), (I), is presented. Investigations into the selective synthesis of [K(18-crown-6)]I_7 (n = 3) and [K(18-crown-6)]I_9 (n = 4) are in progress.

The asymmetric unit in the molecular structure of (I) shows features characteristic of compounds containing the [K(18-crown-6)]$^+$ moiety (Fig. 1). The macrocyclic ligand crystallizes in the usual manner, showing an all-*gauche* conformation with almost D_{3d} symmetry (Pedersen & Frensdorff, 1972). The K^+ ion (4a; C_i symmetry; $\frac{1}{2}$,0,0) is located in the centre of the 18-crown-6 ligand and coordinated by six O atoms. The K—O distances vary between 2.777 (2) and 2.812 (2) Å (Table 1). The position of the K^+ centre deviates by 0.550 (1) Å from the O_6 mean plane (*PARST*95; Nardelli, 1995). Distances and angles within the crown-ether moiety are in good agreement with published data [mean values from the Cambridge Structural Database (Version 5.24; Allen, 2002): $CH_2—O$ = 1.43 (3) Å and $CH_2—CH_2$ = 1.51 (2) Å, and $O—CH_2—CH_2$ = 108.9 (13)° and $CH_2—O—CH_2$ = 111.4 (10)°].



(I)

The pentaiodide ion, as is often observed, forms a V-shaped unit (Tebbe, 1977; Pantenburg & Tebbe, 2001), with the central I1 atom located on the special site 4e (C_2 symmetry; $\frac{1}{2}$,y,$\frac{1}{4}$). This atom is linked to an iodine molecule [I2—I3 = 2.792 (1) Å] *via* a bond length of 3.116 (1) Å. The angle within the triiodide moiety thus formed (I1—I2—I3) is 178.67 (1)°. The angle at the central atom [I2—I1—I2$^{\rm iii}$ = 102.83 (1)°; symmetry code: (iii) $1 - x, y, \frac{1}{2} - z$] is significantly widened from the usually observed values of close to 90°.

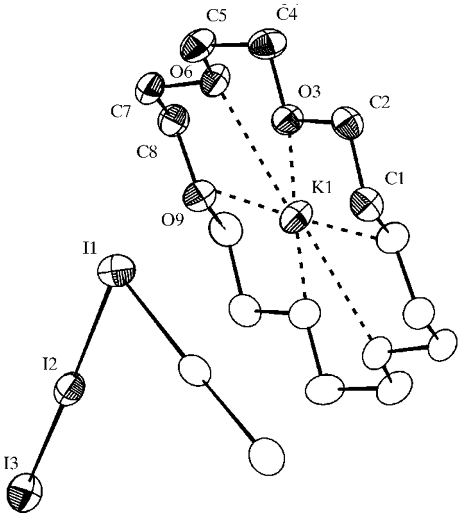


Figure 1
The structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Symmetry-related atoms are drawn as empty ellipsoids, dashed lines denote K—O contacts and H atoms have been omitted for clarity.

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An investigation of possible secondary contacts reveals only I2$\cdots$I3^{iv} of 3.909 (1) Å [symmetry code: (iv) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$], and thus shows that the iodine substructure of (I) consists of essentially isolated pentaiodide units. This result is remarkable, because isolated I_5^- units are rare structural elements. In contrast with the frequently found chains and networks, few examples of this structural motif have been mentioned in the literature (Pantenburg & Tebbe, 2001).

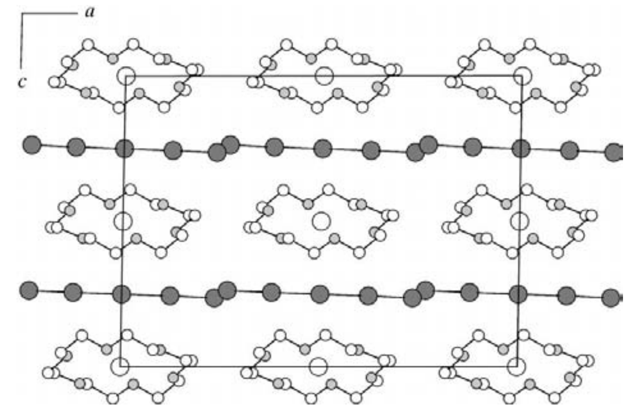

Figure 2
A projection of the structure of (I) along the *ac* plane. H atoms have been omitted for clarity.

In the crystal structure of (I), the ions form planes parallel to (110) (Fig. 2). No significant contacts are observed between the anions and cations of neighbouring planes, as indicated by the distances I3$\cdots$H1*B* = 3.263 (2) Å and I1$\cdots$K1 = 3.686 (1) Å.

Experimental

The title compound was prepared by thoroughly mixing KI (0.083 g, 0.5 mmol), 18-crown-6 (0.132 g, 0.5 mmol) and I_2 (0.380 g, 1.5 mmol) in ethanol (40 ml). Red plate-like crystals of (I) were obtained after a few days by slow evaporation of the solvent under ambient conditions.

Crystal data

$[K(C_{12}H_{24}O_6)]I_5$
M_r = 937.91
Monoclinic, $C2/c$
a = 19.9194 (17) Å
b = 8.6554 (7) Å
c = 14.6049 (14) Å
β = 91.208 (7)°
V = 2517.5 (4) Å^3
Z = 4
D_x = 2.475 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 494 reflections
θ = 1.1–29.8°
μ = 6.36 mm^{-1}
T = 170 (2) K
Plate, red
0.31 × 0.22 × 0.05 mm

Data collection

Stoe IPDS-II image-plate diffractometer
ω and φ scans
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001), after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999)]
T_{min} = 0.193, T_{max} = 0.691
26 538 measured reflections
3513 independent reflections
2779 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 29.6°
h = −27 → 25
k = −11 → 12
l = −20 → 20

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.057
S = 1.02
3513 reflections
113 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 1.2320P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.90 e Å^{-3}
$\Delta\rho_{min}$ = −1.03 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00503 (10)

Table 1
Selected geometric parameters (Å, °).

I1—I2	3.1162 (3)	C2—O3	1.417 (4)
I2—I3	2.7915 (4)	O3—C4	1.420 (4)
I2—I3^{i}	3.9090 (4)	C4—C5	1.498 (5)
I1—K1	3.6857 (3)	C5—O6	1.418 (4)
K1—O3	2.777 (2)	O6—C7	1.424 (4)
K1—O9	2.794 (2)	C7—C8	1.489 (5)
K1—O6	2.812 (2)	C8—O9	1.425 (3)
C1—C2	1.500 (4)	O9—C1^{ii}	1.421 (4)
I2^{iii}—I1—I2	102.83 (1)	I3—I2—I1	178.67 (1)

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

The H atoms were placed in idealized positions and constrained to ride on their parent atom, with C—H distances of 0.97 Å and U_{iso}(H) = 0.038 Å^2.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1580). Services for accessing these data are described at the back of the journal.

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