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The sandwich dimeric form of a Cs^I complex of 18-crown-6 with bridging iodide ions

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Key indicators

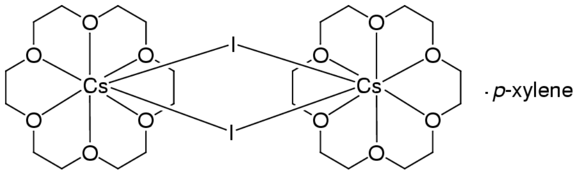
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 23.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The sandwich dimeric structure of di-μ-iodo-bis[(1,4,7,10,13,16-hexaoxacyclooctadecane)caesium(I)] p-xylene solvate, $[Cs_2I_2(C_{12}H_{24}O_6)_2]\cdot C_8H_{10}$, has been characterized by X-ray crystallography. The complex adopts an encapsulate of a molecular dimeric array $[Cs(18\text{-crown-}6)(\mu\text{-I})]_2\cdot C_8H_{10}$. Two $Cs(18\text{-crown-}6)^+$ moieties are doubly linked by two iodide ions. The molecule has crystallographic $2/m$ (C_{2h}) symmetry.

Comment

The chemistry of macrocyclic complexes of alkali metal cations has developed intensively since the end of the 1960′s because of the strong complexing properties of crown ethers. In this case, the complementarity of the macrocyclic cavity and the cation substrate determines the type of complex (Dietrich *et al.*, 1993). A caesium ion is too large for the 18-crown-6 cavity, thus giving a sandwich dimer complex bridged by SCN^- anions (Dobler & Phizackerley, 1974) or water molecules (Rusanova *et al.*, 1999). We report here the sandwich dimer structure of the title compound (I) with bridging iodide ions.



(I)

The title compound adopts a molecular dimeric array consisting of two $[Cs(18\text{-crown-}6)]^+$ units linked *via* two iodide ions as shown in Fig. 1. Two caesium cations are positioned on a mirror plane and two iodide ions are located on a twofold symmetry axis perpendicular to the mirror plane. The asymmetric unit, therefore, consists of a quarter of $Cs_2(18\text{-crown-}6)_2I_2$.

Important bond distances and angles are presented in Table 1. The caesium ion adopts eightfold coordination. The bond distances between Cs and O atoms in the crown ether span a range of 3.050 (3)–3.320 (3) Å and the average distance is 3.198 Å. The caesium ion is located 1.520 (2) Å above the mean O plane of the crown ring, which has a mean deviation of 0.22 Å. This value is slightly larger than those reported previously for the related complexes, 1.44 Å in $[Cs_2(18\text{-crown-}6)_2(SCN)_2]$ (Dobler & Phizackerley, 1974) and 1.48 Å in $[Cs_2(18\text{-crown-}6)_2(H_2O)_2]$ (Rusanova et *al.*, 1999). The dihedral angle between the plane consisting of two caesium and two iodide ions and the mean O plane of the crown ether is 76.75 (4)°.

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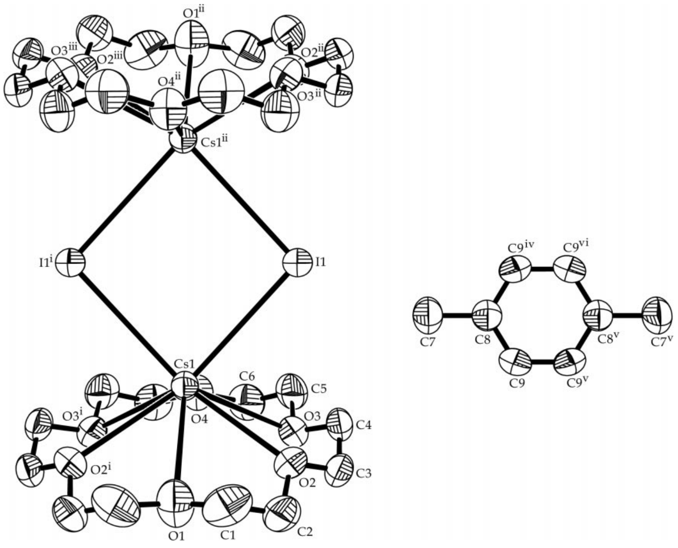

Figure 1
The structure of the title compound with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity. [Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, 1-z$; (iii) $-x, -y, 1-z$; (iv) $-x, y, -z$; (v) $x, 1-y, z$; (vi) $-x, 1-y, -z$]

The *p*-xylene molecules are packed in the voids between the dimer complexes. The centre of *p*-xylene is located on a position of 2/*m* symmetry. We also determined the crystal structure of Cs_2(18-crown-6)$_2I_2$·toluene. The structure is nearly identical to that of the title compound. The toluene molecule is also located at a special position of 2/*m* symmetry in the C2/*m* unit cell, so that the non-centrosymmetric toluene molecules are disordered over the inversion centre to give an image like the *p*-xylene molecule.

Experimental

Equimolar amounts of caesium iodide and 18-crown-6 were dissolved in anhydrous methanol followed by addition of *p*-xylene. Slow evaporation in a calcium chloride desiccator yielded crystals suitable for X-ray analysis.

Crystal data

$[Cs_2I_2(C_{12}H_{24}O_6)_2]\cdot C_8H_{10}$
$M_r = 1154.40$
Monoclinic, $C2/m$
$a = 15.4360$ (10) Å
$b = 17.4317$ (11) Å
$c = 8.1756$ (5) Å
$\beta = 91.195$ (1)°
$V = 2199.4$ (2) Å^3
$Z = 2$
$D_x = 1.743$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7131 reflections
$\theta = 1.8$–28.3°
$\mu = 3.11$ mm^{-1}
$T = 298$ (2) K
Plate, colourless
0.50 × 0.25 × 0.15 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: multiscan (*XPREP*, Siemens, 1996)
$T_{\min} = 0.386$, $T_{\max} = 0.627$
7131 measured reflections
2742 independent reflections
2385 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 28.3°$
$h = -18 \rightarrow 19$
$k = -23 \rightarrow 16$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.09$
2742 reflections
115 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 2.9180P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.20$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cs1—O4	3.050 (3)	Cs1—O3	3.320 (3)
Cs1—O2	3.159 (2)	Cs1—C5	3.793 (4)
Cs1—O1	3.178 (4)	Cs1—I1	3.8940 (3)
I1—Cs1—I1^{i}	84.929 (10)	Cs1—I1—Cs1^{ii}	95.071 (10)

Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, 1-z$.

The C—H atoms were added at their calculated positions ($U = 1.2$ times that of the corresponding C atom) and refined using a riding model.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Siemens, 1996); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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