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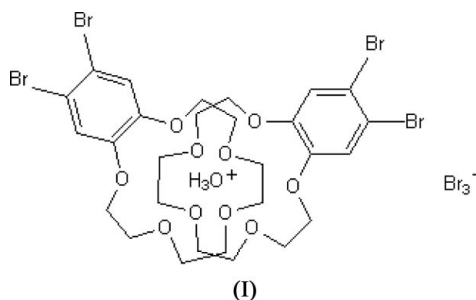
Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å
 R factor = 0.053
 wR factor = 0.133
Data-to-parameter ratio = 16.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(2,3-dibromo-6,7,9,10,12,13,15,16-
octahydro-5,8,11,14,17-pentaoxabenzocyclo-
pentadecene) hydroxonium tribromide

In the title compound, $2\text{C}_{14}\text{H}_{18}\text{O}_5\text{Br}_2 \cdot \text{H}_3\text{O}^+ \cdot \text{Br}_3^-$, the two 15-crown-5 macrocyclic rings are linked by an oxonium cation *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a positively charged unsymmetrical sandwich-like compound with a tribromide counter-anion. The conformations of the two crown-5 fragments have *gauche* C—C and *anti* C—O linkages.

Comment

The reaction of benzo-15-crown-5 with some lanthanide metals normally leads to the formation of a complex *via* metal–oxygen chelation, *e.g.* trichloro(15-crown-5)neodymium (Rogers *et al.*, 1991) and salt-type compounds such as $[\text{M}(\text{H}_2\text{O})_2(15\text{-crown-5})](\text{NO}_3)_2$ (Hao *et al.*, 2005). However, a variety of different products without metal coordination by the crown ether have also been observed, for example (15-crown-5)triaquadichlorodioxouranium (Hassaballa *et al.*, 1998). Similarly, in our study, no complexation product was obtained from a solution mixture containing benzo-15-crown-5, hydrogen bromide and europium nitrate but, instead, bromination of the benzene ring and the formation of a tribromide anion occurred, resulting in the title compound, (I).



In contrast to 4-nitrobenzo-15-crown-5 tetrachloroaurate(III) oxonium monohydrate clathrate (Calleja *et al.*, 2001), compound (I) has two dibromobenzo-15-crown-5 molecules linked by hydrogen bonds between the annular O atoms, O1', O2, O4', O7 and O8 and the H atoms of the oxonium cation (Fig. 1, Table 2). As in the unsubstituted benzo-15-crown-5 (Hanson, 1978), the crown ether molecules maintain their approximate plane of symmetry through O3 and the mid-point of the C9—C14 bond for the first macrocycle and through O8 and the mid-point of the C23—C28 bond for the second ring. The torsion angles (Table 1) also indicate a similar conformation, individual O—C—O segments being ag^-a , g^-g^-a , ag^+g^+ and ag^+a in the two crown ether units. The bond lengths and angles are also close to those in benzo-15-crown-5 [average C—C, 1.485; C—O, 1.360 (5)—

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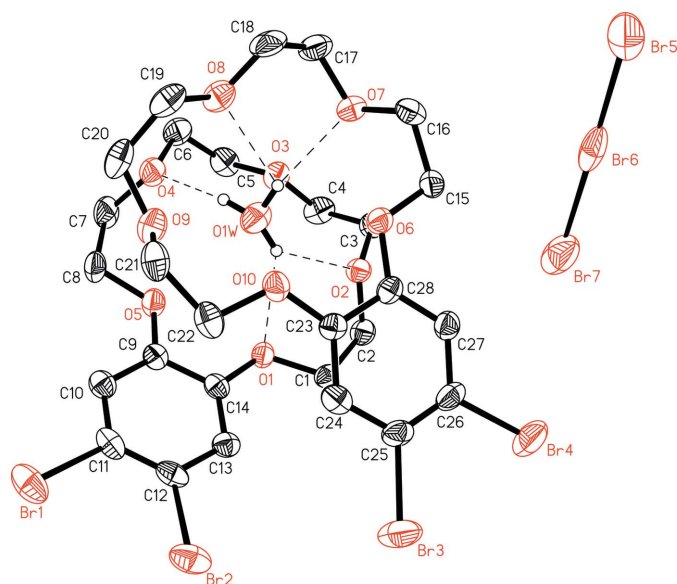


Figure 1

Structure of the title compound, (I), with 30% probability displacement ellipsoids. H atoms of the 15-crown-5 have been omitted for clarity. Dashed lines indicate hydrogen bonds.

1.431 (5) Å], indicating that the hydrogen bonds that link the two molecules together have little effect on the internal structure of the macrocycles. O—H···O and C—H···Br hydrogen bonds stabilize the crystal structure (see Table 2 and Fig. 2).

Experimental

Benzo-15-crown-5 (0.268 g, 1 mmol) in 10 ml of mixed acetonitrile-methanol (3:1 v/v) was added to europium nitrate (0.445 g, 1 mmol) in 10 ml mixed MeCN–methanol (3:1 v/v) solution. HBr (1 ml, 12.5 M, 12.5 mmol) was slowly added to the mixture. The resulting solution was left to evaporate at room temperature. Orange crystals suitable for X-ray investigation were obtained after three weeks (yield 1.55 g, 70%; melting point; 444.4–445.3 K. Microelemental analysis data: Found (calculated) C 30.26 (29.03), H 3.51 (3.62) and O 15.84% (16.5%).

Crystal data

$2C_{14}H_{18}Br_2O_5 \cdot H_3O^+ \cdot Br_3^-$	$Z = 2$
$M_r = 1110.96$	$D_x = 1.882 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.568 (3) \text{ \AA}$	Cell parameters from 957 reflections
$b = 13.590 (3) \text{ \AA}$	$\theta = 1.6\text{--}25.0^\circ$
$c = 13.829 (3) \text{ \AA}$	$\mu = 7.21 \text{ mm}^{-1}$
$\alpha = 70.697 (4)^\circ$	$T = 273 (2) \text{ K}$
$\beta = 66.718 (4)^\circ$	Block, brown
$\gamma = 67.601 (4)^\circ$	$0.50 \times 0.27 \times 0.13 \text{ mm}$
$V = 1960.4 (7) \text{ \AA}^3$	

Data collection

Bruker SMART APEX area-detector diffractometer	6883 independent reflections
ω scan	4087 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{int} = 0.040$
$T_{min} = 0.104$, $T_{max} = 0.392$	$\theta_{max} = 25.0^\circ$
18603 measured reflections	$h = -14 \rightarrow 14$
	$k = -16 \rightarrow 16$
	$l = -16 \rightarrow 16$

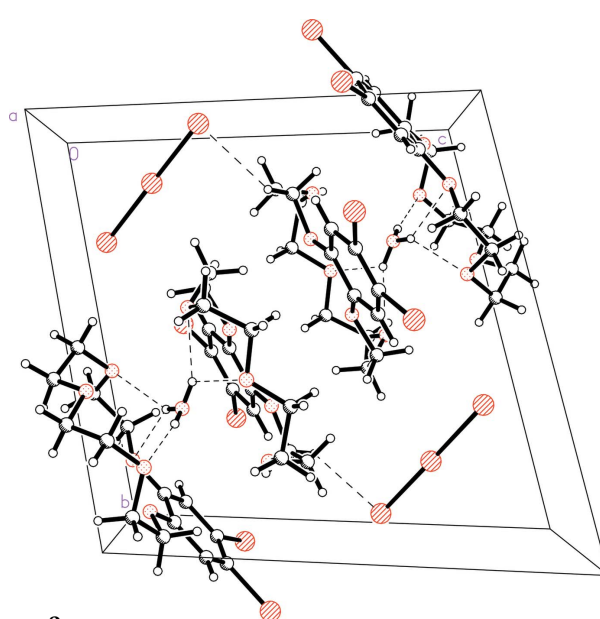


Figure 2

Packing of (I), viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.133$
 $S = 1.02$
 6883 reflections
 424 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 5.5902P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.92 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.85 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Br1—C11	1.908 (6)	O4—C6	1.430 (8)
Br2—C12	1.898 (7)	O5—C9	1.357 (7)
Br3—C25	1.900 (7)	O5—C8	1.436 (7)
Br4—C26	1.899 (7)	O6—C28	1.359 (7)
Br5—Br6	2.516 (2)	O6—C15	1.429 (7)
Br6—Br7	2.558 (2)	O7—C17	1.422 (8)
O1—C14	1.375 (7)	O7—C16	1.430 (7)
O1—C1	1.435 (7)	O8—C18	1.409 (9)
O2—C2	1.425 (7)	O8—C19	1.415 (8)
O2—C3	1.430 (7)	O9—C21	1.420 (8)
O3—C4	1.411 (8)	O9—C20	1.431 (8)
O3—C5	1.431 (8)	O10—C23	1.353 (7)
O4—C7	1.417 (8)	O10—C22	1.429 (7)
O5—C9—C14—O1	0.4 (8)	C23—O10—C22—C21	−177.3 (5)
C9—O5—C8—C7	177.8 (6)	O9—C21—C22—O10	63.6 (7)
O4—C7—C8—O5	−65.1 (8)	C20—O9—C21—C22	−163.7 (6)
C6—O4—C7—C8	163.4 (6)	C21—O9—C20—C19	83.2 (8)
C7—O4—C6—C5	−82.7 (8)	O8—C19—C20—O9	66.6 (8)
O3—C5—C6—O4	−64.9 (8)	C18—O8—C19—C20	−179.0 (6)
C4—O3—C5—C6	172.4 (6)	C19—O8—C18—C17	178.4 (6)
C5—O3—C4—C3	−177.8 (5)	O7—C17—C18—O8	−63.5 (9)
O2—C3—C4—O3	71.2 (7)	C16—O7—C17—C18	−80.2 (8)
C2—O2—C3—C4	84.8 (7)	C17—O7—C16—C15	162.0 (6)
C3—O2—C2—C1	−161.4 (5)	O6—C15—C16—O7	−65.6 (7)
O1—C1—C2—O2	62.5 (6)	C28—O6—C15—C16	−178.7 (5)
C14—O1—C1—C2	−176.5 (5)	C15—O6—C28—C23	−175.7 (5)
C8—O5—C9—C14	−172.5 (5)	C22—O10—C23—C28	170.4 (5)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O1	0.85 (8)	2.40 (8)	3.128 (8)	143 (7)
O1W—H1W1...O2	0.85 (8)	2.18 (8)	2.882 (8)	140 (7)
O1W—H1W2...O7	0.86 (6)	2.16 (5)	2.959 (8)	156 (6)
O1W—H1W2...O8	0.86 (6)	2.34 (9)	2.859 (9)	119 (5)
O1W—H1W3...O4	0.86 (8)	2.06 (8)	2.910 (9)	168 (7)
C22—H22A...Br5 ⁱ	0.97	2.86	3.676 (7)	142

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

After their location in a difference map, all C-bound H atoms were positioned geometrically with C—H = 0.93–0.97 Å and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecule were located in a difference Fourier map and refined isotropically, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ using restraints of O—H = 0.85 (5) and 0.86 (6) Å for the O—H distances.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for

publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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