Tetrabenzo-24-crown-8 tris(1,2-dichloroethane) solvate[1]

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The title compound, $C_{32}H_{32}O_8 \cdot 3C_2H_4Cl_2$, illustrates how tetrabenzo-24-crown-8 may be solvated by a common solvent-extraction diluent, 1,2-dichloroethane (DCE). Two molecules of DCE occupy the crown cavity, forming weak hydrogen bonds to the ether O atoms and the crown arene rings, while the crown adopts its most commonly observed binding conformation. The asymmetric unit is composed of

[1] Alternative name: 2,5,12,15,22,25,32,35-octaoxopentacyclo[34.4.0.0^{6,11}.0^{16,21}.-0^{26,31}]tetraconta-6,8,10,16,18,20,26,28,30,36,38,40-dodecaene tris(1,2-dichloroethane) solvate.

two molecules of tetrabenzo-24-crown-8 and six molecules of DCE.

Comment

Solvation of a host molecule can inhibit guest complexation if the energy of desolvating the host molecule is sufficiently high (Bryan *et al.*, 2001). Solvation can also alter the host conformation, which could facilitate or inhibit the eventual guest complexation (Sachleben *et al.*, 1997). As part of our continuing studies of tetrabenzo-24-crown-8 (Levitskaia *et al.*, 2000; Bryan *et al.*, 2000), we have determined its structure when solvated by three 1,2-dichloroethane (DCE) molecules, to give the title compound, (I).
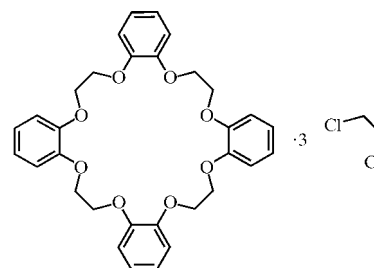
(I)

Two molecules of tetrabenzo-24-crown-8 and six molecules of DCE make up the asymmetric unit of (I) (Fig. 1). Both crown-ether molecules adopt the conformation previously observed when bound to acetonitrile, Cs^+ or Rb^+ (Bryan *et al.*, 2000, 1999; Levitskaia *et al.*, 2000). Two DCE molecules fill
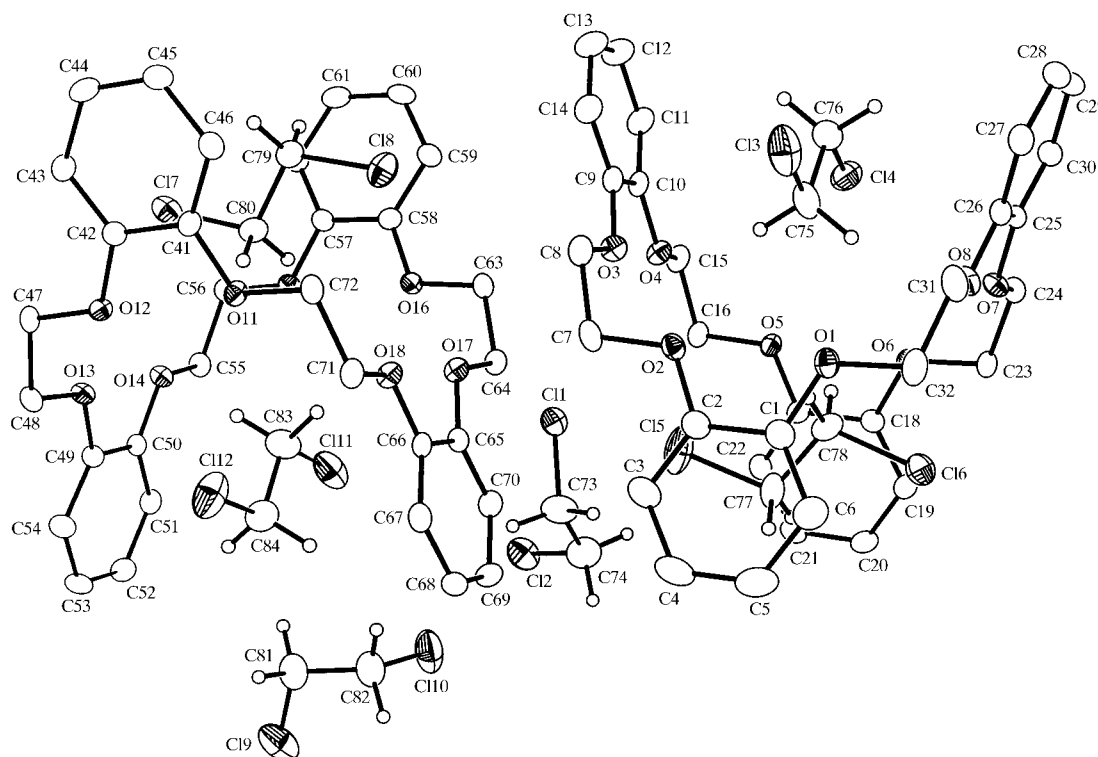

Figure 1
The asymmetric unit of (I) showing 50% displacement ellipsoids. H atoms have been omitted for clarity, except those on 1,2-dichloroethane, and only the major disorder components are shown.

organic compounds

each crown cavity, forming weak C—H···O and C—H···π hydrogen bonds to both the crown O atoms and the arene rings. The geometrical parameters for these interactions, as calculated by *PLATON* (Spek, 2001), are presented in Table 2, with ring centroids represented as $Cg1$ (C1–C6), $Cg2$ (C9–C13) *etc.*

Polar solvents, such as acetonitrile and nitromethane, have often been observed to coordinate crown-ether host molecules (Sachleben *et al.*, 1997), but, to the best of our knowledge, this is the first report of a crown-ether–DCE complex. All four of the included solvent molecules adopt an *anti* configuration. Two additional DCE molecules are observed outside the crown; both adopt a *gauche* conformation and neither appears to engage in hydrogen bonding.

No π-stacking of arene rings is observed in the crystal structure of (I). However, close C_{arene}—H···π contacts, some of which may represent edge–face arene interactions, are clearly present. The geometrical parameters for these inter-actions, as calculated by *PLATON*, are also presented in Table 2.

Experimental

Tetrabenzo-24-crown-8 was prepared as described by Pedersen (1967) and Brown & Foubister (1983). Crystals of (I) were prepared by slow evaporation of a solution in 1,2-dichloroethane.

Crystal data

$C_{32}H_{32}O_8 \cdot 3C_2H_4Cl_2$	$Z = 4$
$M_r = 841.43$	$D_x = 1.418$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.478$ (2) Å	Cell parameters from 25
$b = 14.3841$ (18) Å	reflections
$c = 21.381$ (2) Å	$\theta = 10.0$–14.4°
$\alpha = 97.144$ (10)°	$\mu = 0.49$ mm^{-1}
$\beta = 97.854$ (10)°	$T = 100$ K
$\gamma = 103.405$ (11)°	Hexagonal rod, colorless
$V = 3941.6$ (9) Å^3	$0.56 \times 0.34 \times 0.23$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.025$
diffractometer	$\theta_{max} = 27.5°$
ω scans	$h = -17 \rightarrow 17$
Absorption correction: ψ scan	$k = -18 \rightarrow 18$
(*SHELXTL*; Bruker, 1997)	$l = -20 \rightarrow 27$
$T_{min} = 0.840$, $T_{max} = 0.884$	3 standard reflections
25 644 measured reflections	frequency: 120 min
18 086 independent reflections	intensity decay: 6%
12 891 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2$
$R(F) = 0.044$	$+ 2.861P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
18 086 reflections	$\Delta\rho_{max} = 0.95$ e Å^{-3}
1027 parameters	$\Delta\rho_{min} = -0.76$ e Å^{-3}
H-atom parameters constrained	

Four of the 1,2-dichloroethane molecules were found to be disordered. All were modelled over two sites (occupancy factors C73/C74 72.5:27.5, C75/C76 50:50, C77/C78 52.5:47.5 and C79/C80 78:22) and were freely refined. All non-H atoms were refined anisotropically, and only one (C73*A*) exhibited unusual elongation of its displacement ellipsoid. All H atoms were placed in calculated

Table 1
Selected torsion angles (°).

C32—O1—C1—C2	176.46 (19)	C58—O16—C63—C64	177.67 (17)
C1—O1—C32—C31	174.15 (18)	C65—O17—C64—C63	177.83 (17)
C7—O2—C2—C1	−177.95 (19)	C64—O17—C65—C66	174.69 (17)
C2—O2—C7—C8	−175.11 (18)	C71—O18—C66—C65	−176.56 (17)
C8—O3—C9—C10	−175.13 (18)	C66—O18—C71—C72	−174.92 (17)
C9—O3—C8—C7	−178.52 (17)	O1—C1—C2—O2	−1.0 (3)
C15—O4—C10—C9	175.41 (18)	O2—C7—C8—O3	78.0 (2)
C10—O4—C15—C16	179.31 (17)	O3—C9—C10—O4	0.8 (3)
C17—O5—C16—C15	179.96 (17)	O4—C15—C16—O5	−79.5 (2)
C16—O5—C17—C18	178.01 (18)	O5—C17—C18—O6	−1.3 (3)
C18—O6—C23—C24	−178.72 (17)	O6—C23—C24—O7	76.0 (2)
C23—O6—C18—C17	−173.90 (18)	O7—C25—C26—O8	0.4 (3)
C25—O7—C24—C23	−179.10 (17)	O8—C31—C32—O1	−77.3 (2)
C24—O7—C25—C26	−176.81 (18)	O11—C41—C42—O12	−0.6 (3)
C31—O8—C26—C25	174.84 (18)	O12—C47—C48—O13	−79.68 (19)
C26—O8—C31—C32	179.68 (18)	O13—C49—C50—O14	−1.1 (2)
C41—O11—C72—C71	−177.49 (17)	O14—C55—C56—O15	78.5 (2)
C72—O11—C41—C42	−175.44 (18)	O15—C57—C58—O16	−0.7 (3)
C47—O12—C42—C41	−178.80 (17)	O16—C63—C64—O17	−76.9 (2)
C42—O12—C47—C48	172.20 (17)	O17—C65—C66—O18	0.3 (3)
C49—O13—C48—C47	179.82 (16)	O18—C71—C72—O11	79.5 (2)
C48—O13—C49—C50	175.72 (17)	Cl1—C73—C74—Cl2	−66.3 (4)
C55—O14—C50—C49	−176.73 (17)	Cl3—C75—C76—Cl4	−178.8 (3)
C50—O14—C55—C56	−176.43 (16)	Cl5—C77—C78—Cl6	179.2 (2)
C56—O15—C57—C58	−174.93 (18)	Cl8—C79—C80—Cl7	179.28 (14)
C57—O15—C56—C55	179.16 (17)	Cl9—C81—C82—Cl10	64.2 (2)
C63—O16—C58—C57	176.97 (18)	Cl11—C83—C84—Cl12	178.98 (13)

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

The ring centroids are as follows: $Cg1$ C1–C6, $Cg2$ C9–C14, $Cg3$ C17–C22, $Cg4$ C25–C30, $Cg5$ C41–C46, $Cg6$ C49–C54, $Cg7$ C57–C62 and $Cg8$ C65–C70.

D—H···A	D—H	H···A	D···A	D—H···A
C75—H75A···O8	0.99	2.44	3.302 (6)	145
C75—H75B···O3	0.99	2.55	3.385 (7)	142
C78—H78A···O1	0.99	2.51	3.389 (5)	147
C78—H78B···O6	0.99	2.46	3.310 (4)	143
C80—H80B···O15	0.99	2.58	3.351 (3)	134
C83—H83A···O17	0.99	2.55	3.391 (3)	142
C83—H83B···O14	0.99	2.57	3.404 (3)	142
C3—H3···$Cg8$	0.95	2.90	3.788 (3)	155
C15—H15A···$Cg5^{i}$	0.99	2.94	3.399 (2)	109
C15—H15B···$Cg5^{i}$	0.99	3.09	3.399 (2)	99
C23—H23A···$Cg4^{ii}$	0.99	3.24	3.354 (2)	88
C23—H23B···$Cg4^{ii}$	0.99	2.71	3.354 (2)	123
C27—H27···$Cg1^{iii}$	0.95	3.19	4.124 (3)	167
C43—H43···$Cg6^{iv}$	0.95	2.77	3.684 (2)	162
C51—H51···$Cg7^{v}$	0.95	2.76	3.679 (2)	164
C59—H59···$Cg2$	0.95	3.23	4.144 (2)	162
C71—H71B···$Cg3^{vi}$	0.99	2.76	3.458 (2)	128
C77—H77A···$Cg1$	0.99	2.90	3.611 (5)	129
C77—H77B···$Cg3$	0.99	2.83	3.605 (6)	136
C79—H79A···$Cg5$	0.99	2.92	3.682 (3)	135
C79—H79B···$Cg7$	0.99	2.85	3.639 (3)	137
C84—H84A···$Cg8$	0.99	2.82	3.575 (3)	134
C84—H84B···$Cg6$	0.99	2.92	3.690 (3)	135
C78A—H78C···$Cg3$	0.99	2.98	3.725 (6)	133
C78A—H78D···$Cg1$	0.99	2.80	3.583 (6)	136
C80A—H80C···$Cg7$	0.99	2.86	3.641 (11)	137
C80A—H80D···$Cg5$	0.99	2.82	3.574 (11)	133

Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, 2 - y, 1 - z$; (iii) $3 - x, 2 - y, 1 - z$; (iv) $4 - x, 3 - y, -z$; (v) $3 - x, 3 - y, -z$; (vi) $1 + x, y, z$.

positions, refined using a riding model and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they were attached, with methylene C—H = 0.99 and arene C—H = 0.95 Å. The nine

highest peaks in the final difference map (electron density greater than 0.4 e Å^{-3}) were located near Cl atoms.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1996); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *PLATON* (Spek, 2001).

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