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A tetra-*tert*-butylcalix[4]arene-12-crown-4 *N,N*-dimethylformamide inclusion complex

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The crown ether portion of the title complex, $C_{50}H_{66}O_6 \cdot C_3H_7NO$, is not pre-organized for metal binding to the four calix[4]arene O atoms. *N,N*-Dimethylformamide forms a hydrogen-bond bridge between two calix[4]arene–crown molecules.

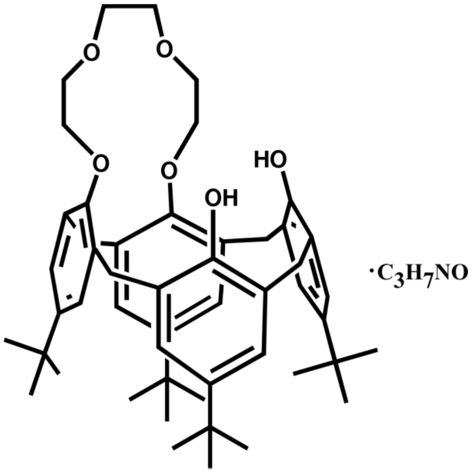
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.058
wR factor = 0.171
Data-to-parameter ratio = 14.8

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

Comment

We are beginning a new research effort investigating tight ion-pair recognition. As a first step, we prepared the title compound (Arduini *et al.*, 1997) in hopes of using its crown ring to partially bind a metal cation and the two remaining phenolic groups as precursors to appendages containing anion-binding groups. The structure of the title compound, (I), was determined to ascertain the degree of pre-organization for cation binding present in this molecule.



(I)

Optimal metal binding will occur when the crown ether adopts a conformation with all O—C—C—O torsion angles *anti*, and all C—O—C—C torsion angles *gauche*. Examination of Table 1 shows this is not the case for the structure reported here. The crown ether is collapsed in upon itself, as is commonly observed in the structures of uncomplexed crown ether molecules (Bryan *et al.*, 2001, and references therein). This collapse forms relatively short C—H···O contacts, one of which is listed in Table 2. As evident in the figures, the two crown atoms O2 and O3 are not well oriented for binding a metal cation together with the O atoms directly attached to the calix[4]arene.

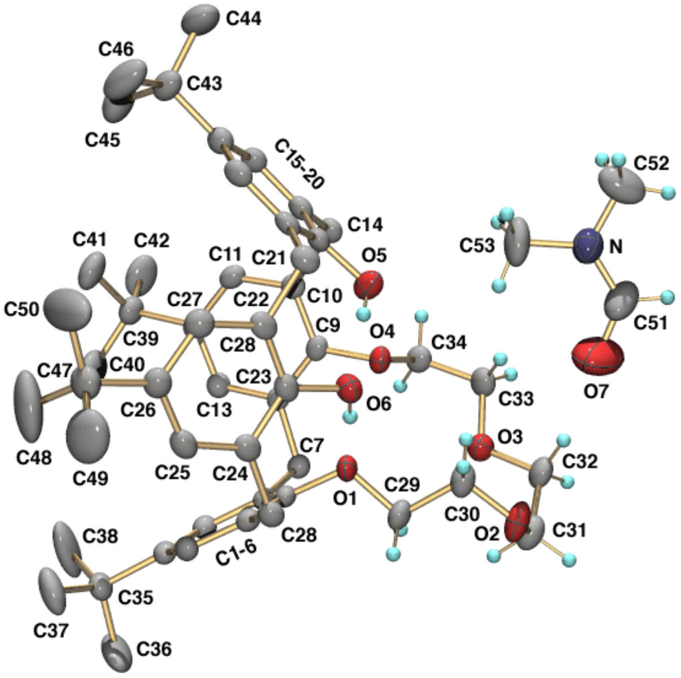


Figure 1
The molecular structure of the title compound, showing 50% displacement ellipsoids.

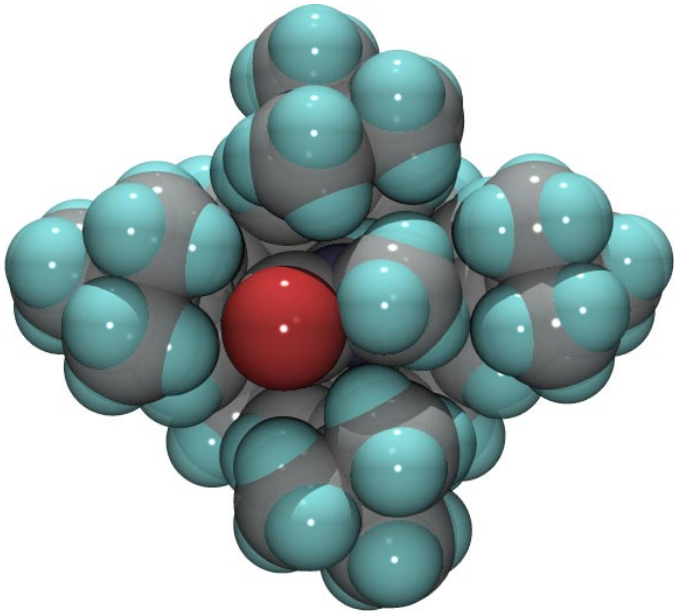


Figure 2
Space-filling model of the title compound, showing DMF (center) surrounded by the calix[4]arene cavity.

The calix[4]arene adopts the cone conformation, as anticipated when two phenolic groups remain unsubstituted (Böhmer, 1995). This conformation facilitates hydrogen bonding between the phenolic H atoms and the calix[4]arene O atoms (Table 2).

The *N,N*-dimethylformamide (DMF) molecule acts as a bridge between two calix–crown molecules. Within the asymmetric unit, C—H···O hydrogen bonds (Table 2) are formed both between the crown ring and the DMF O atom (O7), and between one of the DMF methyl atoms (C53) and a calix phenolic O atom (O5). The DMF molecule is enveloped by a symmetry-equivalent (symmetry code: x, $3/2-y$, $1/2+z$) calix[4]arene cavity (Fig. 2). The DMF carbonyl C atom (C51) and one of its methyl groups (C52) form numerous C—H···π interactions with the interior of the calixarene rings (Table 2, where *C*g1 represents the centroid for C1–6, *C*g2 for C8–13, *C*g3 for C15–20, and *C*g4 for C22–27).

Experimental

The title compound was prepared as previously described (Arduini *et al.*, 1997) and crystallized from *N,N*-dimethylformamide.

Crystal data

$C_{50}H_{66}O_6 \cdot C_3H_7NO$
$M_r = 836.1$
Monoclinic, $P2_1/c$
$a = 12.6115\ (13)$ Å
$b = 20.000\ (3)$ Å
$c = 19.995\ (3)$ Å
$\beta = 107.087\ (9)°$
$V = 4820.7\ (12)$ Å^3
$Z = 4$
$D_x = 1.15$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0–14.4°$
$\mu = 0.08$ mm^{-1}
$T = 173$ K
Fragment, colorless
0.47 × 0.41 × 0.34 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
10485 measured reflections
8451 independent reflections
5151 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 25.0°$
$h = -14 \rightarrow 0$
$k = -23 \rightarrow 13$
$l = -22 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[(F^2 > 2\sigma\ (F^2)] = 0.058$
$wR(F^2) = 0.171$
$S = 1.02$
8451 reflections
570 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 3.2092P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.00$
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O5—H5	0.82 (3)	N—C52	1.429 (5)
O6—H6	0.84 (3)	N—C53	1.454 (5)
O7—C51	1.235 (6)	N—C51	1.315 (5)
C16—O5—H5	109 (2)	C51—N—C53	124.6 (4)
C23—O6—H6	112 (2)	C51—N—C52	119.6 (4)
C52—N—C53	115.8 (3)	O7—C51—N	125.3 (5)
C31—O2—C30—C29	71.8 (4)	C53—N—C51—O7	0.0 (8)
C30—O2—C31—C32	56.6 (4)	O1—C29—C30—O2	−175.7 (3)
C33—O3—C32—C31	154.7 (3)	O2—C31—C32—O3	−85.4 (3)
C32—O3—C33—C34	−172.9 (3)	O3—C33—C34—O4	69.8 (3)
C52—N—C51—O7	176.6 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O6	0.82 (3)	1.88 (4)	2.694 (3)	175 (4)
O6—H6···O1	0.84 (3)	1.85 (3)	2.682 (3)	172 (4)
C30—H30*A*···O3	0.99	2.39	3.011 (4)	120
C32—H32*A*···O7	0.99	2.35	3.324 (6)	168
C53—H53*C*···O5	0.98	2.71	3.220 (4)	113
C51—H51···*Cg*3$^{\rm i}$	0.95	3.04	3.961 (6)	165
C52—H52*A*···*Cg*3$^{\rm i}$	0.98	3.15	4.106 (4)	165
C52—H52*B*···*Cg*1$^{\rm i}$	0.98	2.95	3.590 (4)	124
C52—H52*B*···*Cg*4$^{\rm i}$	0.98	2.97	3.592 (4)	122
C52—H52*C*···*Cg*2$^{\rm i}$	0.98	2.93	3.583 (4)	125

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

The hydroxyl H atoms were located in a difference map, and their coordinates refined, although their O—H bond lengths were restrained to be equal. All other H atoms were placed in calculated positions, and refined using a riding model. All H atoms were given an isotropic displacement parameter equal to 1.2 (CH and CH_2) or 1.5 (OH and CH_3) times the equivalent isotropic displacement parameter of the atom to which they were attached. The C—H distances used depended on the type of C atom: $C_{\rm methyl}$—H = 0.98, $C_{\rm methylene}$—H = 0.99, and C_{sp^2}—H = 0.95 Å. The largest peak of residual electron density in the final difference map is 0.66 e Å^{-3}, and is located roughly 1.3 Å from N, C51 and C52. This peak, along with some unusual variations in the displacement parameters in the the DMF molecule, suggest there is some unresolved disorder in this molecule. The next highest peak is 0.39 e Å^{-3}, and is located near C49.

Data collection: *CAD*-4/*PC* (Nonius, 1996); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2001).

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