

The lithium chloride complex of the *anti* isomer of the bridged spherand $C_{50}H_{48}O_6$

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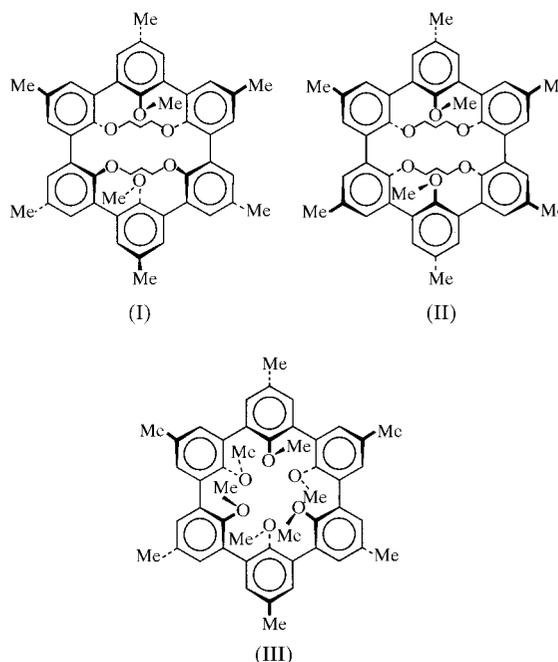
The structure of (11,12,24,25-tetrahydro-28,34-dimethoxy-3,6,16,19,31,37-hexamethyl-1,21[1',3']:8,14[1'',3'']-dibenzeno-10*H*,23*H*-tetrabenzo[*f,h,o,z*][1,5,10,14]tetraoxacyclooctadecane)lithium chloride monohydrate, *anti*-[Li($C_{50}H_{48}O_6$)]Cl·H₂O, at 100 K reveals that the host is less strained than that of the *syn*-bridged isomer. There are two independent complex cations, each lying on a center of symmetry. Four short [1.944 (2)–1.998 (2) Å] and two long [2.381 (2) and 2.455 (2) Å] Li⁺···O distances provide six-coordination in a distorted octahedral environment.

Comment

The synthesis and properties of the bridged spherand host $C_{50}H_{48}O_6$ were first reported in 1979 (Cram *et al.*, 1979). The structure was taken to be that of the *anti* compound, (I), since that is the only structure that can be assembled using CPK molecular models. However, crystal structure analysis (Cram *et al.*, 1981; Knobler *et al.*, 1992) demonstrated that the synthesis had in fact produced the *syn* compound, (II). Since both models and calculations (Kollman *et al.*, 1985) indicated that (I) should complex Li⁺ and Na⁺ ions not only more strongly than (II), but also more strongly than (III), the strongest binder of Li⁺ known at the time (Cram *et al.*, 1981), the synthesis of (I) was pursued further. When (I) was finally isolated some years later, its tenacious hold on the templating Li⁺ confirmed these predictions. Indeed, spherand (I) does not release Li⁺ when the complex is heated at 400 K in methanol-water, whereas (III)⊙Li⁺ decomplexes under these conditions. Thus, (I)⊙Li⁺ may be the first and smallest carceplex, since it probably cannot dissociate unless covalent bonds are broken (Maverick & Cram, 1996a).

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The crystal structure of (I)·Li⁺ reported here demonstrates, as predicted, that the *anti*-bridged host (I) is less strained than (II), both by the absence of very short O···O interactions and in the dihedral angles between adjoining aromatic rings. Model analysis (Cram *et al.*, 1979) showed that spheres of radius 0.65–0.95 Å could be pushed into the cavity of (I). Calculations (Kollman *et al.*, 1985) and the present analysis result in a centrosymmetric distorted octahedral coordination geometry with four short and two long Li⁺···O distances. Distances and angles about the cation appear in Table 1. The structural features of the Li⁺ complexes of (I), (II) and (III) are compared in Table 2.



Data taken in 1993 at room temperature [$a = 44.603$ (9), $b = 12.426$ (3), $c = 17.201$ (4) Å and $\beta = 109.414$ (6)°; Cu $K\alpha$ radiation] gave essentially the same structure as that reported here, except that fewer intensities were measured, precision was lower, and the anion and solvent were more difficult to locate and refine. A drawing of one of the complexes and some structural features were published (Maverick & Cram, 1996b).

The present 100 K Mo $K\alpha$ data set is much more complete, even though the shadow of the beam stop on many of the frames made it necessary to remove 92 redundant reflections. The two half-molecules in the asymmetric unit are similar, but not identical. For example, C39 is better located than C9 (represented by a disorder model), perhaps reflecting the somewhat longer Li⁺···O8 distance. Chloride ions are disordered over two different centers of symmetry, one at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ and one at $(0, 0, \frac{1}{4})$, and solvent water is similarly disordered, such that in this model each partial-occupancy chloride ion is associated with a water O atom, roughly at hydrogen-bonding distance. Again, the disorder is slightly different at the two sites. A drawing showing the anions and water is included in the supplementary data.

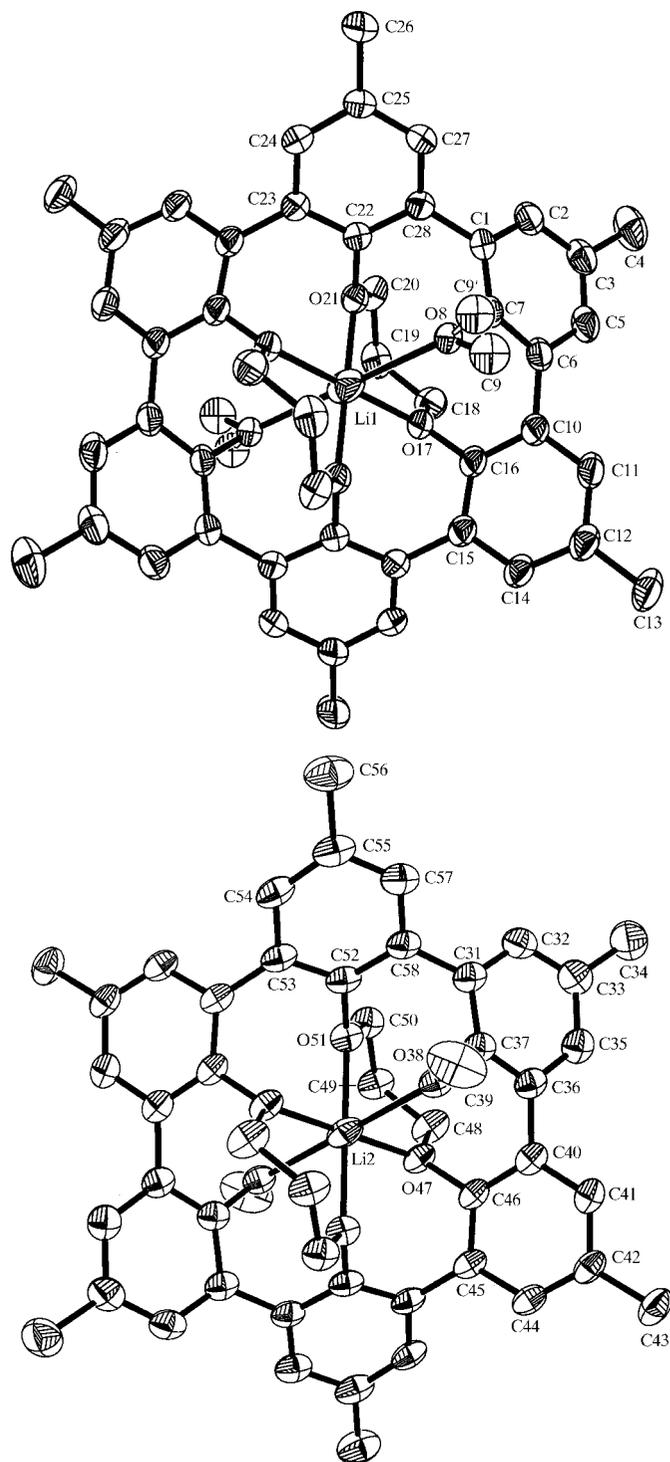


Figure 1
Views of the two independent molecules in the asymmetric unit. Ellipsoids enclose 50% probability. The numbering scheme for non-H atoms is shown; unnumbered atoms are generated from the numbered atoms by the symmetry operations $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ for C1–C28 and $(-x, 1 - y, -z)$ for C31–C58. Chloride ions and solvent water molecules are not shown.

Experimental

The only isomer formed when tetrahydrofuran is the solvent in the final step in the synthesis is (II) (Cram *et al.*, 1985). However, when

the reaction of the precursor dibromide with ferric acetylacetonate is carried out in benzene, both the *syn* and *anti* spherand complexes are formed. The *syn* isomer, (II), decomplexes at 370 K in methanol–water, while the *anti* complex is unchanged by this treatment and therefore crystalline (II) can be removed by filtration. The remaining *anti*-LiCl complex of (I) was isolated by CHCl_3 extraction and recrystallized from methanol.

Crystal data

$[\text{Li}(\text{C}_{50}\text{H}_{48}\text{O}_6)]\text{Cl}\cdot\text{H}_2\text{O}$
 $M_r = 805.29$
 Monoclinic, C_2/c
 $a = 44.486(5) \text{ \AA}$
 $b = 12.1755(13) \text{ \AA}$
 $c = 16.995(2) \text{ \AA}$
 $\beta = 108.958(2)^\circ$
 $V = 8705.8(16) \text{ \AA}^3$
 $Z = 8$

$D_x = 1.229 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 4625 reflections
 $\theta = 2.2\text{--}26.3^\circ$
 $\mu = 0.139 \text{ mm}^{-1}$
 $T = 100(2) \text{ K}$
 Parallelepiped, colorless
 $0.45 \times 0.25 \times 0.15 \text{ mm}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O8–Li1	2.455 (2)	O38–Li2	2.381 (2)
O17–Li1	1.962 (2)	O47–Li2	1.944 (2)
O21–Li1	1.952 (2)	O51–Li2	1.998 (2)
O21–Li1–O17 ⁱ	87.20 (8)	O47–Li2–O51 ⁱⁱ	85.95 (8)
O21–Li1–O8 ⁱ	92.80 (8)	O47–Li2–O51	94.05 (8)
O21–Li1–O8 ⁱ	101.14 (7)	O47–Li2–O38 ⁱⁱ	99.25 (8)
O17–Li1–O8 ⁱ	102.52 (7)	O51–Li2–O38 ⁱⁱ	103.18 (7)
O21–Li1–O8	78.86 (7)	O47–Li2–O38	80.75 (8)
O17–Li1–O8	77.48 (7)	O51–Li2–O38	76.82 (7)

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

Table 2

Geometric features and complexation free energies (\AA , $^\circ$, kJ mol^{-1}) for Li^+ complexes of (I), (II) and (III).

	(I) $\odot \text{Li}^{+c}$	(I) $\odot \text{Li}^{+a}$	(II) $\odot \text{Li}^{+b}$	(II) $\odot \text{Li}^{+a}$	(III) $\odot \text{Li}^{+b}$	(III) $\odot \text{Li}^{+a}$
O...O						
Number < 2.80	4	(6)	7	(6)	6	(6)
Number < 3.00	8	(6)	8	(8)	6	(6)
Shortest	2.70	(2.74)	2.51	(2.41)	2.79	(2.74)
$\text{Li}^+ \cdots \text{O}$						
Number < 2.50	6	(6)	5	(5)	6	(6)
Number < 2.00	4	(0)	0	(0)	0	(0)
Average < 2.50	2.12	(2.10)	2.04	(2.05)	2.14	(2.11)
Range ^d	1.94–2.46	(2.02–2.27)	2.00–2.89	(2.05–2.60)	–	(–)
Li^+ radius ^e	0.72	(0.70)	0.64	(0.65)	0.74	(0.71)
Aryl–aryl dihedral angle						
Average	47	(62)	50	(41)	56	(55)
Range	44–52	(–)	28–51	(8–57)	–	(–)
$-\Delta G^\circ$ of complexation ^f	$\gg 96^g$	(–)	70	(–)	> 96	(–)

Notes: (a) calculated values from Kollman *et al.* (1985) are given in parentheses; (b) from Knobler *et al.* (1992); (c) this work; (d) a survey by Hermansson *et al.* (1977) gives 1.94–1.99 \AA for four-coordinate, 2.04–2.12 \AA for five-coordinate and 2.13–2.17 \AA for six-coordinate Li^+ . For (II) $\odot \text{Li}^+$, the 2.89 \AA distance was deemed non-bonded (Knobler *et al.*, 1992). The wide range for (I) reflects the four short and two long $\text{Li}^+ \cdots \text{O}$ distances in the distorted octahedron (see Table 1); (e) calculated by subtracting an oxygen radius of 1.40 \AA from the average $\text{Li}^+ \cdots \text{O}$ distance. Shannon (1976) gives 0.76 and 0.59 \AA for six- and four-coordination, respectively; (f) Cram & Lein (1985); (g) deduced from the fact that (I) $\odot \text{Li}^+$ does not decomplex at 400 K in methanol/water (see text).

Data collection

Bruker SMART 1 K CCD area-detector diffractometer
 φ and ω scans
 27 872 measured reflections
 10 410 independent reflections
 4825 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -59 \rightarrow 47$
 $k = -15 \rightarrow 15$
 $l = -21 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.074$
 $wR(F^2) = 0.241$
 $S = 0.929$
 10 410 reflections
 556 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1366P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.026$
 $\Delta\rho_{\text{max}} = 0.72 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.64 \text{ e } \text{\AA}^{-3}$

No solvent water H atoms were located. Other H atoms were treated as riding with fixed C—H distances and U_{iso} values equal to $1.2U_{\text{eq}}(\text{C})$. For methyl H atoms, C—O—C—H or C—C—C—H torsion angles were refined and $U_{\text{iso}}(\text{H})$ values were set equal to $1.5U_{\text{eq}}(\text{C})$. The largest shifts in the final cycle involved torsional parameters for methyl groups, with the largest other shifts being 0.01σ .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SHELXTL* (Sheldrick, 1995); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL93* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1274). Services for accessing these data are described at the back of the journal.

References

- Bruker (1999). *SMART* and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cram, D. J., Kaneda, T., Helgeson, R. C., Brown, S. B., Knobler, C. B., Maverick, E. & Trueblood, K. N. (1985). *J. Am. Chem. Soc.* **107**, 3645–3657.
- Cram, D. J., Kaneda, T., Lein, G. M. & Helgeson, R. C. (1979). *J. Chem. Soc. Chem. Commun.* pp. 948–950.
- Cram, D. J. & Lein, G. M. (1985). *J. Am. Chem. Soc.* **107**, 3657–3668.
- Cram, D. J., Lein, G. M., Kaneda, T., Helgeson, R. C., Knobler, C. B., Maverick, E. & Trueblood, K. N. (1981). *J. Am. Chem. Soc.* **103**, 6228–6232.
- Hermansson, K., Thomas, J. O. & Olovsson, I. (1977). *Acta Cryst.* **B33**, 2857–2861.
- Knobler, C. B., Maverick, E. & Trueblood, K. N. (1992). *J. Incl. Phenom. Mol. Recognit. Chem.* **12**, 341–360.
- Kollman, P. A., Wipff, G. & Singh, U. C. (1985). *J. Am. Chem. Soc.* **107**, 2212–2219.
- Maverick, E. & Cram, D. J. (1996a). *Comprehensive Supramolecular Chemistry*, Vol. 2, edited by F. Vögtle, p. 368. Oxford: Elsevier Science Ltd.
- Maverick, E. & Cram, D. J. (1996b). *Comprehensive Supramolecular Chemistry*, Vol. 1, edited by G. W. Gokel, pp. 213–243. Oxford: Elsevier Science Ltd.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
- Sheldrick, G. M. (1995). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.