

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

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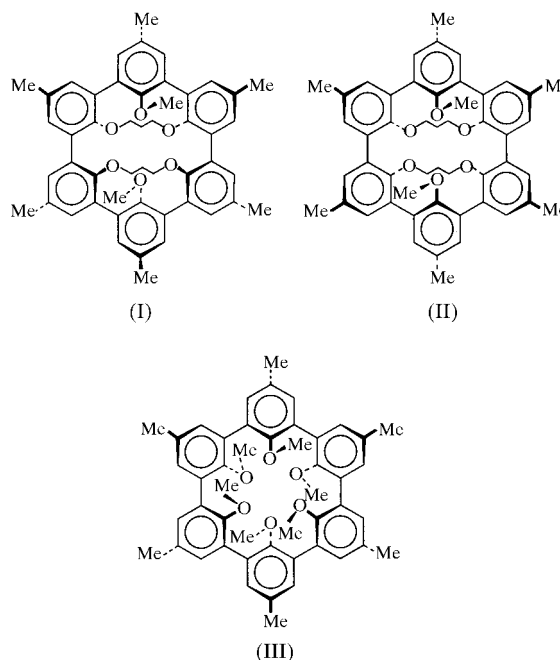
The structure of (11,12,24,25-tetrahydro-28,34-dimethoxy-3,6,16,19,31,37-hexamethyl-1,21[1',3']:8,14[1'',3'']-dibenzeno-10*H*,23*H*-tetrabenzo[*f,h,o,z*][1,5,10,14]tetraoxacyclooctadecane)lithium chloride monohydrate, *anti*-[Li( $C_{50}H_{48}O_6$ )]Cl·H<sub>2</sub>O, at 100 K reveals that the host is 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<sup>+</sup>···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<sup>+</sup> and Na<sup>+</sup> ions not only more strongly than (II), but also more strongly than (III), the strongest binder of Li<sup>+</sup> 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<sup>+</sup> confirmed these predictions. Indeed, spherand (I) does not release Li<sup>+</sup> when the complex is heated at 400 K in methanol-water, whereas (III)⊙Li<sup>+</sup> decomplexes under these conditions. Thus, (I)⊙Li<sup>+</sup> may be the first and smallest carceplex, since it probably cannot dissociate unless covalent bonds are broken (Maverick & Cram, 1996a).

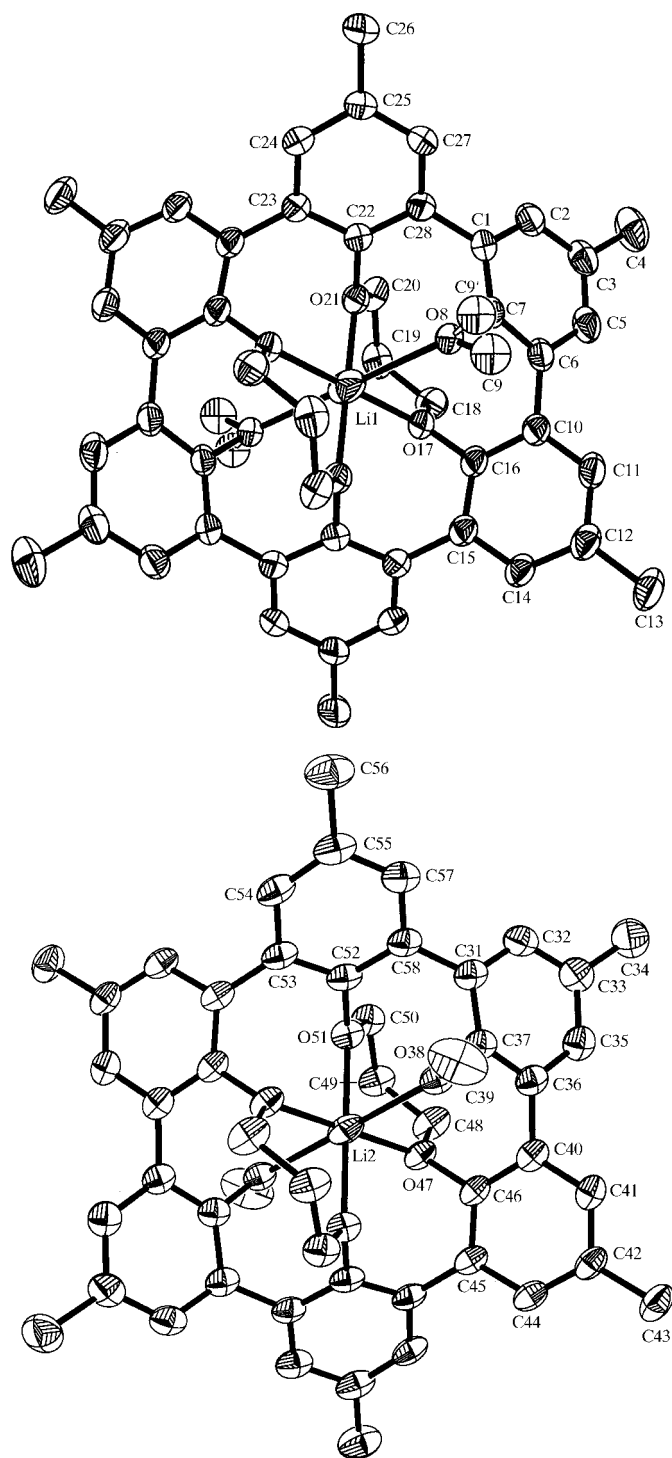
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The crystal structure of (I)·Li<sup>+</sup> reported here demonstrates, as predicted, that the *anti*-bridged host (I) is less strained than (II), both by the absence of very short O···O interactions and in the dihedral angles between adjoining aromatic 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<sup>+</sup>···O distances. Distances and angles about the cation appear in Table 1. The structural features of the Li<sup>+</sup> 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<sup>+</sup>···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  $\text{CHCl}_3$  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 ( $\text{\AA}$ ,  $^\circ$ ).

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 <sup>i</sup>	87.20 (8)	O47–Li2–O51 <sup>ii</sup>	85.95 (8)
O21–Li1–O8 <sup>i</sup>	92.80 (8)	O47–Li2–O51	94.05 (8)
O21–Li1–O8 <sup>i</sup>	101.14 (7)	O47–Li2–O38 <sup>ii</sup>	99.25 (8)
O17–Li1–O8 <sup>i</sup>	102.52 (7)	O51–Li2–O38 <sup>ii</sup>	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 ( $\text{\AA}$ ,  $^\circ$ ,  $\text{kJ mol}^{-1}$ ) for  $\text{Li}^+$  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 <sup>d</sup>	1.94–2.46	(2.02–2.27)	2.00–2.89	(2.05–2.60)	–	(–)
$\text{Li}^+$ radius <sup>e</sup>	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 <sup>f</sup>	$\gg 96^g$	(–)	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  $\text{\AA}$  for four-coordinate, 2.04–2.12  $\text{\AA}$  for five-coordinate and 2.13–2.17  $\text{\AA}$  for six-coordinate  $\text{Li}^+$ . For (II)  $\odot\text{Li}^+$ , the 2.89  $\text{\AA}$  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  $\text{\AA}$  from the average  $\text{Li}^+\cdots\text{O}$  distance. Shannon (1976) gives 0.76 and 0.59  $\text{\AA}$  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  
 $\varphi$  and  $\omega$  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  $U_{\text{iso}}$  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  $0.01\sigma$ .

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.

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