The Crystal and Molecular Structures of Bridged Spherands: The Host $C_{52}H_{52}O_8$, Its Complex $C_{52}H_{52}O_8 \cdot Li^+$, and the Complexes $C_{50}H_{48}O_6 \cdot Li^+$ and $C_{52}H_{52}O_6 \cdot Li^+$

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Abstract. The structures of the title novel hosts and host–guest complexes, synthesized by D. J. Cram and his colleagues, were determined by direct methods from diffractometer data and refined by least-squares. The hosts $C_{52}H_{52}O_8$, **I**, $C_{50}H_{48}O_6$, **II**, and $C_{52}H_{52}O_6$, **III**, are di-bridged derivatives of the prototype spherand $C_{48}H_{48}O_6$, **IV**. In **IV**, six 4-methylanisole units are joined in the 2,6 positions. In **I** two —$CH_2CH_2OCH_2CH_2$— bridges replace four of the methoxy methyl groups, joining pseudo-*meta* oxygen atoms; these two bridges are on the same face of the macrocycle (*syn*). In **II** and **III**, trimethylene and tetramethylene bridges, respectively, are similarly situated, again replacing four methoxy methyls of **IV**. Compounds **Ia**, **IIa** and **IIIa** are Li^+ complexes of these hosts. The lithium ion is essentially hepta-coordinated in **Ia**, penta-coordinated in **IIa** and hexa-coordinated in **IIIa**. These structures are extremely rigid, and the aromatic rings in them are greatly deformed. There are intramolecular oxygen contacts in each complex only slightly greater than 2.5 Å, about 10 percent shorter than the sum of the usual van der Waals radii for oxygen atoms. Thus the structures provide useful data for parameterizing potential functions for molecular mechanics calculations.

Key words. Intramolecular overcrowding, crystal structures, spherand, Li^+ complexes, host, guest.

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1. Introduction

Charles Pedersen's two epoch-making and inspirational papers that created and named the field of crown chemistry [1, 2] had the same title; the first was a communication and the second the promised full paper, which was submitted only three weeks after the first (how often has that been done?). These papers were devoted almost entirely to compounds prepared from aromatic vicinal diols, or substances prepared from such compounds by hydrogenation, the only exception being 18-crown-6, which was prepared by "a special method" in less than 2% yield and was included, although little discussed, "as an example of an unsubstituted crown compound". He reports that "many of these compounds have the unusual property of forming stable complexes with alkali and alkaline earth metal ions", as well as with ammonium ion and transition metal ions, and that the "more effective

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# This paper is dedicated to the memory of the late Dr C. J. Pedersen.
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ligands are those containing 5 to 10 O atoms, each separated from the next by 2 C atoms". He made Fischer–Hirschfelder–Taylor molecular models, and used them to estimate the sizes of the holes in the rings, corresponding to the diameter of the largest sphere that could pass through. Although Pedersen does not mention explicitly the conformational flexibility of any of the 48 substances he prepared, he was clearly aware of the possibilities and implications, mentioning that "when 7 or more O atoms are present in the polyether ring, they cannot arrange themselves in a coplanar configuration, but can arrange themselves around the surface of a right circular cylinder, with the apices of the —C—O—C— angles pointed toward the center".

Readers of this journal know how quickly and in how many directions this field grew. One of the areas pursued by Cram and his coworkers has been that of the chemistry of what he has called 'spherands', which are synthetic hosts that show minimal conformational reorganization upon complexation [3, 4].

The structures of spherand hosts and their complexes are exceptionally rigid [5], with appreciable deformation from conventional geometry because of intramolecular overcrowding in the inner portion of the molecules. We report here the structures of Li^+ complexes of three bridged spherands and of the host of one of them. Each of these structures shows even more severe distortions than do the spherands themselves. Some of these results[1] have been presented earlier [4, 6].

Since systematic names are lengthy and complex [4], a structural formula is given for each host, together with the Roman numeral that will be used to refer to the compound in the text. Previously reported structural studies establish that indeed for the prototype spherand, **IV**, there is essentially no (net) reorganization upon complexation [5], that is, the conformation of the complex is essentially identical to that of the host. All pure spherand hosts, including those of the present compounds, have been prepared only by expulsion of Li^+ from complexes. In the one
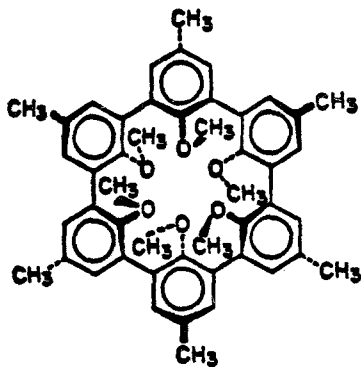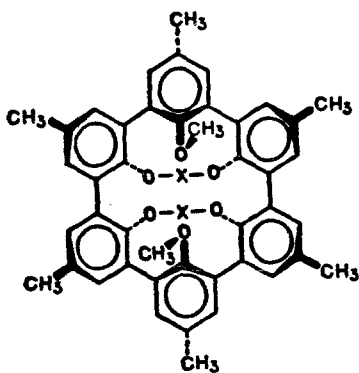
I: X = -CH₂-CH₂-O-CH₂-CH₂-   I V

II: X = -CH₂-CH₂-CH₂-

III: X = -CH₂-CH₂-CH₂-CH₂-

present example in which a comparison of the structure of a host (**I**) and its complex (**Ia**) is possible, there is a small degree of reorganization of one bridge. This implies that with **I**, in contrast to **IV**, after the distortions incident to expulsion of the Li$^+$, the host does not quite relax back to the exact conformation it had in the complex.

2. Experimental

The macrocycles **I–IV** were all first isolated [4] as crystalline LiFeCl$_4$ complexes, and then, after anion-exchange, as LiCl complexes. The pure hosts were prepared by heating the LiCl complexes for varying periods in CH$_3$OH:H$_2$O at 125–130° (**I, IV**) or in H$_2$O:pyridine at 100° (**II**).

   Most of the relevant crystallographic information is summarized in Table I. Crystals of **I**, C$_{52}$H$_{52}$O$_8$; **Ia**, C$_{52}$H$_{52}$O$_8 \cdot$ LiCl $\cdot$ 3H$_2$O; **IIa**, C$_{50}$H$_{48}$O$_6 \cdot$ LiFeCl$_4 \cdot$ 0.5 CH$_2$Cl$_2$; and **IIIa**,[1] C$_{52}$H$_{52}$O$_6 \cdot$ LiCl $\cdot$ 3C$_6$H$_6$, were grown by slow evaporation from the indicated solvents; crystals of **Ia** were grown from non-aqueous solvents, but the complex had earlier been heated in water solutions (see above), and the solvent in the crystals was best characterized as H$_2$O. Monoclinic crystals of **IIb**, the LiCl complex of **II**, were grown from a mixture of toluene and methylene chloride.[2] Although this structure also was solved, there was unresolved disordered solvent present, and after refinement of the structure of **IIa**, we did not pursue the analysis of **IIb**.

2.1. REFINEMENT

All four structures were readily solved: **I, IIa** and **IIIa** with MULTAN [11], and **Ia** with SHELX76 [8]. Most H atoms appeared on difference maps in early stages of refinement. For **Ia** and **IIa**, H positions were refined in early cycles; in the final refinement, H atoms were treated as parts of rigid groups (methyl) or riding (methylene and aromatic) for all four structures [8]. C—H distances were fixed at 1.08 Å, and displacement parameters for H were set to about 0.01 Å^2 more than the equivalent isotropic U value for the attached C atom.

   For **I**, after H atoms had been added and the refinement converged, peaks in the difference map of about 0.5 e$^-$Å^{-3} suggested disorder in four of the *para* methyl groups. The final model contains two partial-occupancy sets of positions for the methyl H atoms for these groups. The largest peaks in the final difference map are near the C and H atoms of one of the bridges.

   For **Ia**, peaks in the difference map after convergence suggested solvent molecules, perhaps water or molecules of another (disordered) solvent. The present model contains one fairly well characterized water molecule (H atoms were refined with O1S; one of them is 2.12 Å from the Cl$^-$ ion), another reasonable O atom, and two rather poorly defined O atoms at 0.5 occupancy. One of the latter is 2.3 Å from its counterpart related by the symmetry operation $1 - x$, $-y$, $-z$, with large displacement parameters suggesting disorder. The observed room-temperature density is more than 5% greater than that calculated for the room-temperature cell with the contents we find at low temperature (a room-temperatue data set was collected first, about six months before the low-temperature one). We suspect that this deficiency of some 5% was caused by the loss of water from the crystals over

Table I. Crystal, data collection and refinement information[a].

Compound	I	Ia	IIa	IIIa
Formula	$C_{52}H_{52}O_8$	$C_{52}H_{52}O_8 \cdot LiCl \cdot 3H_2O$	$C_{50}H_{48}O_6 \cdot LiFeCl_4 \cdot 0.5CH_2Cl_2$	$C_{52}H_{52}O_6 \cdot LiCl \cdot 3C_6H_6$
Solvent[b]	E-C	M-T	M-T	B
M_r (g mol^{-1})	805	901	992	1050
Space Group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
T(K)	128	115	115	295
Crystal dim. (mm^c)	$0.27 \times 0.24 \times 0.51$	$0.15 \times 0.20 \times 0.46$	$0.20 \times 0.38 \times 0.41$	$0.08 \times 0.04 \times 0.50$
$2\theta(°)$, latt. par (# reflns)	9–20 15	23–27 15	24–29 15	16–32 35
a(Å)	11.964(9)	12.773(3)	12.251(3)	24.581(3)
b(Å)	12.717(10)	14.125(3)	22.582(7)	16.458(2)
c(Å)	15.534(12)	15.147(4)	17.236(4)	16.049(2)
$\alpha(°)$	67.05(2)	79.99(2)	90	90
$\beta(°)$	87.27(2)	67.50(2)	101.33(3)	115.036(4)
$\gamma(°)$	75.22(2)	67.72(2)	90	90
V(Å^3)	2101	2335	4676	5883
Z	2	2	4	4
D_x (g cm^{-3})	1.273	1.282	1.409	1.184
D_m (g cm^{-3}) (295 K)	—	1.312(5) ($D_x = 1.250$)	1.354(5)	—
Radiation, λ (Å)	MoK_α, 0.7107	MoK_α, 0.7107	MoK_α, 0.7107	CuK_α, 1.5418
Max. $\sin \theta/\lambda$	0.595	0.650	0.704	0.639

Range of h	-13 to 14	0 to 16	0 to 17	0 to 24
k	0 to 15	-17 to 17	0 to 31	0 to 16
l	-16 to 18	-18 to 18	-24 to 23	-14 to 14
Scan (deg min^{-1})	4.5	2.0	2.0	3.0
Background scan	No	Yes	Yes	No
μ(cm^{-1})	0.48		6.0	9.0
$F(000)$	856	956	2056	2232
No. measd. refl	7425	10823	14626	3365
No. unique refl.	7407	10814	12348	3026
Unobs. $< n\sigma(F)$; $n =$	2	3	3	3
No. unobs. refl	1262	2539	1553	927
No. refl. in L.S	6163	7275	10795	2099
No. params. ref.	541 (2 blocks)	595 (2 blocks)	586 (2 blocks)	309
R	0.057	0.083	0.068	0.102
R_w	0.063	0.073	0.074	0.116
Goodness of fit	1.76	1.71	1.99	3.00
Final Peaks (e^- Å^{-3})	0.35, -0.28	0.53, -0.70	1.07, -1.05	0.47, -0.45

[a] All measured densities were determined by flotation; diffractometer Syntex P1bar, graphite-monochromatized radiation; all low-temperature measurements were made with the device of Strouse [7]; the maximum average deviation of a standard reflection for **I**, **Ia**, **IIa** was 2%, for **IIIa** 4%; all final refinements were done with SHELX76 [8]; all least-squares refinements, based on $|F|$, with weighting inversely proportional to $\sigma^2(F)$; scattering factors were taken from Cromer and Mann [9], and Stewart, Davidson and Simpson [10].

[b] Abbreviations for solvents: B, benzene; E, ethanol, C, chloroform; M, methylene chloride; T, toluene.

[c] Absorption corrections were not made. For the needle-shaped crystal of **IIIa**, transmission factors vary from 0.90 to 0.96.

time (two molecules per asymmetric unit would almost account for the difference). Loss of water is not uncommon from crystals such as these, in which the water is neither strongly hydrogen bonded nor bound to an ion, and it is consistent with the poor definition of some of the solvent molecules. The largest peaks in the final difference map are near the solvent O atoms, or near Cl^-.

The structure of **IIa** refined well, but even before convergence a large solvent peak (about $10\ e^-\ \text{Å}^{-3}$) appeared. It was near the center of symmetry at the origin, about 2.9 Å from its symmetry-equivalent position. Since the crystals had been grown from methylene chloride, and since a peak appeared in a reasonable position for a C atom, we characterized the solvent as disordered CH_2Cl_2. Thus in this model one CH_2Cl_2 molecule (refined with restrained bond lengths and bond angle [8]) is present for two formula units of the complex, in one of two equally probable positions in each solvent 'hole'. In the final difference map, the largest peaks are near the Cl atoms of the counterion, $FeCl_4^-$; attempts to fit these peaks to a disorder model failed, and the displacement parameters for Cl and Fe can be reasonably interpreted as evidence of motion (see below).

Finally, the structure of **IIIa** (space group $C2/c$) contains disorder of two kinds. In contrast to **I**, **Ia** and **IIa**, the asymmetric unit of **IIIa** is a half-molecule, with the Li^+ and Cl^- ions in special positions. The two halves of the macrocycle are related by a two-fold axis; two of the four bridging $—CH_2—$ groups are disordered, with nearly equal occupancies (0.56 and 0.44, respectively) for C(19A)—C(20A) and C(19B)—C(20B). The solvent, benzene, appeared in two regions: quite clearly near 0.2, 0, 0.3, and more ambiguously near a center of symmetry. In both regions, difference maps after refinement suggested alternate positions for benzene molecules. The final model contains benzene molecules (refined as rigid bodies [8]) as follows: two molecules have a total occupancy 1.00 (0.55, 0.45) near 0.2, 0, 0.3; two molecules near the center have a combined occupancy of 0.50 (0.29, 0.21). There are thus 12 molecules per unit cell or three per formula unit. The largest peaks in the final difference map are near these solvent molecules. Since the systematic absences do not distinguish between the space groups $C2/c$ and Cc, we tried to refine in the latter, even though intensity statistics strongly favored a centrosymmetric structure. We began by phasing with half the macrocycle, adding other atoms as they appeared on Fourier maps; three independent solvent molecules (modeled as benzene) developed. The outcome was unsatisfactory for the macrocyclic host, however, with large correlations, high e.s.d.s, and strange bond lengths. The number of observations is also too small for reasonable anisotropic refinement in Cc. We believe that the macrocycle is best described in $C2/c$, but that the solvent may fit the lower-symmetry space group, which suggests that the disorder of benzene molecules, and perhaps also of the bridge atoms, is static. In any event, this structure determination is not precise.

All calculations were done on an IBM 3090 or on DEC VAX 11/750, 11/780 or 3100 computers, with the UCLA Crystallographic Package [12], which includes locally edited versions of CARESS and PROFILE, and with SHELX76 [8], PLUTO78 [13], a local molecular geometry program, and THMA11 [14].

The final positional and isotropic displacement parameters (equivalent values for atoms refined anisotropically, H atoms omitted) are given in Tables IIA through IID.[3] PLUTO stereodrawings in Figures 1 through 4 show conformations and atomic numbering in **I** and in the cationic complexes of **Ia**, **IIa**, and **IIIa**.

Table IIA. Position and displacement* parameters for $C_{52}H_{52}O_8$ (I).

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(1)	0.19877(19)	0.68783(19)	0.42942(16)	0.024
C(2)	0.31490(20)	0.68974(21)	0.42450(16)	0.028
C(3)	0.37821(20)	0.68358(21)	0.34849(17)	0.029
C(4)	0.50451(22)	0.68275(26)	0.34643(19)	0.039
C(5)	0.32126(20)	0.68349(20)	0.27214(16)	0.027
C(6)	0.20476(19)	0.68203(19)	0.27367(16)	0.023
C(7)	0.14758(19)	0.67736(19)	0.35454(16)	0.022
O(8)	0.03815(13)	0.65806(13)	0.36400(11)	0.024
C(9)	0.04367(21)	0.53652(21)	0.38322(19)	0.034
C(10)	0.14085(19)	0.68675(20)	0.19099(16)	0.024
C(11)	0.18097(20)	0.60521(20)	0.15007(16)	0.026
C(12)	0.11822(20)	0.60848(20)	0.07531(16)	0.026
C(13)	0.16399(22)	0.52245(22)	0.02886(18)	0.033
C(14)	0.00966(20)	0.68777(20)	0.04845(15)	0.024
C(15)	−0.04012(20)	0.76692(19)	0.09144(15)	0.024
C(16)	0.03525(19)	0.77337(19)	0.15548(15)	0.023
O(17)	0.00869(13)	0.86517(13)	0.18525(11)	0.024
C(18)	0.05128(21)	0.96388(21)	0.12300(17)	0.029
C(19)	0.15658(22)	0.97607(22)	0.16357(17)	0.033
O(20)	0.15185(14)	0.95662(14)	0.25986(11)	0.030
C(21)	0.04686(23)	1.02037(22)	0.28337(18)	0.033
C(22)	0.03683(21)	0.95913(20)	0.38703(17)	0.028
O(23)	−0.00779(13)	0.85859(13)	0.39962(10)	0.024
C(24)	0.01750(20)	0.77698(19)	0.49001(15)	0.023
C(25)	−0.06297(20)	0.77318(19)	0.55833(16)	0.023
C(26)	−0.01892(20)	0.70404(20)	0.65099(16)	0.025
C(27)	0.09407(20)	0.63285(20)	0.67380(16)	0.027
C(28)	0.13264(22)	0.55638(23)	0.77483(18)	0.036
C(29)	0.16565(20)	0.62700(20)	0.60209(16)	0.026
C(30)	0.12866(19)	0.69692(19)	0.50934(16)	0.024
C(31)	−0.19278(19)	0.81281(19)	0.53864(15)	0.023
C(32)	−0.25358(20)	0.73282(20)	0.59739(16)	0.025
C(33)	−0.36986(20)	0.74222(20)	0.58364(16)	0.026
C(34)	−0.43009(22)	0.65649(22)	0.65194(18)	0.035
C(35)	−0.42697(20)	0.82951(20)	0.50104(16)	0.025
C(36)	−0.37086(19)	0.90934(20)	0.43832(16)	0.024
C(37)	−0.25844(19)	0.90943(19)	0.46158(15)	0.023
O(38)	−0.20909(13)	0.99809(13)	0.40776(11)	0.027
C(39)	−0.28011(21)	1.11838(20)	0.37364(17)	0.028
C(40)	−0.24807(22)	1.18584(20)	0.27616(17)	0.029
O(41)	−0.27986(15)	1.14069(14)	0.21290(11)	0.031
C(42)	−0.23813(22)	1.18659(20)	0.12298(17)	0.029
C(43)	−0.26067(21)	1.12203(20)	0.06408(16)	0.028
O(44)	−0.19175(13)	1.00089(13)	0.10116(11)	0.027
C(45)	−0.23952(19)	0.91405(19)	0.09980(15)	0.023
C(46)	−0.17100(19)	0.81680(19)	0.08189(15)	0.023
C(47)	−0.23188(20)	0.74286(20)	0.06695(15)	0.025
C(48)	−0.35090(20)	0.75812(20)	0.07119(16)	0.025
C(49)	−0.41068(21)	0.67788(22)	0.05153(18)	0.032
C(50)	−0.41157(20)	0.84510(20)	0.10174(16)	0.025
C(51)	−0.35605(19)	0.91848(20)	0.12108(15)	0.024
C(52)	−0.41731(19)	0.97780(19)	0.18278(16)	0.023

Table IIA. (*Continued.*)

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(53)	−0.52933(20)	1.05127(20)	0.16295(16)	0.025
C(54)	−0.58897(19)	1.08880(20)	0.22934(16)	0.025
C(55)	−0.70702(21)	1.17458(21)	0.20587(17)	0.029
C(56)	−0.53707(20)	1.04538(20)	0.31908(16)	0.025
C(57)	−0.42491(19)	0.97215(19)	0.34085(16)	0.023
C(58)	−0.36434(19)	0.94163(19)	0.27166(16)	0.023
O(59)	−0.25102(13)	0.87523(13)	0.29033(11)	0.025
C(60)	−0.23289(20)	0.74939(21)	0.32863(18)	0.031

Table IIB. Position and displacement* parameters for $C_{52}H_{52}O_8 \cdot LiCl \cdot 3H_2O$ (**Ia**).

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(1)	−0.51660(31)	0.43775(28)	0.28536(25)	0.021
C(2)	−0.58177(31)	0.45625(30)	0.22428(26)	0.024
C(3)	−0.57818(32)	0.53273(31)	0.15271(26)	0.025
C(4)	−0.65636(36)	0.55679(34)	0.09122(29)	0.034
C(5)	−0.50232(31)	0.58759(29)	0.13776(26)	0.023
C(6)	−0.43338(31)	0.56978(28)	0.19629(25)	0.022
C(7)	−0.44794(31)	0.49940(28)	0.27232(25)	0.021
O(8)	−0.39374(21)	0.48968(19)	0.33917(17)	0.022
C(9)	−0.45585(36)	0.57676(31)	0.40023(28)	0.031
C(10)	−0.34656(31)	0.62404(27)	0.17901(25)	0.020
C(11)	−0.38139(33)	0.73021(29)	0.17340(26)	0.024
C(12)	−0.29900(33)	0.77792(27)	0.16136(26)	0.023
C(13)	−0.33625(37)	0.89352(31)	0.15388(31)	0.035
C(14)	−0.18408(32)	0.71774(28)	0.16142(25)	0.022
C(15)	−0.14486(30)	0.60968(27)	0.17053(23)	0.017
C(16)	−0.22554(31)	0.56561(27)	0.17000(24)	0.019
O(17)	−0.18846(21)	0.46172(18)	0.15518(17)	0.019
C(18)	−0.16593(34)	0.45300(29)	0.05477(26)	0.025
C(19)	−0.09847(33)	0.34276(28)	0.02762(25)	0.023
O(20)	−0.13522(21)	0.27481(18)	0.10507(17)	0.021
C(21)	−0.25260(33)	0.27386(29)	0.11764(26)	0.023
C(22)	−0.29625(32)	0.22478(28)	0.21334(26)	0.022
O(23)	−0.30524(21)	0.28682(18)	0.28562(17)	0.020
C(24)	−0.40462(31)	0.28547(27)	0.36575(26)	0.021
C(25)	−0.39693(30)	0.21813(26)	0.44455(25)	0.018
C(26)	−0.50581(32)	0.20481(28)	0.50662(26)	0.021
C(27)	−0.61767(32)	0.26406(30)	0.49825(26)	0.024
C(28)	−0.73175(34)	0.24725(32)	0.56792(29)	0.031
C(29)	−0.62237(32)	0.34299(29)	0.42794(26)	0.023
C(30)	−0.51679(31)	0.35459(28)	0.36130(25)	0.020
C(31)	−0.28895(30)	0.17655(26)	0.47693(26)	0.019
C(32)	−0.31697(31)	0.17552(27)	0.57625(26)	0.021
C(33)	−0.23127(32)	0.15476(26)	0.62028(25)	0.020
C(34)	−0.26742(33)	0.15190(31)	0.72709(27)	0.028
C(35)	−0.11501(31)	0.14681(26)	0.56021(26)	0.020
C(36)	−0.08275(30)	0.15137(26)	0.46182(26)	0.020
C(37)	−0.16574(31)	0.15514(25)	0.41992(25)	0.018

Table IIB. (*Continued.*)

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
O(38)	−0.12732(21)	0.14559(18)	0.32244(17)	0.020
C(39)	−0.02187(32)	0.05576(27)	0.28243(26)	0.022
C(40)	0.04284(32)	0.08371(27)	0.18117(26)	0.022
O(41)	0.06494(23)	0.17592(19)	0.18313(18)	0.025
C(42)	0.14205(33)	0.20075(28)	0.09363(27)	0.024
C(43)	0.15175(31)	0.30371(28)	0.09890(26)	0.022
O(44)	0.03280(21)	0.37699(18)	0.14766(18)	0.022
C(45)	0.03185(31)	0.44643(27)	0.20310(25)	0.019
C(46)	−0.03372(30)	0.55323(27)	0.19973(24)	0.018
C(47)	−0.00552(31)	0.61550(27)	0.24424(26)	0.021
C(48)	0.07135(31)	0.57872(28)	0.29606(26)	0.022
C(49)	0.09724(36)	0.65231(30)	0.33951(30)	0.030
C(50)	0.11403(32)	0.47337(27)	0.31306(26)	0.023
C(51)	0.09314(30)	0.40779(27)	0.26931(25)	0.019
C(52)	0.11760(32)	0.30013(27)	0.30779(25)	0.020
C(53)	0.23029(31)	0.23616(28)	0.31350(27)	0.022
C(54)	0.24382(32)	0.14192(28)	0.36352(28)	0.024
C(55)	0.36737(34)	0.07328(30)	0.36667(33)	0.034
C(56)	0.14426(32)	0.11139(27)	0.40945(27)	0.022
C(57)	0.03052(31)	0.17300(27)	0.40399(25)	0.019
C(58)	0.02111(31)	0.26533(27)	0.35152(25)	0.019
O(59)	−0.09177(20)	0.32713(17)	0.34421(17)	0.018
C(60)	−0.16731(33)	0.39842(29)	0.41982(27)	0.026
Li	−0.12040(59)	0.30209(53)	0.22896(46)	0.028
Cl	1.05110(13)	−0.15205(10)	0.13025(9)	0.053
O(1S)[a]	0.85078(37)	0.02933(30)	0.06587(28)	0.076
O(2S)	1.31496(48)	−0.12524(46)	0.02833(35)	0.119
O(3S)	0.46301(96)	0.22282(116)	0.08716(82)	0.174
O(4S)	0.56379(195)	0.02081(194)	−0.06501(173)	0.361

Table IIC. Position and displacement* parameters for $C_{50}H_{48}O_6 \cdot LiFeCl_4 \cdot 0.5\ CH_2Cl_2$ (**IIa**).

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(1)	0.22917(23)	0.19928(12)	0.58522(16)	0.017
C(2)	0.17949(24)	0.25184(13)	0.60416(17)	0.019
C(3)	0.18226(24)	0.30351(13)	0.56098(17)	0.020
C(4)	0.12240(27)	0.35849(13)	0.57845(19)	0.026
C(5)	0.23432(24)	0.30163(12)	0.49545(17)	0.019
C(6)	0.28438(23)	0.24975(12)	0.47477(16)	0.017
C(7)	0.28581(22)	0.20008(12)	0.52254(16)	0.015
O(8)	0.34028(15)	0.14865(8)	0.50459(11)	0.015
C(9)	0.45727(27)	0.15007(15)	0.53747(25)	0.039
C(10)	0.32690(23)	0.24458(12)	0.40033(16)	0.017
C(11)	0.40990(23)	0.28324(12)	0.38570(17)	0.019
C(12)	0.45568(23)	0.27527(12)	0.31899(17)	0.020
C(13)	0.54051(26)	0.31783(13)	0.29864(20)	0.027
C(14)	0.42501(23)	0.22539(12)	0.27309(17)	0.019
C(15)	0.34307(22)	0.18396(12)	0.28514(15)	0.015
C(16)	0.28680(22)	0.19881(12)	0.34701(16)	0.015

Table IIC. (*Continued.*)

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
O(17)	0.19719(15)	0.16592(8)	0.36284(11)	0.015
C(18)	0.09322(22)	0.19723(12)	0.36121(16)	0.018
C(19)	0.01266(22)	0.15777(12)	0.39508(16)	0.016
C(20)	0.03934(22)	0.14086(12)	0.48257(16)	0.017
O(21)	0.13772(15)	0.10230(8)	0.49880(11)	0.015
C(22)	0.18314(21)	0.09183(12)	0.57807(15)	0.014
C(23)	0.20362(22)	0.03410(12)	0.61048(16)	0.016
C(24)	0.23454(27)	0.03287(14)	0.69418(17)	0.024
C(25)	0.24956(29)	0.08194(15)	0.74256(17)	0.028
C(26)	0.27711(44)	0.07507(17)	0.83142(20)	0.054
C(27)	0.24498(26)	0.13776(14)	0.70706(17)	0.024
C(28)	0.21678(23)	0.14190(12)	0.62556(16)	0.017
C(29)	0.21237(21)	−0.02510(12)	0.56999(16)	0.015
C(30)	0.23324(22)	−0.07662(13)	0.61698(16)	0.018
C(31)	0.26731(23)	−0.13024(13)	0.59091(17)	0.020
C(32)	0.29184(28)	−0.18267(14)	0.64618(20)	0.028
C(33)	0.28312(23)	−0.13470(12)	0.51345(18)	0.019
C(34)	0.25869(22)	−0.08653(11)	0.46274(16)	0.016
C(35)	0.21829(21)	−0.03393(12)	0.49017(15)	0.014
O(36)	0.18440(15)	0.00902(8)	0.43337(11)	0.013
C(37)	0.07071(21)	0.00062(12)	0.38995(16)	0.015
C(38)	0.06512(22)	0.00338(12)	0.30110(16)	0.016
C(39)	0.11810(22)	0.05627(12)	0.26907(16)	0.016
O(40)	0.23287(15)	0.06527(8)	0.31092(11)	0.014
C(41)	0.30537(22)	0.07141(12)	0.25897(15)	0.015
C(42)	0.34020(22)	0.12716(12)	0.23746(15)	0.015
C(43)	0.39212(24)	0.12633(13)	0.17069(17)	0.020
C(44)	0.41466(25)	0.07510(14)	0.13317(17)	0.022
C(45)	0.46363(32)	0.07785(16)	0.05949(20)	0.034
C(46)	0.39347(24)	0.02026(13)	0.16491(17)	0.020
C(47)	0.33880(23)	0.01833(12)	0.22817(16)	0.017
C(48)	0.30995(23)	−0.03845(12)	0.26322(16)	0.017
C(49)	0.25176(24)	−0.08257(13)	0.21482(17)	0.020
C(50)	0.20467(25)	−0.13098(13)	0.24683(18)	0.022
C(51)	0.14059(30)	−0.17760(14)	0.19402(21)	0.032
C(52)	0.21170(24)	−0.13268(12)	0.32856(18)	0.020
C(53)	0.26899(22)	−0.08959(12)	0.37821(16)	0.016
C(54)	0.32587(22)	−0.04518(12)	0.34570(16)	0.016
O(55)	0.38990(16)	−0.00596(9)	0.39743(11)	0.018
C(56)	0.50209(24)	0.00264(15)	0.38687(19)	0.026
Li	0.24694(40)	0.09060(21)	0.42369(28)	0.019
Cl(S)[b]	1.00278(45)	0.46517(23)	0.41397(32)	0.094
Cl(S)′	1.00162(83)	0.51301(31)	0.56383(47)	0.163
C(s)	1.08191(114)	0.51074(65)	0.48713(77)	0.102
Fe	0.77145(4)	0.17332(2)	0.08558(3)	0.021
Cl(1)	0.63087(7)	0.22174(4)	0.11695(6)	0.038
Cl(2)	0.88373(8)	0.23653(4)	0.04504(7)	0.049
Cl(3)	0.85818(9)	0.12322(6)	0.18813(6)	0.054
Cl(4)	0.71319(9)	0.11090(6)	−0.01030(6)	0.057

Table IID. Position and displacement* parameters for $C_{52}H_{52}O_6 \cdot LiCl \cdot 3C_6H_6$(**IIIa**).

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(1)	0.33325(42)	0.16000(53)	0.71559(56)	0.039
C(2)	0.27471(42)	0.13029(56)	0.67639(61)	0.046
C(3)	0.24480(41)	0.11614(55)	0.57956(63)	0.045
C(4)	0.18189(44)	0.08359(63)	0.53727(64)	0.061
C(5)	0.27670(43)	0.13242(57)	0.52666(58)	0.045
C(6)	0.33476(42)	0.16019(54)	0.56386(57)	0.040
C(7)	0.36132(40)	0.17881(54)	0.65629(64)	0.042
O(8)	0.41869(28)	0.21449(39)	0.69603(39)	0.052
C(9)	0.41617(56)	0.30058(74)	0.70857(108)	0.118
C(10)	0.37051(43)	0.17037(55)	0.50949(56)	0.041
C(11)	0.34562(40)	0.20898(54)	0.42482(62)	0.045
C(12)	0.37910(44)	0.21766(55)	0.37281(57)	0.045
C(13)	0.35242(46)	0.25428(66)	0.27721(63)	0.070
C(14)	0.43952(44)	0.19666(54)	0.41361(57)	0.044
C(15)	0.46825(40)	0.16074(50)	0.50369(56)	0.038
C(16)	0.42872(44)	0.14021(53)	0.54358(55)	0.038
O(17)	0.44505(26)	0.08728(37)	0.61876(36)	0.045
C(18)	0.42258(47)	0.00642(63)	0.58680(64)	0.061
C(19A)[c]	0.3865(8)	−0.0309(10)	0.6345(10)	0.039(4)
C(19B)	0.4240(11)	−0.0502(13)	0.6572(15)	0.049(6)
C(20A)	0.4189(9)	−0.0500(12)	0.7396(12)	0.063(6)
C(20B)	0.3852(11)	−0.0321(14)	0.7119(15)	0.050(7)
C(21)	0.41291(49)	0.00595(58)	0.80562(66)	0.061
O(22)	0.44157(25)	0.08431(35)	0.80905(36)	0.043
C(23)	0.42468(43)	0.13928(53)	0.86076(54)	0.038
C(24)	0.46384(39)	0.16243(51)	0.95011(58)	0.036
C(25)	0.43483(45)	0.20486(59)	0.99823(61)	0.053
C(26)	0.37564(48)	0.22723(63)	0.95983(62)	0.058
C(27)	0.34765(51)	0.27229(93)	1.01584(75)	0.112
C(28)	0.34062(42)	0.21427(60)	0.86324(64)	0.053
C(29)	0.36609(42)	0.17042(56)	0.81671(60)	0.042
Li	0.50000	0.12343(140)	0.75000	0.062
Cl	0.00000	0.75945(27)	0.25000	0.083
C(1S)[d]	0.2483(10)	0.0490(14)	0.2986(19)	0.084(8)
C(2S)	0.1900	0.0673	0.2354	0.100(8)
C(3S)	0.1415	0.0243	0.2365	0.117(9)
C(4S)	0.1513	−0.0372	0.3008	0.147(11)
C(5S)	0.2096	−0.0556	0.3640	0.121(9)
C(6S)	0.2581	−0.0125	0.3629	0.117(9)
C(7S)[e]	0.1371(8)	−0.0103(21)	0.2534(22)	0.110
C(8S)	0.1756	−0.0526	0.3314	0.110
C(9S)	0.2375	−0.0416	0.3654	0.110
C(10S)	0.2610	0.0118	0.3213	0.110
C(11S)	0.2224	0.0541	0.2433	0.110
C(12D)	0.1605	0.0431	0.2094	0.110
C(13S)[f]	0.4736(25)	0.5205(34)	0.0734(29)	0.096(19)
C(14S)	0.4910	0.4417	0.0648	0.095(22)
C(15S)	0.5160	0.4247	0.0033	0.076(18)
C(16S)	0.5236	0.4866	−0.0498	0.101(21)
C(17S)	0.5061	0.5654	−0.0412	0.099(20)
C(18S)	0.4811	0.5824	0.0204	0.093(22)

Table IID. (Continued.)

Atom	x/a	y/b	z/c	$\langle u^2 \rangle$
C(19S)[g]	0.4907(20)	0.4363(24)	0.1100(27)	0.082
C(20S)	0.4733	0.5157	0.1172	0.082
C(21S)	0.4841	0.5780	0.0673	0.082
C(22S)	0.5124	0.5609	0.0102	0.082
C(23S)	0.5299	0.4816	0.0029	0.082
C(24S)	0.5191	0.4193	0.0529	0.082

* Displacement parameters are commonly called vibration or thermal parameters. Units of $\langle u^2 \rangle$ are Å². Units of each e.s.d. in parentheses are those of the least significant digit of the corresponding parameter. E.s.d.'s of displacement parameters are given for atoms refined isotropically.

Equivalent isotropic values are $[1/(8\pi^2)]$ times the 'equivalent B value' for an anisotropic atom as defined by Hamilton [15].

[a] Occupancies for solvent O atoms: O(1S), 1.0, O(2S), 1.0, O(3S), 0.5, O(4S), 0.5.

[b] Occupancy for solvent CH_2Cl_2 atoms: 0.5.

[c] Occupancy for C(19A)–C(20A): 0.56; for C(19B)–C(20B): 0.44.

[d] Pivot atom in rigid group. Occupancy for C(1S)–C(6S): 0.55.

[e] Pivot atom in rigid group. Occupancy for C(7S)–C(12S): 0.45.

[f] Pivot atom in rigid group. Occupancy for C(13S)–C(18S): 0.29.

[g] Pivot atom in rigid group. Occupancy for C(19S)–C(24S): 0.21.
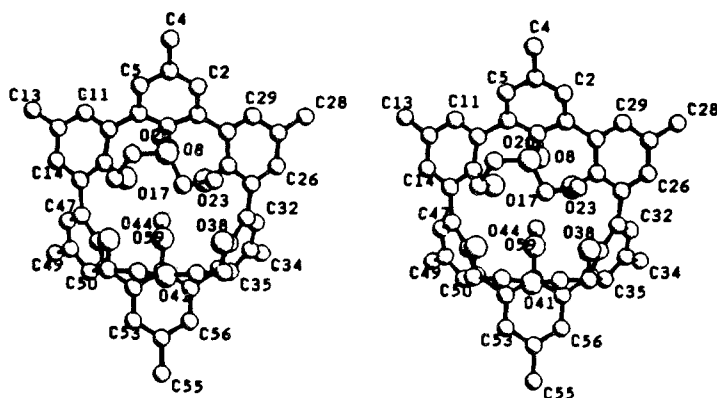
Fig. 1. PLUTO [13] stereoview of I. H atoms, and labels for some C atoms, have been omitted to avoid clutter.

3. Results and Discussion

Many of the distinctive properties of these compounds are due to the fact that they have, unexpectedly [4, 6], *syn* bridges. The hosts can only be prepared around Li$^+$; the pure hosts are then formed by expelling the cation [4]. Calculations [16] indicate that, as models suggest, the isomer of **II** with *anti* bridges should be much more stable, and presumably the same situation obtains for **I** and **III**.
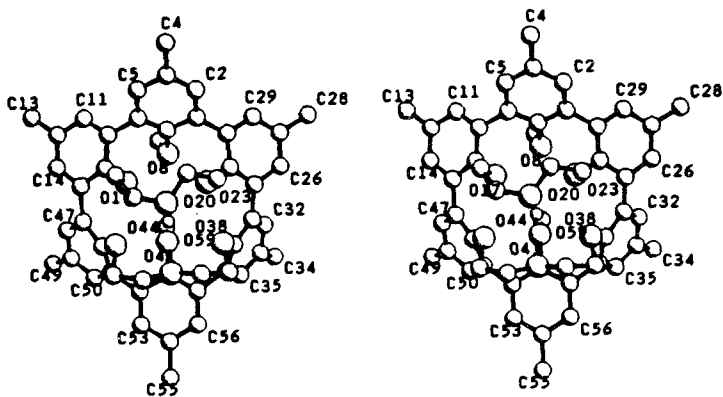
Fig. 2. Stereoview of **Ia**. Solvent and chloride ion have been omitted.
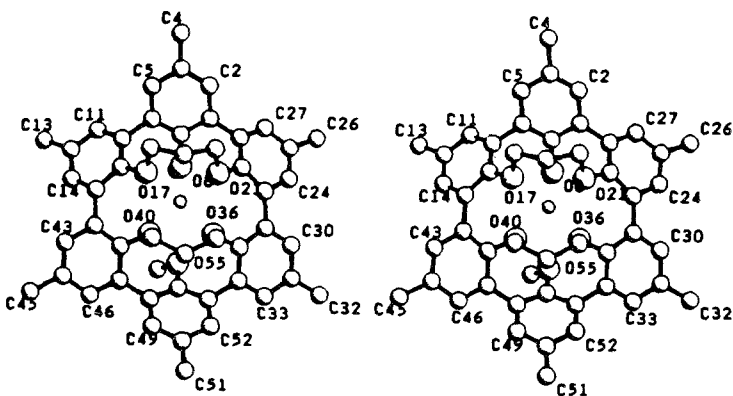

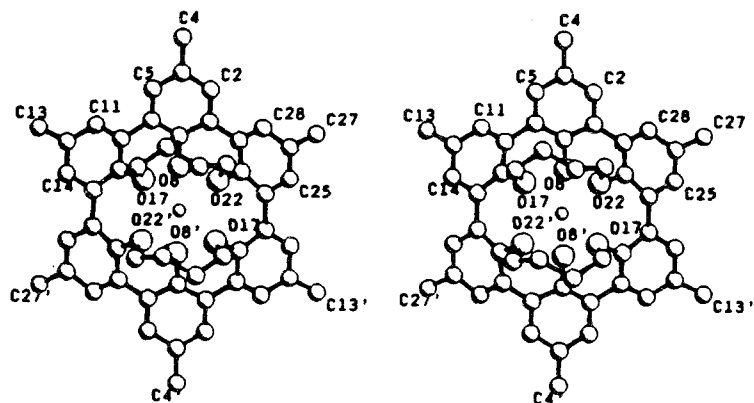Fig. 3. Stereoview of **IIa**. Solvent and $FeCl_4^-$ ion have been omitted.

Fig. 4. Stereoview of **IIIa**. The two halves of the macrocycle are related by the symmetry operation $1 - x$, y, $3/2 - z$; positions for the disordered bridge atoms are those of C(19B)—C(20B). The solvent, the chloride ion and C(19A)—C(20A) have been omitted.

Among the consequences of the fact that the bridges are *syn* that are most relevant in the present context are: (a) the aromatic rings do not tip alternately up and down relative to the median plane (or to the molecular axis), as they do in **IV** [4, 5]; and (b) the arrangement of the six O atoms attached to the aromatic rings approaches more closely a trigonal prism in each of these structures than it does the approximately regular octahedron characteristic of **IV** [4, 5]. These features are evident in the stereoviews of the structures (Figures 1–4).

A third consequence of the *syn* bridges, not apparent from the Figures, is that there is extreme intramolecular overcrowding in these molecules, and resulting geometrical distortions. Some of the relevant geometrical data are summarized in Tables III and IV, where pertinent properties of **IV** and **IVa** [5] are also shown for comparison; more details are given with the supplementary material. Table III is concerned with the arrangement of the O atoms and the coordination of the Li^+ in the complexes. In **Ia**, seven of the eight O atoms are coordinated to the cation; in **IIa**, five of the six O atoms are, and in **IIIa** (which has a two-fold axis), all six Os are coordinated to Li^+. The free energy of binding [20] might be expected to be related to the coordination number and to the cavity size; generally binding is favored by large total r_i^{-2}, where r_i are the Li^+—O distances. In this respect **IIa** and **IVa** are about the same, while **Ia** is more favored; the fact that **IVa** has much greater binding energy is presumably due chiefly to the absence of short repulsive O···O contacts in **IVa**. The effect of the small cation, with its strong field, in contracting the cavity lined with O atoms can be seen by comparing the number of O···O contacts shorter than the sum of the van der Waals radii (2.8 Å) in **I** (only three) and in **Ia** (seven). On the other hand, the numbers of distances below 3.0 Å (those between 2.8 and 3.0 Å involving little strain) are almost the same (ten and eleven respectively). The O···O distances below 2.8 Å involving atoms coordinated to Li^+ in **Ia** are shorter, by an average of 0.14 Å, than the corresponding distances in **I**.

Comparison of Figures 1 and 2, as well as a detailed study of the respective geometries, shows that the host structure in the pure host (**I**) is very similar to that in the complex (**Ia**). The major difference is in the position of O(20), which is more than 2 Å farther from O(41) in the pure host (5.06 Å vs. 2.99 Å), and also 1.3–1.4 Å farther from O(38) and O(44). It appears that when the Li^+ is expelled from the complex, it escapes by a path that involves moving O(20) (and its adjoining bridge) out of the way. In **I**, the conformation allows short H···O distances, for example O(38)···H(22A) and O(44)···H(18B), both about 2.3 Å.

The fact that some O···O distances, even in the pure host **I**, are distinctly shorter than the sum of the van der Waals radii is an indication of the strain built into the structures. The final ring-closing step in the synthesis of the complexes involves what is probably [4] a Li^+-templated coupling of two aryl radicals with the release of sufficient energy to allow the considerable molecular deformations that are found. Some information about these deformations is summarized in Table IV. In an unperturbed aromatic system, the atoms of the ring and the atoms immediately attached to the ring are all coplanar. In the present molecules, as in **IV** and related unbridged spherands [5], the aromatic rings are folded or buckled, and the immediately attached atoms are often far out of the mean aromatic plane. The distortions in the *anisyl* rings in each of the present

Table III. Short intramolecular O···O and Li$^+$···O distances and complexation energies.

	Ia	IIa	I	IIIa	IV	IVa
O···O						
No. of distances						
smaller than 2.8Å	7[a]	3	7	6	0	6
smaller than 3.0Å	11	10	8	6	6	6
Shortest O···O distance	2.57Å	2.62Å	2.51Å	2.53Å	2.92Å	2.79Å
Li$^+$···O						
No. of atoms within 2.5Å of Li$^+$	7[b]	—	5[c]	6	—	6
Ave. distance, r	2.26Å	—	2.04Å	2.17Å	—	2.14Å
Range[d] of distances	2.03–2.43	—	2.00–2.08	2.05–2.35	—	—
Effective Li$^+$ radius[e]	0.86	—	0.64	0.77	—	0.74
Sum[f] of r_i^{-2}	1.47Å^{-2}	—	1.33Å^{-2}	1.28Å^{-2}	—	1.31Å^{-2}
$-\Delta G^o$(kJ mol^{-1}) of complexation[g]	67	—	70	—	—	>96

a Six of these 7 shortest O···O distances in **Ia** are shorter than the corresponding distances in **I**, by an average of 0.14Å. Only O(8)···O(23) is longer in **Ia** than in **I**, by 0.06Å, and O(8) is not coordinated to Li$^+$.

b O(8) is 3.47Å from Li$^+$.

c O(55) is 2.89Å from Li$^+$; one aromatic C, C(16), is as close to Li$^+$ (2.87Å).

d This range of distances is in agreement with a survey by Hermansson et al. [17], 2.04–2.12Å for 5-coordinate and 2.13–2.17Å for 6-coordinate Li$^+$; Reiss et al. [18] find a range of 1.99–2.20Å, mean 2.06Å for a 5-coordinate Li$^+$ complex.

e This radius is calculated by subtracting an oxygen radius of 1.40Å from the average Li$^+$···O distance. Shannon [19] gives 0.76Å as the radius for 6-coordination; he also calculates the radius as 0.92Å for 8-coordination, so the value here for 7-coordination is reasonable.

f Over all O atoms.

g From Ref. [20].

Table IV. Comparison of some features of the molecular geometry[a].

		I	Ia	IIa	IIIa	IV	IVa
Ave. fold angle of aryl ring along CH_3—C···C—O line	Anisyl	5°	4°	6°	4°	6°	3°
	Bridge[b]	9	10	9	10	—	—
Ave. abs. dev. of aryl C atoms from aryl plane	Anisyl	0.023Å	0.018Å	0.026Å	0.020Å	0.032Å	0.014Å
	Bridge	0.042	0.045	0.040	0.046	—	—
Ave. abs. dev. of attached O atom from aryl plane	Anisyl	0.17Å	0.12Å	0.11Å	0.20Å	0.21Å	0.06Å
	Bridge	0.29	0.32	0.24	0.46	—	—
Ave. abs. dev. of attached aryl C from aryl plane	Anisyl	0.19Å	0.17Å	0.28Å	0.14Å	0.17Å	0.13Å
	Bridge	0.43	0.40	0.29	0.33	—	—
Interplanar angle between adjacent rings[c]	Average	52°	50°	43°	40°	52°	56°
	Range	43–66	40–61	28–51	33–46	—	—
Tilt of aryl rings relative to mean plane of the four attached bridge O atoms[d]	Average	37°	35°	28°	26°	30°	33°
	Range	2–67	1–61	12–43	21–31	—	—

[a] Values for **IV** and **IVa** are taken from Ref. [5].

[b] 'Bridge' means the aryl (aromatic) rings attached to the O atoms leading to the bridges.

[c] The angle between the normals to the least-squares planes of adjacent aryl rings.

[d] The angle between the normal to the least-squares plane of the aryl ring and the normal to the least-squares plane of the four bridge O atoms that are attached to aryl rings.

molecules, given in Table IV, are comparable to those in **IV** and its complexes [5] (which contain anisyl rings but no bridges), and are, on the average, about half those in the aromatic rings directly linked to the bridges. This is not surprising, since the source of much of the strain in each structure is the unusually short O···O contacts, which always involve the bridge O atoms attached to the aromatic rings. Thus, while the evidence in Table IV shows that complexation relieves some of the strain present in **I** and **IV** as pure hosts, **Ia**, **IIa** and **IIIa** all show more geometrical distortion than **IVa**, presumably because of the short O···O contacts in **Ia**, **IIa** and **IIIa** (Table III).

The dihedral angles between adjacent rings are comparable to those in **IV** and related molecules [5], but the latter have $\bar{3}$ symmetry, or approximate it, with rings tipped up and down alternately, while the present molecules do not. The considerable variation in the degree of tip of the different rings, and especially the extreme tip of two of the bridging rings in **I** and **Ia** relative to the molecular axis (the viewing direction in Figures 1 and 2), has no counterpart in **IV** and related species.

The bond distances and bond angles in the present structures are all quite normal; e.g. the average aromatic C—C distances in **I**, **Ia**, **IIa**, and **IIIa** are 1.399, 1.399, 1.398 and 1.40 Å. (The results for **IIIa** are much less precise than for the other three, as can be seen from Tables I and II.) The fact that these and other distances are not foreshortened is in accord with the lack of both overall and internal molecular motion (except for some wagging of the anisyl methyl groups, and possibly of the bridge atoms in **IIIa**).

The *overall* libration of the host molecules, estimated from the U^{ij} values for the individual atoms, is very small in each of these structures: the *maximum* rms librational amplitudes are about 1° for **I**, **Ia**, and **IIa** and 2° for **IIIa** (**IIIa** was done at room temperature, the others at low temperature). There is, however, evidence of significant torsional oscillation (libration) of the methoxy methyl groups about the C—O bonds in each compound, the rms librational amplitudes being in the range 5 to 10° for the low temperature structures, and 18° for **IIIa** (Table V). Because the overall libration is so small, the corrections to most bond distances for such motion are negligible, only a fraction of the e.s.d. of the distance. On the other hand, some corrections to the O—CH$_3$ distances are appreciable, an order of magnitude larger (up to as much as 0.06 Å). These distances have been corrected in the supplementary tables.

For bonds of the kinds present in the hosts of these structures, Hirshfeld has pointed out that the difference in mean square displacement amplitudes (MSDAs) of the bonded atoms along the bond direction should be of the order of 0.0010 Å^2 or less [21] if the data are of good quality. The quality of U values, as estimated from the mean e.s.d. of U^{ij}, is reasonably good for **I** and **IIa**, fair for **Ia**, and poor for **IIIa** (Table V). The data for **I**, **Ia** and **IIa** fit the Hirshfeld criterion as well as can be expected, given the quality of the data; for **IIIa**, the U values are so imprecise that the test is hardly meaningful, but nonetheless, the 'fit' is in accord with the mean e.s.d. of U.

Study of the data in Table V (and the more extensive tables of MSDA differences with the supplementary material) shows that the hosts in these structures are indeed very rigid, except for the appreciable librational motion of the methoxy methyl groups about the C—O bonds and a small degree of wagging of

Table V. Some results of analysis[a] of the anisotropic displacement parameters.

	I	Ia	IIa	IIIa	IV	IVa
Rms libration amplitude of						
CH$_3$ about the C$_{Ar}$—O bond	6.6°	6.2°	10.3°[b]	17.8°	10.5°	10.9°
	5.0	5.2	5.5			
Mean MSDA differences[c]:						
(1) between bonded atoms along bonded direction	16 pm^2	20 pm^2	11 pm^2	85 pm^2	9 pm^2	8 pm^2
(2) between all atoms within the individual aryl rings	17	21	13	72	13	13
(3) between non-bonded atoms in different aryl rings	23	34	18	83	17	17
(4) between methoxy methyl C atoms and atoms in aryl rings						
same rings	23	29	34	177	126	60
other rings	186	166	214	1344	437	360
Mean e.s.d.[d] of U^{ij}	11	17	12	63	13	12
T	128 K	115 K	115 K	295 K	295 K	295 K

[a] All calculations were made with THMA11 [14]. Numbers in parentheses represent e.s.d.s, given in units of the least significant digit of the corresponding quantity. See discussion in text concerning the significance of MSDA differences, Data for IV and IVa taken from Ref. [5]. Detailed tables of these quantities for each structure are included with the supplementary material.

[b] For IIa, this larger libration amplitude is, somewhat surprisingly, for C(9), on the methoxy O closer to Li$^+$.

[c] Units of MSDA differences are $Å^2 \times 10^{-4}$, or pm^2.

[d] The mean e.s.d. of a difference in MSDA values would be expected to be about 1.4 times the mean e.s.d. of an individual U^{ij} term.

the *para* methyl groups. The MSDA differences between non-bonded atoms within each aromatic ring are scarcely larger than those between bonded atoms, and the differences between atoms in *different* aromatic rings are only slightly larger. A much more common situation in compounds containing many aromatic rings is that the differences in MSDA values for atoms in different rings are much larger than those within a ring, indicating significant relative motion [22]. The fact that the MSDA differences for the methoxy methyl groups are much larger relative to atoms in other aromatic rings than relative to those in rings to which they are attached is a manifestation of the fact that if atomic motion is approximately normal to the interatomic vector in question, the MSDA difference may be small even though appreciable internal motion is present. In other words, large MSDA differences are a sufficient but not a necessary condition for the presence of internal motion.

The FeCl$_4^-$ counterion in IIa has tetrahedral geometry (bond angles 108.2–111.0°, average 109.5°) with an average Fe—Cl distance (corrected for libration) of 2.209 Å (range 2.205 to 2.215 Å), quite in accord with the average of 17 precise structures in the Cambridge Structural Data Base [23], 2.217 (14) Å. The Cl

atoms have rather large displacement parameters; the apparent motion of the anion fits the rigid-body approximation extremely well.

4. Conclusions

Compared to the prototype spherand **IV**, the 'augmented' spherand **I** provides more cation$\cdots$O contacts and a greater cavity size (which should favor Na$^+$), and the 'diminished' spherand **II** provides a smaller cavity size (which should favor Li$^+$). In fact, **IV** is most strongly bonded to each of these cations; for Na$^+$ the order of binding is **IV** > **I** > **II**, and for Li$^+$ the order is **IV** > **II** > **I** [20]. The present structural study shows that a high degree of strain remains in the complexes of **I** and **II**, in the form of short O$\cdots$O distances and out-of-plane deformations, and that, in addition, at least for **I**, minor rearrangement occurs upon complexation. These results also suggest that **III** will not bind Li$^+$ as strongly as **IV**, for although the average Li$^+$—O distance is only 0.03 Å longer in **IIIa** than in **IVa**, and there are two very short Li$^+$—O distances of 2.05 Å in **IIIa** the short O$\cdots$O contacts necessitated by the *syn* configuration will render this complex less stable relative to the pure host than **IVa** is relative to **IV**.

Acknowledgments

Notes

[1] The new complex **IIIa** was prepared by R. C. Helgeson; its properties will be published elsewhere.
[2] Crystal data: $a = 22.791(5)$, $b = 16.716(4)$, $c = 16.138(3)$ Å, $\beta = 104.32(2)°$ at 296 K, $V = 5957$ Å^3, space group $I2/a$, $Z = 4$, $D_m = 1.192(3)$ g cm^{-3}, $D_x = 1.186$ g cm^{-3} for the host with LiCl and three molecules of toluene.
[3] Lists of structure factors (Tables 1S through 4S) have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82121 (154 pages); atomic positions with anisotropic displacement parameters, (Tables 5S through 8S), bond distances, bond angles and torsion angles (9S through 12S), and tables of differences of mean square displacement amplitudes (Tables 13S through 16S) have been deposited as Supplementary Publication No. SUP 82122 (36 pages).

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