Hydrogen bonds‡

Atoms 1···2···3	O43···O52···N51	O40···O54···O50
Distance 1···2	2.868 (11)	2.822 (12)
Distance 2···3	2.861 (14)	3.024 (12)
Angle 1···2···3	119.3 (4)	105.2 (4)

† Ring 1 starts with C1, ring 2 with C10, and ring 3 with C19. ‡ The angle O52···N51—C50 in (II) is 149.4 (9)°.

The low-temperature device used was that described by Strouse (1976). The largest shift/error ratios in the final least-squares cycle for (I) were for torsion angles of the methyl groups: 0.47 for C22 and 0.25 for C4. No other ratio was larger than 0.07. These torsion angles are inherently imprecise and tend to converge at best slowly during refinement. For (II), the largest shift/error value in the final cycle (0.16) was for the torsion angle about the C3—C4 bond, involving the methyl H atoms on C4; no other shift/error ratio was as large as 0.10. For (III), the largest shift/error value in the final cycle (0.69) was for the torsion angle about the C21—C22 bond, again depending upon imprecise methyl H-atom positions on C22; no other shift/error value was as large as 0.10. The unusually large peaks in the final difference map for (III) were all near disordered atoms (three O atoms of the perchlorate ion, and O43). We were unable to find more suitable models for these disordered regions.

Data collection: Syntex $P\bar{1}$ diffractometer software for (I); *UCLA Crystallographic Package* (1984) for (II) and (III). Cell refinement: Syntex $P\bar{1}$ diffractometer software for (I); *LEAST* (*UCLA Crystallographic Package*, 1984) for (II) and (III). For all compounds, data reduction: *CARESS* (*UCLA Crystallographic Package*, 1984). Program(s) used to solve structures: *YZARC* (Declercq, Germain & Woolfson, 1979) for (I); *SHELXS*86 (Sheldrick, 1990) for (II) and (III). For all compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1279). Services for accessing these data are described at the back of the journal.

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An Na$^+$ Complex and a Bis-BH$_3$ Complex of a [1.1]Cryptahemispherand

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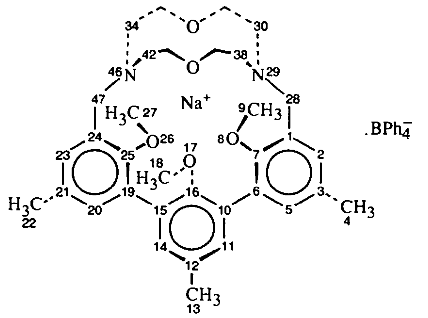
Abstract

The [1.1]cryptahemispherand host 30,31,32-trimethoxy-5,10,15-trimethyl-22,27-dioxa-1,19-diazapentacyclo[$17.5.5.1^{3,7}.1^{8,12}.1^{13,17}$]dotriaconta-3,5,7(30),8,10,12(31),13,15,17(32)-nonaene forms a crystalline complex, (I), with sodium tetraphenylborate, $[Na(C_{34}H_{44}N_2O_5)](C_{24}H_{20}B)$, and also forms a coordination complex, (II), with two molecules of BH$_3$, μ-{30,31,32-trimethoxy-5,10,15-trimethyl-22,27-dioxa-1,19-diazapentacyclo[$17.5.5.1^{3,7}.1^{8,12}.1^{13,17}$]dotriaconta-3,5,7(30),8,10,12(31),13,15,17(32)-nonaene}-N^1:N^{19}-bis(trihydroboron),

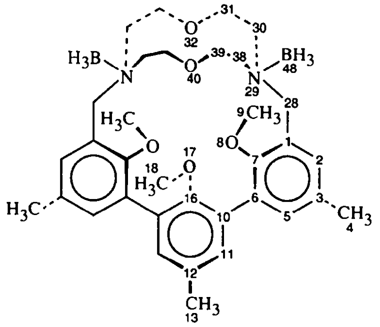
$C_{34}H_{50}B_2N_2O_5$, which crystallizes as a CH_2Cl_2 hemisolvate. The host of (I) complexes Na^+ more strongly than it does any other alkali metal ion, consistent with the nearly ideal coordination of Na^+ reported here. The N atoms, which are only about 2.6 Å from the Na^+ ion, are unusually close to each other in (I), being separated by about 4.63 Å. The solvent in the structure of (I) is disordered and unidentifiable. The structure of (II) was determined at 115 K. It contains two independent molecules in the asymmetric unit, each with site symmetry *m*; they have very similar conformations. The BH_3 groups attached to the N atoms are directed outward from the cavity of each molecule, giving the molecules the uncommon *exo-exo* conformation. The N atoms in (II) are about 1.3 Å farther apart than those in (I). Because the N atoms are tetrasubstituted, (II) is a poor complexer. One $-CH_2CH_2OCH_2CH_2-$ bridge in each cryptand moiety in (II) adopts a 'crown' conformation, while the other bridge has *trans* $-CH_2CH_2-$ torsion angles. The cavity of the host in (II) is filled, and the conformation is stabilized by typical C—H···O interactions.

Comment

Cryptahemispherands are part spherand and part cryptand (Cram, Ho, Knobler, Maverick & Trueblood, 1986). Uncomplexed cryptahemispherands are more highly pre-organized for binding than are cryptands, but less so than are spherands; they are more flexible than spherands. Most cryptahemispherands bind cations rapidly and strongly because they have many converging ligating atoms and are at once flexible and partially pre-organized. The present host forms a strong complex with Na^+, (I), with nearly ideal coordination to the five O and two N atoms; it is much better suited for complexing Na^+ than is the [2.2] analog (Maverick, Knobler, Trueblood & Ho, 1997). However, when the present host forms a complex with two BH_3 groups, (II), the N atoms at the cryptand-moiety bridgeheads become quaternary, and the molecule becomes a poor complexing agent. The N atoms are inverted relative to those in (I), in which the unshared pairs are directed towards the center of the cavity. Consequently, the N atoms are 1.3 Å farther apart in (II) than in (I).



(I)



(II)

The general geometrical features of the host are quite similar to those reported for the hosts in the first paper of this series (Maverick *et al.*, 1997). Some features unique to these structures are given in Tables 2 and 3. The two bridges in (I) are conformationally different, as should be apparent from Fig. 1 and from the torsion angles; the C—C torsion angles all range (in absolute value) from 48 to 54°, but the C—O torsion angles in the C30–C34 bridge are both antiperiplanar, 175.4 (6) and −167.4 (6)°, whereas those in the C38–C42 bridge are −177.2 (8) and 82.0 (10)°.

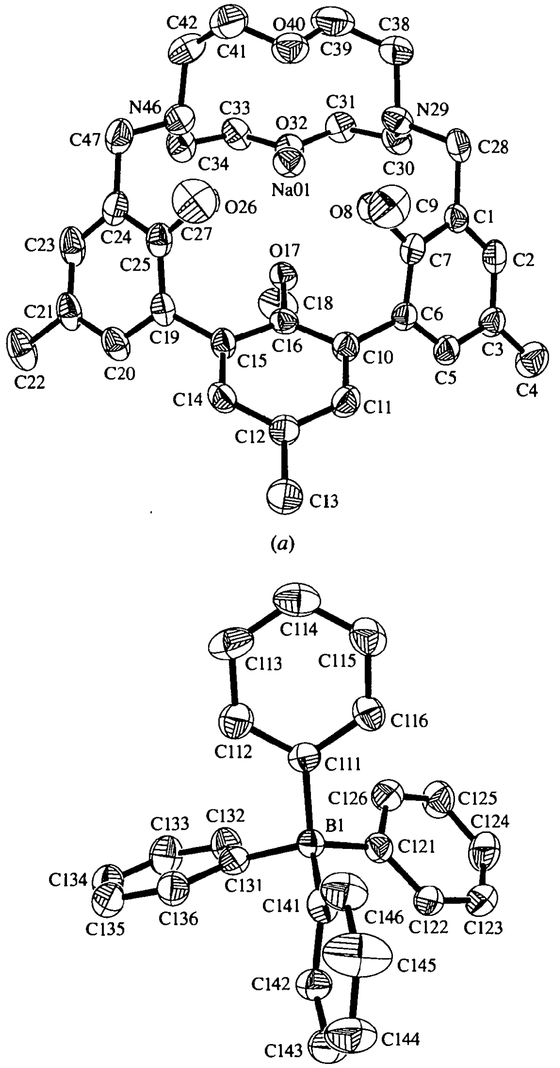
The two independent molecules of (II) have very similar but not identical conformations; within each molecule, the two cryptand bridges have quite distinct conformations (Fig. 2). The chief difference between the two molecular structures is in the angle between the normals to the planes of the adjacent aromatic rings (66° in molecule 1 and 54° in molecule 2). There are also small differences in the conformation of one of the $-CH_2CH_2OCH_2CH_2-$ links. For each molecule, the cavity is filled by inward-turned H atoms of the diethyleneoxy bridges, with the borane moieties situated outside the cavity.

The trianisyl groups in these structures are similar to those found in the [2.2]cryptahemispherands (Maverick *et al.*, 1997) and in the prototype hexaanisyl spherand (Trueblood, Maverick & Knobler, 1991). The methoxy methyl groups of the anisyls nearer the cryptand bridgeheads are *syn* to each other and *anti* to the OCH_3 group of the remaining anisyl. Some of the rings are significantly distorted from planarity, although most of them less so than in the spherands; aryl folds along the O–Ar–CH_3 axis range from 2 to 5°.

The tetraphenylborate ion in (I) was initially included with idealized aromatic rings, but a survey of such ions in the Cambridge Structural Database (Allen *et al.*, 1991) showed that, invariably, the '*ipso*' angle (the C—C—C angle at the C atom attached to the central B atom) is very close to 115°, with accompanying distortions of the bond distances. Refinement of the rings in the present ion showed exactly this pattern; the '*ipso*' angles all refined to values close to 115° (Table 2). This was especially encouraging because the 'solvent' in this structure could not be identified. The crystals had been exposed to CH_3OH, CH_2Cl_2 and ethyl acetate, but we were never able to find in difference maps any chemically reasonable pattern corresponding to any of these. The final refinement included two low-occupancy (0.3 and 0.2) constrained C—O pairs and two even lower-occupancy (0.15) bent Cl—C—Cl groups, also constrained, but these did not fit the difference maps better than other models that were less reasonable chemically (*e.g.* six C atoms). The closest approach of any solvent atom to any atom of the host or either ion is 3.46 (5) Å. Despite our failure to resolve the solvent, which contributed to the uncommonly high *R* value for this structure (the data set for which had a large proportion of weak reflections), the internal consistency of the geometry of both the ionic complex of the host and the tetraphenylborate ion gives us confidence that the significant details of the structure are correct.

In (I), each of the seven heteroatoms of the host is coordinated to Na^+, at close to the standard distances of 2.45 Å for O and 2.6 Å for N (for sevenfold coordination; Shannon, 1976). The bridges of the host adopt a crown conformation (Fig. 1), with *gauche* C—C torsion angles; the N· · ·N distance is only 4.63 (1) Å.

The B—N distances in (II), 1.632 (7) and 1.631 (6) Å, are nearly identical to that found in $(CH_3)_3N.BH_3$ [1.638 (10) Å; microwave spectroscopy (Cassoux, Kuczkowski, Bryan & Taylor, 1975)] and in 1,7-diaza-4,10,15-trioxabicyclo[5.5.5]heptadecane-borane [1.633 (4) Å; Metz & Weiss, 1978], and somewhat shorter than that of 1.657 (6) Å found in another BH_3 compound



(*a*)

(*b*)

Fig. 1. Views of (*a*) the cationic complex and (*b*) the anion of (I) (*SHELXTL*; Sheldrick, 1995). Displacement ellipsoids are drawn to enclose 30% probability; H atoms and solvent have been omitted.

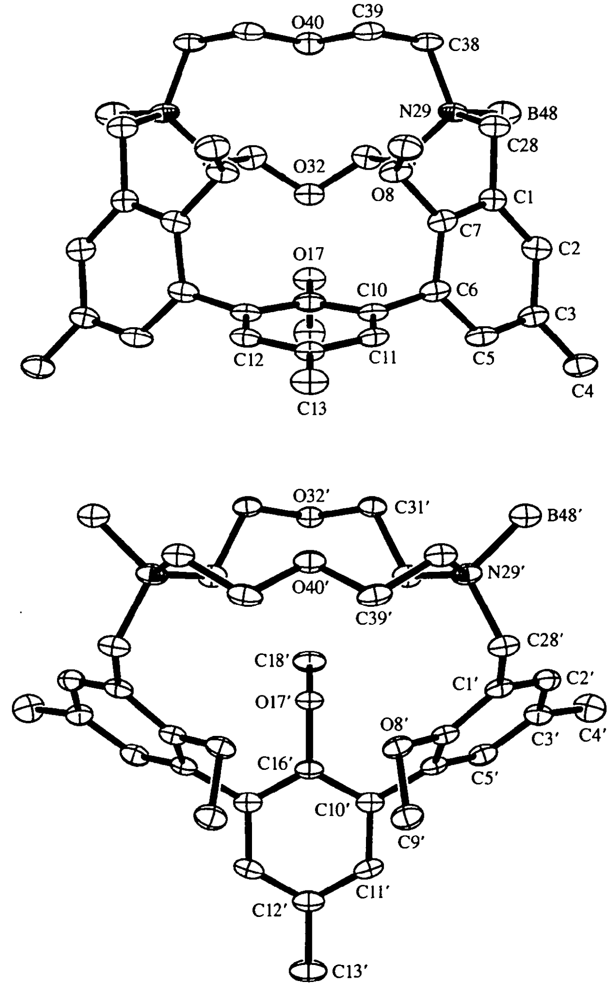


Fig. 2. The two independent molecules of (II) in their mutual orientation in the crystal. Displacement ellipsoids are drawn to enclose 30% probability. N atoms are shaded. The mirror plane is vertical. H atoms and solvent have been omitted. Rotation of the upper molecule (molecule 1) by 90° about an axis normal to the mirror plane, in a direction that moves the upper half of the molecule toward the viewer, puts it in approximately the orientation of the lower molecule (molecule 2).

containing $-NCH_2CH_2OCH_2CH_2OCH_2CH_2N-$ linkages (Metz, Moras & Weiss, 1976). Examination of B—N and N—C distances in these and comparable compounds suggests that the geometry is sensitive to the nature of the substituents on the B atom and to overcrowding, which is not uncommon in such structures.

There are no unusual intermolecular distances in either structure. In (I), all the shortest distances are between the host and the counterion, but there are none below 3.4 Å not involving H atoms. The shortest distances between the (calculated) positions of H atoms are greater than 2.4 Å. In (II), there are some apparent intramolecular C—H···O interactions (Table 3) between strands, from C30 and C31 to O40 in each molecule, and from one strand to a methoxy O atom (C39 to O8) in molecule 1 and from C18′ to O32′ in molecule 2. There is also a possible C—H···Cl interaction to the solvent (Table 3). There are no intermolecular distances in (II) shorter than 3.5 Å not involving either H atoms or solvent. The solvent sites in the crystal are not fully occupied (see *Experimental*).

The displacement parameters are too imprecise to warrant any detailed discussion of overall or internal librational motion (Dunitz, Maverick & Trueblood, 1988). However, the general pattern is the same as in the other spherand and hemispherand structures: overall libration is small, and the methoxy methyl groups are moving significantly with respect to most of the rest of the host molecule.

Experimental

The title compounds were prepared as described by Cram *et al.* (1986). Compound (I) was crystallized from methanol–CH_2Cl_2–ethyl acetate and (II) from methanol–CH_2Cl_2.

Compound (I)

Crystal data

[Na($C_{34}H_{44}N_2O_5$)]($C_{24}H_{20}B$)
$M_r = 902.97$
Monoclinic
$P2_1/n$
$a = 19.919\ (2)$ Å
$b = 14.725\ (2)$ Å
$c = 21.387\ (2)$ Å
$\beta = 111.850\ (3)°$
$V = 5822.3\ (10)$ Å^3
$Z = 4$
$D_x = 1.030$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 4.8–9.0°$
$\mu = 0.073$ mm^{-1}
$T = 295$ K
Platelet
0.40 × 0.35 × 0.08 mm
Colorless

Data collection

Modified Picker FACS-1 (Crystal Logic) diffractometer
$\theta/2\theta$ scans
Absorption correction: none
10739 measured reflections
10278 independent reflections
3744 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 25.00°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 17$
$l = -25 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.117$
$wR(F^2) = 0.388$
$S = 1.016$
10278 reflections
651 parameters
H atoms riding; fixed C—H distances, $\langle u^2\rangle(H) = 1.2U_{\rm eq}(C)$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond

$w = 1/[\sigma^2(F_o^2) + (0.2052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.300$
$\Delta\rho_{\rm max} = 0.639$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.270$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{34}H_{50}B_2N_2O_5.0.5CH_2Cl_2$
$M_r = 630.84$
Monoclinic
$P2_1/m$
$a = 15.605\ (11)$ Å
$b = 15.799\ (7)$ Å
$c = 15.023\ (7)$ Å
$\beta = 94.43\ (5)°$
$V = 3693\ (4)$ Å^3
$Z = 4$
$D_x = 1.135$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 7.5–11.0°$
$\mu = 0.143$ mm^{-1}
$T = 115\ (2)$ K
Irregular
0.5 × 0.3 × 0.2 mm
Colorless

Data collection

Syntex (Crystal Logic) diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7056 measured reflections
6803 independent reflections
3340 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ not known
$\theta_{\rm max} = 25.06°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 14%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.183$
$S = 1.034$
5680 reflections
445 parameters
H atoms riding; fixed C—H distances, $\langle u^2\rangle(H) = 1.2U_{\rm eq}(C)$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond

$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.335$
$\Delta\rho_{\rm max} = 0.248$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.287$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0007 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$U_{eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}
C1	−0.1779 (3)	0.9807 (3)	0.4166 (3)	0.0354 (11)
C2	−0.1606 (3)	1.0384 (3)	0.3504 (3)	0.0390 (12)
C3	−0.0875 (3)	1.0328 (3)	0.3032 (3)	0.0398 (12)
C4	−0.0696 (3)	1.0953 (3)	0.2319 (3)	0.0523 (14)
C5	−0.0322 (3)	0.9649 (3)	0.3230 (3)	0.0432 (13)
C6	−0.0460 (2)	0.9049 (3)	0.3888 (3)	0.0368 (12)
C7	−0.1194 (3)	0.9153 (3)	0.4358 (3)	0.0368 (11)
O8	−0.1385 (2)	0.8563 (2)	0.4998 (2)	0.0407 (8)
C9	−0.0883 (3)	0.8656 (3)	0.5836 (3)	0.0500 (14)
C10	0.0062 (2)	0.8273 (3)	0.4049 (2)	0.0356 (11)
C11	0.0898 (2)	0.8257 (3)	0.4461 (2)	0.0370 (11)
C12	0.1320 (4)	3/4	0.4657 (4)	0.033 (2)
C13	0.2240 (4)	3/4	0.5106 (4)	0.047 (2)
C16	−0.0326 (4)	3/4	0.3841 (4)	0.038 (2)
O17	−0.1156 (2)	3/4	0.3422 (2)	0.0421 (12)
C18	−0.1142 (4)	3/4	0.2468 (4)	0.052 (2)
C28	−0.2586 (2)	0.9844 (3)	0.4652 (3)	0.0403 (12)
N29	−0.3366 (2)	0.9365 (2)	0.4200 (2)	0.0376 (10)
C30	−0.3083 (2)	0.8682 (3)	0.3593 (2)	0.0368 (11)
C31	−0.3820 (3)	0.8266 (3)	0.3026 (3)	0.0435 (12)
O32	−0.3536 (2)	3/4	0.2636 (2)	0.0412 (12)
C38	−0.3873 (2)	0.9021 (3)	0.4934 (3)	0.0422 (13)
C39	−0.3495 (3)	0.8256 (3)	0.5428 (3)	0.0436 (12)
O40	−0.3800 (3)	3/4	0.4975 (2)	0.0429 (12)
B48	−0.3964 (3)	1.0068 (4)	0.3653 (4)	0.056 (2)
C1′	0.3418 (3)	0.9817 (3)	0.0836 (3)	0.0355 (11)
C2′	0.2936 (3)	1.0446 (3)	0.0381 (3)	0.0398 (12)
C3′	0.2760 (3)	1.0401 (3)	−0.0543 (3)	0.0396 (12)
C4′	0.2270 (3)	1.1109 (3)	−0.1042 (3)	0.0556 (14)
C5′	0.3046 (3)	0.9708 (3)	−0.0993 (3)	0.0390 (12)
C6′	0.3527 (3)	0.9064 (3)	−0.0567 (3)	0.0339 (11)
C7′	0.3752 (2)	0.9162 (3)	0.0356 (3)	0.0343 (11)
O8′	0.4273 (2)	0.8563 (2)	0.0804 (2)	0.0377 (8)
C9′	0.5163 (3)	0.8667 (3)	0.0634 (3)	0.0467 (13)
C10′	0.3757 (2)	0.8267 (3)	−0.1016 (2)	0.0337 (11)
C11′	0.4226 (3)	0.8255 (3)	−0.1777 (3)	0.0428 (12)
C12′	0.4439 (4)	3/4	−0.2173 (4)	0.050 (2)
C13′	0.4890 (6)	3/4	−0.3034 (5)	0.085 (3)
C16′	0.3499 (4)	3/4	−0.0682 (4)	0.034 (2)
O17′	0.2950 (2)	3/4	0.0003 (2)	0.0320 (10)
C18′	0.2068 (4)	3/4	−0.0343 (4)	0.046 (2)
C28′	0.3576 (2)	0.9820 (3)	0.1843 (2)	0.0392 (12)
N29′	0.2878 (2)	0.9379 (2)	0.2341 (2)	0.0377 (10)
C30′	0.2436 (2)	0.8688 (3)	0.1781 (2)	0.0363 (11)
C31′	0.1686 (2)	0.8265 (3)	0.2204 (3)	0.0348 (11)
O32′	0.1459 (2)	3/4	0.1755 (2)	0.0329 (10)
C38′	0.3304 (3)	0.9029 (3)	0.3191 (2)	0.0391 (12)
C39′	0.3855 (2)	0.8249 (3)	0.3129 (3)	0.0416 (12)
O40′	0.3338 (2)	3/4	0.3120 (2)	0.0397 (11)
B48′	0.2193 (3)	1.0095 (4)	0.2617 (3)	0.0454 (15)
Cl1†	0.3219 (2)	1/4	0.1705 (2)	0.0722 (11)
Cl2†	0.1386 (3)	1/4	0.1180 (3)	0.0897 (13)
C56†	0.2190 (8)	1/4	0.2073 (8)	0.061 (4)
Cl3‡	0.0079 (6)	−0.0628 (4)	0.0407 (6)	0.099 (3)
Cl4‡	−0.0143 (5)	0.1070 (4)	−0.0374 (5)	0.086 (2)
C57‡	0.0581 (7)	0.0328 (7)	0.0141 (15)	0.072 (7)

† Site occupancy = 0.56. ‡ Site occupancy = 0.23.

Table 2. *Some geometrical features of compounds (I) and (II) (Å, °)*

Interplanar angles between adjacent aromatic rings†

	(I)	(II) (unprimed)	(II) (primed)
1 to 2	54.4 (2)	65.9 (1)	53.5 (1)
2 to 3	53.8 (2)		

Tetraphenylborate ion in (I)

B—C distances	1.65 (2)
Angle at C on B	114.7 (5)

Na⁺ coordination in (I)

	Minimum	Maximum	Average
$Na^+\cdots O$	2.334 (6)	2.451 (5)	2.39 (5)
$Na^+\cdots N$	2.602 (6)	2.636 (7)	2.62 (2)

	(I)		(II) (unprimed)	(II) (primed)
N29···N46	4.627 (9)	N29···N29*M*‡	5.891 (8)	5.938 (8)
C28···C47	7.037 (10)	C28···C28*M*	7.408 (10)	7.331 (10)
C1···C24	7.056 (10)	C1···C1*M*	7.290 (10)	7.322 (10)

† Ring 1 begins with C1, ring 2 with C10, and ring 3 with C19.
‡ Atoms designated with a final *M* are mirror-related to those without.

Table 3. *Some C—H···X interactions in (II) (Å, °)*

C—H distances are constrained to 0.96 or 0.97 Å.

	H···*X*	C···*X*	C—H···*X*
Inter-strand			
C30—H30*A*···O40			
Molecule 1	2.59	3.068 (5)	111
Molecule 2	2.55	3.019 (5)	109
C31—H31*A*···O40			
Molecule 1	2.64	3.166 (5)	115
Molecule 2	2.55	3.075 (5)	114
Strand to outer aryl O			
C39—H39*A*···O8			
Molecule 1	2.51	3.439 (5)	160
Molecule 2	2.74	3.635 (5)	154
C18 to strand			
C18—H18*A*···O32			
Molecule 1	2.96	3.763 (8)	143
Molecule 2	2.48	3.360 (7)	153
C13′ to solvent Cl1 at $(1-x, 1-y, -z)$			
C13′–H13*B*′···Cl1	2.68	3.43 (1)	135

The low-temperature device was that described by Strouse (1976). The refinement of (I) went smoothly except for the difficulties in modeling the solvent. The only large shift/error ratios in the final cycles were for low-occupancy solvent atoms. There were no significant shifts in the parameters of other atoms. The unit cell for structure (II) contains two crystallographically unrelated cryptahemispherand molecules, each of which possesses C_s symmetry. The ^{1}H NMR spectrum suggests that each molecule also possesses a mirror plane in solution (Cram *et al.*, 1986). The solvent was modeled with two separate disordered methylene chloride molecules; occupancies and positions were refined initially, then positions and displacement parameters were refined, keeping occupancies fixed. For one of these molecules [occupancy factor of 0.278 (2)], C and Cl lie on a mirror plane; for the other solvent molecule, which lies near a center of symmetry and has an occupancy factor of 0.228 (2), C—Cl distances were restrained to be about 1.77 Å and the Cl—C—Cl angle was restrained to be about 112°. For structure (II), the largest shift/error value in the final least-squares cycle (0.335) was in the torsion angle for the rotation of a methyl, C4, corresponding to a positional shift in H4*A* of 0.010 Å, which we do not regard as meaningful. The largest shift in any non-H atomic position parameter in the final least-squares cycle was 0.0014 Å; all others were smaller than 0.001 Å. There were a few shift/error values in the range 0.10–0.16, and one of 0.21, for displacement parameters, but these parameters are neither accurate nor precise in this structure.

Data collection: Picker (Crystal Logic) system for (I); Syntex (Crystal Logic) system for (II). Cell refinement: Picker (Crystal Logic) system for (I); Syntex (Crystal Logic) system for (II). For both compounds, data reduction: *UCLA Crystallographic Package* (1984); program(s) used to solve structures: *MULTAN*80 (Declercq, Germain & Woolfson, 1979); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1282). Services for accessing these data are described at the back of the journal.

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A K^+ Complex of a [2.1]Cryptahemispherand at 295 K

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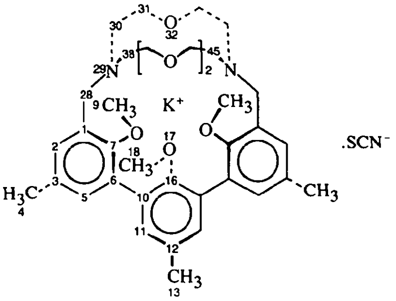
Abstract

The potassium complex of the [2.1]cryptahemispherand 33,34,35-trimethoxy-5,10,15-trimethyl-22,25,30-trioxa-1,19-diazapentacyclo[$17.8.5.1^{3,7}.1^{8,12}.1^{13,17}$]pentatriaconta-3,5,7(33),8,10,12(34),13,15,17(35)-nonaene, crystallizes from ethyl acetate with a thiocyanate counterion $\{[K(C_{36}H_{48}N_2O_6)]SCN\}$. The space group is *Pnma*. The longer cryptand-like bridge is disordered, departing from mirror symmetry because it is constrained to fold unsymmetrically by the geometry of the rest of the host. Five of the O atoms and the two N atoms of the host, as well as the N of the SCN^- ion, are coordinated by the K^+ ion. The sixth O atom of the host is at 3.211 (3) Å from the K^+ ion, about 0.5 Å farther than the closest O atoms.

Comment

The general properties of cryptahemispherands have been discussed in the two immediately preceding papers (Maverick, Knobler, Trueblood & Ho, 1997*a*; Knobler, Maverick, Trueblood & Ho, 1997). In contrast to the [2.2] analog (Maverick *et al.*, 1997*a*), the present host binds to Na^+, K^+ and Rb^+ with nearly equal strength (Cram & Ho, 1986). A suitable crystal of the complex with KSCN was grown from ethyl acetate.



(I)

The structure, (I), is illustrated in Fig. 1 and some geometrical features are given in Table 2. The longer

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