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Three Complexes of a [2.2]Cryptahemispherand

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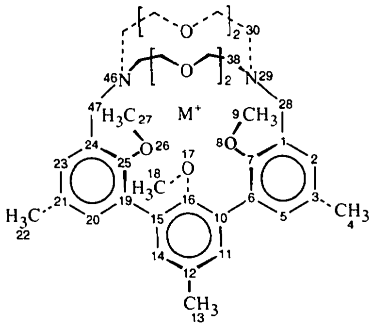
Abstract

The macrocyclic host 36,37,38-trimethoxy-5,10,15-trimethyl-22,25,30,33-tetraoxa-1,19-diazapentacyclo-[17.8.8.$1^{3,7}$.$1^{8,12}$.$1^{13,17}$]octatriaconta-3,5,7(36),8,10,-12(37),13,15,17(38)-nonaene contains a somewhat flexible cavity lined with seven O atoms and two N atoms. The structures of three of its complexes are reported here: that with sodium thiocyanate, (I) {[Na($C_{38}H_{52}N_2O_7$)]SCN}, at 296 K, and those with potassium thiocyanate, (II) {[K($C_{38}H_{52}N_2O_7$)]SCN.H_2O}, and caesium perchlorate, (III) {[Cs($C_{38}H_{52}N_2O_7$)]ClO_4.H_2O}, at 156 K. The host adapts well to Cs^+, with effective ninefold coordination; it adapts nearly as well to K^+, but is not sufficiently flexible to be a good complexer for the much smaller Na^+ ion. In structures (II) and (III), a water molecule forms hydrogen bonds between an O atom of the host and an atom of the anion [N of SCN^- in (II) and O of ClO_4^- in (III)].

Comment

Cryptahemispherands (Cram, Ho, Knobler, Maverick & Trueblood, 1986; Cram & Ho, 1986) contain a trianisyl group, linked in the 2 and 6 positions and joined at its ends to –CH_2N< or –C(=O)N< groups, which are in turn joined by two –$CH_2(CH_2OCH_2)_nCH_2$– strands. The trianisyl group is self-organizing, as in the spherands (Cram, Kaneda, Helgeson & Lein, 1979; Trueblood, Knobler, Maverick, Helgeson, Brown & Cram, 1981; Trueblood, Maverick & Knobler, 1991), and the >$NCH_2(CH_2OCH_2)_nCH_2N$< moieties are a common feature of cryptands (Lehn, 1978); in the present structures, n = 2. Molecular models had suggested that the blend of rigidity and flexibility of a combination of the trianisyl group with cryptand strands would yield structures with very high and specific binding capacities for alkali metal ions. This proved to be the case (Cram & Ho, 1986). The host in the present structures [(I), (II) and (III)] complexes Cs^+ most strongly, by about one order of magnitude more strongly than it binds Rb^+, two orders of magnitude more strongly than it binds K^+, and six orders of magnitude more strongly than it binds Na^+. It is a very selective discriminator for K^+ over Na^+, by a factor of about 10^4, a property that has been used in ion-selective chromogenic ionophores (Helgeson, Czech, Chapoteau, Gebauer, Kumar & Cram, 1989).



(I) M^+ = Na^+; counterion = SCN^-
(II) M^+ = K^+; counterion = SCN^-; solvent = H_2O
(III) M^+ = Cs^+; counterion = ClO_4^-; solvent = H_2O

Some atom numbers for the host are shown in the scheme above; most are also shown in Fig. 1. Because we are simultaneously reporting structures of other cryptahemispherands (Knobler, Maverick, Trueblood & Ho, 1997*a*,*b*; Maverick, Knobler, Trueblood & Ho, 1997), we have, in order to simplify comparisons, chosen a numbering scheme that can be adapted for the other structures. Since our preliminary report (Cram *et al.*, 1986), the structure of the complex with Na^+, (I), has been refined further, and the structures of the complexes with K^+, (II), and Cs^+, (III), have been significantly improved by data collection at low temperature and subsequent refinement. Our earlier discussion of the general structural features is still germane. All three complexes were illustrated in stereo earlier (Chart II, p. 2994, Cram *et al.*, 1986). The general features shown in those low-resolution views are unaltered, although some details are different, particularly with regard to the disorder in one cryptand link in (II), as well as a few other details of the structure of (II), and the role of the water molecules in (II) and (III).

Both (II) and (III) are partially disordered. For (II), disorder in the cryptand moiety was modeled with isotropic atoms C36 and C36′, and with the pairs C44/C45 and C44′/C45′, and appropriate partial-occupancy H atoms. Bond distances and $\langle u^2 \rangle$ values for disordered atoms were restrained. For (III), no improved model was found for O43, but its severe anisotropy, apparent in Fig. 1(*c*), clearly indicates disorder and renders distances involving O43 imprecise. In addition, rotational disorder about the Cl49—O50 bond of the ClO_4^- ion in (III) was modeled with partial-occupancy isotropic atoms, O51/O52/O53 and O51′/O52′/O53′.

The aromatic rings of the hosts are not greatly distorted, unlike those in the hexaanisyl spherands and the

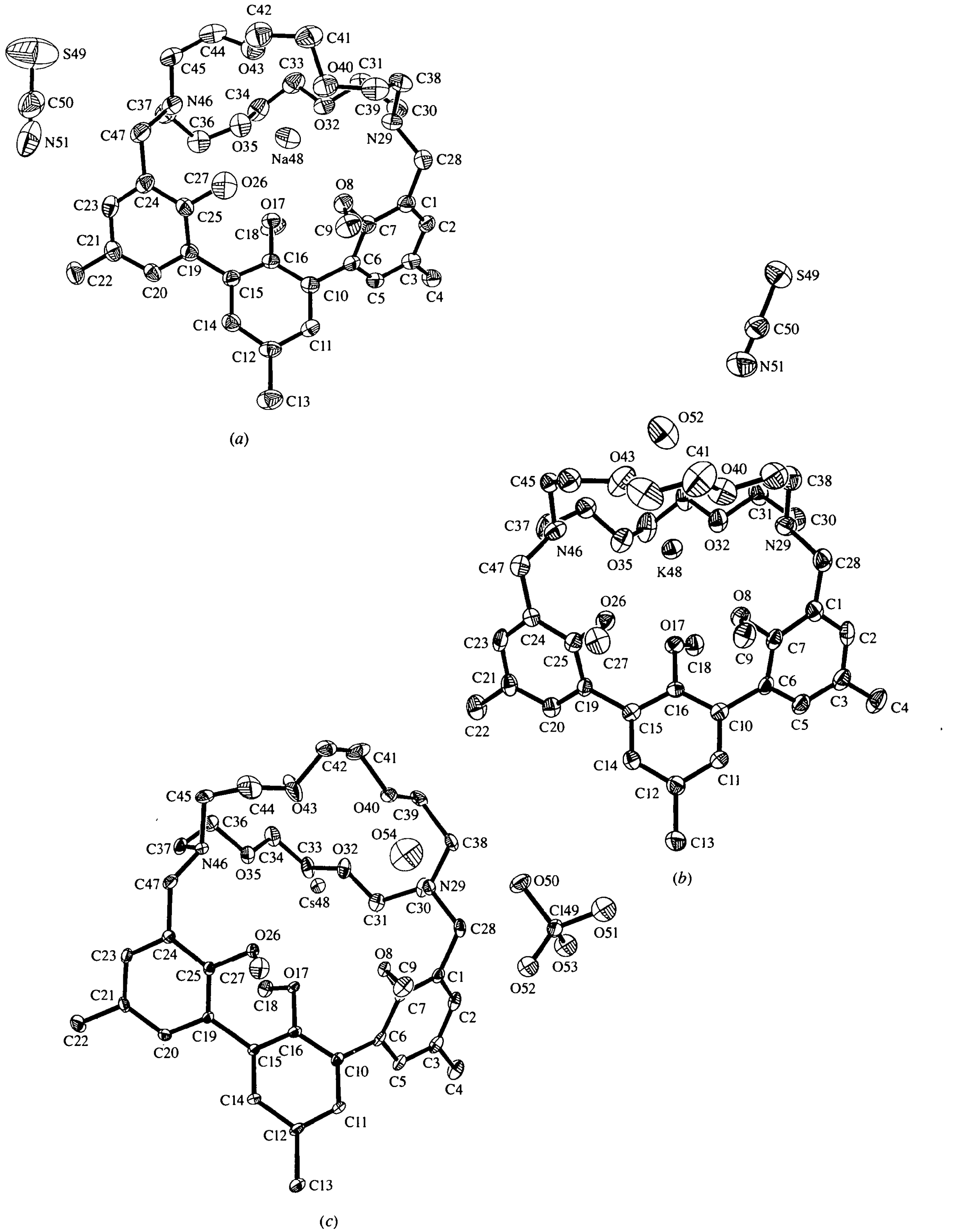


Fig. 1. Minimum-overlap views of the structures (*SHELXTL*; Sheldrick, 1995): (*a*) (I), (*b*) (II) and (*c*) (III). Lower-occupancy disordered atoms are not shown. A few atom labels have been omitted for clarity; most are also given in the accompanying scheme. [For stereoviews of (I), (II) and (III), as well as of the structures in the three accompanying papers (Knobler *et al.*, 1997*a*,*b*; Maverick *et al.*, 1997), see Cram *et al.* (1986).] Ellipsoids are drawn at 30% probability.

related, severely overcrowded, bridged spherands (Trueblood *et al.*, 1991; Knobler, Maverick & Trueblood, 1992). A table illustrating some of those distortions is given on page 903 of the report by Trueblood, Maverick, Knobler & Goldberg (1995). The differences between the three host molecules in the present structures arise almost entirely as a consequence of differing adaptation to coordination with Na^+, K^+ and Cs^+, which have quite different effective radii. Small structural differences arise also because the counterion in (III) is ClO_4^-, whereas that in each of (I) and (II) is SCN^-, and because a water molecule is associated with each host in (II) and (III), but not in (I).

There are seven potentially ligating O atoms in the host, three of them being the ether O atoms of the trianisyl group. The other four O atoms, as well as the two N atoms of the host, are in an 18-membered ring. Although this ring superficially resembles an 18-crown ring, *i.e.* it has the formula $(CH_2CH_2X)_6$, with X = N in the 1 and 10 positions and X = O in the other four positions, it is restricted in its conformational freedom by the fact that there is a third, longer, bulkier and less flexible bridge between the two N atoms, consisting of 11 C atoms of the dimethylene–trianisyl group. This third bridge prevents the 18-membered macrocycle from adopting a crown conformation, as does the third strand in cryptates. The conformation at the N atoms in each of the present structures is *endo-endo*, *i.e.* the lone pairs are directed inwards.

In the usual 18-crown-6 ring, the heteroatoms opposite each other (*e.g.* in the 1 and 10 positions) are about 5.7 Å apart (Dobler, 1981). In the present structures, the N atoms are separated by 6.36 Å or more (Table 1); the O atoms in the 4 and 13 positions (O32 and O43) and those in the 7 and 16 positions (O35 and O40) are closer than 5.7 Å because of the folding of the ring about the N···N line. This cryptand part of the host is much flatter in (II) than in (I) or (III), as may be seen both from Fig. 1 and from the cross-ring O···O distances in Table 1. The angle between the normals to the N–O–O–N planes that correspond to each strand of the cryptand is 27.3 (2) in (II), 43.3 (4) in (I), and 65.7 (2)° in (III). The pronounced difference in this fold between (II) and (III) presumably results from a complex interplay of the cation coordination, the hydrogen bonding of the water molecule and the packing of the quite different-shaped anions. The atoms in these four-atom N–O–O–N planes show the greatest divergence from coplanarity in (I) (see Fig. 1). Although the torsion angles about all C—C bonds in the 18-membered macrocycle of each of the present structures are *gauche*, the ring folding is reflected in the fact that only about two thirds of the C—O and C—N bonds are antiperiplanar (all would be so in a true crown).

The host adapts best to the Cs^+ ion, the radius of which, according to Shannon (1976), is about 1.70 Å for coordination number (CN) seven (and about 1.78 Å for CN nine). With the standard O radius of 1.40 Å (Shannon, 1976), this implies a Cs^+···O distance of between 3.1 and 3.2 Å, at the upper end of the range found (Table 1). Shannon's radius for K^+ for CN seven is 1.46 Å, which leads to an expected K^+···O distance of 2.86 Å, in good agreement with the present results (Table 1). If one considers the N atoms to be coordinated to K^+ (see below), then the CN is nine, for which Shannon gives a K^+ radius of 1.55 Å, corresponding to an expected K^+···O distance of 2.95 Å, not much greater than the average value in (II) of 2.89 Å. On the other hand, the Na^+···O distances indicate clearly that the host is unable to coordinate all O atoms to this smaller ion. Shannon's radius for Na^+ is 1.02 Å for CN six, and 1.12 Å for CN seven, which correspond to Na^+···O distances of 2.42 and 2.52 Å, respectively; the former is well below all of the Na^+···O distances in (I), and the latter below all but the distance to O35 by 0.1 to more than 0.3 Å.

The 'standard' M^+···N distances (Shannon, 1976) are 2.74, 3.05 and 3.28 Å (for CN nine) for (I), (II) and (III), respectively. The last of these values is within 0.08–0.10 Å of the values found in (III), consistent with CN nine for Cs^+. The second value, 3.05 Å, is only 0.16–0.21 Å smaller than the values found in (II), so it is not unreasonable to say that the CN for K^+ in (II) approaches nine. However, the distance 2.74 Å, corresponding to an Na^+···N distance for CN nine (it would be even smaller for lower CN), is more than 0.4 Å smaller than the shorter of the two disparate Na^+···N distances in (I), and 0.9 Å smaller than the longer of the two. This is again consistent with the inability of the host to contract enough to coordinate all its O and N atoms to Na^+, manifested also in the asymmetry of the cryptand-like strands, which is reflected (Table 1) in the disparity in (I) between the comparable inter-strand O···O distances. For the '4,6' and '7,13' distances, this disparity amounts to 23% in (I), but to only 3% in (II), and 6% in (III); for the '4,13' and '7,16' distances, it is 27% in (I), 2% in (II), and 1% in (III). The structural differences in the adaptation of the host to these ions are entirely consistent with the relative strengths of complexing and the strong discrimination this host shows between K^+ and Na^+.

The O atom of the water molecule (O52) in (II) is at about the same distance from the K^+ ion as N29 and N46 (Table 1). This water molecule serves as a hydrogen-bonding bridge between O43 of the host and the N atom of the counterion; the relevant geometrical parameters are given in Table 1. This hydrogen-bonding interaction with the thiocyanate ion is quite in accord with those described by Tchertanov & Pascard (1996), even though no H-atom positions in the water molecule were found for (II). In structure (III), the water molecule plays a comparable role in linking O40 and the perchlorate O50 atom, the only non-disordered O atom of that anion. Because of the encapsulation of each cation by the host, there are no short cation–anion contacts in any of these structures.

In structures (II) and (III), complexes are paired around centers of symmetry. This is illustrated for (III) in Fig. 2; the pairing in (II) is very similar. Because structure (I) is non-centrosymmetric, the packing is necessarily quite different. There are no 'short' contacts between molecules or ions other than those noted in Table 1. The closest approach of host non-H atoms in any of the structures is greater than 3.5 Å. The closest contact involving the anion in structure (I) is between N51 (in SCN^-) and C23 [3.482 (12) Å]; in structure (II), the shortest such distance is between S49 and C44 [3.49 (2) Å]. Two of the disordered O atoms of the perchlorate ion in (III) appear to be only about 3.2 Å from host C atoms, but the positions of those O atoms are not well defined. The positions of the H atoms in these structures were calculated, being adjusted as refinement proceeded; they cannot be considered precise. There are short intermolecular H···H distances of about 2.2 Å in (I), between molecules related by the *c*-glide (H4*A*···H22*C* and H13*A*···H34*A*), and a similar distance in (III) between H18*C* atoms of two molecules related by the center of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Atom H18*C* is on the methoxy methyl group of the central anisyl ring and one can see this interaction in Fig. 2. The shortest H···H contact in (II) is about 2.4 Å; the H18*C*···H18*C* distance across the center of symmetry in this structure is about 2.6 Å.

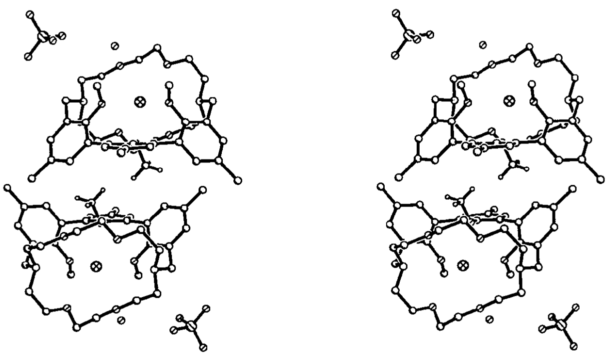


Fig. 2. Stereoview of a pair of complexes in (III), related by a center of symmetry ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). H atoms have been omitted, except for those on C18. Lower-occupancy positions in the perchlorate anion (O51′, O52′ and O53′) have been omitted. This view shows the close contact H18*C*···H18*C*, 2.2 Å, and the hydrogen-bonded approach of the water O atoms at the top and bottom center to O50 of the perchlorate (see also Table 1).

The precision of the displacement parameters for the atoms in these structures is low, as evidenced both by their e.s.d.'s and by the fit of differences in the mean-square displacement amplitudes for bonded atoms to the Hirshfeld (1976) test. Nonetheless, these parameters are more than adequate to establish that the host molecules show very little librational motion in the crystal, with no overall r.m.s. librational amplitude greater than 2.9°. The methyl C atoms of the three methoxy groups in each structure are, however, wagging appreciably, with average r.m.s. amplitudes of about 9° for (I), and 6° for both (II) and (III). If one assumes that this motion is classical, and corrects for the higher temperature at which structure (I) was measured, all three amplitudes are about the same, and comparable to those found for the similar groups in the spherands. There is an anomaly in the U^{ij} (and hence in the U_{eq}) values for (II) that we have been unable to explain. Perusal of Fig. 1 or of the U_{eq} values in the supplementary material, as well as comparison with those for similar structures determined at room temperature and at low temperature, might lead one to conclude that the intensity data for structure (II) were collected at room temperature, not at 156 K. In fact, we first determined the structures of (II) and (III) at room temperature, as reported earlier (Cram *et al.*, 1986). The U_{eq} values for the K^+ complex at room temperature are about 50% higher than those found for (II) in the present work, and are also distinctly higher on average than those reported here for the Na^+ complex, (I), at room temperature. The U_{eq} values for the Cs^+ complex at room temperature are quite similar to those found for (I).

Experimental

The compounds were prepared as described by Cram *et al.* (1986). Each was crystallized from ethyl acetate.

Compound (I)

Crystal data

$[Na(C_{38}H_{52}N_2O_7)]SCN$
$M_r = 729.89$
Monoclinic
Cc
$a = 16.907\,(6)$ Å
$b = 12.543\,(4)$ Å
$c = 20.860\,(7)$ Å
$\beta = 117.89\,(3)°$
$V = 3910\,(2)$ Å^3
$Z = 4$
$D_x = 1.240$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 10.4$–$14.6°$
$\mu = 0.145$ mm^{-1}
$T = 296\,(2)$ K
Chunk
0.50 × 0.34 × 0.26 mm
Colorless

Data collection

Syntex $P\bar{1}$ diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none
3875 measured reflections
3468 independent reflections
2814 reflections with $I > 2\sigma(I)$
R_{int} not known

$\theta_{max} = 25.07°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 14$
$l = -24 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.152$

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.468$

$S = 1.064$
3468 reflections
466 parameters
H atoms riding; fixed C—H distances, $\langle u^2 \rangle(H) = 1.2U_{eq}(C)$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond

$\Delta\rho_{max} = 0.316$ e Å^{-3}
$\Delta\rho_{min} = -0.251$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.4 (4)

Compound (II)

Crystal data

[K($C_{38}H_{52}N_2O_7$)]SCN.H_2O
$M_r = 764.01$
Monoclinic
$P2_1/c$
$a = 13.921$ (12) Å
$b = 11.397$ (11) Å
$c = 25.53$ (2) Å
$\beta = 101.74$ (2)°
$V = 3966$ (6) Å^3
$Z = 4$
$D_x = 1.280$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 4.7–8.8°$
$\mu = 0.240$ mm^{-1}
$T = 156$ K
Parallelepiped
0.35 × 0.27 × 0.16 mm
Colorless

Data collection

Modified Picker FACS-1 (Crystal Logic) diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none
7045 measured reflections
6768 independent reflections
2462 reflections with $I > 2\sigma(I)$

$R_{int} = 0.082$
$\theta_{max} = 25.00°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -30 \rightarrow 29$
3 standard reflections every 97 reflections intensity decay: ~2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.218$
$S = 1.056$
6763 reflections
480 parameters
H atoms riding; fixed C—H distances, $\langle u^2 \rangle(H) = 1.2U_{eq}(C)$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond

$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 12.2089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.16$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (III)

Crystal data

[Cs($C_{38}H_{52}N_2O_7$)]ClO_4.H_2O
$M_r = 899.19$
Monoclinic
$P2_1/c$
$a = 11.252$ (10) Å
$b = 14.272$ (13) Å
$c = 25.99$ (2) Å
$\beta = 104.72$ (2)°
$V = 4038$ (6) Å^3
$Z = 4$
$D_x = 1.450$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 4.5–7.9°$
$\mu = 1.043$ mm^{-1}
$T = 156$ K
Parallelepiped
0.22 × 0.16 × 0.14 mm
Colorless

Data collection

Modified Picker FACS-1 (Crystal Logic) diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none
12 306 measured reflections
11 776 independent reflections
6057 reflections with $I > 2\sigma(I)$

$R_{int} = 0.045$
$\theta_{max} = 30.00°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 20$
$l = -36 \rightarrow 35$
3 standard reflections every 97 reflections intensity decay: ~1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.227$
$S = 1.040$
11 772 reflections
491 parameters
H atoms riding; fixed C—H distances, $\langle u^2 \rangle(H) = 1.2U_{eq}(C)$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond

$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 27.6179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.69$
$\Delta\rho_{max} = 1.98$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Some geometrical features (Å, °)*

	(I)	(II)	(III)
Interplanar angles between adjacent aromatic rings†			
1 to 2	63.8 (2)	53.6 (2)	56.1 (2)
2 to 3	50.1 (2)	56.1 (2)	56.0 (2)
Some aspects of the coordination geometry			
$M^+\cdots$O(host)			
Range	2.51–2.84	2.80–3.00	2.91–3.12
Average	2.68 (10)	2.89 (6)	3.02 (7)
$M^+\cdots$O(water molecule)			
	–	3.237 (9)	3.487 (11)
$M^+\cdots$N			
$\cdots$N29	3.167 (7)	3.207 (7)	3.381 (6)
$\cdots$N46	3.626 (7)	3.257 (7)	3.356 (6)
O32$\cdots$O40	4.102 (6)	4.551 (8)	3.866 (8)
O35$\cdots$O43	3.326 (8)	4.696 (9)	4.090 (10)
N29$\cdots$N46	6.646 (8)	6.357 (10)	6.650 (8)
O32$\cdots$O43	3.769 (8)	5.287 (8)	4.884 (11)
O35$\cdots$O40	4.804 (7)	5.416 (8)	4.908 (8)

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),