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

Carolyn B. Knobler,[a] Emily F. Maverick,[a]
Kenneth N. Trueblood[a] and Siew Peng Ho[b]

[a]*Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA, and* [b]*DuPont Merck Pharmaceutical Company, PO Box 80-400, Experimental Station, Bldg 400/5219, Wilmington, DE 19880-0400, USA. E-mail: knt@chem.ucla.edu*

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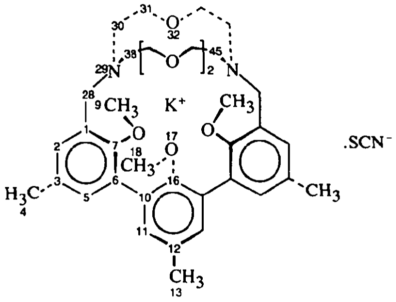
Abstract

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 bridge (C38 to C45) does not have the mirror symmetry characteristic of the rest of the structure. The structure is disordered in *Pnma*, but refines well if the close atoms are kept isotropic (to minimize correlation of position parameters with anisotropic displacement parameters) and restraints are used on C—C, C—O and C—N distances. In this model, the distances between the half-atoms in each pair that corresponds to a single atom in the ordered model ranged from 0.44 to 0.94 Å.

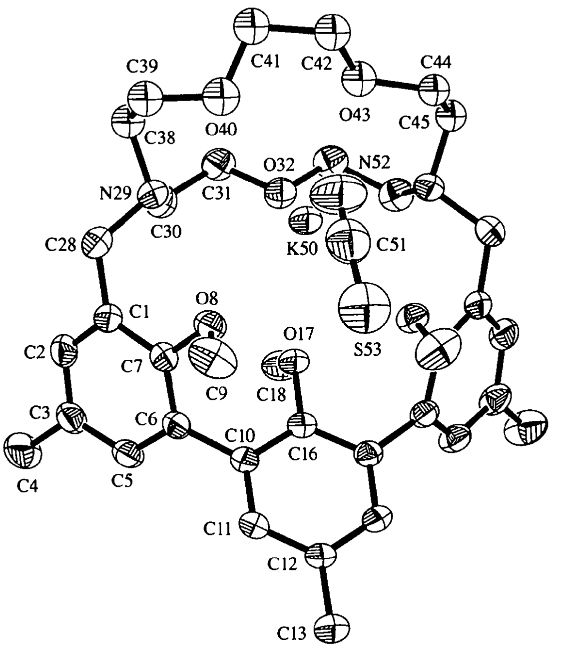


Fig. 1. *SHELXTL* (Sheldrick, 1995) view of the title compound. Displacement ellipsoids are drawn to enclose 30% probability. Atoms without labels are generated by a mirror plane at $y = \frac{1}{4}$. The atoms so generated for the disordered region (C38 to C45) are not shown.

The trianisyl group is similar to those found in the [2.2]cryptahemispherands (Maverick *et al.*, 1997*a*) and in the other cryptahemispherands (Maverick, Knobler, Trueblood & Ho, 1997*b*; Knobler *et al.*, 1997). The C atoms of the (equivalent) outer aromatic rings show significant deviations from coplanarity and these rings are folded about the CH_3—C···C—O line by nearly 5°, but the central ring does not depart significantly from planarity. The geometry of the coordination with K^+ is quite normal (Table 2). The torsion angles about the C—C bonds are all synclinal, ranging (in absolute value) from 63.7 (8) to 72.8 (7)° in the two bridges; those about the C—O bonds are all nearly antiperiplanar with one exception, C39—O40, which is 88.3 (8)°.

It is not clear just what combination of factors causes O17 (the central methoxy O atom of the trianisyl group) not to approach the K^+ ion more closely (see Table 2), although the fact that eight other atoms are coordinated to K^+ doubtless plays a role. Atom O17 is 0.3 to 0.5 Å farther from the K^+ ion than the other five O atoms of the host, four of which are closer than the 'standard' $K^+\cdots O$ distance of 2.91 Å for eightfold coordination (Shannon, 1976), three of them being about 0.2 Å closer. This situation is consistent with the fact that this host binds K^+ about one order of magnitude more strongly than does the analogous [2.2] compound (Cram & Ho, 1986). The three $K^+\cdots N$ distances are about 0.1 Å longer than the 'standard' distance of about 3.0 Å.

There are no unusual intermolecular distances. The shortest intermolecular distance not involving a H atom is 3.618 (5) Å, from an aromatic ring atom, C2, to a methyl C atom, C13 at ($1-x$, $-y$, $1-z$). The shortest distances from (calculated positions of) H atoms to non-H atoms range from 2.95 to 3.1 Å, from H atoms on the methyl atoms C9, C13 and C18 to aromatic ring atoms or atoms in the disordered bridge in nearby molecules. The shortest intermolecular H···H distances, 2.3 to 2.5 Å, again involve either methyl groups or the cryptand-like bridges, or both.

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 examination of the differences in mean-square displacement amplitudes for all pairs of atoms along the line between them shows that the methoxy methyl groups are moving significantly (presumably wagging) with respect to most of the rest of the host molecule.

Experimental

The title compound was prepared as described by Cram, Ho, Knobler, Maverick & Trueblood (1986) and crystallized from ethyl acetate.

Crystal data

$[K(C_{36}H_{48}N_2O_6)]SCN$
$M_r = 701.94$
Orthorhombic
Pnma
$a = 21.210\,(9)$ Å
$b = 14.745\,(6)$ Å
$c = 11.807\,(5)$ Å
$V = 3693\,(3)$ Å^3
$Z = 4$
$D_x = 1.263$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$10.5°$
$\mu = 0.248$ mm^{-1}
$T = 295\,(2)$ K
Cut parallelepiped
0.54 × 0.43 × 0.30 mm
Colorless

Data collection

Syntex $P\bar{1}$ (Crystal Logic) diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none

$\theta_{max} = 27.00°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 15$

4189 measured reflections
4189 independent reflections
2721 reflections with $I > 2\sigma(I)$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.221$
$S = 1.071$
4189 reflections
232 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
$w = 1/[\sigma^2(F_o^2) + (0.0902P)^2 + 2.7738P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.351$
$\Delta\rho_{max} = 0.427$ e Å^{-3}
$\Delta\rho_{min} = -0.389$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (*Å^2*)

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

	x	y	z	U_{eq}
K50	0.28232 (5)	1/4	0.38642 (9)	0.0598 (3)
C1	0.3724 (2)	0.0007 (2)	0.2993 (3)	0.0629 (9)
C2	0.4085 (2)	−0.0531 (2)	0.2285 (4)	0.0748 (11)
C3	0.4728 (2)	−0.0445 (3)	0.2181 (3)	0.0741 (10)
C4	0.5116 (2)	−0.1076 (4)	0.1435 (5)	0.113 (2)
C5	0.5012 (2)	0.0257 (2)	0.2764 (3)	0.0669 (9)
C6	0.46748 (14)	0.0834 (2)	0.3466 (3)	0.0554 (8)
C7	0.4034 (2)	0.0670 (2)	0.3617 (3)	0.0566 (8)
O8	0.36864 (10)	0.1184 (2)	0.4366 (2)	0.0621 (6)
C9	0.3853 (2)	0.1078 (4)	0.5524 (3)	0.0970 (15)
C10	0.49627 (13)	0.1675 (2)	0.3912 (3)	0.0517 (7)
C11	0.54589 (14)	0.1695 (2)	0.4685 (3)	0.0556 (8)
C12	0.5710 (2)	1/4	0.5082 (4)	0.0528 (10)
C13	0.6220 (2)	1/4	0.5971 (4)	0.0645 (12)
C16	0.4721 (2)	1/4	0.3529 (4)	0.0516 (10)
O17	0.42149 (14)	1/4	0.2793 (3)	0.0557 (8)
C18	0.4376 (3)	1/4	0.1623 (5)	0.083 (2)
C28	0.3024 (2)	−0.0125 (3)	0.3099 (4)	0.0768 (11)
N29	0.26323 (12)	0.0642 (2)	0.2697 (3)	0.0627 (7)
C30	0.2772 (2)	0.0861 (3)	0.1514 (3)	0.0762 (10)
C31	0.2470 (2)	0.1711 (3)	0.1059 (3)	0.0730 (10)
O32	0.2722 (2)	1/4	0.1580 (3)	0.0646 (9)
C38†	0.1977 (3)	0.0341 (7)	0.2641 (6)	0.071 (2)
C39†	0.1730 (4)	0.0460 (5)	0.3831 (6)	0.073 (2)
O40†	0.1707 (3)	0.1361 (4)	0.4266 (5)	0.082 (2)
C41†	0.1126 (3)	0.1796 (4)	0.3997 (7)	0.077 (2)
C42†	0.1177 (3)	0.2763 (3)	0.4415 (6)	0.074 (2)
O43†	0.1598 (2)	0.3229 (3)	0.3684 (4)	0.0741 (13)
C44†	0.1691 (3)	0.4140 (4)	0.4046 (6)	0.059 (2)
C45†	0.1965 (2)	0.4589 (6)	0.3001 (7)	0.063 (2)
C51	0.2763 (4)	1/4	0.7110 (7)	0.097 (2)
N52	0.2434 (3)	1/4	0.6417 (6)	0.118 (2)
S53	0.32092 (11)	1/4	0.8199 (2)	0.1147 (7)

† = Site occupancy = 0.50.

Table 2. *Some geometrical features* (*Å*, *°*)

Atoms designated with a prime (*e.g* N29′) are at $x, \frac{1}{2} - y, z$.

N29···N29′	5.480 (6)	C1···C1′	7.352 (7)
C28···C28′	7.741 (7)		

Interplanar angle between adjacent aromatic rings	62.3 (1)

$K^+\cdots$	O8 O8′	O17	O32	O40	O43	N29 N29′	N52
	2.733 (2)	3.211 (3)	2.705 (3)	2.942 (6)	2.821 (5)	3.094 (3)	3.125 (7)

The unit cell contains four molecules and all indications are that the space group is centrosymmetric, *Pnma*, with each molecule lying on a mirror plane. Because of the difficulty in fitting a model of the second bridge, we tried refining that bridge in $Pn2_1a$, with the remainder of the molecule fixed (and mirror-equivalent atoms generated). However, there was no significant improvement over the model described in the text. The refinement reported here was performed with the *PART* and *DFIX* options of *SHELXL*93 (Sheldrick, 1993); each atom in a disordered pair (C38 to C45) was assigned an occupancy factor of 0.50. The largest shift/error in the final least-squares cycle (0.35) was in the scale factor, but it amounted to only 0.001 of that value; the largest shift in any atomic position was 0.003 Å for H9*B* (a methyl H atom) and no change in any displacement parameter was as large as 0.001 Å^2.

Data collection: *UCLA Crystallographic Package* (1984). Cell refinement: *UCLA Crystallographic Package* (1984). Data reduction: *UCLA Crystallographic Package* (1984). Program(s) used to solve structure: *MULTAN*80 (Declercq, Germain & Woolfson, 1979). Molecular graphics: *SHELXTL* (Sheldrick, 1995). Software used to prepare material for publication: local programs.

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