Data collection

Enraf–Nonius CAD-4 diffractometer	1183 reflections with $I > 2\sigma(I)$
Non-profiled ω scans	$\theta_{max} = 27.47°$
Absorption correction:	$h = 0 \rightarrow 30$
ψ scan (North *et al.*, 1968)	$k = 0 \rightarrow 9$
	$l = 0 \rightarrow 12$
$T_{min} = 0.304$, $T_{max} = 0.674$	3 standard reflections
1930 measured reflections	frequency: 60 min
1930 independent reflections	intensity decay: 2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R(F) = 0.040$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
$wR(F^2) = 0.112$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
$S = 1.028$	Extinction correction:
1930 reflections	SHELXL97 (Sheldrick,
135 parameters	1997)
H atoms constrained	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2$	0.0006 (4)
$+ 0.26P]$	Scattering factors from
where $P = [\text{Max}(F_o^2,0)$	*International Tables for*
$+ 2F_c^2]/3$	*Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Br1—C9	1.905 (5)	C8a—C9	1.412 (7)
Br2—C10	1.903 (5)	C9—C9a	1.401 (7)
C4a—C10	1.392 (7)	C10—C10a	1.409 (7)
C9a—C9—Br1	118.2 (4)	C4a—C10—Br2	118.6 (4)
C8a—C9—Br1	119.0 (4)	C10a—C10—Br2	118.8 (4)

A difference Fourier map clearly indicated two regions of electron density suggestive of disorder for with 'Bu group. C atoms were inserted and the sum of occupancies of the relevant C atoms were constrained to unity and then refinement continued to convergence both on positions and occupancies.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms & Wocadlo, 1995). Program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *WinGX* (Farrugia, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1224). Services for accessing these data are described at the back of the journal.

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The *tert*-butylammonium perchlorate complex of 2,3-naphtho-18-crown-6 at 115 K

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Abstract

In the title complex, *tert*-butylammonium perchlorate–2,5,8,11,14,17-hexaoxatricyclo[16.8.0.0^{20,25}]hexacosa-1(26),18,20(25),21,23-pentaene–ethyl acetate–dichloromethane (4/4/1/1), $C_4H_{12}N^+ \cdot C_{20}H_{26}O_6 \cdot ClO_4^- \cdot 0.25C_4H_8O_2 \cdot 0.25CH_2Cl_2$, the *tert*-butylammonium cation binds to the macrocyclic host (Chemical Abstracts name: 2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-hexaoxanaphtho[2,3-*b*]cyclooctadecin) in the expected tripod arrangement, while the perchlorate anion links naphthyl groups in the crystal through C—H⋯O—Cl—O⋯H—C interactions. Thermal motion analysis indicates that the *tert*-butylammonium group and the perchlorate anion each librate with respect to the host, with amplitudes of 6.2 (4) and 11.4 (2)°, respectively.

Comment

The host in the title compound, (I), has been used as a standard in solution studies of structures of hosts and their complexing affinities; see, for example, Kyba *et al.* (1977) and Helgeson *et al.* (1979). The *tert*-butyl-

† Deceased 7 May 1998.

ammonium ion has been used as the standard guest. These two moieties were chosen because the complex is lipophilic enough to be soluble in relatively non-polar solvents, and because the naphtho group and the *tert*-butyl group both give useful signals in ^1H NMR spectra. Perchlorate, hexafluorophosphate and picrate were standard anions in the aforementioned studies.

(I)
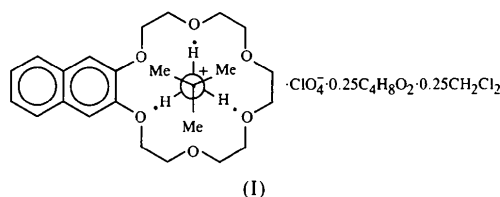
The first X-ray data for (I) were measured at 295 K in 1976 [Cu $K\alpha$ radiation, $a = 11.141\,(2)$, $b = 11.696\,(2)$, $c = 13.169\,(2)$ Å, $\alpha = 101.98\,(1)$, $\beta = 111.26\,(1)$, $\gamma = 100.66\,(1)^\circ$ and $V = 1550.4\,(4)$ Å^3]. The present data at 115 K were collected in 1978, and the structure appeared in the literature as early as 1981 (Cram & Trueblood, 1981; Lingenfelter *et al.*, 1981). The cation and anion refined well at both temperatures, but unidentified solvent filled the space around the center of symmetry at ($\frac{1}{2}$,0,0) and we were unable to complete either refinement satisfactorily.

The solvent is now described as a disordered mixture of ethyl acetate and dichloromethane. The structure displays the tripod staggered arrangement which was predicted on the basis of CPK model examination (Cram & Trueblood, 1981), with the *tert*-butylammonium ion perching above the macro-ring (Fig. 1). The naphtho group in the host prevents the 18-crown-6 moiety from attaining the 'ideal crown' conformation in the complex (Trueblood *et al.*, 1982). All aliphatic O—C—C—O torsion angles are *gauche*, but three C—O—C—C torsion angles have values in the range 82–87° instead of the ideal *trans* conformation of 165–180° (Table 1).

Three nearly linear hydrogen bonds are formed (Table 2). The N atom is 0.912 (2) Å above the plane of the three hydrogen-bonded O atoms and 0.996 (2) Å above the plane of all six O atoms. The angle between the normals to these planes is 5.52 (4)°. Thermal motion analysis shows that the anisotropic displacement parameters are of good quality. The differences in mean square displacement amplitudes between bonded atoms (except for C24—O23, see below) are less than 2.5 times the mean standard uncertainty of the U values themselves (Hirshfeld, 1976; Schomaker & Trueblood, 1998). Although the host does not fit the rigid-body model well, both the *tert*-butylammonium ion and the perchlorate anion do. The anion may be described as a librating rigid body with an amplitude about the principal axis of 129 (5)°^{2}, leading to bond length corrections for Cl—O (to 1.455–1.462 Å) of 11–14 s.u. Description of the mo-
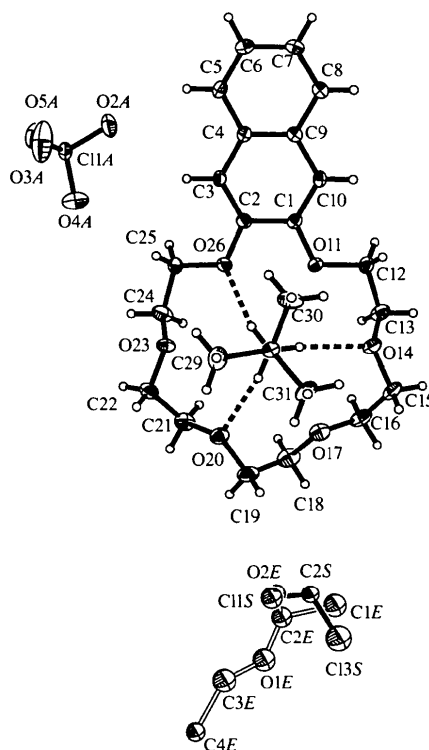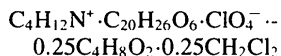

Fig. 1. View of the asymmetric unit of (I), approximately down the C28—N27 bond (*SHELXTL*; Sheldrick, 1995). C28 and N27 are not labeled as they are superimposed. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines. The minor occupancy O23′ atom is not shown. Both solvent molecules (with the exception of H atoms) are shown.

tion of the guest as an internal torsional libration about the C—N bond in the cationic complex leads to an amplitude of 38 (6)°^{2} or 6.2 (4)°, a calculated barrier to threefold rotation of the *tert*-butyl group of 19 kJ mol^{-1} (Dunitz *et al.*, 1988) and to C—C bond-length corrections in the *tert*-butyl group of 2–3 s.u. The thermal motion analysis for the *tert*-butylammonium perchlorate complex of monopyrido-18-crown-6 (Maverick *et al.*, 1979) at 113 K gave very similar results, as did that for *tert*-butylammonium chloride at 115 K (Trueblood, 1987), although hydrogen bonding and packing are quite different in the three structures.

Experimental

The 2,3-naphtho-18-crown-6 host was synthesized by Dr Thomas Tarnowski, using the method published by Pedersen (1967). The title complex, (I), was prepared by extracting solid *tert*-butylammonium perchlorate into a chloroform solution of the host to form a 1:1 complex. The crystals formed by evaporation of the solvent were recrystallized from ethyl acetate/methylene chloride. The low-temperature device was that described by Strouse (1976).

Crystal data

$C_4H_{12}N^+ \cdot C_{20}H_{26}O_6 \cdot ClO_4^- \cdot$
$0.25C_4H_8O_2 \cdot 0.25CH_2Cl_2$
$M_r = 579.26$
Triclinic
$P\bar{1}$
$a = 10.996\,(3)$ Å
$b = 11.423\,(3)$ Å
$c = 13.501\,(3)$ Å
$\alpha = 102.36\,(2)°$
$\beta = 111.79\,(2)°$
$\gamma = 100.28\,(2)°$
$V = 1474.7\,(7)$ Å^3
$Z = 2$
$D_x = 1.305$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 15
reflections
$\theta = 8.62-12.76°$
$\mu = 0.230$ mm^{-1}
$T = 115\,(2)$ K
Chunk
$0.35 \times 0.25 \times 0.20$ mm
Colorless

Data collection

Syntex $P\bar{1}$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7816 measured reflections
6812 independent reflections
5547 reflections with
$I > 2\sigma(I)$
R_{int}: see below

$\theta_{max} = 27.57°$
$h = -5 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.249$
$S = 1.06$
6811 reflections
366 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1728P)^2 + 0.9323P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.038$
$\Delta\rho_{max} = 1.19$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected torsion angles (°)*

O11—C1—C2—O26	2.3 (3)	O17—C18—C19—O20	65.4 (3)
C2—C1—O11—C12	173.5 (2)	C18—C19—O20—C21	87.1 (3)
C1—O11—C12—C13	−169.7 (2)	C19—O20—C21—C22	165.2 (2)
O11—C12—C13—O14	−66.2 (3)	O20—C21—C22—O23	68.5 (3)
C12—C13—O14—C15	−170.1 (2)	C21—C22—O23—C24	87.3 (3)
C13—O14—C15—C16	−82.6 (3)	C22—O23—C24—C25	173.5 (2)
O14—C15—C16—O17	−68.3 (3)	O23—C24—C25—O26	66.1 (3)
C15—C16—O17—C18	−179.5 (2)	C1—C2—O26—C25	−168.1 (2)
C16—O17—C18—C19	176.1 (2)	C24—C25—O26—C2	168.9 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N27—H27A···O14	0.89	2.08	2.963 (3)	170
N27—H27B···O26	0.89	2.11	2.979 (3)	167
N27—H27C···O20	0.89	2.08	2.961 (3)	170

The title structure is essentially isomorphous with the room-temperature one, in which the solvent appears to be CH_2Cl_2. The crystals reported here were dissolved and shown by ^1H NMR to contain ethyl acetate, as well as the expected dichloromethane. Friedel pairs were equivalent within experimental error and only one of each pair was retained. Since each solvent cavity in the crystal could contain one molecule of CH_2Cl_2 or one molecule of ethyl acetate but not both, and

the cavity is centrosymmetric; the occupancy of 0.25 for each solvent atom assumes equal populations of the two solvents, each disordered about the center. All solvent atoms were refined isotropically. The host atom O23 is also disordered. The minor O23' atom in the final disorder model has an occupancy of 0.15; the distances O23'—C22 and O23'—C24 were restrained. The disorder at O23 may be due in part to strain associated with the C—O—C—C torsion angle (Table 1) and perhaps also in part to the differing spatial requirements of the two solvent molecules. For example, Cl1S approaches the host atom O23($-1 - x$, $-y$, $-1 - z$) at a distance of 3.347 (5) Å, while the comparable distance O2E···O23 is 3.65 (1) Å. The highest peak in the final difference map, 1.19 e Å^{-3}, is in the solvent region, 0.6 Å from the center of symmetry (O1E). All H atoms were constrained as riding, with fixed C—H distances and $<u^2>_H = 1.2U_{eq}$ of the attached C (1.5 for CH$_3$ and NH$_3^+$). The H—C—C—N torsion angles for CH$_3$ groups and the H—N—C—C torsion angle for the NH$_3^+$ group were refined.

Data collection: $P\bar{1}$ software. Cell refinement: $P\bar{1}$ software. Data reduction: *UCLA Crystallographic Package* (1984). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1995). Software used to prepare material for publication: local programs.

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