Crystals were obtained from methanol solution by slow evaporation. A parallelepiped crystal fragment was cut from a larger crystal and mounted in a Lindemann capillary to prevent its sublimation. During the data collection intensities of the standard reflections ($\bar{2}\bar{2}1$, 004 and 400) dropped by up to 89% of their initial values. Data were corrected for crystal decay.

We thank Professor Herbert Mayr, Technische Hochschule Darmstadt, for synthetic hints.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and ring-puckering parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55627 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1017]

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Acta Cryst. (1993). C**49**, 402–404

Structure of 1,3-Xylyl-(18-crown-5)–Ammonium Catecholborate (1/1)

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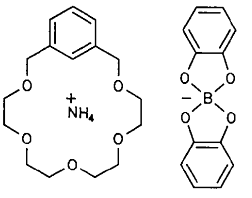
(*Received* 23 *July* 1992; *accepted* 5 *October* 1992)

Abstract

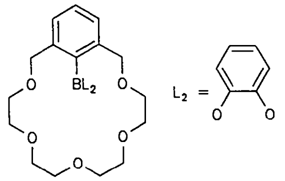
In the title compound, 3,6,9,12,15-pentaoxabicyclo-[15.3.1]henicosa-1(21),17,19-triene–ammonium bis(1,2-benzenediolato)borate (1/1), the ammonium cation is hydrogen bonded by three of its H atoms to the crown ether, and by the remaining H atom to the O atom of the catecholborate anion. Thus the crown ether competes favourably with the catechol ligands for hydrogen bonding with the ammonium cation.

Comment

The title compound (1) was obtained as a by-product of the reaction of ammonia with the crown ether borate 1,3-xylyl-(18-crown-5)-2-catecholborate (2) (Reetz, Niemeyer, Hermes & Goddard, 1992). Dry ammonia was passed through a dry solution of 0.6 mmol of the crown ether borate dissolved in 10 ml of dichloromethane for 30 s at 273 K. The solution immediately became cloudy. The solution was then diluted fivefold and filtered to remove any insoluble deposits. Careful layering with diethyl ether resulted in the formation of crystals of the title compound together with those of the NH_3 adduct of the crown ether borate (Reetz, Niemeyer, Hermes & Goddard, 1992). We report here the structure of the title compound.



(1)



(2)

The results of the structure analysis are summarized in Fig. 1 which shows an ion-pair complex comprising ammonium catecholborate attached to a macrocyclic crown ether. The ammonium cation is bonded on one side by three hydrogen bonds to a 1,3-xylyl-(18-crown-5) polyether and on the other through a single hydrogen bond to a catecholborate anion. Interestingly, the ammonium cation forms hydrogen bonds preferentially with the O atoms of the crown ether in spite of the fact that the catecholborate anion is negatively charged and carries four O atoms that are eminently suited to form hydrogen bonds. By way of comparison, ammonium tetrafluoroborate crystallizes as a three-dimensional structure with each H atom of the ammonium cation hydrogen bonded, albeit weakly (Pendred & Richards, 1955), to an F atom of a neighbouring tetrafluoroborate anion (Clark & Lynton, 1969; Van Rensburg & Boeyens, 1972; Stromme, 1974). The crown ether thus competes effectively with the borate for hydrogen bonding. This is reflected in the similar N···O hydrogen-bonded distances to the crown ether and the borate anion [N···O1 2.978(4), N···O3 2.827(4), N···O5 2.999(4), N···O8 2.827(4) Å]. The H···O distances are also comparable [H1···O1 1.98(4), H3···O3 2.00(3), H2···O5 2.13(3), H4···O8 1.98(4) Å] although

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these are less well determined. Although O2 and O4 in the macrocycle do not appear to form hydrogen bonds with the ammonium cation, the N···O distances to these atoms are not appreciably longer [N···O2 3.042(4), N···O4 3.061(4) Å] and so a restricted rotation of the ammonium cation cannot be ruled out. The proximity of the ammonium cation to O8 results in a lengthening of the B—O8 bond which at 1.502(4) Å is significantly longer than the other B—O distances in the anion [mean 1.470(3) Å]. The catecholborate anion has also been reported in the structure of triethylammonium catecholborate catechol solvate (Mohr, Heller, Timper & Woller, 1990). Examination of the interatomic non-bonding distances indicates that there is an additional weak interaction between the borate anion and the crown ether through O7 and H4a [O7···C4 3.405(5), H4a—C4 (calculated) 0.95 Å]. The mean Csp^3—Csp^3 bond length in the macrocyclic ring is 1.477(8) Å and the mean C—O bond length is 1.416(12) Å, in agreement with similar molecules containing 18-crown-5 macrocyclic ethers (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985). The remaining bond lengths and angles are as expected.

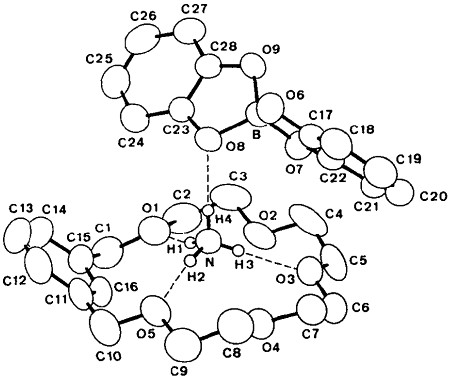

Fig. 1. View of the molecular structure. Thermal ellipsoids are shown at 50% probability levels; H atoms attached to N are drawn as circles of arbitrary radius.

Experimental

Crystal data

$C_{16}H_{24}O_5.H_4N^+.C_{12}H_8BO_4^-$
$M_r = 541.4$
Monoclinic
$P2_1/c$
$a = 14.930$ (2) Å
$b = 11.193$ (1) Å
$c = 17.211$ (1) Å
$\beta = 99.896$ (5)°
$V = 2833.5$ (4) Å^3
$Z = 4$
$D_x = 1.27$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.5$–17.2°
$\mu = 0.088$ mm^{-1}
$T = 293$ K
Prism
0.42 × 0.42 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7007 measured reflections
6448 independent reflections
3239 observed reflections [$I \geq 2.0\sigma(I)$]

$\theta_{\max} = 27.41°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.060$
$wR = 0.059$
$S = 1.97$
3239 reflections
368 parameters
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max} = 0.71$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}

Extinction correction: not applied
Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A (C, B, N, O) and 2.2C (H)]

Data collection: Enraf–Nonius CAD-4. Cell refinement: *LSCELD* (Davis, 1969). Data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *GFLMX* (modified *ORFLS*; Busing, Martin & Levy, 1962). Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *DAESD* (Davis & Harris, 1970).

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

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

	x	y	z	$U_{\rm eq}$
O1	0.7594 (1)	−0.3403 (2)	0.8695 (1)	0.063 (2)
O2	0.5947 (1)	−0.2134 (2)	0.8355 (1)	0.071 (2)
O3	0.6096 (2)	0.0396 (2)	0.8172 (1)	0.070 (2)
O4	0.7699 (2)	0.1488 (2)	0.7903 (1)	0.068 (2)
O5	0.9342 (1)	0.0268 (2)	0.8371 (1)	0.067 (2)
O6	0.7289 (1)	0.1140 (2)	0.1184 (1)	0.057 (1)
O7	0.6231 (1)	0.0243 (2)	0.0199 (1)	0.057 (1)
O8	0.7733 (1)	−0.0679 (2)	0.0557 (1)	0.055 (1)
O9	0.6693 (1)	−0.0847 (2)	0.1428 (1)	0.055 (1)
N	0.7700 (2)	−0.0765 (3)	−0.1090 (2)	0.051 (2)
C1	0.8267 (3)	−0.4105 (3)	0.8421 (2)	0.072 (3)
C2	0.6729 (3)	−0.3955 (4)	0.8594 (2)	0.080 (3)
C3	0.6079 (3)	−0.3134 (5)	0.8870 (2)	0.086 (3)
C4	0.5308 (2)	−0.1298 (4)	0.8550 (2)	0.086 (3)
C5	0.5270 (2)	−0.0272 (5)	0.8004 (2)	0.087 (3)
C6	0.6096 (3)	0.1429 (5)	0.7722 (2)	0.093 (3)
C7	0.6911 (3)	0.2144 (4)	0.8006 (2)	0.087 (3)
C8	0.8513 (3)	0.2093 (3)	0.8160 (2)	0.084 (3)
C9	0.9288 (3)	0.1378 (4)	0.7973 (2)	0.080 (3)
C10	1.0080 (2)	−0.0444 (4)	0.8212 (2)	0.083 (3)
C11	1.0014 (2)	−0.1660 (3)	0.8553 (2)	0.066 (3)
C12	1.0689 (2)	−0.2123 (5)	0.9126 (3)	0.085 (3)
C13	1.0602 (3)	−0.3241 (5)	0.9428 (3)	0.094 (3)
C14	0.9832 (3)	−0.3887 (4)	0.9186 (2)	0.080 (3)
C15	0.9141 (2)	−0.3450 (3)	0.8631 (2)	0.061 (2)
C16	0.9252 (2)	−0.2347 (3)	0.8298 (2)	0.060 (2)
C17	0.6797 (2)	0.1981 (3)	0.0723 (2)	0.050 (2)
C18	0.6869 (2)	0.3192 (3)	0.0790 (2)	0.065 (3)
C19	0.6262 (3)	0.3873 (3)	0.0273 (3)	0.075 (3)
C20	0.5607 (3)	0.3358 (3)	−0.0287 (2)	0.068 (3)
C21	0.5542 (2)	0.2111 (3)	−0.0358 (2)	0.059 (2)

C22	0.6154 (2)	0.1452 (3)	0.0140 (2)	0.047 (2)
C23	0.7774 (2)	−0.1795 (3)	0.0887 (2)	0.048 (2)
C24	0.8326 (2)	−0.2724 (3)	0.0766 (2)	0.066 (3)
C25	0.8221 (3)	−0.3780 (3)	0.1168 (2)	0.078 (3)
C26	0.7597 (3)	−0.3881 (3)	0.1666 (2)	0.075 (3)
C27	0.7052 (2)	−0.2932 (3)	0.1788 (2)	0.061 (2)
C28	0.7149 (2)	−0.1882 (3)	0.1398 (2)	0.047 (2)
B	0.6980 (2)	−0.0025 (4)	0.0850 (2)	0.050 (2)
H1	0.767 (2)	−0.164 (4)	−0.124 (2)	0.10 (1)
H2	0.821 (2)	−0.053 (3)	−0.123 (2)	0.07 (1)
H3	0.724 (2)	−0.040 (3)	−0.131 (2)	0.06 (1)
H4	0.774 (2)	−0.070 (3)	−0.057 (2)	0.06 (1)

Table 2. *Geometric parameters* (Å, °)

O1—C1	1.419 (5)	C2—C3	1.474 (6)
O1—C2	1.415 (5)	C4—C5	1.478 (7)
O2—C3	1.421 (5)	C6—C7	1.468 (6)
O2—C4	1.418 (5)	C8—C9	1.487 (6)
O3—C5	1.429 (5)	C10—C11	1.492 (6)
O3—C6	1.393 (5)	C11—C12	1.385 (6)
O4—C7	1.425 (5)	C11—C16	1.381 (5)
O4—C8	1.396 (5)	C12—C13	1.371 (7)
O5—C9	1.415 (5)	C13—C14	1.361 (6)
O5—C10	1.425 (4)	C14—C15	1.370 (5)
O6—C17	1.362 (4)	C15—C16	1.384 (5)
O6—B	1.467 (4)	C17—C18	1.364 (5)
O7—C22	1.361 (4)	C17—C22	1.396 (4)
O7—B	1.472 (4)	C18—C19	1.385 (5)
O8—C23	1.369 (4)	C19—C20	1.377 (6)
O8—B	1.502 (4)	C20—C21	1.403 (5)
O9—C28	1.349 (4)	C21—C22	1.359 (5)
O9—B	1.472 (4)	C23—C24	1.366 (5)
N—H1	1.02 (4)	C23—C28	1.391 (4)
N—H2	0.88 (3)	C24—C25	1.392 (5)
N—H3	0.83 (3)	C25—C26	1.376 (6)
N—H4	0.89 (4)	C26—C27	1.375 (5)
C1—C15	1.488 (5)	C27—C28	1.374 (5)
C2—O1—C1	113.7 (3)	C16—C15—C14	118.6 (3)
C4—O2—C3	113.5 (3)	C16—C15—C1	120.1 (3)
C6—O3—C5	113.9 (3)	C14—C15—C1	121.2 (3)
C8—O4—C7	113.8 (3)	C15—C16—C11	121.1 (3)
C10—O5—C9	112.3 (3)	C22—C17—C18	121.1 (3)
B—O6—C17	106.5 (2)	C22—C17—O6	111.2 (3)
B—O7—C22	107.6 (2)	C18—C17—O6	127.7 (3)
B—O8—C23	106.7 (2)	C19—C18—C17	117.4 (3)
B—O9—C28	107.7 (2)	C20—C19—C18	121.9 (3)
H4—N—H3	109 (3)	C21—C20—C19	120.5 (3)
H4—N—H2	110 (3)	C22—C21—C20	117.2 (3)
H4—N—H1	110 (3)	C21—C22—C17	121.9 (3)
H3—N—H2	114 (3)	C21—C22—O7	128.8 (3)
H3—N—H1	111 (3)	C17—C22—O7	109.3 (3)
H2—N—H1	103 (3)	C28—C23—C24	122.1 (3)
C15—C1—O1	106.8 (3)	C28—C23—O8	109.9 (3)
C3—C2—O1	109.1 (3)	C24—C23—O8	128.1 (3)
C2—C3—O2	108.5 (3)	C25—C24—C23	116.7 (3)
C5—C4—O2	108.5 (3)	C26—C25—C24	121.7 (4)
C4—C5—O3	109.9 (3)	C27—C26—C25	120.9 (3)
C7—C6—O3	110.3 (3)	C28—C27—C26	118.1 (3)
C6—C7—O4	109.4 (3)	C27—C28—C23	120.5 (3)
C9—C8—O4	109.7 (3)	C27—C28—O9	128.3 (3)
C8—C9—O5	110.4 (3)	C23—C28—O9	111.2 (3)
C11—C10—O5	109.2 (3)	O9—B—O8	104.1 (3)
C16—C11—C12	118.5 (4)	O9—B—O7	111.8 (3)
C16—C11—C10	119.3 (3)	O9—B—O6	113.6 (3)
C12—C11—C10	122.2 (3)	O8—B—O7	111.0 (3)
C13—C12—C11	120.5 (4)	O8—B—O6	111.2 (3)
C14—C13—C12	120.0 (4)	O7—B—O6	105.3 (3)
C15—C14—C13	121.2 (4)		

Data were corrected for Lorentz and polarization effects. $\sigma(F)$ was calculated from $[\sigma(I)^2 + (Ik)^2]^{1/2}/2F$, where $k = 0.02$. The H atoms attached to the N atom were located on a difference Fourier map and refined with isotropic temperature factors. The remaining H atoms were fixed at calculated positions [d(C—H) = 0.95 Å; $U_H = 0.05$ Å^2].

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55685 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1034]

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Acta Cryst. (1993). C**49**, 404–406

Structure of 1:1 Clathrate between Tris(2,3-naphthalenedioxy)cyclotriphosphazene and *p*-Xylene

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(*Received* 28 *April* 1992; *accepted* 24 *August* 1992)

Abstract

The host molecule lies on the crystallographic two-fold axis. The centroid of the guest, *p*-xylene, is located at a center of symmetry. The host forms a cage-type 1:1 clathrate with *p*-xylene. The *p*-xylene is