The Crystal Structure of the Ammonium Bromide Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6), $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$

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(Received July 1, 1977)

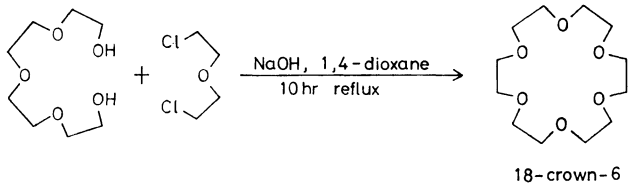
Ammonium bromide forms a 1 : 1 complex with cyclic polyether "18-crown-6." The crystals of $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$ are orthorhombic, with the space group of Pnam and with cell constants of $a=10.002(3)$, $b=12.716(4)$, $c=15.073(4)$ Å, and $Z=4$. The structure was solved by the conventional heavy-atom technique and refined by the full matrix least-squares method to $R=0.099$ for 1033 independent reflections. The 18-crown-6 has a conformation with a pseudo D_{3d} symmetry. The ammonium cation is displaced by 1.00 Å from the mean oxygen plane of the 18-crown-6 and interacts with the nearest bromide anion. The relationship between the cation and the 18-crown-6 resembles those of the $C_{12}H_{24}O_6 \cdot RbNCS$ and $C_{12}H_{24}O_6 \cdot CsNCS$ complexes. On the difference Fourier maps, four electron-density peaks were detected at reasonable positions for the hydrogen atoms of the amonium cation.

Macrocyclic polyethers, often called "crown" compounds, form complexes with many different inorganic cations, such as alkaline metal, alkaline-earth metal, and ammonium cations.[1] They have the possibility to increase the salt solubility and the anion reactivity in organic solvents.

In the last decade, therefore, many macrocyclic polyethers have been studied as catalysts for organic syntheses,[2,3] reagents for solvent extraction in analytical chemistry,[4,5] and packing material for the separation of *d,l*-amino acids by column chromatography.[7-9] Our main interest in the present structure study of $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$ lies in the difference between the interaction of an alkaline or alkaline-earth metal cation-crown compound[10-16] and that of an ammonium cation-crown compound.

Experimental

18-Crown-6 was synthesized from bis(2-chloroethyl) ether and tetraethylene glycol according to the following scheme:[17,18]



18-crown-6

The crystal of $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$ was obtained from an aqueous solution of the 18-crown-6 and ammonium bromide (18-crown-6 : NH_4Br = 1 : 1). The crystal used was made nearly spherical, and its radius was 0.18 mm.

The intensities of the reflections were measured with a Rigaku automatic four-circle diffractometer (graphite monochrometer, Mo $K\alpha$ radiation, ω-2θ scan method). The scanning range was determined according to the formula of $1.2°+0.6° \tan\theta$, and the scanning rate was 0.5° per min in ω when $2\theta<60°$. Background counts of 10 s were taken at both limits of the scanning range. Three reference reflections were measured after every 50 reflections; no significant changes were observed over the period of data collection. The intensities of 1033 reflections ($\sigma(F)>3.0$) were adopted for the structure determination.

The crystal data are: $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$, orthorhombic, space group Pnam, $a=10.002(3)$, $b=12.716(4)$ $c=15.073(4)$ Å, $U=1917.1(9)$ Å^3 at 23 °C, $Z=4$, $D_m=1.35$, $D_x=1.380$ g cm^{-3}, $F.W.=398.29$ and μ(Mo $K\alpha$) = 23.07 cm^{-1}.

Structure Determination

The structure was solved by the heavy-atom technique and refined by the full matrix least-squares program LINUS.[19] The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2(F)$. The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography, Vol. IV.[20] Corrections for anomalous dispersion and absorption were included in the refinement. An extinction correction was applied at the final stage of the refinement, but the R value, 0.099 ($R=\Sigma w||F_o|-|F_c||/\Sigma w|F_o|$), did not change. The R value was relatively large, possibly because of the sensitivity of the crystal to X-ray, but possibly also because of the release of water molecules from the crystal during the measurement. In a test of the R-factor ratio based on the hypothesis that $Pna2_1$ was the correct space group, the R-factor ratio, $R(\text{Pnam})/R(Pna2_1)$, was found to be 1.016. We could not reject, at the 50% significance level, the hypothesis that Pnam was the correct space group. However, the result for $Pna2_1$ indicated unreasonable values in the bond distances and bond angles. Hence, we selected centro-symmetric Pnam as the space group of the crystal.[21] The atomic coordinates and temperature factors are listed in Tables 1—3. The F_o-F_c table is kept at the office of this Bulletin as Document No. 7807.

Results and Discussion

Crystal Structure. The two oxygen atoms of the 18-crown-6, O(1) and O(4), the nitrogen atom and two hydrogen atoms, H_{Br} and $H_{O(4)}$, of the ammonium cation and the bromide anion lie on the mirror plane at $z=1/4$ and 3/4. The cation interacts with the 18-crown-6 and the nearest bromide anion, which is weakly bound to four water molecules. The NH_4^+–Br^- distance (3.438 Å) is slightly longer than the sum of the two corresponding ionic radii (3.39 Å = 1.43 + 1.96 Å). The Br^-–OH_2 distances (average, 3.365 Å) are in fair agreement with the sum of corresponding ionic and van der Waals radii (3.36 Å = 1.96 + 1.40 Å). There is

Table 1. Fractional coordinates (and estimated standard deviations) of the non-hydrogen atoms (Values are $\times 10^4$)

	x	y	z
Br	1456(2)	1412(2)	2500
O(1)	−338(13)	2169(11)	7500
O(2)	562(9)	1250(8)	9120(5)
O(3)	3138(9)	356(8)	9177(6)
O(4)	4072(14)	−370(12)	7500
O(H_2O)	3716(14)	2850(12)	3629(10)
N	1308(16)	196(11)	7500
C(1)	−1120(16)	2128(16)	8280(11)
C(2)	−224(19)	2178(14)	9073(11)
C(3)	1329(16)	1204(15)	9910(10)
C(4)	2196(17)	268(17)	9862(10)
C(5)	3959(20)	−546(16)	9047(13)
C(6)	4875(17)	−347(15)	8273(13)

Table 2. Fractional coordinates (and estimated standard deviations) of the hydrogen atoms (Values are $\times 10^3$)

	x	y	z
H(1)	−164(11)	147(8)	829(7)
H(1)*	−174(11)	247(8)	828(7)
H(2)	−78(11)	226(9)	963(7)
H(2)	35(10)	282(8)	902(7)
H(3)	74(11)	116(8)	1044(7)
H(3)*	190(10)	184(8)	995(7)
H(4)	165(11)	−36(8)	976(7)
H(4)	265(11)	17(9)	1044(7)
H(5)	341(11)	−118(8)	892(7)
H(5)*	448(11)	−69(8)	959(7)
H(6)	553(11)	−92(8)	824(7)
H(6)*	530(11)	39(9)	834(7)
H_{Br}	69(16)	−51(13)	750
$H_{O(2)}$	108(10)	56(8)	803(6)
$H_{O(4)}$	220(18)	0(14)	750

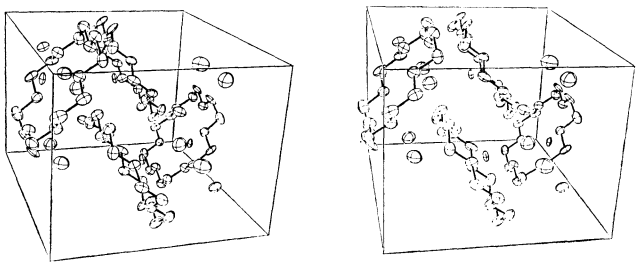


Fig. 1. Stereoscopic view of the crystal structure looking along the c axis. The c axis vertical, the a axis horizontal.

no direct interaction between the cation and the water molecules. The TG measurement of $C_{12}H_{24}O_6·NH_4Br·2H_2O$ showed that the water molecules of crystallization were released from the crystal lattice at *ca.* 55 °C. They are distributed in the holes of the crystal lattice as is shown in Fig. 1.

The Structure of the NH_4^+·18-Crown-6 Complex Cation. The pseudo D_{3d} symmetrical conformation of the 18-crown-6 is the same as those found in the KNCS, RbNCS, and CsNCS complexes.[22] Table 4 shows the bond distances, the bond angles, and the torsion angles in the 18-membered ring. The six oxygen atoms of the 18-crown-6 are alternately 0.25 Å above and below their mean plane and form a nearly planar hexagon of approximately 2.84 Å (2.819—2.853 Å; average, 2.840 Å). The C–C distances (1.474—1.506 Å; average, 1.492 Å) and the C–O distances (1.403—1.424 Å; average, 1.416 Å) appear to be somewhat shorter than those in the $C_{12}H_{24}O_6$·KNCS complex, possibly because of the internal motion in the ring, as is observed in other complexes.[16-20,22] The temperature factors of the oxygen and carbon atoms are remarkably anisotropic (Table 3). The C–O–C bond angles (110.8—115.1°; average, 113.0°) are larger than the C–C–O bond angles (106.8—111.5°; average, 109.0°). The average of the torsion angles about C–C bonds is 67.9°, while that about C–O bonds is 4.3°. All the C–H distances are between 0.96 and 1.05 Å.

The nitrogen atom of the ammonium cation has the smallest thermal ellipsoid of all the non-hydrogen atoms,

Table 3. Anisotropic vibration parameters (Å^2) of the $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ form (Values are $\times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	58(1)	105(2)	76(2)	−21(2)	0	0
O(1)	58(9)	87(12)	59(8)	15(8)	0	0
O(2)	68(6)	74(8)	45(5)	4(5)	−5(5)	−9(5)
O(3)	61(6)	73(7)	65(6)	−5(5)	1(5)	13(6)
O(4)	53(8)	88(12)	72(10)	10(8)	0	0
O(H_2O)	120(11)	155(14)	153(12)	0(10)	1(11)	−39(11)
N	73(10)	20(7)	33(7)	−11(8)	0	0
C(1)	68(11)	80(14)	73(11)	13(10)	8(9)	1(10)
C(2)	94(13)	59(12)	59(9)	6(10)	9(10)	−11(8)
C(3)	55(9)	100(14)	49(8)	−16(10)	11(8)	−7(9)
C(4)	74(11)	110(16)	42(9)	−34(12)	6(8)	32(10)
C(5)	99(14)	74(13)	80(13)	22(11)	−28(12)	4(11)
C(6)	69(10)	81(13)	102(14)	55(11)	−5(10)	−11(12)

TABLE 4. BOND DISTANCES (Å), BOND ANGLES (°), AND TORSION ANGLES (°) IN THE 18-REFER MEMBERED RING

Prime marks as superscripts refer to the following equivalent position: x, y, $3/2-z$.

Atoms				Distance	Angle	Torsion angle
1	2	3	4	2-3	1-2-3	1-2-3-4
C (1')-	O (1)-	C (1)	-C (2)	1.414	112.6	0.18
O (1)	-C (1)-	C (2)	-O (2)	1.496	109.4	67.10
C (1)	-C (2)-	O (2)	-C (3)	1.420	109.6	6.20
C (2)	-O (2)-	C (3)	-C (4)	1.418	112.1	4.97
O (2)	-C (3)-	C (4)	-O (3)	1.474	108.1	65.20
C (3)	-C (4)-	O (3)	-C (5)	1.403	111.5	3.96
C (4)	-O (3)-	C (5)	-C (6)	1.424	115.1	2.12
O (3)	-C (5)-	C (6)	-O (4)	1.506	108.8	71.36
C (5)	-C (6)-	O (4)	-C (6')	1.415	106.8	8.79
C (6)	-O (4)-	C (6')	-C (5')	1.415	110.8	8.79

TABLE 5. DISTANCES (Å) INVOLVING THE AMMONIUM AND BROMIDE IONS

Roman numerals refer to the following equivalent positions:

I; $-1/2+x$, $1/2-y$, $1/2-z$

II; x, y, $1/2-z$

III; $-1/2+x$, $1/2-y$, z.

N-O(1)	3.000	Br-N	3.438
N-O(2)	2.884	Br-H_{Br}	2.43
N-O(3)	3.128	Br-O(H_2O)	3.369
N-O(4)	2.857	Br-O(H_2O) I	3.360
N-H_{Br}	1.09	Br-O(H_2O) II	3.369
N-$H_{O(2)}$	0.95	Br-O(H_2O) III	3.360
N-$H_{O(4)}$	0.93		

suggesting that the cation strongly interacts with the 18-crown-6 as is shown in Figs. 2 and 3. This nitrogen atom is displaced by 1.00 Å from the mean oxygen plane of the 18-crown-6. The ammonium cation is too large to fit in the cavity of the 18-crown-6. Dunitz *et al.*[22] reported that, in the RbNCS and CsNCS complexes of the 18-crown-6, the cations were displaced from the mean oxygen plane by 1.19 Å (Rb^+) and 1.44 Å (Cs^+). The distance, 1.00 Å for NH_4^+, is a suitable length considering the size of the cations and that of the cavity of the 18-crown-6 (cavity $< NH_4^+ < Rb^+ < Cs^+$). The straight line passing through the bromine and nitrogen atoms intersects the mean oxygen plane at an angle of 68.8° (Fig. 3). The N–O distances are divided into two groups (3.000—3.128 Å; average, 3.064 Å for N–O(1), N–O(3) and N–O(3'); 2.857—2.844 Å; average, 2.871 Å for N–O(2), N–O(2') and N–O(4)). On the difference Fourier maps, four electron-density peaks (0.6—0.8 e/Å^3) were detected at reasonable positions for the hydrogen atoms of the ammonium caion. The electron-densities of the ghost peaks around the nitrogen atom were lower than 0.55 e/Å^3. Three peaks are between N and O(2), N and O(2'), and N and O(4), suggesting the existence of three hydrogen bonds (Fig. 2). The last peak is between N and Br^- (Fig. 3). The N–H distances are between 0.9 and 1.1 Å. Table 5 shows the distances in-

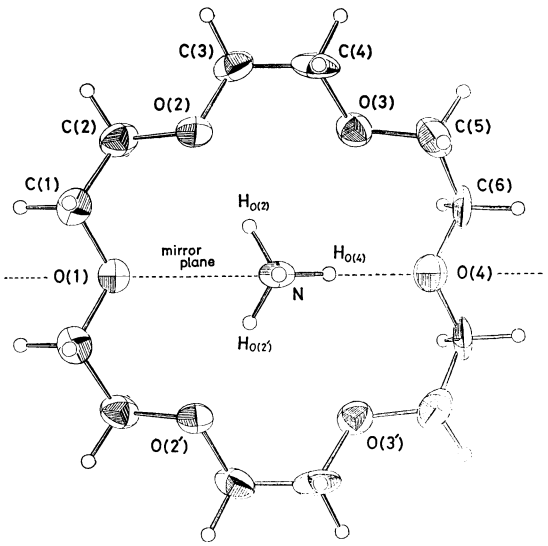


Fig. 2. $NH_4^+ \cdot C_{12}H_{24}O_6$ complex cation viewed in direction normal to the mean plane. The vibration ellipsoids are drawn at the 30% probability level.[23]

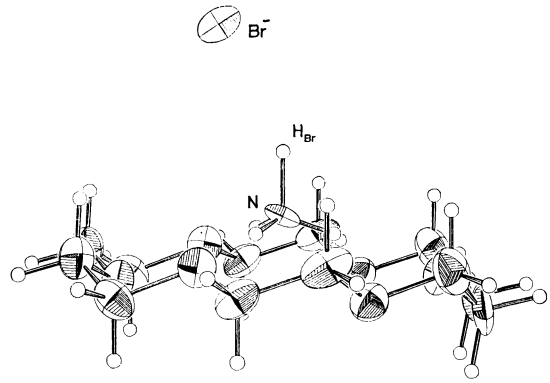


Fig. 3. $NH_4^+ \cdot C_{12}H_{24}O_6$ complex cation viewed along a direction in the mean plane. The vibration ellipsoids are drawn at the 30% probability level.[23]

volving the ammonium and bromide ions. The structure of NH_4^+·18-crown-6 closely resembles those of Rb^+·18-crown-6 and Cs^+·18-crown-6, but the distortion from the D_{3d} symmetry in NH_4^+·18-crown-6 is slightly larger than those in Rb^+·18-crown-6 and Cs^+·18-crown-6 because of the hydrogen bonds. In brief, the present complex differs from alkaline or alkaline-earth metal salts-"crown" complexes in the presence of the hydrogen bonds.

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