variable temperature probe. The chemical shifts were referenced to external tetramethylsilane.

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Registry No. 1, 17964-42-0; **2**, 80515-45-3; **3**, 80515-46-4; **4**, 17922-21-3; **5**, 30274-47-6; **7**, 53173-00-5; **10**, 40965-54-6; **12**, 13411-48-8; **13**, 5908-41-8; **14**, 80515-47-5; **15**, 80515-48-6; **16a**, 73502-43-9; **16b**, 80515-49-7; **16c**, 5272-33-3; **16d**, 80515-50-0; **17**a, 80515-51-1; **17b**, 80515-52-2; **17c**, 80515-53-3; **17d**, 80532-00-9; **18**a, 80515-54-4; **18b**, 80515-55-5; **18c**, 80515-56-6; **19**a, 38252-96-9; **19b**, 80515-57-7; 19c, 53474-96-7; **19d**, 80515-58-8; benzyltrimethylsilane, 770-09-2; (α,α-dibromotolyl)-α-trimethylsilane, 17921-71-0; (trimethylsilyl)acetylene, 1066-54-2; *tert*-butylacetylene, 917-92-0; $CH_3C(O)CMe_3$, 75-97-8; $CH_3C(OH^+)CMe_3$, 68706-39-8; $PhC(O)CMe_3$, 938-16-9; $PhC(OH^+)$-CMe_3, 80515-59-9.

Structures of the 1:1 Complexes of 18-Crown-6 with Hydrazinium Perchlorate, Hydroxylammonium Perchlorate, and Methylammonium Perchlorate

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Abstract: The structures of the crystalline 1:1 complexes of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with hydrazinium perchlorate, hydroxylammonium perchlorate, and methylammonium perchlorate have been determined by X-ray diffractometry. The first two structures were determined at 115 K, the last at 296 K. The hydrazinium complex (**1**) has space group $Pn2_1a$, with a = 14.567 (3) Å, b = 13.652 (2) Å, c = 9.244 (2) Å, and Z = 4. The hydroxylammonium complex (**2**), which crystallizes as a hemihydrate, has space group $C2/c$, with a = 19.410 (5) Å, b = 10.231 (3) Å, c = 21.321 (5) Å, β = 116.71°, and Z = 8. The methylammonium complex (**3**) has space group $C2/c$, with a = 24.518 (4) Å, b = 8.594 (2) Å, c = 21.447 (4), β = 117.04 (1)°, and Z = 8. Each structure was solved by direct methods and refined by full-matrix least squares. The radiation used, number of unique reflections, and final value of R are: for **1**, Mo Kα, 4198, 0.057; for **2**, Mo Kα, 6898, 0.066; for **3**, Cu Kα, 3590, 0.086. The perchlorate ion in room-temperature structure **3** exhibits apparent high-amplitude librational motion. The macrocycle in each of these structures is in the ideal crown conformation, with all C–C bonds gauche and all C–O bonds trans. The hydrazinium complex, **1**, is unique among complexes of crowns with ammonium and substituted ammonium ions in that the $-NH_3^+$ nitrogen atom lies close to the median plane of the six oxygen atoms of the crown ring, in a nesting position just 0.11 Å from this plane. It is hydrogen bonded to the *lower* triangle of oxygen atoms; the $-NH_2$ group is hydrogen bonded in turn to two oxygen atoms of the *upper* triangle in the host, one of these bonds being weakly bifurcated, involving a perchlorate oxygen atom as well. The assertion that the diameter of NH_4^+ is too large to permit this ion to be in a nesting position in a complex is clearly incorrect; the depth of penetration of an ammonium or substituted ammonium ion appears to depend on the relative strengths of the ion's interactions within and external to the complex. In the hydroxylammonium complex, **2**, the nitrogen of the $-NH_3^+$ group lies 0.68 Å from the plane of the oxygens of the crown ring; the hydrogen atoms of this $-NH_3^+$ group are involved in bifurcated hydrogen bonds, each to two adjacent oxygen atoms of the crown ring. The hydroxyl group of the hydroxylammonium ion is hydrogen bonded to a water molecule that lies on a twofold axis; the water molecule is in turn hydrogen bonded to two perchlorate ions. The nitrogen atom of the $-NH_3^+$ group in **3** lies 0.83 Å above the plane of the six oxygens of the crown ring, with the $-NH_3^+$ group perching on the upper triangle of oxygen atoms. In structures **1** and **2**, for which atomic vibrational parameters could be measured with fair precision, the 18-crown-6 ring is rigid and holds the $-NH_3^+$ group quite firmly. The atoms attached to the $-NH_3^+$ group undergo considerably greater motion, in directions predictable from their patterns of hydrogen bonding. It appears that in structures of this kind the orientation of the $N^+\cdots O$ line relative to the tetrahedral and trigonal directions at each C–O–C group of a crown ring is governed primarily by the depth of penetration of the $-NH_3^+$ into the ring, irrespective of the disposition of hydrogen bonds to the ring oxygen atoms.

The structures of many complexes of crown ethers with ammonium ion and substituted ammonium ions have been reported.[1] All so far described have the $-NH_3^+$ group in the *perching*[2] position, about 1 Å out of the best plane of the oxygen atoms of the crown ring, rather than in the *nesting*[2] position, essentially in the plane and encircled by the crown ring. For example, in the crystalline complex of ammonium bromide with 18-crown-6 (which has also two molecules of water per formula unit),[1a] the ammonium ion is 1.0 Å above the best plane of the six oxygens of the crown ring. In contrast, in the crystalline complex[3] of potassium thiocyanate with 18-crown-6, the potassium ion lies at the center of the crown ring, in the ideal nesting position. These findings have been widely interpreted as a consequence of the relative diameters of potassium ion (about 1.33 Å) and ammonium ion (1.48 Å), the latter almost the same as that of rubidium ion, which perches[4] about 1.19 Å out of the plane of 18-crown-6.

Studies of complexes of diammonium ions with crown ethers have been reported by several groups,[5,6] but attempts to prepare

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Table I. Crystal and Data-Collection Parameters for 18-Crown-6 Complexes

structure	1	2	3
guest	hydrazinium perchlorate	hydroxylammonium perchlorate hemihydrate	methylammonium perchlorate
formula wt, amu	396.8	406.8	395.8
cryst dimensions, mm	0.30 × 0.34 × 0.44	0.30 × 0.38 × 0.38	0.15 × 0.20 × 0.45
T, K	115	115	296
a, Å	14.657 (3)	19.410 (5)	24.518 (4)
b, Å	13.652 (2)	10.231 (3)	8.594 (2)
c, Å	9.244 (2)	21.321 (5)	21.447 (4)
β, °	90.0	116.71 (2)	117.04 (1)
space group	$Pn2_1a$	$C2/c$	$C2/c$
Z	4	8	8
d_{calcd}, g cm^{-3}	1.434	1.429	1.306
radiation	Mo Kα	Mo Kα	Cu Kα
λ_{av}, Å	0.71073	0.71073	1.54184
max ($\sin\theta/\lambda$), Å^{-1}	0.81	0.76	0.63
μ, cm^{-1}	2.20	2.66	20.0
scan speed 2θ, deg min^{-1}	4.0	4.0	6.0
final no. of variables	341	359	346
no. of unique reflections measd	4198	6898	3590
no. of reflections with $F_o \geq 2\sigma(F)$	3629	5512	2991
error in observation of unit weight	1.2	1.6	2.6
R (all reflections)	0.074	0.090	0.099
R ($F_o \geq 2\sigma(F)$)	0.057	0.066	0.086

2:1 complexes of crown ethers with $H_3NNH_3^{2+}$ have not been successful. We have, however, prepared a 1:1 crystalline complex of hydrazinium perchlorate, $H_2NNH_3^+ClO_4^-$, with 18-crown-6 and determined its structure. Surprisingly, the $-NH_3^+$ nitrogen atom is almost in the plane of the crown ring. This finding led us to prepare and determine the structure of the complexes of 18-crown-6 with hydroxylammonium perchlorate, $HONH_3^+ClO_4^-$ (as a hemihydrate), and with methylammonium perchlorate, $CH_3NH_3^+ClO_4^-$, as well. In these complexes, the ammonium nitrogen atoms are in intermediate positions, about 0.68 and 0.83 Å from the best oxygen plane. Haymore has recently determined the structures[7] of an ammonium complex and a hydronium complex of dicyclohexano-18-crown-6 in which the NH_4^+ and H_3O^+ ions lie 0.86 and 0.54 Å above the plane of five of the six oxygens of the crown ring (which has an envelope conformation, one oxygen being significantly displaced from the plane of the other five).

Experimental Section

Materials. The following chemicals were obtained from the indicated suppliers: hydrazine dihydrochloride (Eastman); hydroxylamine hydrochloride (Mallinckrodt); lithium perchlorate (34.5% H_2O) (Alfa); methylamine hydrochloride (Matheson, Coleman, and Bell). The ammonium salts were purified according to Perrin et al.[8] 18-Crown-6 was prepared by the method of Cram and Gokel.[9] The complexes of 18-crown-6 with the ammonium salts were prepared as follows: Ammonium salt (1 mmol) was dissolved in 1.0 mL of 4.0 M $LiClO_4$. To this solution was added 1.1 mL of a 1.0 M aqueous solution of 18-crown-6. The resulting precipitate was collected and allowed to dry in air. For each salt the yield was essentially quantitative.

18-Crown-6·Hydrazinium Perchlorate (1). The complex was recrystallized by dissolution in methylene chloride followed by dropwise addition of benzene to the point of cloudiness. Slow evaporation provided clear colorless rod-shaped crystals. Although we had hoped to obtain a 2:1 complex of 18-crown-6 with $N_2H_6^{2+}$, both the chemical analysis and the structure determination showed that the complex obtained was the 1:1 complex with $N_2H_5^+ClO_4$. Anal. Calcd for $C_{12}H_{29}ClN_2O_{10}$: C, 36.31; H, 7.31; N, 7.06. Found: C, 36.61; H, 7.03; N, 7.03.

18-Crown-6·Hydroxylammonium Perchlorate (Hemihydrate) (2). The complex was recrystallized by dissolution in chloroform followed by dropwise addition of hexane to the point of cloudiness. Slow evaporation produced colorless needles. The degree of hydration was established from the structural study (see below). Anal. Calcd for $C_{12}H_{29}ClO_{10.5}$: C, 35.48; H, 7.39; N, 3.45. Found: C, 36.02; H, 7.26; N, 3.53.

18-Crown-6·Methylammonium Perchlorate (3). The complex was recrystallized by dissolution in methylene chloride followed by dropwise addition of hexane to the point of cloudiness. Slow evaporation yielded colorless needles. Anal. Calcd for $C_{13}H_{30}ClNO_{10}$: C, 39.44; H, 7.58; N, 3.54. Found: C, 39.73; H, 7.59; N, 3.63.

Pertinent data about the crystals and the measurement of diffraction intensities are summarized in Table I. The intensities used for refinement of structures **1** and **2** were measured at low temperature[10] (115 K) with Mo Kα radiation; more limited data sets were also collected for **2** with Cu Kα radiation at both 115 and 296 K (see below). Intensity data for **3** were measured only at room temperature because the diffraction maxima appeared to split when the crystal was cooled to 115 K.

Photographic and diffractometer measurements of intensities for **1** gave systematic absences consistent with space groups *Pnma* (No. 62)[11] and $Pn2_1a$ (No. 33). The intensity statistics strongly indicated that the latter (noncentrosymmetric) space group was correct and this was confirmed by the successful refinement. For **2** and **3**, systematic absences were consistent with either $C2/c$ (No. 15) or Cc (No. 9). For each structure the intensity statistics strongly indicated the centrosymmetric space group, $C2/c$, and the refinement confirmed this choice.

Unit-cell dimensions were measured and intensity data collected with a Syntex P$\bar{1}$ diffractometer. Cell dimensions were obtained by least-squares fit to the angles measured for 15 automatically centered reflections (2θ ranges: 23–30° for **1**, 28–32° for **2**, and 61–81° for **3**). Each structure was solved by direct methods with the MULTAN78 package[12] and was refined by full-matrix least squares using all reflections with $F_o \geq 2\sigma(F)$. After all the nonhydrogen atoms had first been refined anisotropically, the hydrogens were located with difference maps. All were found unambiguously except those on the $-NH_3^+$ group of the $HONH_3^+$ in **2**, which are partially disordered. Hydrogen positions and isotropic temperature factors were refined, at the same time that the other atoms were again refined anisotropically, to convergence. We were able to find tentative positions for two sets of three hydrogen atoms in difference maps for structure **2** near the final stage of refinement and attempted to define them better by refinement with varying occupancy factors. One set, listed in the parameter tables and shown in Figures 2 and 4, refined well, with occupancy about 0.7, but no other definitive positions could be found. Except for MULTAN78, all computer programs used were local programs. Atomic scattering factors were taken from the "International Tables".[13] No absorption corrections were made; they would have been significant only for structure **3**. No final shift in position for an atom[14]

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(13) "International Tables for X-Ray Crystallography"; Kynoch Press, Birmingham, England, Vol. IV, pp 73, 75, 102.

(14) Because of the polar axis in structure **1**, the *y* value of the Cl atom was fixed at an arbitrary value. The numbering of atoms was similar in each structure: the 18-crown-6 ring with numbers from 1 to 18, starting with an oxygen atom; the N$^+$ atom and its attached N, O or C, 19 and 20; and the perchlorate oxygens 22–25.

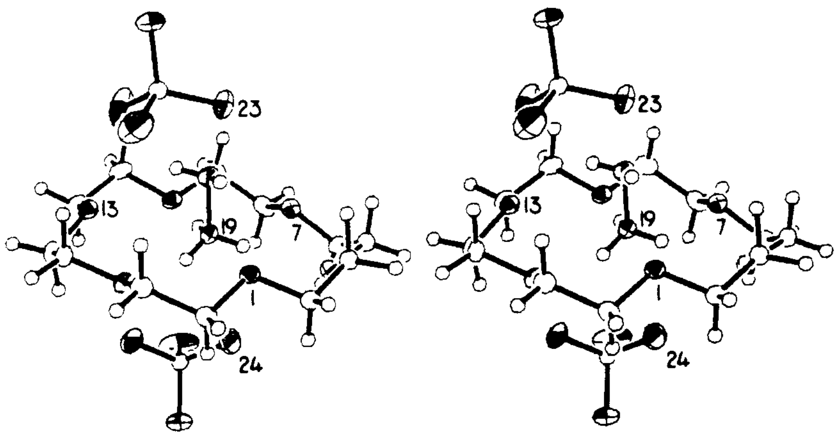

Figure 1. Stereoview of the hydrazinium perchlorate complex. Two symmetry-related perchlorate ions are shown. One oxygen atom of the upper perchlorate is involved in a weak bifurcated hydrogen bond from the $-NH_2$ group. A different oxygen atom of the lower perchlorate lies not far from an extension of the N–N axis, below the $-NH_3^+$ group, 3.03 Å from the nitrogen atom. (Nitrogen and oxygen atoms are partially shaded in this and the other figures.)

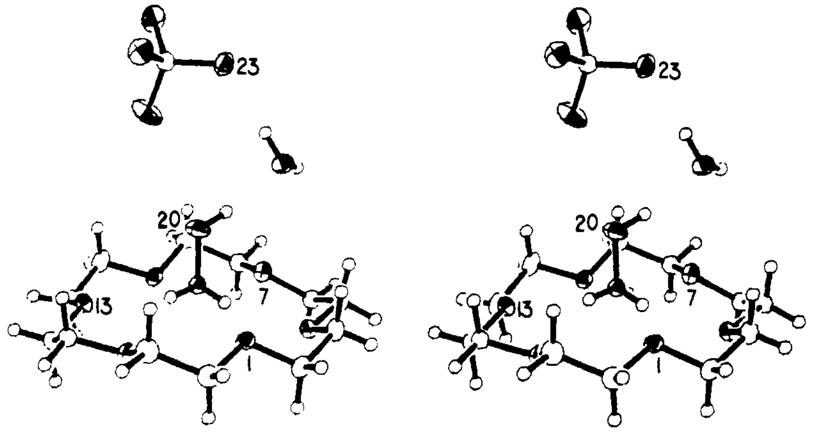

Figure 2. Stereoview of the hydroxylammonium perchlorate hemihydrate complex. The bifurcation of the N–H···O hydrogen bonds is quite evident. The water molecule lies on a twofold axis, accepting a hydrogen bond from each of two –OH groups of hydroxylammonium ions (only one shown here) and acting as a hydrogen-bond donor to each of two perchlorate ions (only one shown here). See also Figure 4.

other than hydrogen in structures **1** and **2** was larger than half the corresponding esd and none for a hydrogen atom (for which the esd's are underestimates of the actual errors) larger than 0.8 times the corresponding esd, except for H(19B) in **2**. For structure **3**, the final shift in y of C(6) was 1.1 times the esd, and the shifts in the position parameters of H(6B) were 1.2–2.2 times the corresponding esd's. The final difference map of structure **1** had no peaks higher than 0.5 e A^{-3}, and the highest peaks were within 1 Å of the chlorine atom. For structure **2**, the three highest peaks in the final difference map were in the range 0.4–0.7 e Å^{-3}, and each was near a bond: C(8)–C(9), C(17)–C(18), and Cl–O(23), the latter the highest. There were no definitive peaks representing possible disordered hydrogen atoms on the nitrogen atom. In structure **3**, done at room temperature and having no hydrogen bonding, there is evidence of apparent high thermal motion, especially of the perchlorate group (see below). The Gaussian ellipsoid model for anisotropic vibration parameters is inadequate for this group, but we did not attempt to use a higher cumulant or other higher-order model.[15] There was one unexplained peak in the final difference map for **3**, of height just below 1 e Å^{-3}. It was close to one of the threefold axes of the perchlorate ion, about 1.6 Å from the Cl atom, and is almost certainly attributable to static or dynamic disorder. We did not feel it worthwhile to attempt further refinement with a more elaborate model for the disorder of the ClO_4^-, which is not of intrinsic structural interest.

The final parameters and their esd's are given in Table II, and the final values of F_o and F_c in Table III (in the supplementary material). The structures of the complexes are illustrated[16] in Figures 1, 2, and 3, and a stereoview of the unit cell of **2** is shown in Figure 4.

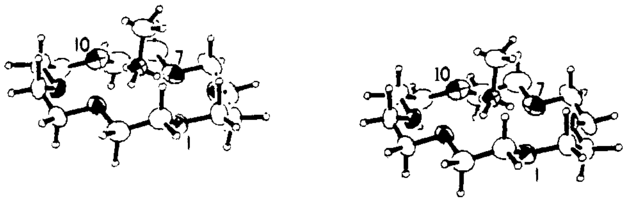

Figure 3. Stereoview of the methylammonium complex. The perchlorate ion is not shown here.

Discussion

We consider first the conformation and other geometrical features of the host molecules, then their interactions with the guests, and finally the intermolecular interactions and packing arrangements in the different structures. It should be noted that the precision (as well as the accuracy) of the room-temperature structure of the methylammonium complex, **3**, is appreciably lower than that of the low-temperature structures, **1** and **2**, in part at least because there is much higher apparent librational motion, especially of the perchlorate ion (Table VI). Consequently, we shall not emphasize the fine metric details in discussing structure **3**.

Hosts. As is apparent from Figures 1, 2, and 3, the 18-crown-6 ring in each structure is in nearly the ideal crown formation, with all C–C torsion angles gauche (*sc*) and all C–O and O–C torsion angles trans (*ap*). Because of the near D_{3d} symmetry of each ring, only the average values and the ranges of the relevant bond

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[16] All hydrogen atoms in the drawings are represented as spheres of radius 0.1 Å. The ellipsoids of the other atoms in the low-temperature structures (Figures 1, 2, and 4) are drawn at the 50% probability level; those for the methylammonium perchlorate structure, which has much higher motion, are drawn at the 33% level in Figure 3.

Table II. Position and Vibration Parameters[a]

A. Hydrazinium Perchlorate Complex of 18-Crown-6

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
O(1)	0.27564(13)	0.96372(15)	0.43181(21)	1.5	H(3A)	0.4556(24)	0.9272(27)	0.4976(37)	1.9(7)
C(2)	0.31958(20)	0.88059(23)	0.49390(29)	1.6	H(3B)	0.4526(22)	0.9373(25)	0.4381(35)	1.1(7)
C(3)	0.41488(19)	0.87327(22)	0.43508(30)	1.5	H(5A)	0.5380(20)	0.8715(22)	0.2496(32)	0.4(5)
O(4)	0.40958(13)	0.84050(16)	0.28746(20)	1.5	H(5B)	0.5284(28)	0.7636(32)	0.2702(43)	2.9(9)
C(5)	0.49716(19)	0.81829(22)	0.22880(32)	1.7	H(6A)	0.4313(21)	0.7631(23)	0.0460(31)	0.8(6)
C(6)	0.48746(19)	0.80325(20)	0.06853(31)	1.7	H(6B)	0.5387(19)	0.7745(22)	0.0302(29)	0.5(5)
O(7)	0.46950(13)	0.89592(16)	0.00462(21)	1.5	H(8A)	0.5171(25)	0.8766(30)	-0.1781(41)	2.3(8)
C(8)	0.46329(21)	0.89237(25)	-0.14976(30)	1.8	H(8B)	0.4185(28)	0.8441(31)	-0.1786(42)	2.4(9)
C(9)	0.43653(21)	0.99251(26)	-0.20279(31)	2.0	H(9A)	0.4451(23)	0.9925(28)	-0.3059(38)	1.9(7)
O(10)	0.34208(14)	1.00815(16)	-0.17076(21)	1.6	H(9B)	0.4745(24)	1.0394(26)	-0.1593(36)	1.5(7)
C(11)	0.30721(23)	1.09956(23)	-0.22339(32)	2.0	H(11A)	0.3449(28)	1.1537(31)	-0.1862(45)	3.1(9)
C(12)	0.20800(24)	1.10720(25)	-0.18582(31)	2.0	H(11B)	0.3183(22)	1.1056(24)	-0.3228(36)	1.0(6)
O(13)	0.19836(16)	1.12033(16)	-0.03243(21)	1.6	H(12A)	0.1765(25)	1.0534(29)	-0.2088(40)	2.0(8)
C(14)	0.10467(21)	1.11189(23)	0.01068(33)	1.8	H(12B)	0.1840(28)	1.1615(31)	-0.2387(48)	3.0(9)
C(15)	0.09826(21)	1.12758(22)	0.17240(33)	1.7	H(14A)	0.0679(25)	1.1554(26)	-0.0376(36)	1.1(7)
O(16)	0.13866(14)	1.04466(16)	0.24349(21)	1.5	H(14B)	0.0810(28)	1.0492(33)	-0.0134(45)	3.0(9)
C(17)	0.13721(21)	1.05546(23)	0.39746(31)	1.7	H(15A)	0.0375(24)	1.1386(25)	0.1938(35)	1.3(6)
C(18)	0.18017(19)	0.96540(22)	0.46411(31)	1.6	H(15B)	0.1323(20)	1.1875(24)	0.1967(34)	0.7(6)
N(19)	0.30918(17)	0.98614(19)	0.12886(26)	1.3	H(17A)	0.1684(26)	1.1162(30)	0.4252(40)	2.1(8)
N(20)	0.35630(19)	1.07450(20)	0.17379(31)	1.8	H(17B)	0.0832(25)	1.0594(28)	0.4255(36)	1.7(7)
CL(21)	0.82228(4)	0.28900(0)	0.07561(7)	1.4	H(18A)	0.1547(23)	0.9069(26)	0.4253(37)	1.5(6)
O(22)	0.86804(19)	0.38163(19)	0.06237(32)	3.0	H(18B)	0.1694(24)	0.9658(29)	0.5650(42)	1.6(8)
O(23)	0.88593(17)	0.21120(18)	0.04699(25)	2.2	H(19A)	0.2538(22)	0.9827(23)	0.1422(33)	0.5(6)
O(24)	0.74792(20)	0.28498(25)	-0.02451(35)	4.3	H(19B)	0.3174(25)	0.9875(30)	0.0349(44)	2.1(8)
O(25)	0.78717(22)	0.27824(23)	0.21909(30)	4.1	H(19C)	0.3391(24)	0.9382(30)	0.1570(42)	2.0(8)
H(2A)	0.3194(19)	0.8858(23)	0.5937(32)	0.4(5)	H(20A)	0.3492(23)	1.0755(25)	0.2663(38)	1.0(6)
H(2B)	0.2846(24)	0.8284(27)	0.4752(36)	1.0(7)	H(20B)	0.3302(29)	1.1138(33)	0.1298(46)	3.3(9)

B. Hydroxylammonium Perchlorate Hemihydrate of 18-Crown-6

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
O(1)	0.39151(8)	0.46332(13)	0.71911(7)	1.5	H(3A)	0.4907(14)	0.4044(25)	0.8816(13)	2.2(5)
C(2)	0.42702(13)	0.49954(20)	0.79146(11)	1.8	H(3B)	0.5066(14)	0.3525(24)	0.8226(13)	2.2(5)
C(3)	0.46686(12)	0.38280(21)	0.83534(11)	1.8	H(5A)	0.4669(12)	0.2047(21)	0.9208(11)	1.0(4)
O(4)	0.41102(8)	0.28433(13)	0.82674(7)	1.4	H(58)	0.4873(13)	0.1384(23)	0.8655(11)	1.4(5)
C(5)	0.44581(12)	0.17584(20)	0.87270(10)	1.6	H(6A)	0.3434(12)	0.1085(22)	0.8683(11)	1.2(4)
C(6)	0.38653(12)	0.07220(20)	0.85984(10)	1.6	H(6B)	0.4112(13)	0.0032(22)	0.8955(12)	1.5(5)
O(7)	0.35748(8)	0.02853(14)	0.78891(7)	1.6	H(8A)	0.2688(13)	-0.0681(22)	0.7892(12)	1.4(4)
C(8)	0.30889(12)	-0.08399(20)	0.77552(11)	1.7	H(8B)	0.3391(13)	-0.1583(24)	0.8052(12)	2.0(5)
C(9)	0.27293(12)	-0.11335(20)	0.69856(11)	1.7	H(9A)	0.2396(14)	-0.1949(24)	0.6924(12)	2.2(5)
O(10)	0.22526(8)	-0.00566(14)	0.66155(7)	1.6	H(9B)	0.3099(14)	-0.1246(25)	0.6830(12)	2.0(5)
C(11)	0.18006(14)	-0.03328(22)	0.58873(11)	2.0	H(11A)	0.1441(14)	-0.0965(26)	0.5857(13)	2.5(5)
C(12)	0.13352(12)	0.08534(23)	0.55413(11)	2.0	H(11B)	0.2129(13)	-0.0575(23)	0.5696(12)	1.8(5)
O(13)	0.18495(8)	0.18798(13)	0.55783(7)	1.6	H(12A)	0.1030(13)	0.1113(24)	0.5785(12)	2.0(5)
C(14)	0.14582(11)	0.30308(22)	0.52141(11)	1.7	H(12B)	0.0988(14)	0.0690(24)	0.5088(13)	1.8(5)
C(15)	0.20368(12)	0.40143(21)	0.52382(10)	1.7	H(14A)	0.1118(14)	0.3429(25)	0.5431(13)	2.6(5)
O(16)	0.25285(8)	0.43480(14)	0.59549(7)	1.6	H(14B)	0.1144(13)	0.2796(22)	0.4751(12)	1.6(5)
C(17)	0.31023(13)	0.52732(22)	0.60073(12)	2.0	H(15A)	0.1784(14)	0.4783(26)	0.4995(13)	2.4(5)
C(18)	0.35261(13)	0.57129(20)	0.67564(12)	1.9	H(15B)	0.2354(13)	0.3644(22)	0.5024(12)	1.5(4)
N(19)	0.32953(11)	0.20743(19)	0.68106(10)	1.4	H(17A)	0.2901(14)	0.6004(26)	0.5703(13)	2.5(6)
O(20)	0.38161(9)	0.15160(16)	0.65888(9)	2.4	H(17B)	0.3481(13)	0.4849(23)	0.5881(12)	1.7(5)
CL	0.94572(3)	0.29738(5)	0.58193(3)	1.6	H(18A)	0.3177(14)	0.6114(25)	0.6923(13)	2.3(5)
O(22)	0.94892(11)	0.16441(17)	0.56195(10)	3.5	H(18B)	0.3894(14)	0.6353(25)	0.6771(12)	2.2(5)
O(23)	1.00816(10)	0.31783(16)	0.65165(8)	2.6	H(19A)	0.3517(20)	0.2582(37)	0.7141(19)	3.3(8)
O(24)	0.95499(10)	0.38623(18)	0.53401(9)	2.8	H(19B)	0.3159(25)	0.1633(48)	0.7019(24)	6.6(12)
O(25)	0.87387(10)	0.32237(18)	0.58343(11)	3.4	H(19C)	0.2979(19)	0.2377(34)	0.6502(18)	2.5(7)
OW	1.00000(0)	0.50251(22)	0.25000(0)	2.0	H(20)	0.4148(16)	0.1007(29)	0.6915(15)	3.8(7)
H(2A)	0.3880(15)	0.5386(25)	0.8032(13)	2.4(5)	HW	1.0030(20)	0.5573(32)	0.2190(16)	5.2(8)
H(2B)	0.4667(14)	0.5679(25)	0.7972(13)	2.4(5)					

C. Methylammonium Perchlorate Complex of 18-Crown-6

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
O(1)	0.8449(1)	0.2476(4)	0.3720(2)	5.4	H(3A)	0.859(2)	0.007(6)	0.450(2)	6.4(11)
C(2)	0.8951(3)	0.2277(8)	0.4401(3)	6.7	H(3B)	0.936(3)	0.042(8)	0.514(4)	13.4(20)
C(3)	0.9023(3)	0.0616(8)	0.4575(3)	7.2	H(5A)	0.883(3)	-0.246(7)	0.427(3)	10.8(17)
O(4)	0.9199(1)	-0.0167(4)	0.4106(2)	6.2	H(5B)	0.968(4)	-0.194(8)	0.471(4)	13.8(22)
C(5)	0.9325(3)	-0.1793(8)	0.4259(4)	7.9	H(6A)	0.987(2)	-0.183(6)	0.375(2)	6.1(11)
C(6)	0.9521(3)	-0.2481(9)	0.3765(5)	8.3	H(6B)	0.971(3)	-0.351(8)	0.394(3)	10.3(17)
O(7)	0.9014(2)	-0.2462(4)	0.3085(2)	6.8	H(8A)	0.928(3)	-0.417(9)	0.272(4)	10.9(23)
C(8)	0.9146(4)	-0.3195(9)	0.2575(6)	9.5	H(8B)	0.953(2)	-0.261(6)	0.258(2)	6.8(13)
C(9)	0.8601(5)	-0.3118(8)	0.1893(6)	9.0	H(9A)	0.873(3)	-0.356(9)	0.154(4)	11.8(21)
O(10)	0.8484(2)	-0.1522(4)	0.1660(2)	6.9	H(9B)	0.823(3)	-0.336(7)	0.183(3)	8.2(20)
C(11)	0.7978(4)	-0.1347(9)	0.0980(4)	8.3	H(11A)	0.803(3)	-0.197(7)	0.064(3)	8.1(15)
C(12)	0.7880(3)	0.0352(9)	0.0789(3)	7.3	H(11B)	0.758(3)	-0.188(7)	0.096(3)	9.7(17)
O(13)	0.7744(1)	0.1125(4)	0.1281(1)	5.5	H(12A)	0.755(2)	0.061(6)	0.022(3)	6.9(12)
C(14)	0.7608(3)	0.2751(7)	0.1115(3)	6.3	H(12B)	0.824(2)	0.073(5)	0.077(2)	6.2(12)
C(15)	0.7443(2)	0.3471(7)	0.1632(3)	6.2	H(14A)	0.729(3)	0.288(6)	0.066(3)	8.3(14)
O(16)	0.7951(1)	0.3450(3)	0.2297(2)	5.1	H(14B)	0.799(3)	0.329(7)	0.107(3)	9.6(17)
C(17)	0.7828(3)	0.4178(7)	0.2823(3)	6.1	H(15A)	0.707(2)	0.282(6)	0.162(3)	7.8(13)
C(18)	0.8370(3)	0.4056(7)	0.3510(3)	6.5	H(15B)	0.725(2)	0.461(7)	0.150(3)	8.3(14)
N(19)	0.8786(2)	0.0880(6)	0.2694(3)	4.4	H(17A)	0.769(3)	0.525(8)	0.268(3)	10.0(17)
C(20)	0.9344(4)	0.1546(11)	0.2732(6)	8.1	H(17B)	0.741(2)	0.360(6)	0.281(2)	6.5(11)
CL	0.4208(1)	0.8889(2)	0.0804(1)	5.7	H(18A)	0.830(2)	0.462(6)	0.388(3)	7.4(13)
O(22)	0.4660(2)	0.9142(6)	0.0601(3)	11.8	H(18B)	0.877(2)	0.451(6)	0.348(2)	7.1(12)
O(23)	0.4402(3)	0.9161(7)	0.1500(2)	14.0	H(19A)	0.884(2)	0.063(6)	0.303(3)	5.9(16)
O(24)	0.4113(4)	0.7259(8)	0.0759(5)	17.9	H(19B)	0.866(2)	0.033(6)	0.242(2)	5.1(14)
O(25)	0.3675(3)	0.9508(13)	0.0388(4)	19.6	H(19C)	0.850(3)	0.163(9)	0.269(4)	11.6(21)
H(2A)	0.894(3)	0.275(7)	0.477(3)	9.6(18)	H(20A)	0.951(4)	0.232(10)	0.314(5)	13.7(30)
H(2B)	0.935(3)	0.274(7)	0.433(3)	8.9(15)	H(20B)	0.925(4)	0.190(10)	0.240(4)	12.4(31)
					H(20C)	0.974(4)	0.083(9)	0.289(4)	12.8(23)

[a] Units of isotropic *B* are angstroms squared. Units of each ESD, in parentheses, are those of the least significant digit of the corresponding parameter. If *B* has no ESD, it is equivalent isotropic *B* for an atom refined anisotropically.

distances, bond angles, and absolute values of the torsion angles for each structure are given in Table IV; the individual values are given with the supplementary material. The observed values of the various geometrical parameters are in good accord with those found in other structural studies of 18-crown-6 and related macrocyclic polyethers.[17] In particular, in structures **1** and **2**, for which the bond-length corrections for apparent molecular libration[18] of the crown ring are small (averaging 0.001 Å) and the range of observed C–C distances relatively small, the C–C distances average[19] very close to 1.500 Å, significantly smaller than the standard distance between bonded sp^3 carbon atoms in

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[17] Summarized, for example, by Goldberg, I. "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogs", Supplement E1; Patai, S., Ed.; Wiley: London, 1980; pp 175–214.

[18] Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *B24*, 63–76.

[19] The average C–C distance in the hydroxylammonium complex structure refined with low-temperature Cu Kα data is essentially the same, 1.499 Å, whereas for the same structure refined with room-temperature Cu Kα data, the mean C–C distance (after a libration correction averaging 0.004 Å) is about 1.487 Å, and that in structure **3** is 1.482 Å.

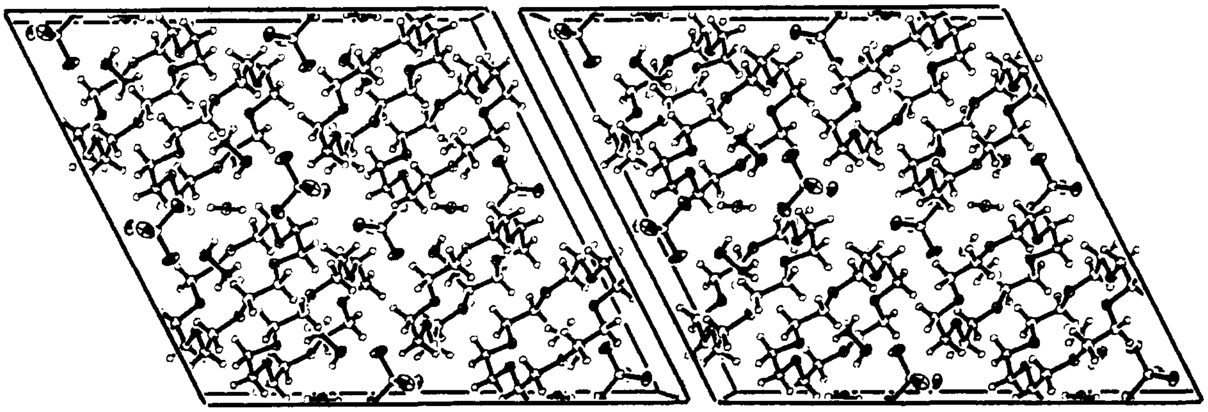

Figure 4. Stereoview of the unit cell of the hydroxylammonium perchlorate hemihydrate complex, viewed along *b*, with *c* horizontal. The twofold axes through the water molecules are apparent here (see legend of Figure 2).

Table IV. Structural Parameters[a] for the 18-Crown-6 Rings[b]

structure guest	1 $H_2NNH_3^+$	2 $HONH_3^+$	3 $H_3CNH_3^+$
bond distances, Å			
average C–C	1.503 (4)	1.498 (3)	1.482 (10)
range of C–C	1.491–1.514	1.493–1.501	1.471–1.511
average C–O	1.429 (4)	1.430 (3)	1.431 (8)
range of C–O	1.420–1.439	1.423–1.435	1.409–1.448
average C–H	0.95 (4)	0.97 (3)	1.04 (7)
range of C–H	0.83–1.04	0.90–1.04	0.90–1.35
bond angles, deg			
average C–O–C	112.3 (2)	111.8 (2)	112.7 (5)
range of C–O–C	111.1–113.8	111.1–112.9	111.6–113.6
average C–C–O	108.7 (2)	109.0 (2)	109.1 (6)
range of C–C–O	107.8–109.5	108.4–109.7	108.5–109.8
absolute values of torsion angles, deg			
average C–C	71.1 (3)	62.8 (2)	65.9 (7)
range of C–C	68.4–73.8	61.2–65.1	61.2–68.9
average C–O	175.6 (3)	175.4 (2)	177.5 (6)
range of C–O	169.5–179.7	171.3–179.0	175.8–179.7

[a] Values corrected for librational motion. For the two low-temperature structures, the corrections to bond distances are only 0.001 Å; for structure 3, they amount to 0.006–0.007 Å. Corrections to bond angles and torsion angles are negligible for all structures. [b] Estimated standard deviations of individual distances and angles given in parentheses in units of the least significant digit.

Table V. Average Structural Parameters of Guests[a]

structure guest	1 $H_2NNH_3^+$	**2** $HONH_3^+$	**3** $H_3CNH_3^+$
ammonium ions; distances, Å			
X–N	1.449 (4)	1.415 (3)	1.450 (10)
N–H	0.84 (4)	0.77 (5)	0.79 (6)
X–H	0.82 (4)	0.88 (3)	0.93 (8)
ammonium ions; angles, deg			
τ_{X-N}	58 (4)[a]	39 (4)	53 (7)[a]
perchlorate ions; distances, Å			
Cl–O[b]	1.431 (3) 1.457	1.439 (2) 1.458	1.368 (9) 1.502
water molecule			
H–O, distance, Å		0.89 (3)	
H–O–H, angle, deg		102 (4)	

[a] Absolute value of the smallest H–X–N–H torsion angles (average of two for **1** and of three for 3). [b] Lower value is after correction for apparent molecular libration. [c] Estimated standard deviations of individual distances and angles given in parentheses, in units of the least significant digit.

Table VI. Selected Rigid-Body Motion Parameters[a,b]

		2		
	1 (115 K)	115 K	296 K	**3** (296 K)
	18-Crown-6 Ring			
$L_{ii}^{1/2}$, deg	1.8	1.9	3.6	5.0
	1.4	1.4	2.9	2.4
	1.3	1.3	2.4	c
R_{wU}	0.145	0.149	0.113	0.192
av $\vert\Delta(\mathrm{MSVA})\vert/\mathrm{Å}^2$				
C–C, C–O bonds	0.0017	0.0011		0.0190
nonbonded	0.0024	0.0016		0.0160
$N^+\cdots O$	0.0022	0.0014		0.0107
X···ring atoms[d]	0.0066	0.0132		0.0320
av esd of Δ	0.0018	0.0015		0.0063
	Perchlorate Ion			
$L_{ii}^{1/2}$, deg	11.1	8.3	20.3	21.7
	6.4	5.7	12.0	17.9
	4.1	5.5	9.5	13.3
R_{wU}	0.014	0.022	0.042	0.092
av $\vert\Delta(\mathrm{MSVA})\vert$, $\mathrm{Å}^2$				
Cl–O bonds	0.0012	0.0014		0.0185
O···O	0.0014	0.0024		0.0304
av esd of Δ	0.0015	0.0011		0.0063

[a] R_{wU} is a weighted measure of the agreement of the observed and calculated values of the components of the individual atomic vibrational tensors.[22] |Δ(MSVA)| is the absolute value of the difference in the mean-square atomic vibration amplitudes along interatomic lines. A low value of Δ indicates rigidity. [b] For comparison, some results from the room-temperature refinement of structure 2 are also included. [c] The smallest principal component of the librational tensor for the 18-crown-6 ring of structure 3 was slightly negative (−0.2 degrees squared). [d] Atom X is the atom attached to the NH_3^+ group, N in structure 1, O in structure 2, and C in structure 3. For all three structures, all or all but one of these differences were positive, that is, X was vibrating more than the ring atom along the line from X to that atom.

hydrocarbons, about 1.533 Å. The C–O distances average slightly below 1.43 Å in all three structures, a distance characteristic of similar molecules.[17] The bond angles and torsion angles are much less sensitive to librational corrections than the bond distances. The bond angles at oxygen and at carbon average 112–113° and about 109°, respectively, in all three structures, quite typically. The (absolute values of the) C–C torsion angles are significantly higher in **1**, averaging about 71°, than in **2** and **3**, where the averages are close to 63° and 66°, respectively. The absolute C–O torsion angles all average rather close to 180°.

Guests and Anions. Structural information on the ammonium and perchlorate ions is summarized in Table V. Both the hydrazinium and methylammonium ions, in which all protons were located unambiguously, have a staggered conformation. As already mentioned, the $-NH_3^+$ group of structure **2** is disordered[20]

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(20) The disorder of the $-NH_3^+$ group of the $HONH_3^+$ was found as well with the low-temperature Cu Kα data set (collected from the same crystal) and with the room-temperature Cu Kα data set (collected from a different crystal).

Table VII. Hydrogen-Bonding Parameters

structure		angle, deg	distance, Å	
		X–H···O	X···O	H···O
1	N(19)–H(19C)···O(4)	162 (4)	2.871 (3)	2.07 (4)
	–H(19B)···O(10)	172 (4)	2.827 (3)	1.96 (4)
	–H(19A)···O(16)	146 (3)	2.816 (3)	2.10 (4)
	N(20)–H(20A)···O(1)	132 (3)	3.059 (4)	2.41 (4)
	···O(23)[a]	130 (3)	3.214 (4)	2.59 (4)
	–H(20B)···O(13)	140 (3)	3.053 (4)	2.42 (4)
2	N(19)–H(19A)···O(1)	132 (3)	2.843 (3)	2.22 (4)
	–H(19A)···O(4)	147 (3)	2.890 (3)	2.16 (4)
	N(19)–H(19B)···O(7)	142 (5)	2.795 (3)	2.16 (5)
	–H(19B)···O(10)	129 (4)	2.875 (3)	2.34 (5)
	N(19)–H(19C)···O(13)	141 (3)	2.862 (3)	2.25 (4)
	–H(19C)···O(16)	143 (3)	2.918 (3)	2.30 (4)
	O(20)–H(20)···OW[b]	167 (2)	2.744 (2)	1.88 (3)
	OW–HW···O(23)[c]	178 (3)	2.846 (2)	1.96 (3)
3	N(19)–H(19A)···O(4)	169 (6)	2.863 (6)	2.17 (5)
	–H(19B)···O(10)	168 (5)	2.865 (6)	2.17 (5)
	–H(19C)···O(16)	154 (6)	2.865 (6)	1.98 (7)

[a] This O(23) is in the perchlorate ion at $-\frac{1}{2} + x, 1 + y, \frac{1}{2} - z$. [b] This OW is at $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. [c] This O(23) is in the perchlorate ion at $x, 1 - y, -\frac{1}{2} + z$.

Table VIII. Structural Parameters Relevant to Host–Guest Interaction[a]

structure guest	**1** $H_2NNH_3^+$	**2** $HONH_3^+$	**3** $H_3CNH_3^+$
distances, Å			
N^+ from best O_6 plane	0.11	0.68	0.84
N^+ from upper O_3 plane	−0.13	0.49	0.64
N^+ from lower O_3 plane	0.36	0.87	1.04
O···O in upper O_3 group	4.96	4.83	4.84
O···O in lower O_3 group	4.88	4.78	4.83
N^+···O to upper O_3 group	2.87	2.83	2.86
N^+···O to lower O_3 group	2.84	2.89	2.98
upper to lower O_3 plane[b]	0.49	0.38	0.40
angles, deg			
between X–N bond and the normal to O_6 plane	5.5	5.6	2.0
average absolute C–C torsion angle	71	63	66
from N^+···O line to tetrahedral[c] direction at O			
upper O_3 group	6	27	28
lower O_3 group	8	4	5
from N^+···O line to trigonal[d] direction at O			
upper O_3 group	48	28	26
lower O_3 group	47	52	58

[a] "Upper" refers to the side of the crown ring on which the bulk of the guest lies. The "O_6 plane" is the least-squares plane through the six oxygen atoms of the crown ring. [b] Along normal to O_6 plane through N^+. [c] Tetrahedral directions at O are defined as lines at 109.5° to each other and equally inclined to the two O–C vectors. [d] Trigonal direction at O is defined as a line in the C–O–C plane that makes equal angles with the two O–C vectors and is directed away from them.

about the O–N bond; one set of hydrogen positions of weight about 0.7 is fairly well defined, corresponding to a conformation intermediate between staggered and eclipsed, with a torsion angle of about 39°. Possible reasons for this disorder, which is unique among more than a dozen complexes that we have studied in which there is interaction of a $-NH_3^+$ group with a crown-like host, are considered below.

There is appreciable thermal motion of the perchlorate ions in all three structures. The fit to the rigid-body model is excellent (Table VI) for the low-temperature structures. The model is demonstrably inadequate for the perchlorate ion of structure **3**, for which the apparent principal rms amplitudes of libration range from 13 to 22° (0.2–0.4 radian). The geometry of the ClO_4^- ion in structure **3** is accordingly not meaningfully measured by this study. On the other hand, for structures **1** and **2**, after corrections for libration, the Cl–O distances average close to 1.458 Å for each structure, a value essentially identical with that found in other precise studies on perchlorate ions for which there are also appreciable but meaningful libration corrections.[21,22]

Interaction of Host and Guest. The variation in the interaction of the $X-NH_3^+$ guests with the host among these structures and relative to other comparable structures provides some illuminating contrasts. Relevant structural parameters are summarized in Table VII, which gives information about hydrogen bonds, and in Table VIII.

As is evident in Figures 1, 2, and 3, the oxygen atoms of the crown rings in these structures are, as is common, displaced alternately above and below the median plane of the ring, forming two approximately parallel and nearly equilateral triangles, rotated 60° relative to one another. Table VIII contains information about the displacement of the ammonium nitrogen atom from the planes of these triangles and from the median plane as well. Examination of the figures and of Table VIII shows clearly that the ammonium nitrogen atom in the hydrazinium complex lies between these two three-oxygen planes, only 0.11 Å from the median plane of all six oxygen atoms, while in the other two structures it is "above" both O_3 planes, as hydrogen-bonding guests are in all other known structures of crown complexes. As indicated in the introduction, this finding belies arguments that the ammonium ion is *too large* to fit within the crown ring. The uniqueness of structure **1** seems to be a consequence of the fact that the $-NH_2$ group of the hydrazinium ion also interacts (although only weakly) by hydrogen bonding with crown oxygen atoms. These bonds are about 0.2 Å longer than the other NH···O bonds and are distinctly nonlinear (Table VII), both features a consequence of the elevation of the $-NH_2$ above the ring. One of these hydrogen bonds is very weakly bifurcated, involving also one perchlorate oxygen atom; this can be seen in Figure 1. Because of these interactions of the $-NH_2$ group, the N–N axis is tipped nearly 6° away from the normal to the best plane of the six ring oxygen atoms. The $-NH_3^+$ group is hydrogen bonded to the lower O_3 triangle, encircled by the crown ring; this structure particularly well illustrates nesting complexation. One additional factor that may help to draw the ammonium group into the ring is the fact that one perchlorate oxygen atom, O(24), lies just 3.03 Å below the N^+ atom, not far from the extension of the N–N line (see Figure 1). In contrast, the ammonium ion in the structure[1a] of 18-crown-6·NH_4Br·$2H_2O$ is weakly hydrogen bonded to a bromide ion lying above it.

The hydroxylammonium complex structure is held together not only by the interactions of the $-NH_3^+$ group with the ring, but by hydrogen bonds from the –OH group to a water molecule and from that water molecule to two perchlorate ions (well illustrated in Figure 4, and in part, in Figure 2). The disorder of the $-NH_3^+$ group is presumably related to the position of the N^+ atom, intermediate between the nesting position found in structure **1** and the almost classic "perching" position of structure **3** (see Figure 3). The view in Figure 2 shows the set of hydrogen atoms that could be definitely located. They are involved in bifurcated hydrogen bonds (Table VII) a finding that is not unexpected (although unique in this kind of system) in view of the position of the $-NH_3^+$ group relative to the oxygen planes (compare in Table VIII the relative positions of the N^+ and the upper and lower triangles of oxygens in structures **1**, **2**, and **3**). The N–O axis of the hydroxylammonium ion is tipped, again nearly 6°, away from the normal to the best plane of the six ring oxygens, in the direction of the water molecule (toward O(7) and C(6) of the ring). Both O–H···O hydrogen bonds in this structure are nearly linear (Table VII), and the water molecule is so oriented that the line from O(20), the hydroxylammonium oxygen atom, to it is only about 16° from a tetrahedral direction defined by the positions of the

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hydrogen atoms of the water molecule. This small departure from tetrahedrality is apparent in Figure 4.

Structure **3** exemplifies a perching interaction, with the $-NH_3^+$ group hydrogen bonded to the upper triangle of oxygens. The fact that the hydrogen atoms of this group were readily located and were refined without difficulty, despite the much lower precision and much higher molecular motion in this room-temperature structure, attests to the lack of disorder in the hydrogen-bonding pattern. The C–N axis of the methylammonium ion is tipped only 2° from the normal to the best plane of the six ring oxygens; there are no specific interactions or close contacts of the methyl group with other groups in the crystal, its nearest neighbors being three perchlorate oxygens at 3.52–3.74 Å and a methyl group of a neighboring methylammonium ion.

One indicator of the validity of individual atomic vibration parameters is the "rigid-bond test" suggested by Hirshfeld:[23] with data of the highest quality, the difference between the mean-square vibration amplitudes along the bonding direction for a pair of bonded atoms of comparable mass is no larger than about 0.0010 Å^2. If the average esd of the U values is not much larger than 0.0010 Å^2, this difference should be comparable with the esd or, more precisely, with the esd of the difference, evaluated along the direction of the interatomic line, a value normally somewhat greater than the esd of the individual U's. (When the average esd of the U values is many times larger, the data are manifestly unreliable.) A generalization of the rigid-bond test can be used[24] to test for rigidity of a molecule or molecular fragment, since rigidity implies that *all* interatomic distances within the moiety are invariant, not just those involving bonds. Table VI gives the results of applying these tests to the present structures. The average esd of the individual U values (given in the supplemental tables) is about 0.0011 Å^2 for structure **1**, about 0.0008 Å^2 for structure **2**, and close to 0.0040 Å^2 for structure **3**. Thus we might expect these tests for rigidity to be meaningful for the components of structures **1** and **2**, but not for those of **3**, and the data of Table VI support this view. For both **1** and **2**, the differences in mean-square vibration amplitudes for the bonds in the crown ring and in the perchlorate ion are small and comparable to the esd's of these differences. Furthermore, the differences are also small for pairs of nonbonded atoms within the crown ring and along the lines from the ammonium nitrogen atoms to the crown oxygen atoms. These results demonstrate clearly that the crown ring is itself essentially rigid and that the N^+ atom is held tightly in it. The rigidity of the crown rings in **1** and **2** is quite in contrast to the situation with uncomplexed 18-crown-6, for which there are significant internal torsional vibrations[25] in crystals, even at 100 K.

In each structure, the atom attached to N^+ (N in **1**, O in **2**) is vibrating much more than the crown atoms. The anisotropy of this vibration in structure **2** is especially noteworthy; the pattern of hydrogen bonding is such that one might anticipate that the hydroxyl oxygen atom would be vibrating much more in directions normal to the plane containing the N–O axis and the water oxygen atom than in this plane and normal to the N–O bond, and that is just what is found. The average excess mean-square vibration amplitude of O(20) relative to the ring atoms is about 0.0061 Å^2 in the plane and more than 3 times as great, about 0.0197 Å^2, normal to it. The second N atom of the hydrazinium ion in **1**, N(20), is also vibrating more than the ring atoms, but the difference is smaller and less anisotropic, presumably because this atom is to some extent restrained by the weak N–H···O bonds (see Figure 1 and Table VII).

As mentioned at the start, the thermal parameters for structure **3** are of such low precision and accuracy (among other reasons because no absorption correction was made) that they indicate little, except in a most general way. Even with these poor data, however, the results in Table VI suggest that the methyl group, C(20), is much freer to move than are the ring atoms, as anticipated. Its motion relative to the ring atoms has little apparent anisotropy. The situation of the $-NH_3^+$ in **3** is much like that of the $-NH_3^+$ in the recently reported[1c] structure of the complex of 18-crown-6 with benzylammonium thiocyanate.

We had noticed[21] in several earlier structural studies of $-NH_3^+$ complexes of various crownlike hosts that there was a significant difference in mean-square vibration amplitudes along $N^+\cdots O$ lines in hydrogen-bonding and nonhydrogen-bonding directions, the former being much smaller. However, we do not find any such effect in the present structures. Another aspect of the $N^+\cdots O$ interaction that has been discussed in a number of places[1b,2b,21] concerns the orientation of the $N^+\cdots O$ line relative to the crown-ether oxygen atom and its attached carbon atoms. The generalization made on the basis of most previous studies of the interactions of $-NH_3^+$ groups with a great variety of hosts was that the $N^+\cdots O$ line tended to be oriented very near the tetrahedral direction at the O atom for nonhydrogen-bonding interactions and a little closer to the trigonal than the tetrahedral direction at the O for the hydrogen-bonding $N^+\cdots O$ lines. Table VIII gives the average angles for these interactions in the present structures, presented, however, in terms of the upper and lower triangles of oxygen atoms. The hydrogen bonding is to the lower triangle in **1**, to both upper and lower triangles in **2**, and to the upper triangle in **3**.

Structure **3** is in accord with the generalization cited above—the $N^+\cdots O$ line is nearly in the tetrahedral direction for the oxygens of the lower triangle, the nonhydrogen-bonded set of oxygen atoms. However, the results for **1** and **2** belie the generalization. Study of Figures 1–3 or of a model of 18-crown-6 in its conformation in these structures suggests that the primary factor governing the geometry of the interaction at the ether oxygen atoms is the depth of penetration of the $-NH_3^+$ group, irrespective of whether hydrogen bonding is involved. For *perching* complexes (such as **3** and all those previously studied), with hydrogen bonding to the upper triangle, the hydrogen-bonding $N^+\cdots O$ line necessarily points nearer the trigonal than the tetrahedral direction at oxygen because the C–O–C planes are tipped upward, toward the N^+. On the other hand, the nonhydrogen-bonding $N^+\cdots O$ line, directed at the lower oxygens, comes close to the tetrahedral direction at these atoms because the C–O–C planes are tipped down and away from the N^+. In contrast, for a $-NH_3^+$ group in the *nesting* position near the center of the ring, as in **1**, all the C–O–C planes are tipped away from the N^+, and the $N^+\cdots O$ lines come close to the tetrahedral directions at all six oxygen atoms. For structure **2**, with the NH_3^+ well above the upper triangle, the geometry of the $N^+\cdots O$ interactions at the oxygen atoms is close to that of **3** and other truly perching structures. There may, of course, also be minor effects of the position of the N^+ and the hydrogen bonds on the C–C and C–O torsion angles of the crown ring, which in turn will have minor effects on the orientation of the $N^+\cdots O$ lines at the oxygen atoms.

For an approximately fixed set of bond distances, bond angles, and C–O torsion angles in an 18-crown-6 molecule in the conformation observed in the present structures, an increase in the C–C torsion angle will result in increases in the separation of the upper and lower triangles of oxygen atoms and in the separation of oxygen atoms within each triangle. Such an effect is evident in Table VIII, and similar trends are found with data for other 18-crown-6 complexes,[3,21,26] although small variations in the C–O torsion angles and in other geometric parameters make exact comparisons impossible. We do not yet see just what factors govern the particular values of the C–C torsion angles and the corresponding separation between the O_3 planes in any particular structure.

18-Crown-6 forms 1:2 host-guest complexes with the neutral molecules dinitrophenylhydrazine,[27] benzenesulfonamide,[28] and

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dimethylsulfone,[29] as well as with the guanidinium ion.[30] In each structure, the two guest molecules approach from the opposite sides of the crown ring, with N–H···O or C–H···O hydrogen bonds stabilizing the interaction. The 18-crown-6 ring in the sulfonamide complex has an elliptical shape, with a conformation different from that of the uncomplexed molecule[25] and from that found here, although all C–C torsion angles are gauche, near 66°. The 18-crown-6 ring in the guanidinium complex[30] has also a conformation different from that of the uncomplexed molecule and that found here, with the guanidinium ions tipped at rather high angles to the median crown plane and each joined to the crown ring by only a single hydrogen bond. The crown ring in the dinitrophenylhydrazine complex[27] has the nearly ideal crown conformation; each ring oxygen is involved in a N–H···O hydrogen bond. In the complex with dimethylsulfone,[29] one methyl group of each dimethylsulfone molecule is more or less centered over the crown ring, which also has the nearly ideal crown conformation. This arrangement is similar to that in the complex of 18-crown-6 with dimethyl acetylenedicarboxylate.[26] Cationic repulsion would make such an arrangement of two perching RNH_3^+ groups on opposite faces of a single crown ring unstable.

Molecular and Ionic Packing. We have commented already on some features of the packing in these structures; that for **2** is illustrated in Figure 4. There are no unusually short contacts in any of the structures. In each structure the shortest apparent intermolecular H···H distances are around 2.25–2.4 Å, but their significance is questionable because the hydrogen positions are of limited precision and are on the average about 0.1 Å too close to the atoms to which the hydrogens are bonded, as is common with X-ray structure determinations. The shortest intermolecular C···O distances are in the range 3.24–3.4 Å, usually involving perchlorate oxygen atoms, and do not seem of any particular significance.

Conclusion. Our principal findings are as follows. (1) Despite arguments that an ammonium or substituted ammonium ion is too large to fit into an 18-crown-6 ring, it can readily move almost to the center of the ring, as in the hydrazinium complex, if its stability in such a position is even moderately enhanced by other interactions. (2) The 18-crown-6 ring in the present structures for which we were able to measure vibrational parameters precisely is itself rigid and holds the $-NH_3^+$ group firmly as well. The atoms attached to the $-NH_3^+$ group undergo considerably greater motion, in directions predictable from their patterns of hydrogen bonding. (3) The orientation of the N^+···O line relative to the tetrahedral and trigonal directions at each C–O–C group of a crown ring is governed primarily by the depth of penetration of the NH_3^+ into the ring, irrespective of the disposition of hydrogen bonds to the ring oxygen atoms.

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Supplementary Material Available: The *U* values for all anisotropic atoms (Tables IIA, IIB, IIC), observed and calculated structure factors (amplitudes for **1**) (Tables IIIA, IIIB, IIIC), and values of individual bond lengths, bond angles, and torsion angles (Tables IVA, IVB, and IVC) (84 pages). Ordering information is given on any current masthead page.

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Complete Kinetic Analysis of the Thermal Stereomutations of (+)-(1*S*,2*S*,3*R*)-*r*-1-Cyano-*t*-2-methyl-1,2,*t*-3-trideuteriocyclopropane

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Abstract: (+)-(1*S*,2*S*,3*R*)-*r*-1-Cyano-*t*-2-methyl-1,2,*t*-3-trideuteriocyclopropane has been synthesized in optically pure form. The kinetics of thermal stereomutations which interconvert this and seven other isomeric cyclopropanes have been followed: at 335.4 °C in the gas phase, the title compound undergoes stereomutations with rate constants ($\times 10^5$ s) $k_1 = 0.55$, $k_2 = 0.61$, $k_3 = 0.10$, $k_{12} = 0.88$, $k_{13} = 0.083$, and $k_{23} = 0$; the *cis*-1-cyano-2-methyl-1,2,3-trideuteriocyclopropanes exhibit stereomutation rate constants ($\times 10^5$ s) $k'_1 = 0.62$, $k'_2 = 0.69$, $k'_3 = 0.15$, $k'_{12} = 1.31$, $k'_{13} = 0.09$, and $k'_{23} = 0$. While cyclopropanes 1,2-disubstituted with potent radical-stabilizing groups such as phenyl, cyano, and vinyl give stereomutation products by way of C(1)–C(2) bond cleavage only, the deuterium-labeled 1-cyano-2-methylcyclopropanes experience thermal stereomutations consistent with the intermediacy of two distinct trimethylene diradicals, one formed through cleavage of the C(1)–C(2) bond, the other by breaking C(1)–C(3).

Even though the thermal stereomutations of cyclopropanes have been studied most intensively, they remain imperfectly understood.[1] These stereomutations may involve epimerization at one carbon, or at two carbons simultaneously; which of the two types of epimerization predominates in a given cyclopropane is often hard to rationalize in conformity with existing theory and cannot in general be predicted.[1,2]

Earlier experimental studies with unconstrained cyclopropanes have frequently been interpreted with the aid of an assumption: that only processes arising from cleavage of the most substituted

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