

## A Host–Guest Complex: *tert*-Butylammonium Perchlorate Complex of 3,6,9,12,15-Pentaoxa-21-azabicyclo[15.3.1]heneicosa-1(20),17,19-triene (Monopyrido-18-crown-6) at 113 K

BY EMILY MAVERICK, LINDA GROSSENBACHER AND K. N. TRUEBLOOD

*Department of Chemistry, University of California, Los Angeles, California 90024, USA*

(Received 12 December 1978; accepted 3 May 1979)

**Abstract.**  $C_{15}H_{23}NO_5 \cdot C_4H_{12}N^+ \cdot ClO_4^-$ , orthorhombic,  $Pna2_1$ ,  $a = 12.309$  (2),  $b = 20.821$  (3),  $c = 9.237$  (1) Å,  $U = 2367.2$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.321$  Mg m<sup>-3</sup>. Least-squares refinement for 2568 reflections (measured at 113 K) gave a final discrepancy index  $R(F) = 0.038$ . The crown-ether *tert*-butylammonium cation complex has approximate  $m$  symmetry; the *tert*-BuNH<sub>3</sub><sup>+</sup> forms hydrogen bonds to two O atoms and the pyridine N atom in the macrocyclic ring.

**Introduction.** The title compound is an example of a host–guest complex for which several structures appear to be possible (Newcomb, Timko, Walba & Cram, 1977): the *tert*-butylammonium ion might form H-bonds to three O atoms in the crown-ether ring, or to the pyridine N atom and two of the O atoms, and the pyridine ring might tip toward the *tert*-BuNH<sub>3</sub><sup>+</sup> ('nesting') or away from it ('perching' conformation: Moore, Tarnowski, Newcomb & Cram, 1977; Newcomb, Moore & Cram, 1977). The present crystal-structure analysis was undertaken because of the importance of the compound in studies of the free energy of host–guest binding.

Single crystals were supplied by S. S. Moore and D. J. Cram. The intensities for a nearly cubic crystal with sides 0.4 mm were measured on a Syntex automated diffractometer, with graphite-monochromatized Mo  $K\alpha$  radiation, at 113 K (Strouse, 1976). The systematic absences ( $Ok\ell$ ,  $k + \ell$  odd;  $h0\ell$ ,  $h$  odd) indicated that the space group was  $Pna2_1$  or  $Pnam$ . A little more than a complete octant of reflections to  $2\theta = 55^\circ$  ( $\sin \theta/\lambda = 0.65$  Å<sup>-1</sup>) included 3476 intensity measurements. Of these, 2903 were unique and 2568 had  $F \geq 3\sigma(F)$ ; the latter were used in the subsequent refinement of the structure.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Intensity statistics suggested a non-centrosymmetric space group, and the analysis confirmed the choice of  $Pna2_1$ . 15 of the 31 heavy atoms were located on the  $E$  map and were used in a Fourier synthesis; the remaining 16 atoms appeared on the map in their correct positions. Isotropic full-matrix least-squares

refinement converged at  $R = 0.10$ . All but three H atoms were located on a difference map at this stage; positions for the others were calculated. Anisotropic refinement of heavy atoms and isotropic refinement of H atoms led to a final agreement factor  $R = 0.038^*$  ( $R = 0.050$  for all reflections). At convergence, the error of fit was 1.17; with the scale factor, a total of 420 parameters were refined. No absorption correction was made. A final difference map showed no peaks of height greater than  $0.2 e \text{ \AA}^{-3}$ .

Fig. 1 illustrates the structure of the complex of the *tert*-butylammonium ion with the macrocycle and shows the torsion angles around the macrocycle and the numbering of the atoms in the cation. Fig. 2 shows that the complex has the 'perching' conformation and demonstrates the displacement of the ammonium N(22) atom from the least-squares plane of the hetero-

\* Scattering factors for N, O, C<sub>val</sub>, Cl and bonded H were taken from *International Tables for X-ray Crystallography* (1974).

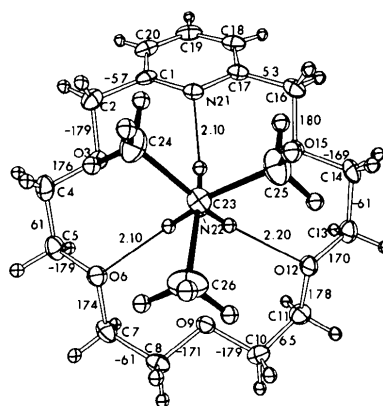


Fig. 1. A perspective view of the monopyrido-18-crown-6-*tert*-butylammonium ion complex. The numbering of the atoms and the torsion angles ( $^\circ$ ) around the macrocycle are shown; the average estimated standard deviation of a torsion angle is  $0.3^\circ$ . The H-bond distances N(21)···H(22A), O(12)···H(22B), and O(6)···H(22C) have estimated standard deviations of about 0.04 Å. Solid bonds are used for H-bonds and for the bonds in the *tert*-butylammonium ion; thermal ellipsoids enclose 50% probability (Johnson, 1965).

atoms in the macrocycle. It also shows the numbering in the  $ClO_4^-$  ion. Bond distances and angles around the ring are shown in Fig. 3, together with the  $N(22) \cdots O$  and  $N(22) \cdots N(21)$  distances. Atomic positions are given in Tables 1 and 2.\*

Distances and angle ranges for the  $tert$ - $BuNH_3^+$  and perchlorate ions are given in Table 3.

**Discussion.** The macrocycle–cation complex nearly has  $m$  symmetry. This can be most clearly seen in Fig. 1, which also shows the torsion-angle pattern to be nearly synclinal about C–C bonds, nearly antiplanar about C–O bonds, as found in most parts of other crown-ether complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974; Goldberg, 1978; Mercer & Truter, 1973). The geometry about the  $tert$ - $BuNH_3^+$  N atom,

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34394 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

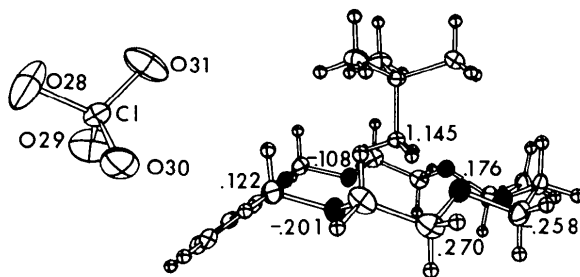


Fig. 2. A view of the asymmetric unit, including the numbering of atoms in the  $ClO_4^-$  ion, the displacements (Å) of the heteroatoms in the ring [N(21), O(3), O(6), O(9), O(12) and O(15)] from their least-squares plane, and the displacement from that plane of N(22). O(3) and O(6) are nearer the viewer. The pyridine ring (left) is tilted away from the  $tert$ - $BuNH_3^+$ . The equation of the least-squares plane of the heteroatoms is  $0.0933X - 0.8556Y + 0.5091Z - 0.3485 = 0$ , where  $X$ ,  $Y$  and  $Z$  are orthogonal coordinates (Å) parallel to  $a$ ,  $b$  and  $c$ . Thermal ellipsoids enclose 50% probability.

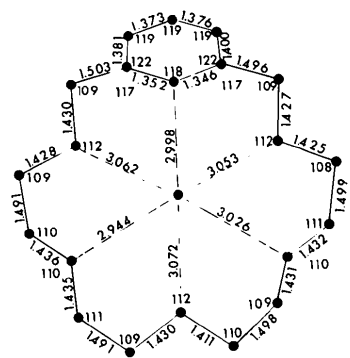


Fig. 3. Distances (Å) and angles ( $^\circ$ ) in the macrocycle. Angles have e.s.d.'s of  $0.2^\circ$ ; they are rounded to the nearest degree for clarity. Bond lengths have e.s.d.'s of  $0.003$ – $0.004$  Å. Dashed lines are  $N \cdots N(22)$  and  $O \cdots N(22)$  distances: e.s.d.  $0.003$  Å.

Table 1. Atomic fractional coordinates ( $\times 10^4$ ) for C, N, O and Cl (e.s.d.'s are in parentheses)

	x	y	z
C(1)	2644 (2)	763 (1)	3639 (3)
C(2)	2078 (2)	624 (2)	2232 (4)
O(3)	989 (2)	425 (1)	2539 (2)
C(4)	406 (3)	274 (2)	1247 (3)
C(5)	-690 (3)	26 (2)	1647 (4)
O(6)	-1278 (2)	513 (1)	2422 (2)
C(7)	-2331 (3)	280 (2)	2835 (4)
C(8)	-2904 (2)	754 (1)	3773 (4)
O(9)	-2284 (1)	849 (1)	5065 (3)
C(10)	-2855 (2)	1212 (2)	6106 (4)
C(11)	-2162 (2)	1306 (2)	7423 (4)
O(12)	-1233 (2)	1684 (1)	7048 (2)
C(13)	-582 (3)	1803 (2)	8305 (3)
C(14)	486 (3)	2095 (2)	7886 (4)
O(15)	1040 (2)	1651 (1)	6973 (3)
C(16)	2146 (2)	1828 (1)	6737 (4)
C(17)	2674 (2)	1341 (1)	5775 (4)
C(18)	3645 (2)	1044 (1)	6195 (4)
C(19)	4102 (2)	595 (1)	5287 (4)
C(20)	3600 (2)	454 (2)	3997 (4)
N(21)	2178 (2)	1205 (1)	4514 (3)
N(22)	-180 (2)	1520 (1)	4111 (3)
C(23)	-288 (2)	2141 (1)	3265 (3)
C(24)	441 (3)	2091 (2)	1950 (4)
C(25)	66 (3)	2685 (1)	4248 (4)
C(26)	-1478 (3)	2221 (2)	2834 (4)
Cl	4698 (1)	1168 (0.3)	99*
O(28)	5465 (2)	1257 (2)	-1030 (4)
O(29)	5231 (3)	1162 (1)	1465 (3)
O(30)	4141 (2)	577 (1)	-139 (3)
O(31)	3926 (2)	1680 (1)	35 (4)

\* Not refined; fixes the origin on the polar axis.

N(22), is very similar to those about  $Rb^+$  and  $NH_4^+$  in the 18-crown-6 complexes of  $RbNCS$  (Dunitz *et al.*, 1974) and  $NH_4Br$  (Nagano, Kobayashi & Sasaki, 1978). The heteroatoms in the macrocycle fall into two groups; they are displaced alternately above [O(6), O(12), N(21)] and below [O(3), O(9), O(15)] their least-squares plane (Fig. 2). N(22) is situated  $1.14$  Å above that plane; the corresponding displacements are  $1.00$  Å in the  $NH_4^+$  complex and  $1.19$  Å in the  $Rb^+$  complex. The H atoms of the  $-NH_3^+$  group lie along the lines joining N(22) to O(6), O(12) and N(21); the other three heteroatoms are slightly further away from N(22) (Fig. 3). Thus all six electron-donor atoms approach either the H or the N of the  $-NH_3^+$  because of the *gauche* C–C torsion angles around the ring (Timko, Moore, Walba, Hiberty & Cram, 1977). The arrangement of the electron-donor heteroatoms may also be described in terms of their nominal electron-pair geometry (Mercer & Truter, 1973). Each of the vectors  $N(22) \cdots O$  to the non-hydrogen-bonded atoms O(3), O(9), and O(15) lies essentially in the plane bisecting the corresponding C–O–C angle (Fig. 3) and is oriented very nearly at the tetrahedral angle to the

Table 2. Atomic fractional coordinates ( $\times 10^3$ ) for H atoms (e.s.d.'s are in parentheses)

	x	y	z
H(2A)	208 (3)	100 (1)	171 (4)
H(2B)	245 (2)	34 (1)	167 (3)
H(4A)	37 (3)	65 (2)	65 (4)
H(4B)	79 (2)	-7 (1)	72 (4)
H(5A)	-111 (2)	-10 (1)	75 (4)
H(5B)	-64 (2)	-34 (1)	224 (3)
H(7A)	-273 (3)	22 (1)	205 (4)
H(7B)	-227 (2)	-9 (1)	337 (4)
H(8A)	-361 (3)	62 (1)	401 (4)
H(8B)	-300 (2)	116 (1)	328 (3)
H(10A)	-353 (3)	104 (1)	639 (3)
H(10B)	-308 (3)	161 (2)	571 (4)
H(11A)	-257 (3)	150 (2)	822 (4)
H(11B)	-194 (2)	88 (1)	782 (4)
H(13A)	-93 (2)	208 (1)	893 (4)
H(13B)	-46 (3)	139 (2)	879 (4)
H(14A)	39 (3)	253 (2)	742 (3)
H(14B)	85 (3)	218 (2)	875 (4)
H(16A)	214 (2)	225 (1)	630 (3)
H(16B)	247 (3)	185 (1)	762 (4)
H(18)	393 (3)	115 (2)	710 (5)
H(19)	473 (3)	40 (2)	558 (4)
H(20)	391 (3)	18 (2)	342 (4)
H(22A)	54 (3)	145 (1)	427 (4)
H(22B)	-49 (3)	153 (2)	491 (5)
H(22C)	-46 (3)	121 (2)	366 (4)
H(24A)	41 (3)	250 (2)	145 (4)
H(24B)	24 (2)	176 (2)	139 (4)
H(24C)	117 (3)	203 (2)	220 (4)
H(25A)	4 (3)	311 (2)	373 (4)
H(25B)	76 (3)	263 (2)	454 (4)
H(25C)	-39 (3)	271 (2)	508 (5)
H(26A)	-155 (3)	260 (2)	234 (4)
H(26B)	-193 (3)	223 (2)	372 (4)
H(26C)	-172 (2)	188 (1)	226 (3)

C—O vectors at each O atom (Table 3), pointing at the presumed position of one of the unshared electron pairs. The deviations from the tetrahedral angle average only 2°. On the other hand, the vectors from N(22) to the H-bonded atoms N(21), O(6), and O(12), while also lying very nearly in the planes bisecting the respective C—X—C angles, make angles averaging 32° with the tetrahedral direction (and 23° with the trigonal direction) at X. The hydrogen bonds are essentially linear, the N—H...O and N—H...N angles lying between 172 and 175°.

Fig. 3 shows that most chemically equivalent bond distances (and bond angles) agree very well. We have no explanation for the apparent discrepancy between C(1)—C(20) (1.381 Å) and C(17)—C(18) (1.400 Å), or that between C(8)—O(9) (1.430 Å) and O(9)—C(10) (1.411 Å), each nearly five times the respective e.s.d.

The three separate fragments of the molecule (macrocycle, *tert*-BuNH<sub>3</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup>) were treated as rigid bodies in an analysis of their thermal motion (Schomaker & Trueblood, 1968) (Table 4). The

Table 3. Some distances (Å) and angles (°) with e.s.d.'s in parentheses

	Only distances and angles not shown in Fig. 3 are given here.		
	Uncorrected	Corrected for thermal motion*	
N(22)—C(23)	1.516 (3)	1.518	
C(23)—C(24)	1.513 (4)	1.520	
C(23)—C(25)	1.515 (4)	1.524	
C(23)—C(26)	1.528 (4)	1.536	
Cl—O(28)	1.419 (3)	1.462	
Cl—O(29)	1.421 (3)	1.447	
Cl—O(30)	1.425 (2)	1.460	
Cl—O(31)	1.429 (2)	1.461	
N—H	(av.) 0.86 (4) (range 0.83–0.91)		
Aromatic C—H	(av.) 0.90 (3) (range 0.87–0.93)		
Aliphatic C—H	(av.) 0.95 (4) (range 0.88–1.01)		
C—C(23)—C	(av.) 111.1 (2) (range 110.5–111.5)		
C—C(23)—N(22)	(av.) 107.8 (2) (range 107.6–108.1)		
O—Cl—O	(av.) 109.5 (2) (range 108.5–110.6)		
N(22)...O(3)—C(2)	109	N(22)...O(6)—C(5)	122
...O(3)—C(4)	109	...O(6)—C(7)	121
...O(9)—C(8)	106	...O(12)—C(11)	120
...O(9)—C(10)	112	...O(12)—C(13)	120
...O(15)—C(14)	110	...N(21)—C(1)	119
...O(15)—C(16)	111	...N(21)—C(17)	120

\* See Table 4 and Discussion.

differences in the mean-square vibration amplitudes for bonded atoms along the bonding directions (Hirshfeld, 1976) are small, comparable to their e.s.d.'s, indicating that the 'thermal' vibration parameters are meaningful. The macrocycle does not fit the rigid-body model particularly well; however, the librational motion is small (maximum amplitude about 2°). For the *tert*-BuNH<sub>3</sub><sup>+</sup>, the maximum libration, nearly 6°, is about an axis at an angle of only 7° to the N(22)—C(23) bond; bond-length corrections are at the border of significance (Table 3). As suggested by the orientation of the ellipsoids of the methyl C atoms (Fig. 1), most of this apparent motion of the *tert*-BuNH<sub>3</sub><sup>+</sup> can be ascribed to a torsional libration about the N—C bond. Analysis of this motion (Trueblood, 1978) in the *tert*-BuNH<sub>3</sub><sup>+</sup>—macrocycle complex showed that it has an r.m.s. amplitude of 5.5° (Table 4). We have found similar torsional librations in other *tert*-BuNH<sub>3</sub><sup>+</sup> crown-ether complexes, with r.m.s. amplitudes ranging from around 4° (Goldberg, 1975) to as much as 11° (Trueblood & Maverick, unpublished).

One unexpected finding relates to the differences in the mean-square vibration amplitudes of the amino N atom and the ether O (or pyridyl N) atoms along the lines between them. For the three hydrogen-bonded contacts, these differences are all small, averaging 0.0007 Å<sup>2</sup>; for the other three N...O directions the differences are large, averaging 0.0053 Å<sup>2</sup>, more than twice their e.s.d.'s. The same pattern is found in the *tert*-BuNH<sub>3</sub><sup>+</sup> complex studied by Goldberg (1975), the

Table 4. Results of the thermal-motion analysis

Eigenvectors are given as direction cosines parallel to the crystal axes.  $\Omega$  is the mean-square amplitude of libration of the *tert*-butyl group about the N(22)–C(23) bond. Coordinates of the center of mass are in the crystal system. **T** is the reduced **T** (Schomaker & Trueblood, 1968). The eigenvalues and eigenvectors for the macrocycle taken alone were similar to those given in (a), the average deviation of corresponding vectors being 7°. Note the interchange of the first two eigenvectors of **L** between (a) and (b). The improvement in fit in (a) relative to (b) is highly significant (Trueblood, 1978).

	Eigenvalues	Eigenvectors	Center of mass	
Complex of pyridine crown and <i>tert</i> -BuNH <sub>3</sub> <sup>+</sup> (26 atoms)				
(a) With internal torsion about N(22)–C(23) bond	<b>L</b>	4.0 (2) (°) <sup>2</sup>	0.274, -0.768, 0.579	x = 0.0396
		3.4 (4)	0.961, 0.239, -0.139	y = 0.1224
		1.0 (2)	-0.032, 0.594, 0.804	z = 0.4516
	<b>T</b> × 10 <sup>4</sup>	184 (7) Å <sup>2</sup>	0.710, -0.649, 0.273	
		155 (7)	0.307, -0.064, -0.949	
		132 (7)	0.634, 0.758, 0.154	
<b>Ω</b>	31 (3) (°) <sup>2</sup>	(-0.088, 0.852, -0.516)		
$\langle(\Delta U)^2\rangle^{1/2} = 0.0024 \text{ \AA}^2$ , weighted $R = 0.130$				
(b) Without internal torsion	<b>L</b>	4.4 (5) (°) <sup>2</sup>	0.995, 0.103, -0.008	
		3.9 (3)	-0.086, 0.777, -0.624	
		1.7 (3)	-0.059, 0.621, 0.781	
	<b>T</b> × 10 <sup>4</sup>	174 (9) Å <sup>2</sup>	0.809, -0.574, -0.127	
		159 (10)	-0.211, -0.081, -0.974	
		123 (10)	0.549, 0.815, -0.186	
$\langle(\Delta U)^2\rangle^{1/2} = 0.0031 \text{ \AA}^2$ , weighted $R = 0.172$				
ClO <sub>4</sub> <sup>-</sup> (5 atoms)	<b>L</b>	139 (3) (°) <sup>2</sup>	0.812, -0.070, 0.580	x = 0.4692
		62 (2)	0.039, 0.997, 0.065	y = 0.1169
		33 (2)	-0.582, -0.030, 0.812	z = 0.0084
	<b>T</b> × 10 <sup>4</sup>	288 (3) Å <sup>2</sup>	0.848, -0.437, 0.300	
		214 (5)	0.528, 0.751, -0.398	
		156 (4)	-0.052, 0.496, 0.867	
$\langle(\Delta U)^2\rangle^{1/2} = 0.0006 \text{ \AA}^2$ , weighted $R = 0.016$				

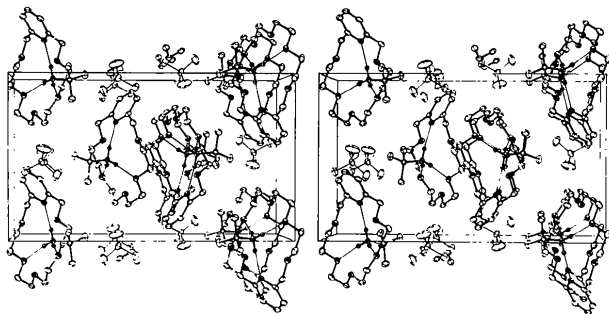


Fig. 4. Stereoview of the packing of the crown-cation complexes and the ClO<sub>4</sub><sup>-</sup> counterions. The drawing includes more than the complete unit cell, in order to show complete molecules. Line bonds are used in the ClO<sub>4</sub><sup>-</sup> ion and for H-bonds in the complex. Other H atoms are omitted; ring heteroatoms are shaded. The crystal axis **a** is vertical, **b** horizontal, **c** is directed away from the viewer. The cavity surrounding the ClO<sub>4</sub><sup>-</sup> ion can best be seen on the right side of the drawing, halfway up **a** (see text).

corresponding values being 0.0014 and 0.0043 Å<sup>2</sup>, and in a number of other structures we have studied, implying a rigidity of the hydrogen bond and a looseness of the other interaction.

The ClO<sub>4</sub><sup>-</sup> ion fits the rigid-body model very well; the apparent motion is large, but this might reflect static

disorder. The eigenvector corresponding to the largest eigenvalue (an amplitude of libration of about 12°) makes an angle of 27° with the Cl–O(29) bond, and an angle of 96° with the normal to the plane of the pyridine ring. The ion lies in a cavity best described by the shortest distances between the respective perchlorate O atoms and neighboring C atoms: O(28)···C(11) 3.25, O(29)···C(8) 3.25, O(30)···C(19) 3.28, and O(31)···C(26) 3.49 Å (see Fig. 4). The negative ion may thus have some freedom to move within this cavity. The corrected Cl–O bond lengths (average 1.458 Å, e.s.d. 0.007 Å) agree well with the corrected distances in the precisely determined structure (Berglund, Thomas & Tellgren, 1975) of NaClO<sub>4</sub>·H<sub>2</sub>O (uncorrected, 1.426 Å; corrected, 1.457 Å). Many recently reported structures containing ClO<sub>4</sub><sup>-</sup> give precise uncorrected distances around 1.42–1.43 Å; because thermal parameters are usually not now published, we cannot conveniently calculate distances for these structures.

This work was supported in part by National Science Foundation Grants 72-04385 and GP-28248. The authors are grateful to Stephen S. Moore and Professor

D. J. Cram for the crystals, to Dr Carolyn Knobler for helpful discussions, and to the UCLA Office of Academic Computing.

### References

- BERGLUND, B., THOMAS, J. O. & TELLGREN, R. (1975). *Acta Cryst.* **B31**, 1842–1846.
- DUNITZ, J. D., DOBLER, M., SEILER, P. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2733–2738.
- GOLDBERG, I. (1975). *Acta Cryst.* **B31**, 2592–2600.
- GOLDBERG, I. (1978). *Acta Cryst.* **B34**, 2224–2228.
- HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 73, 75, 102. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MERCER, M. & TRUTER, M. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2215–2220.
- MOORE, S. S., TARNOWSKI, T. L., NEWCOMB, M. & CRAM, D. J. (1977). *J. Am. Chem. Soc.* **99**, 6398–6405.
- NAGANO, O., KOBAYASHI, A. & SASAKI, Y. (1978). *Bull. Chem. Soc. Jpn.* **51**, 790–793.
- NEWCOMB, M., MOORE, S. S. & CRAM, D. J. (1977). *J. Am. Chem. Soc.* **99**, 6405–6410.
- NEWCOMB, M., TIMKO, J. M., WALBA, D. M. & CRAM, D. J. (1977). *J. Am. Chem. Soc.* **99**, 6392–6398.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STROUSE, C. E. (1976). *Rev. Sci. Instrum.* **47**, 871–876.
- TIMKO, J. M., MOORE, S. S., WALBA, D. M., HIBERTY, P. C. & CRAM, D. J. (1977). *J. Am. Chem. Soc.* **99**, 4207–4219.
- TRUEBLOOD, K. N. (1978). *Acta Cryst.* **A34**, 950–954.

*Acta Cryst.* (1979). **B35**, 2237–2241

## 1,9-Dimethyladeninium Chloride\*

BY CHIAN C. CHIANG, LEON A. EPPS, LUIGI G. MARZILLI AND THOMAS J. KISTENMACHER  
*Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, USA*

(Received 8 February 1979; accepted 23 April 1979)

**Abstract.** C<sub>7</sub>H<sub>10</sub>N<sub>5</sub><sup>+</sup> · Cl<sup>-</sup>, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 17.474 (4), *b* = 13.718 (4), *c* = 7.639 (2) Å, β = 96.03 (2)°, *V* = 1820.9 Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.46 (1), *D<sub>c</sub>* = 1.46 Mg m<sup>-3</sup>. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms included but not refined) based on 3439 counter-collected *F<sub>o</sub>*'s led to final *R* and weighted *R* values of 0.076 and 0.054 respectively. The two crystallographically independent 1,9-dimethyladeninium cations are related by a pseudo center of symmetry and form hydrogen-bonded dimers in the crystal. The exocyclic amino group of one of the cations donates a hydrogen bond to the imidazole-ring nitrogen atom N(7) of the other cation and *vice versa*. Several interactions of the type *D*—H ··· Cl<sup>-</sup> are noted between the purine cations and the chloride anions.

**Introduction.** Chiang, Epps, Marzilli & Kistenmacher (1979) have recently determined the crystal and molecular structure of a cobalt(III) complex containing the 1,9-dimethyladeninium cation as a ligand in an

initial attempt at elucidating the metal-coordination properties of N(1)-alkylated purines. Such N(1)-alkylated purines are to be found in natural, biologically important systems, including some tRNA's (McCloskey & Nishimura, 1977; Rich, 1977). Many of these N-methylated purines are located in essentially invariant and pivotal regions of tRNA (McCloskey & Nishimura, 1977). In one important example (Rich, 1977), it was found that N(1)-methylated adenosine occurs at residue 58 in the TC loop of tRNA<sup>Phe</sup> and this 1-methyladenosine residue is hydrogen bonded to a thymidine base (residue 54 in the TC loop) *via* a reversed Hoogsteen scheme (Hoogsteen, 1963). This reversed loop hydrogen bonding clearly plays a major role in determining the tertiary structure of tRNA<sup>Phe</sup>, but it is unknown as to whether such intraloop hydrogen bonding affects the functional behavior of various tRNAs. In this paper, we present a structural analysis of the uncomplexed 1,9-dimethyladeninium cation, as the chloride salt, in the course of our studies on the effects on the molecular structural parameters in purine ligands owing to metal coordination (Kistenmacher & Marzilli, 1977) and to probe further the nature of the

\* This investigation was supported by the National Institutes of Health, Public Health Service Grant No. GM 20544.