Crystal Structure of the Dihydroperchlorate of 1,4,8,11-Tetra-azacyclotetradecane (Cyclam)

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Three-dimensional crystal structure analysis by Patterson and Fourier methods has shown that the title compound consists of centrosymmetrical cations, two of the nitrogen atoms being protonated, and perchlorate ions. There is one formula unit $[C_{10}H_{26}N_4][ClO_4]_2$ in a triclinic unit cell of dimensions a = 8·081(3), b = 8·657(3), c = 8·219(2) Å, α = 119·23(2), β = 95·05(3), γ = 111·37(2)°, space group $P\bar{1}$. Refinement by least-squares gave R 0·049 on 1009 diffractometer observations. In the perchlorate ion mean Cl–O is 1·405(3) Å, uncorrected for libration. The cationic ring contains two centrosymmetrically related protonated nitrogen atoms (N–C 1·504 and 1·490, N–H 0·94 and 0·99 Å), and two secondary amine nitrogen atoms (N–C 1·464 and 1·470, N–H 0·91 Å). An approximately tetrahedral arrangement about the latter type is completed by a hydrogen atom from the former type which may be forming a weak hydrogen bond. Evidence for N–H · · · O hydrogen bonding is equivocal.

INVESTIGATION of the behaviour of lithium salts with 1,4,8,11-tetra-azacyclotetradecane (cyclam) revealed a complicated situation because of the tendency of the lithium salts to undergo hydrolysis in warm methanol yielding the [dihydronium(cyclam)]$^{2+}$ cation and lithium hydroxide.[1] This was resolved partly by chemical investigation and partly by the crystal-structure analysis described here.

Cyclam dihydroperchlorate, for crystallographic investigation, was prepared initially as a by-product of the reaction between lithium perchlorate and cyclam in warm methanol; two crystalline forms α and β were obtained from the same solution which also yielded a lithium perchlorate : cyclam (1 : 1) complex, lithium hydroxide, and lithium perchlorate trihydrate.

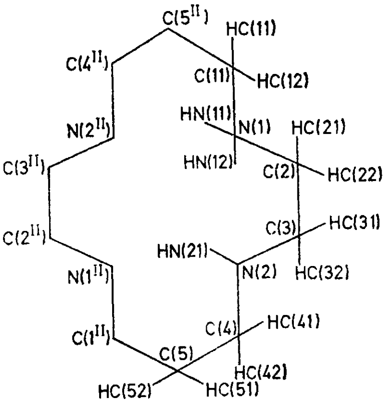

FIGURE 1 The designation of the atoms, including hydrogen, in the crystal chemical unit of [H$_2$cyclam]$^{2+}$, and an indication of the centrosymmetrically related half of the molecule, without hydrogen atoms; the Roman numeral superscript II indicates the centrosymmetrical relation.

A less equivocal synthesis was later achieved from cyclam and excess of perchloric acid in methanol, the first product being the tetrahydroperchlorate which on warming with cyclam in equimolar ratio in methanol yielded the α- and β-forms of the dihydroperchlorate. All crystals of the β-form were twinned monoclinic with four formula units in the asymmetric unit.

Crystals of the α-form proved suitable for crystal-structure analysis, having one formula unit in a triclinic unit cell. One perchlorate ion and half a [H$_2$cyclam]$^{2+}$ ion constitute the crystal chemical unit. The numbering of the atoms in the cation is shown in Figure 1; the centre of this ion occupies a crystallographic centre of symmetry. The structure was solved by conventional methods and all the hydrogen atoms were located unequivocally in an electron-density difference map. Full-matrix least-squares refinement was used to give the parameters in Table 1.

TABLE 1

Atomic co-ordinates ($\times 10^4$) and vibration parameters ($\times 10^3$ Å^2), with standard deviations in the least significant digits in parentheses

	x/a	y/b	z/c	U
Cl	−2280(1)	3043(2)	1234(2)	*
O(1)	−1639(4)	2395(5)	2300(5)	*
O(2)	−3102(7)	1474(8)	−775(5)	*
O(3)	−752(5)	4621(7)	1401(8)	*
O(4)	−3618(4)	3680(5)	1871(5)	*
C(1)	3262(6)	5121(6)	3290(6)	47(1)
N(1)	2790(5)	4329(5)	1133(4)	39(1)
C(2)	1909(6)	2106(6)	−227(6)	44(1)
C(3)	1796(6)	1499(7)	−2304(6)	44(1)
N(2)	3682(4)	2254(5)	−2445(5)	40(1)
C(4)	3626(6)	1853(7)	−4411(6)	48(1)
C(5)	5587(6)	2632(7)	−4554(7)	54(1)
HC(12)	2010(50)	4518(51)	3516(50)	49(11)
HC(11)	3869(45)	4406(49)	3473(46)	36(9)
HN(11)	3873(61)	5064(61)	977(59)	71(13)
HN(12)	2018(56)	4896(59)	881(57)	70(13)
HC(21)	563(56)	1614(56)	−144(53)	59(12)
HC(22)	2732(48)	1700(49)	260(49)	45(10)
HC(31)	1135(46)	2131(50)	−2736(48)	42(10)
HC(32)	1124(51)	30(58)	−3207(54)	54(11)
HN(21)	4243(50)	1628(53)	−2167(52)	50(11)
HC(41)	3017(43)	2582(47)	−4618(45)	32(9)
HC(42)	2840(55)	307(66)	−5441(60)	68(13)
HC(51)	5447(62)	2150(67)	−6065(71)	100(17)
HC(52)	6274(44)	2041(47)	−4168(45)	33(9)

* Anisotropic vibration parameters are in the form: exp $[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Cl	45(1)	61(1)	48(1)	36(1)	23(1)	36(1)
O(1)	83(2)	98(3)	95(3)	58(2)	37(2)	75(2)
O(2)	198(5)	202(5)	50(3)	150(5)	10(3)	16(3)
O(3)	81(3)	166(4)	269(6)	83(3)	96(3)	183(5)
O(4)	73(2)	99(3)	94(3)	65(2)	50(2)	58(2)

RESULTS AND DISCUSSION

The positions of the hydrogen atoms show clearly that a pair of nitrogen atoms, N(1) and N(1^{II}), are protonated so that the structure consists of perchlorate ions and [H$_2$cyclam]$^{2+}$ cations. From the bond lengths (Table 2) it can be seen that the C–H lengths lie in the range 0·97—1·04 Å, reasonable for determination by X-ray diffraction, and that the N–H bonds are in a shorter range,

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[1] D. E. Fenton, C. Nave, and M. R. Truter, *J.C.S. Chem. Comm.*, 1972, 1303; 1974, 116.

0·91—0·99 Å. The protonated nitrogen N(1) is in a tetrahedral environment (Table 2) with mean N(1)–C bond lengths 1·497 Å; the other nitrogen has three bonds pyramidally arranged and may (see later) be a recipient for a hydrogen bond from a protonated nitrogen; mean N(2)–C bond lengths are 1·467 Å. In the cation the chemically equivalent pairs of bonds differ by 0·014, 0·006, and 0·015 Å so that the difference of 0·030 Å between the mean C–N(1) and C–N(2) bonds, shows only a possibly significant increase in C–N bond length on protonation.

TABLE 2

(*a*) Bond lengths (Å)

Cl–O(1)	1·401(3)	C(1)–HC(11)	0·97(4)
Cl–O(2)	1·404(4)	C(1)–HC(12)	1·04(4)
Cl–O(3)	1·403(4)	N(1)–HN(11)	0·94(5)
Cl–O(4)	1·413(3)	N(1)–HN(12)	0·99(5)
		C(2)–HC(21)	1·04(5)
C(1)–N(1)	1·504(5)	C(2)–HC(22)	0·99(4)
N(1)–C(2)	1·490(5)	C(3)–HC(31)	1·04(4)
C(2)–C(3)	1·503(6)	C(3)–HC(32)	0·98(5)
C(3)–N(2)	1·464(5)	N(2)–HN(21)	0·91(4)
N(2)–C(4)	1·470(5)	C(4)–HC(41)	0·99(4)
C(4)–C(5)	1·520(6)	C(4)–HC(42)	1·04(5)
C(5)–C(1^{II})	1·505(6)	C(5)–HC(51)	1·08(6)
		C(5)–HC(52)	1·00(4)

(*b*) Bond angles (°)

O(1)–Cl–O(2)	109·4(3)	HC(11)–C(1)–HC(12)	100(4)
O(1)–Cl–O(3)	109·6(2)	HN(11)–N(1)–HN(12)	97
O(1)–Cl–O(4)	112·8(2)	HC(21)–C(2)–HC(22)	116
O(2)–Cl–O(3)	107·1(3)	HC(31)–C(3)–HC(32)	110
O(2)–Cl–O(4)	108·6(2)	HC(41)–C(4)–HC(42)	111
O(3)–Cl–O(4)	109·1(2)	HC(51)–C(5)–HC(52)	110
C(5^{II})–C(1)–N(1)	111·1(3)	C(1)–N(1)–HN(11)	107(3)
C(1)–N(1)–C(2)	114·7(3)	C(1)–N(1)–HN(12)	107
N(1)–C(2)–C(3)	110·3(3)	C(2)–N(1)–HN(11)	116
C(2)–C(3)–N(2)	110·5(3)	C(2)–N(1)–HN(12)	113
C(3)–N(2)–C(4)	112·0(3)	C(3)–N(2)–HN(21)	106
N(2)–C(4)–C(5)	111·9(4)	C(4)–N(2)–HN(21)	111
C(4)–C(5)–C(1^{II})	114·5(4)		

The actual value of the C–N(2) bond length is not significantly different from that found [2] for other three-covalent nitrogen compounds [1·472(5) Å], while the C–N(1) bond is longer than the quoted value for four-covalent nitrogen compounds [1·479(5) Å].

Our results are among the most accurate available, since the heaviest atom is chlorine, the perchlorate ion is not disordered, and observations were collected with a diffractometer. All these conditions are also fulfilled by the structure of 2,2′,2″-triaminotriethylamine trihydrochloride [3] which has a H_3N^+–C 1·457 Å and N(tert)–C 1·474 Å (values corrected for libration 1·474 and 1·492 Å), *i.e.* a shorter bond to the nitrogen with more atoms, and more hydrogen atoms, bonded to it; this contrasts with our results. There is no evidence to suggest that our values for the C–N bond lengths are too short as a result of systematic error, so that the relatively short carbon–carbon bond lengths (mean 1·509 Å) are unlikely to be artefacts but further examples of the effect already observed in cyclic [4] and bicyclic [5] compounds with oxygen and nitrogen atoms in large rings.

For the perchlorate ion the mean Cl–O bond length (1·405 Å, uncorrected) is shorter than accurate values obtained in low-temperature studies [1·437(4) (ref. 6) and 1·45(1) Å (ref. 7)]. Our mean is a minimum value, the vibration parameters of the oxygen atoms being greater than those for the chlorine atom (Table 1). This vibration appears larger for atoms O(2) and O(3) which may be involved in hydrogen bonding than for atoms O(1) and O(4) which are definitely not so involved, and is one of the reasons for uncertainty about the existence of this bonding (see later).

Four nitrogen atoms are coplanar, by crystallographic symmetry, as they are in the complex with nickel chloride, $NiCl_2$(cyclam),[8] and some comparison can be made; N(1) is 2·11 and N(2) 1·98 Å from the centre of symmetry, distances comparable with 2·066 and 2·050(8) Å in the nickel complex. All the quoted bond lengths (Table 3) in the ligand molecule are longer than the corresponding ones in the diprotonated molecule, the mean C–N bond length being 1·513 Å and the mean C–C 1·571 Å both quoted as ±0·015 Å. The torsion angle about the C(2)–C(3) bond (Table 4) is gauche in the present com-

TABLE 3

Contacts (Å) <2·81 Å between hydrogen and oxygen or nitrogen atoms

(*a*) From methylene H to O atoms

HC(12) ··· O(1)	2·61	HC(32) ··· O(1^{VIII})	2·69
HC(12) ··· O(3)	2·76	HC(41) ··· O(4^{III})	2·71
HC(11) ··· O(4^{I})	2·62	HC(42) ··· O(2^{IX})	2·79
HC(21) ··· O(1)	2·80	HC(51) ··· O(1^{X})	2·80
HC(22) ··· O(1^{VIII})	2·81	HC(51) ··· O(2^{IX})	2·65
HC(22) ··· O(4^{I})	2·61	HC(51) ··· O(4^{X})	2·63
HC(31) ··· O(3^{III})	2·62		

(*b*) From amine H atoms to O atoms, and the angle N–H ··· O

HN(12) ··· O(3)	2·27	[N(1)–HN(12) ··· O(3)]	129°
HN(12) ··· O(3^{III})	2·34	[N(1)–HN(12) ··· O(3^{III})]	145
HN(21) ··· O(2^{I})	2·42	[N(2)–HN(21) ··· O(2^{I})]	154

(*c*) From amine H atoms to N atoms, and the angle N–H ··· N

HN(11) ··· N(2^{II})	2·06	[N(1)–HN(11) ··· N(2^{II})]	143°
HN(11) ··· N(2)	2·61	[N(1)–HN(11) ··· N(2)]	100

(*d*) Angles subtended at potential hydrogen-bond receptor atoms

Cl–O(2) ··· HN(21^{XI})	108	C(3)–N(2) ··· HN(11^{II})	138
Cl–O(3) ··· HN(12)	131	C(4)–N(2) ··· HN(11^{II})	94
Cl–O(3) ··· HN(12^{III})	104	HN(21)–N(2) ··· HN(11^{II})	93

Roman numeral superscripts relate to the atom at x, y, z in Table 1 by:

I $x + 1, y, z$
II $1 - x, 1 - y, -z$
III $-x, 1 - y, -z$
IV $1 - x, 1 - y, 1 - z$
V $x, y, z + 1$
VI $1 - x, -y, -z$
VII $x, y + 1, z + 1$
VIII $-x, -y, -z$
IX $-x, -y, -z - 1$
X $1 + x, y, z - 1$
XI $x - 1, y, z$

TABLE 4

Torsion angles (°)

C(4^{II})–C(5^{II})–C(1)–N(1)	−67	C(5^{II})–C(1)–N(1)–C(2)	171
C(1)–N(1)–C(2)–C(3)	−170	N(1)–C(2)–C(3)–N(2)	64
C(2)–C(3)–N(2)–C(4)	−174	C(3)–N(2)–C(4)–C(5)	−180
N(2)–C(4)–C(5)–C(1^{II})	−67		

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[2] *Chem. Soc. Special Publ.*, No. 18, 1965.

[3] R. G. Hazell and S. E. Rasmussen, *Acta Chem. Scand.*, 1968, **22**, 348.

[4] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2469, and refs. therein; M. Herceg and R. Weiss, *Bull. Soc. chim. France*, 1972, 549.

[5] D. Moras, B. Metz, and R. Weiss, *Acta Cryst.*, 1973, **B29**, pp. 383, 388, 396, 400.

[6] J. Almlof, J.-O. Lundgren, and I. Olovsson, *Acta Cryst.*, 1971, **B27**, 898.

[7] B. Dickens, *Acta Cryst.*, 1969, **B25**, 1875.

[8] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

pound and in most complexes derived from ethylenediamine, including the nickel one. However, the ' ring ' formed by treating the centre of symmetry as a sixth atom would be boat-shaped. The structures of nickel complexes of three isomers of a hexamethyl derivative of cyclam have recently been reported.[9] The conformations found vary from one isomer to another but all have the four nitrogen atoms more or less coplanar, and since the nickel is only four-co-ordinate Ni–N distances are less than in $NiCl_2$(cyclam).[8] In the two isomers which do not show disorder the Ni–N distances range from 1·897 to 1·940 Å; mean C–N is 1·495 and mean C–C 1·505 Å. When one of the isomers occupied four positions in an octahedrally co-ordinated nickel [10] the mean Ni–N distance was 2·13 and mean N–C and mean C–C were 1·49 and 1·54 Å.

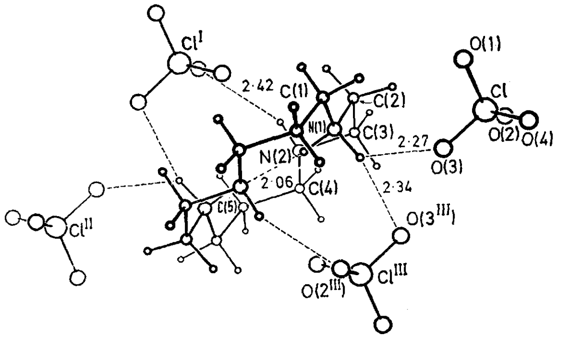

FIGURE 2 One $[H_2cyclam]^{2+}$ cation and the surrounding perchlorate ions. Roman numeral superscripts are defined in Table 3. Hydrogen atoms are represented by the smallest circles. Broken lines from these to neighbouring oxygen atoms show contacts <2·5 Å, at the distances marked. One of the hydrogen atoms on the quarternary nitrogen, HN(12), makes two such contacts, the other NH(11) makes an intercation contact of 2·06 Å to N(2^{II})

Hydrogen Bonding and Molecular Packing.—There are three hydrogen atoms which may take part in hydrogen bonding but the evidence for this is somewhat equivocal. The two bands at 3270 and 3190 cm^{-1} in the i.r. spectrum of the neutral cyclam molecule have been attributed [11] to an N–H ··· N hydrogen bond pattern within the molecule. For the hexamethyl analogue of cyclam both anhydrous and hydrated forms were obtained [12] and the changes in the i.r. spectra attributable to hydrogen bonding are not readily distinguished from the changes obtained in making the tetrahydroperchlorates where the frequencies correspond to $\nu(NH_2^+)$.

From the crystallographic evidence we have to consider the H ··· A (A = acceptor) distance and the angles subtended at the hydrogen and at the acceptor atoms. Relevant facts are given in Figure 2 and Table 3.

The shortest D ··· A distance (D = donor) is N(1) ··· N(2^{II}), corresponding to a pair of intracation hydrogen bonds with the hydrogen atom HN(11) completing a six-membered ring comprising also N(1), C(1), C(5^{II}), C(4^{II}), and N(2^{II}). The HN(11) ··· N(2^{II}) distance (2·06 Å) is matched by C–H ··· N distances where the carbon and nitrogen atoms are adjacent, but for carbon atoms further away these distances are 2·6 Å or more. Around the acceptor nitrogen N(2) bond angles involving HN(11^{II}) differ considerably from the ideal values for a tetrahedron (see Table 3) and the angle at the hydrogen atom is 143°, which is at the small end of the range for hydrogen-bonded contacts. On balance, we consider that there are probably two weak intracationic hydrogen bonds.

Possible hydrogen-bonding contacts from the cation to the surrounding anions are HN(12) ··· O(3^{III}) and HN(21) ··· O(2^{I}). Both give an angle close to 109·5° at the receptor oxygen and of *ca.* 150° at the hydrogen atom; the D ··· A distances (2·98 and 3·26 Å) do not suggest strong hydrogen bonding nor do the vibration parameters (Table 1) which are larger for O(2) and O(3) than for the other oxygen atoms. The shortest contact, HN(12) ··· O(3), is not even a possible hydrogen bond, as judged by the angles subtended at O(3) and HN(12) (Table 3). The NH ··· O contacts are shorter than the shortest CH ··· O contacts so there may be some small reinforcement of the electrostatic attraction which would be expected to operate from N(1) to the perchlorate ion.

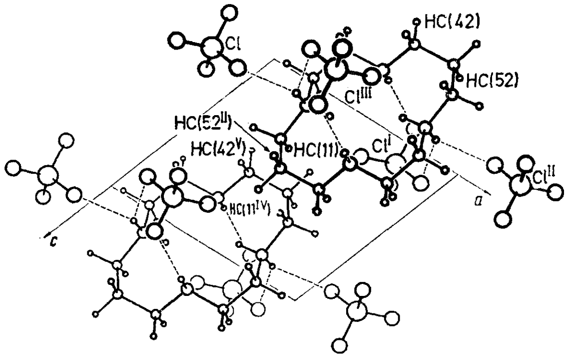

FIGURE 3 The structure projected on the (010) plane. Broken lines, as in Figure 2, show H ··· O contacts <2·5 Å. H ··· H contacts of <2·5 Å between cations alternate along the *b* axis, being between symmetry-related pairs of HC(11) atoms at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and between atoms of type HC(42) and HC(52) at $\frac{1}{2},0,\frac{1}{2}$ and $\frac{1}{2},1,\frac{1}{2}$. The contacts shown [HC(11) ··· HC(11^{IV}) 2·45 Å] are about the centre of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. About the centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$, HC(42^{V}) and HC(52^{V}) make contact with HC(52^{VI}) and HC(42^{VI}) respectively 2·28 Å below the plane of the paper. These are repeated at $\frac{1}{2},1,\frac{1}{2}$ from HC(42^{II}) and HC(52^{II}), to HC(52^{VII}) and HC(42^{VII}), which are above the plane of the paper. Roman numeral superscripts are defined in Table 3

In Figure 3 the packing of the content of more than one unit cell is shown with broken lines for the N–H ··· O contacts; these are in the *ab* plane and the platy habit of the crystals is consistent with there being stronger contacts in this plane than normal to it. In fact, along the normal there are van der Waals' contacts between methylene carbon atoms of successive cations (see Figure 3).

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[9] N. F. Curtis, D. A. Swann, and T. N. Waters, *J.C.S. Dalton*, 1973, 1963.

[10] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

[11] H. Stetter and K. H. Mayer, *Chem. Ber.*, 1961, **94**, 1410.

[12] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

EXPERIMENTAL

Preliminary measurements were made on both α and β forms from Weissenberg and precession photographs.

Crystal Data.—(i) β-*form*. $C_{10}H_{26}Cl_2N_4O_8$, $M = 401{\cdot}26$, Monoclinic, $a = 26{\cdot}15$, $b = 13{\cdot}61$, $c = 20{\cdot}80$ Å, $\beta = 92{\cdot}8°$, $U = 7393{\cdot}9$ Å^3, $D_c = 1{\cdot}44$, $Z = 16$, $D_m = 1{\cdot}45$, $F(000) = 3392$. Space group $P2_1/n$, uniquely determined from systematic absences. There are four formula units in the asymmetric unit. There are two ways in which diprotonation of cyclam can take place and several possible conformations for each protonated species, so that all four of the entities in the asymmetric unit may be different, and the β-form may, or may not, be related to the α-form only by differences in packing.

For the α-form unit-cell dimensions were obtained from 27 lines on a powder photograph taken with a Guinier camera, and agreed, within the standard deviation, with those obtained from 10 reflections centred on a Picker four-circle diffractometer.

Crystal Data.—(ii) α-*form*. $C_{10}H_{26}Cl_2N_4O_8$, $M = 401{\cdot}26$, Triclinic, $a = 8{\cdot}081(3)$, $b = 8{\cdot}657(3)$, $c = 8{\cdot}219(2)$ Å, $\alpha = 119{\cdot}23(2)$, $\beta = 95{\cdot}05(3)$, $\gamma = 111{\cdot}37(2)°$, $U = 441{\cdot}5(3)$ Å^3, $D_c = 1{\cdot}51$, $Z = 1$, $D_m = 1{\cdot}52$, $F(000) = 212$. Space group $P\bar{1}$ by structure determination. Mo-K-radiation, $\lambda = 0{\cdot}7093$ Å (1 Å = 10^{-10}m); μ(Mo-$K_{\alpha1}$) 4·2 cm^{-1}. Guinier powder photographs with monochromated Cu-$K_{\alpha1}$ radiation ($\lambda = 1{\cdot}5405$ Å) for unit-cell dimensions and a Picker four-circle diffractometer with Mo-K_α radiation for intensity measurement. No absorption correction applied.

For intensity measurements a trapezoid-shaped crystal (0·24—0·49 × 0·23 × 0·035 mm) was mounted on a quartz fibre on a Picker single-crystal four-circle diffractometer in the Corporate Laboratory of Imperial Chemical Industries Ltd., and the procedure followed was as described ref. 13. 1156 reflections $h\bar{k}l$, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$, and $\bar{h}\bar{k}\bar{l}$ were measured from 2θ 2—45° by the 2θ—ω scan technique with niobium-filtered Mo-K_α radiation. The scan was from $2\theta_{\alpha1} - 0{\cdot}55°$ to $2\theta_{\alpha2}$ 0·55° at 2° min^{-1} with background counts of 10 s. Reflections were scaled from three standard reflections (100, 030, and 003) measured every 100 observations and rejected if $I < 2\sigma(I)$ and $I < 30$ counts. The variation in intensities of the standards was <2% throughout. Intensities were corrected [14] for Lorentz and polarisation effects to yield 1009 observations which were used for structure determination.

Structure Determination.—In the space group $P\bar{1}$ the two perchlorate ions must be related by a centre of symmetry, and the cyclam molecule must be centrosymmetrical. In $P1$ the formula unit is the asymmetric unit, no conditions are imposed on the cyclam molecule, and the two perchlorate ions are crystallographically independent; the origin of the unit cell is not fixed and may be chosen as a point equidistant from the two chlorine atoms. A Patterson synthesis was calculated and the highest peak assumed to be a Cl · · · Cl vector.

A Fourier synthesis based on this showed the chlorine atom surrounded by eight peaks, corresponding to the superposition of two centrosymmetrically-related perchlorate ions. Further investigation indicated that the true position of the chlorine atoms corresponded to a vector giving the seventh highest peak on the Patterson synthesis. (After the structure had been solved it became clear that two planes had been mis-measured and in a correct Patterson synthesis the Cl · · · Cl vector was the second highest peak.)

Once the perchlorate ion had been located structure factors were calculated (R 0·63) and a Fourier synthesis located the non-hydrogen atoms of the cyclam ring; with the chlorine at $x = -0{\cdot}23$, $y = 0{\cdot}30$, $z = 0{\cdot}12$, the cyclam ring was located about the centre of symmetry at $\frac{1}{2},\frac{1}{2},0$. Full-matrix refinement with isotropic vibration parameters, and all cyclam atoms given the scattering factor of carbon, reduced R to 0·24. Two atoms had low temperature factors, B_{iso} 1·0 Å^2, indicating that these were the nitrogen atoms.

A difference electron-density synthesis revealed all the hydrogen atom positions, including two on N(1), thus showing unequivocally that the compound was a hydroperchlorate not a lithium complex. Further confirmation was obtained by subjecting the crystal used for structure analysis to a flame test for lithium with a negative result.

The difference synthesis also indicated that the perchlorate ion was undergoing anisotropic thermal motion, so final refinement was carried out with anisotropic vibration parameters for chlorine and oxygen, and isotropic vibration parameters for carbon, nitrogen, and hydrogen. Scattering factors for chlorine, oxygen, carbon, and nitrogen were taken from ref. 15, and for hydrogen from ref. 16. In the full-matrix least squares refinement with the program NUCLS [17] the function minimised was $R' = \Sigma w(|F_o| - |F_c|)^2$ and to obtain a similar value of R' for ranges of $|F_o|$ and of sin θ/λ it was found necessary to modify the weights given by the counting statistics, $\sigma(F_o)$, by $w = 1/(\sigma^2(F_o) \times [0{\cdot}51 + 0{\cdot}079|F_o| + 0{\cdot}0026|F_o|^2])$.

Two cycles of refinement reduced R to 0·049 for 1009 observations, the most significant shift being 0·04σ. Many correlation coefficients were >0·5, and the program ORFFE [18] was used to obtain the bond lengths and angles with their standard deviations. These high correlation coefficients were for each atom in the perchlorate group between the co-ordinates and temperature factors, while for the other atoms the effect was shown between their y- and z-co-ordinates.

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21083 (8 pp., 1 microfiche).* Interatomic distances and angles in Table 3 and Figure 2 were calculated on an IBM 1130 computer, as were the torsion angles in Table 4.[14]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[13] J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1968, 1473.

[14] *X*-RAY ARC, IBM 1130 Program System, for details see P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818.

[15] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—212.

[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1955, **42**, 3175.

[17] NUCLS, IBM 360 full-matrix least-squares program, R. J. Doedens and J. A. Ibers.

[18] North Western University version of Program ORFFE, W. A. Busing, K. O. Martin, and H. A. Levy, run on the University College IBM 360 Computer.