

violurate de cuivre, les atomes sont peu agités. Une projection des ellipsoïdes de vibration thermique a été réalisée par le programme *ORTEP* (Johnson, 1965) (Fig. 5). Les atomes d'azote N(1) et N(4) se révèlent avec une anisotropie nettement marquée, contrairement aux atomes d'azote des deux autres fonctions imine N(2) et N(5).

Ce travail a été effectué par Mme Lepicard à qui je tiens à exprimer tous mes remerciements.

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The Crystal Structure of a 1:1 Octahydrate Complex of Calcium Chloride with 1,4,7,10-Tetraoxacyclododecane

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(Received 14 March 1975; accepted 23 May 1975)

A single-crystal X-ray diffraction study has established the structure of $\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, where $\text{C}_8\text{H}_{16}\text{O}_4$ represents the heterocyclic ligand 1,4,7,10-tetraoxacyclododecane. This complex crystallizes in the orthorhombic space group *Fdd2* (No. 43, C_{2v}^{12}). The lattice parameters are $a = 20.104 \pm 0.005$, $b = 28.464 \pm 0.007$, and $c = 7.328 \pm 0.002$ Å, and the calculated density is 1.366 g cm^{-3} for formula weight 431.32 and $Z = 8$. A Picker four-circle diffractometer (θ - 2θ scan mode) and $\text{Mo K}\alpha$ radiation were used to measure the intensities of 1297 unique reflections. The structure was solved by Patterson and Fourier methods and all hydrogen atoms were ultimately located. Full-matrix least-squares refinement of atomic positions, hydrogen isotropic temperature factors, and anisotropic thermal parameters for the Ca, Cl, O, and C atoms converged at a value of $R_1 = 3.1\%$ for the 1142 reflections above background. The calcium ion is situated on a crystallographic C_2 axis and is coordinated to eight oxygen atoms arranged at the apices of a distorted square antiprism. Four of these oxygens belong to the cyclomer (which adopts approximate C_4 symmetry) and approximate a square with sides 2.728(3) and 2.737(4) Å. The remaining four oxygens in the coordination polyhedron belong to water molecules.

Introduction

Our present commitment to the determination of structures of crystalline complexes formed by 1,4,7,10-tetraoxacyclododecane with mono- and di-valent cations stems from two interesting properties of these com-

pounds. The first arises as a consequence of the flexibility of the macrocyclic ring, which has the capacity to act as a tetradentate ligand by adopting at least two entirely different conformations. For certain alkali halide salts (Boer & van Remoortere, 1974), and for sodium hydroxide (Boer, Neuman, Steiner & van

Remoortere, 1974), novel complexes of 2:1 stoichiometry are found: $\text{MX} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 5\text{H}_2\text{O}$ (I), $\text{NaOH} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 8\text{H}_2\text{O}$ (II), where the cation is sandwiched between two rings each with C_4 symmetry to form an eight-coordinate complex of overall D_4 symmetry. In $\text{CuCl}_2 \cdot \text{C}_8\text{H}_{16}\text{O}_4$ (III) (van Remoortere, Boer & Steiner, 1975) the complex and the heterocyclic ligand approximate C_s symmetry. A third conformation, of symmetry C_i , is known in $\text{MgCl}_2 \cdot \text{C}_8\text{H}_{16}\text{O}_4 \cdot 6\text{H}_2\text{O}$ (IV) where the 12-membered heterocycle links $[\text{Mg}(\text{H}_2\text{O})_6]^{+2}$ units *via* hydrogen bonds to the ether oxygens, but does not coordinate to the metal ion directly (Neuman, Steiner, van Remoortere & Boer, 1975).

The second property concerns the mechanism by which the crystals are able to stabilize the anions. The D_4 complexes above are hydrates with unusual infinite two- or three-dimensional hydrogen-bonded networks in which the negative charges are embedded. In brief, the overall structure appears to be governed by two effects: (1) the interaction of the heterocycle and the cation, which may be influenced by such factors as ion size, the ability of the oxygen lone-pair orbitals to direct themselves at the positive charge center, and the chemical affinity of the cation for water; and (2) the capacity of the crystal for suitably 'solvating' the negative ions.

The crystal structure of $\text{CaCl}_2 \cdot \text{C}_8\text{H}_{16}\text{O}_4 \cdot \text{H}_2\text{O}$ described below is intermediate between the D_4 alkali ion complexes, where two cyclomer molecules are bound to the metal, and the $\text{MgCl}_2 \cdot \text{C}_8\text{H}_{16}\text{O}_4 \cdot 6\text{H}_2\text{O}$ complex where the cyclomer is not directly bound to the cation at all.

Experimental

The complex was prepared by adding 20g (114 mmol) of 1,4,7,10-tetraoxacyclododecane to a solution of CaCl_2 (11.1g, 100 mmol) in water (36g, 2000 mmol). The product was obtained as a copious crystalline precipitate. The mixture was warmed to cause dissolution of the complex and then cooled slowly to produce crystals suitable for X-ray diffraction analysis. Two habits are observed: hexagonal prisms elongated on c and bounded by the $\{100\}$, $\{110\}$, and $\{110\}$ faces, and

flat needles with large $\{010\}$ faces again elongated on c . The crystal used in our X-ray study was of the hexagonal variety, 0.22–0.255 mm in diameter by 1.12 mm long. It extinguished sharply along the needle axis under the polarizing microscope.

This crystal was sealed in a thin-walled Lindemann glass capillary to prevent loss of water of hydration, and secured to a goniometer head. The alignment of the needle axis with the goniometer axis was refined with oscillation photographs and preliminary Weissenberg and precession photographs were obtained. The orthorhombic space group $Fdd2$ (C_{2v}^{19} , No. 43) was established from the diffraction symmetry D_{2h} and the reflection conditions hkl : $h+k, k+l, (l+h)=2n$; $0kl, k+l=4n$ ($k, l=2n$); and $h0l$: $l+h=4n$ ($l, h=2n$). The crystal was aligned on the four-circle goniostat of a Picker diffractometer. The lattice parameters obtained by least-squares refinement of the setting angles of ten reflections measured with Mo $K\alpha$ radiation ($\lambda=0.7107\text{\AA}$) at 25°C , are: $a=20.104 \pm 0.005$, $b=28.464 \pm 0.007$, and $c=7.328 \pm 0.002$ \AA . The calculated density is 1.366 g cm^{-3} assuming an octahydrate complex

$\text{C}_8\text{H}_{32}\text{O}_{12}\text{CaCl}_2$ (F.W. 431.32) and $Z=8$. These assumptions are confirmed by the structure determination. The precision of measurement for the lattice constants, as determined from the estimated standard deviations calculated in the least-squares analysis, was a factor of 10 better than the errors assigned above, which reflect our experience with systematic errors and reproducibility of results under different experimental conditions. The presence of eight formula units per unit-cell requires C_2 symmetry for the complex.

Mo $K\alpha$ radiation, for which the complex has a linear absorption coefficient of 5.726 cm^{-1} , was monochromatized with the 002 reflection of a highly oriented graphite crystal and used to obtain intensity data for 1297 reflections on the Picker diffractometer (θ - 2θ scan mode). The X-ray tube was set at a 3° take-off angle and a detector aperture 4 mm square was placed 31.5 cm from the crystal; 1.5 mm diameter incident- and exit-beam collimators were used. Attenuators were used to prevent the count rate from exceeding 12000 c.p.s. The scan speed was 2° min^{-1} over 2θ angles of

Table 1. Final structure parameters with standard deviations in parentheses

(a) Heavy atoms (anisotropic thermal parameters)

The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, and have been multiplied by 10^5 .

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.0	0.0	0.0	141 (2)	79 (1)	98 (1)	2 (1)	0	0
Cl	-0.03009 (4)	0.19593 (3)	0.4606 (2)	242 (2)	126 (1)	175 (2)	13 (1)	33 (5)	24 (4)
O(1)	-0.0131 (1)	0.06797 (7)	0.2218 (4)	242 (6)	116 (3)	166 (5)	13 (3)	-12 (2)	-7 (1)
O(4)	0.0943 (1)	0.00885 (7)	0.2217 (3)	206 (5)	129 (3)	156 (5)	10 (3)	-8 (1)	3 (1)
O(7)	0.0697 (1)	0.05266 (9)	-0.1644 (4)	237 (6)	125 (3)	249 (6)	2 (4)	18 (2)	18 (1)
O(8)	0.0725 (1)	-0.05331 (9)	-0.1583 (4)	221 (6)	120 (3)	210 (6)	3 (4)	15 (2)	-7 (1)
O(9)	0.0005 (2)	0.13635 (9)	-0.1924 (5)	427 (9)	103 (3)	199 (6)	-1 (5)	-8 (2)	4 (1)
O(10)	0.2105 (1)	-0.0511 (1)	-0.1717 (5)	261 (7)	133 (3)	197 (6)	3 (4)	-6 (2)	4 (13)
C(2)	0.0361 (2)	0.0739 (1)	0.3619 (6)	30 (1)	138 (5)	203 (9)	-4 (6)	-24 (3)	-17 (2)
C(3)	0.1004 (2)	0.0567 (1)	0.2840 (6)	237 (9)	142 (5)	225 (9)	-40 (5)	-22 (2)	-6 (2)
C(5)	0.1033 (2)	-0.0250 (1)	0.3650 (6)	230 (9)	164 (6)	186 (8)	28 (6)	-14 (2)	12 (2)
C(6)	0.0805 (2)	-0.0711 (1)	0.2896 (5)	253 (9)	140 (5)	189 (8)	68 (6)	9 (22)	13 (2)

Table 1 (cont.)

(b) Hydrogen atoms (isotropic thermal parameters)				(c) Root mean-square thermal amplitude along principal axes*				
	x	y	z	B		Axis 1	Axis 2	Axis 3
H(2A)	0.022 (2)	0.054 (1)	0.489 (6)	2.7 (8)				
H(2B)	0.040 (2)	0.110 (1)	0.391 (7)	3.5 (9)	Ca	0.163	0.170	0.180
H(3A)	0.138 (2)	0.058 (2)	0.385 (8)	4 (1)	Cl	0.214	0.217	0.236
H(3B)	0.117 (2)	0.076 (1)	0.159 (8)	4 (1)	O(1)	0.192	0.211	0.246
H(5A)	0.076 (2)	-0.018 (1)	0.480 (6)	3 (1)	O(4)	0.188	0.219	0.233
H(5B)	0.150 (2)	-0.026 (1)	0.391 (6)	2.6 (8)	O(7)	0.187	0.221	0.289
H(6A)	0.083 (2)	-0.096 (1)	0.394 (7)	2.1 (7)	O(8)	0.192	0.221	0.257
H(6B)	0.109 (2)	-0.083 (1)	0.174 (6)	2.2 (8)	O(9)	0.203	0.233	0.297
H(7A)	0.062 (2)	0.080 (2)	-0.174 (6)	2.3 (9)	O(10)	0.221	0.234	0.242
H(7B)	0.110 (2)	0.052 (1)	-0.194 (6)	2.7 (9)	C(2)	0.178	0.245	0.287
H(8A)	0.061 (2)	-0.084 (2)	-0.158 (7)	3 (1)	C(3)	0.176	0.254	0.269
H(8B)	0.113 (2)	-0.056 (2)	-0.156 (8)	4 (1)	C(5)	0.180	0.242	0.272
H(9A)	0.012 (2)	0.153 (2)	-0.117 (8)	3 (1)	C(6)	0.174	0.226	0.281
H(9B)	-0.000 (2)	0.151 (2)	-0.272 (8)	4 (1)				
H(10A)	0.213 (2)	-0.023 (2)	-0.194 (7)	4 (1)				
H(10B)	0.222 (2)	-0.054 (1)	-0.091 (6)	1 (1)				

* Ordered on increasing magnitude.

$2.3^\circ + \Delta$, where Δ is the separation of the $K\alpha$ doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Background counts of 10 s were taken at each end of the scan. A 2θ range of $0-54.9^\circ$, equivalent to the Cu $K\alpha$ sphere, was examined. The 660 reflection was monitored after every 50 measurements and showed good stability, giving a root-mean-square deviation of 1% and a maximum deviation of less than 3%. An error $\sigma(I) = [(0.025I)^2 + N_o + k^2 N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects. The 155 reflections for which $I/\sigma(I) < 3.3$ were denoted absent and were omitted from the refinement. No absorption corrections were applied because of the low linear absorption coefficient and the nearly uniform diameter of the crystal. An absolute scale factor and overall temperature factor ($B_o = 3.1 \text{ \AA}^2$) were computed by Wilson's (1942) method.

Structure determination and refinement

A sharpened three-dimensional Patterson map was used to locate the Ca and Cl atoms. The oxygen atoms were then found in an electron-density map based on the Ca and Cl phases, and a subsequent Fourier map revealed the carbon atoms of the heterocycle. Five cycles of full-matrix least-squares refinement, in which atom positions and isotropic temperature factors were varied, resulted in a reduction of $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ from 0.16 to 0.068 and $R_2 = \{\sum w(F_o - F_c)^2 / \sum wF_o^2\}^{1/2}$ from 0.22 to 0.090. A difference map computed after one cycle of least squares in which anisotropic temperature factors were introduced showed peaks ranging from 0.25 to 0.36 e \AA^{-3} at the calculated positions for the methylene hydrogens. However, the water hydrogens could not be unambiguously identified at this stage.

Three additional cycles of refinement were performed in which the methylene hydrogens were included with isotropic temperature factors. The water hydrogens associated with peak heights ranging from 0.21 to 0.30 e \AA^{-3} , were located in an electron-density difference map, which followed, and their identities were subsequently confirmed by the reasonable values obtained

Table 2. Interatomic distances (\AA)

Symmetry transformations applying to the second atom are: (a) $-x, -y, z$; (b) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (c) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (d) $x, y, z + 1$; (e) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$.

Calcium-oxygen distances		Carbon-oxygen bonds	
Ca-O(1)	2.540 (2)	O(1)-C(2)	1.436 (4)
Ca-O(2)	2.509 (2)	O(1)-C(6) ^a	1.445 (4)
Ca-O(7)	2.380 (2)	O(4)-C(3)	1.441 (4)
Ca-O(8)	2.402 (2)	O(4)-C(5)	1.436 (4)
Carbon-carbon bonds		Oxygen-hydrogen bonds	
C(2)-C(3)	1.497 (6)	O(7)-H(7A)	0.79 (4)
C(5)-C(6)	1.496 (5)	O(7)-H(7B)	0.84 (4)
Carbon-hydrogen bonds		O(8)-H(8A)	0.90 (5)
C(2)-H(2A)	1.14 (4)	O(8)-H(8B)	0.81 (5)
C(2)-H(2B)	1.04 (4)	O(9)-H(9A)	0.77 (5)
C(3)-H(3A)	1.05 (6)	O(9)-H(9B)	0.71 (6)
C(3)-H(3B)	1.12 (5)	O(10)-H(10A)	0.82 (5)
C(5)-H(5A)	1.02 (4)	O(10)-H(10B)	0.64 (4)
C(5)-H(5B)	0.96 (4)	Oxygen-oxygen distances (hydrogen bonded)	
C(6)-H(6A)	1.04 (4)	O(7)···O(9)	2.766 (4)
C(6)-H(6B)	1.08 (4)	O(8)···O(9) ^a	2.792 (4)
Oxygen-chlorine distances (hydrogen bonded)		O(8)···O(10)	2.777 (4)
Cl-O(10) ^c	3.118 (3)	O(9)···O(10) ^b	2.779 (4)
Cl-O(9) ^d	3.122 (3)	Oxygen-oxygen distances (nonbonded)	
Cl-O(7) ^c	3.135 (3)	O(1)-O(4) ^a	2.728 (3)
Cl-O(10) ^b	3.141 (3)	O(1)-O(4)	2.737 (4)
Hydrogen bonds (to oxygen)		O(7)-O(8) ^a	2.859 (4)
O(9)···H(7A)	2.04 (4)	O(7)-O(8)	3.017 (4)
O(9)···H(8A) ^a	1.95 (5)	Hydrogen bonds (to chlorine)	
O(10)···H(8B)	1.98 (5)	Cl···H(7B) ^c	2.30 (4)
O(10)···H(9A) ^e	2.01 (5)	Cl···H(10A) ^c	2.30 (5)
		Cl···H(9B) ^d	2.43 (5)
		Cl···H(10B) ^b	2.51 (5)

Atomic parameters and their standard deviations (as computed from the least-squares analysis) are given in Table 1. Errors for the interatomic distances and angles, summarized in Tables 2 and 3 respectively, were computed from the variance-covariance matrix generated in the final least-squares cycle.*

Discussion

The calcium ions are situated on the crystallographic twofold axes and are coordinated to eight oxygen atoms in a square antiprismatic geometry (Fig. 1). Although there are minor differences, the conformation of the heterocycle closely resembles that observed in (I) and (II), and exhibits an approximate non-crystallographic fourfold (C_4) axis. In $\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ the sides of the approximate square formed by the ether oxygens, 2.728 (3) and 2.737 (4) Å, are somewhat shorter than those found in the sodium complexes, which ranged between 2.777 and 2.809 Å. The perpendicular distance from the cation to the least-squares plane (Table 4) through the four oxygens is substantially larger, 1.625 Å, for the Ca complex than the values (1.528, 1.497, 1.505 Å) observed for the sodium compounds. The least-squares planes through the two chemically distinct types of carbon atoms in the C_4 conformation, previously (Boer & van Remoortere, 1974) labelled α and β , are 2.102 and 2.663 Å distant from the cation (Table 4) for the α and β carbons respectively, or again about 0.10 Å further than the corresponding values in the $\text{Na}^+(\text{C}_8\text{H}_{16}\text{O}_4)_2$ structures. The average Ca-O distance for the ether oxygens is 2.525 Å, slightly longer than the average value of 2.489 Å in the sodium complexes. The difference may be related to the difference in ion radius between Na^+ (0.95 Å) and Ca^{2+} (0.99 Å). Small but significant differences occur in the internal bond angles and torsion angles of the heterocycle as compared to the average values (in brackets) found for $\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{Cl} \cdot 5\text{H}_2\text{O}$ and $\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{OH} \cdot 8\text{H}_2\text{O}$, but differences in bond distances are probably not

significant. The internal angles at the α carbons are 110.9 (3) and 111.1 (3)° [112.6°]; at the β carbons, 106.3 (3) and 106.5 (3)° [107.7°]; and at oxygen, 113.0 (3) and 113.1 (3)° [113.5°]. For the three types of torsion angles (ignoring H atoms), the comparisons are, $\text{C}_\alpha\text{-O}$ 84.0 (3) and 83.9 (4)° [80.3°]; O-C_β , -164.5 (3) and -167.5 (3)° [163.6°]; and $\text{C}_\alpha\text{-C}_\beta$, 55.2 (4) and 56.2 (4)° [58.6°]. The methylene hydrogens are very well staggered. The average C-O and C-C bond distances found in the five metal ion complexes of tetraoxacyclododecane studied to date are 1.430 and 1.495 Å for 40 and 20 individual measurements respectively. All the values found here but one [O(1)-C(6)', 1.445 (4) Å] are within three standard deviations of these mean values (atoms related by the diad are designated by primes). The average C-H bond distance of 1.05 Å reflects the systematic shortening from the true internuclear separation [about 1.09 Å (Sutton, 1958)] that results from the shift of electron density from hydrogen upon bond formation (Stewart, Davidson & Simpson, 1965) and from the effects of thermal vibrations (Hamilton & Ibers, 1968). All individual C-H distances are within three standard deviations of the mean value, and all bond angles involving the methylene hydrogens are within 3σ of the tetrahedral angle.

Table 4. Selected least-squares planes

Atoms in brackets were not included in the plane calculation. Atoms related by the twofold axes are designated by primes. The planes are all orthogonal to the z axis.

	Plane 1	Plane 2	Plane 3 (α carbons)	Plane 4 (β carbons)
1	O(7), O(7)'	O(1), O(1)'	C(3), C(3)'	C(2), C(2)'
2	O(8), O(8)'	O(4), O(4)'	C(6), C(6)'	C(5), C(5)'
3	O(9), O(9)'	[Ca]	[Ca]	[Ca]
4	O(10), O(10)'			
5	[H(7A), H(7A)']			
6	[H(7B), H(7B)']			
7	[H(8A), H(8A)']			
8	[H(8B), H(8B)']			
9	[Ca]			
Δd_1	0.053	0.003	-0.021	-0.011
Δd_2	0.098	0.003	0.021	0.011
Δd_3	-0.152	-1.625	-2.102	-2.663
Δd_4	0.000			
Δd_5	0.000			
Δd_6	-0.167			
Δd_7	0.010			
Δd_8	0.117			
Δd_9	1.258			

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31165 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

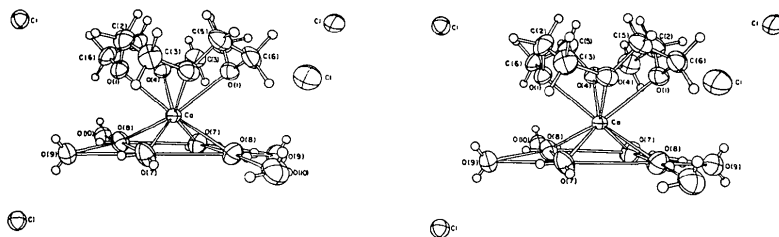


Fig. 1. Three-dimensional stereo pair diagram of the basic structural unit in $\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2 \cdot 8\text{H}_2\text{O}$. The crystallographic twofold axis is vertical and passes through the cation. The thermal ellipsoids are drawn at 50% probability.

The remaining four ligands in the distorted square antiprism are the oxygen atoms O(7), O(7)', O(8), and O(8)'. These atoms are considerably nearer the calcium ion [Ca-O(7), 2.380 (2) Å; Ca-O(8), 2.402 (2) Å] than the ether oxygens and form a parallelogram with sides 3.017 (4) and 2.859 (4) Å and angles 88.6 (1) and 91.4 (1)° (Fig. 2). By comparison the two unique Ca-O distances in CaCl₂·6H₂O, where the Ca is coordinated to nine oxygen atoms, are 2.446 and 2.592 Å. The distances separating oxygens in the water quadrangle from those in the cyclomer square are all well above the sum (2.8 Å) of two oxygen van der Waals radii.

Atoms O(7), O(8), O(9), O(10) and their symmetry-related pairs form an approximately planar structure (Fig. 2). The least-squares plane through these atoms is described in Table 4. Atom O(9) is held by the hydrogen bonds to form a nearly equilateral triangle whose base is the short edge of the {O(7), O(8), O(7)', O(8)'} parallelogram. On the other hand O(10) is bound to this parallelogram by a single hydrogen bond and is essentially collinear with the O(7)' → O(8) vector. The remaining hydrogen atom associated with the water

parallelogram, namely H(7B), forms a hydrogen bond to chloride. The hydrogens on O(10) form hydrogen bonds to two separate chloride ions; a fourth hydrogen bond to chloride utilizes H(9B) of O(9). H(9A) is donated in a hydrogen bond joining O(9) with O(10) of a calcium polyhedron related by a diagonal glide. The chloride ion is bound by a distorted tetrahedron of hydrogen bonds. The observed H···Cl distances, the H···Cl···H angles, and the appropriate symmetry transformations are given in Tables 2 and 3. This tetrahedral arrangement contrasts with the structure of CaCl₂·6H₂O (Agron & Busing, 1969) where the chloride ions occupy octahedral sites with unique O···Cl distances of 3.188 and 3.209 Å. The O(9)···O(10) hydrogen bond links Ca (C₈H₁₆O₄) (H₂O)₈ units together in interlocked helical arrays centered on the screw diads parallel to z. Portions of these helices are apparent in the crystal structure diagram, Fig. 3.

The O-H bonds, which average 0.79 Å are subject to systematic shortening for the same reasons as the methylene hydrogens (Stewart, Davidson & Simpson, 1965; Hamilton & Ibers, 1968). In a neutron diffrac-

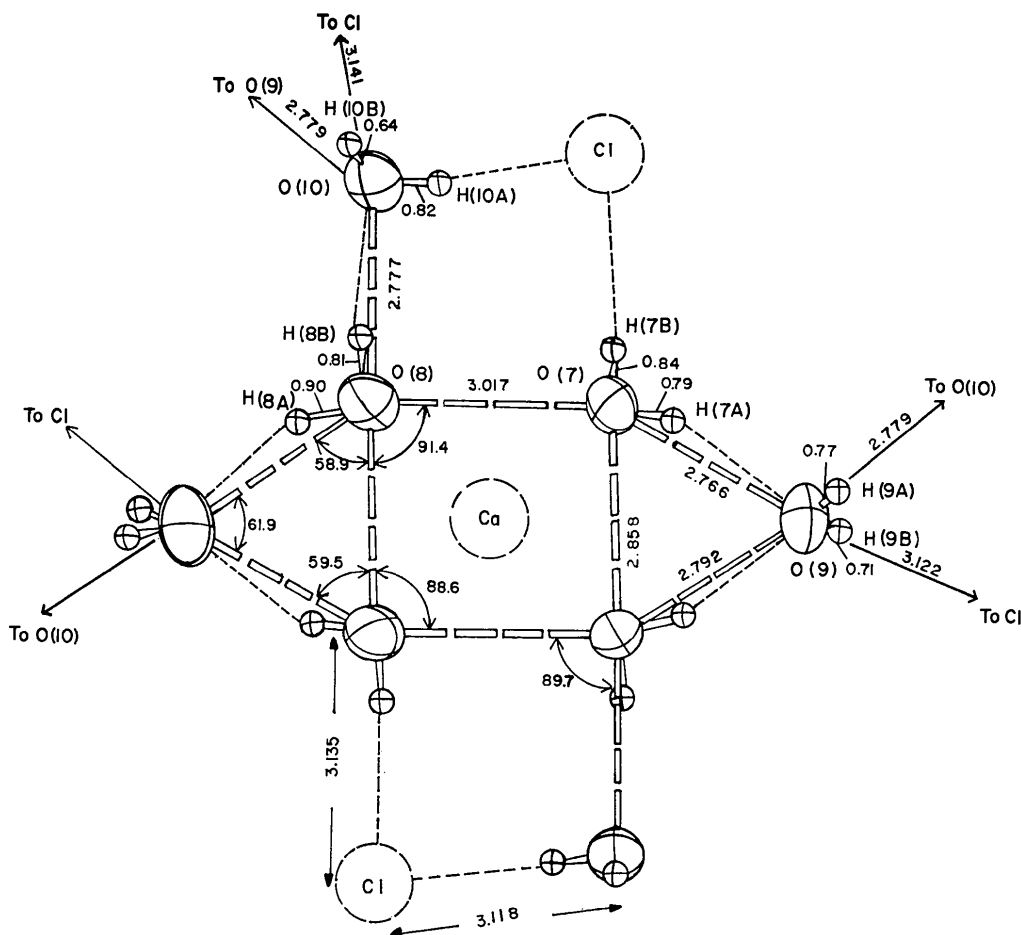


Fig. 2. Diagram of the water plane in Ca(C₈H₁₆O₄)Cl₂·8H₂O showing some of the hydrogen bonds.

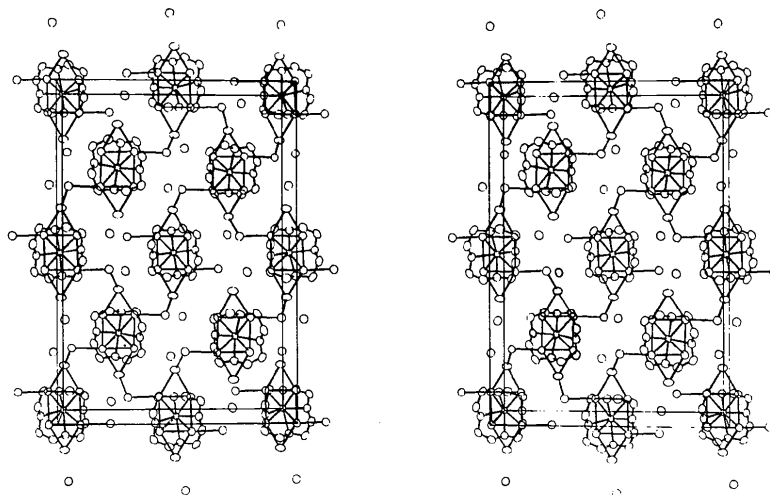


Fig. 3. Three-dimensional stereo pair diagram of a unit cell of $\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ as viewed down the z axis. The y axis is vertical and x is horizontal.

tion study (Agron & Busing, 1969) of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ the O–H distances were 0.949 and 0.963 Å. Thus the magnitude of the shortening appears to be somewhat greater for the water molecules than for the methylene groups, and is in fact of the same order as found in the X-ray study (Boer, Neuman, Steiner & van Remoortere, 1975) of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2 \cdot \text{C}_8\text{H}_{16}\text{O}_4$, where an average O–H distance of 0.80 Å was found, compared with neutron diffraction (Agron & Busing, 1969) values of 0.966 to 0.988 Å in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The H–O–H bond angles found in the present study are all very reasonable: 99 (4)°, 100 (4)°, 103 (5)°. Of the hydrogen bonds to oxygen, two show bond angles with moderate variations from linearity [O(7)–H(7A)···O(9), 153 (4)° and O(8)–H(8A)···O(9), 155 (4)°]. These are part of the near equilateral triangle described above. The O–H···Cl angles range from 166 to 177° (Table 3).

The ellipsoids of thermal motion are drawn (Johnson, 1965) in Figs. 1 and 2, and the root-mean-square components along the principal axes are summarized in Table 1(c). None of the amplitudes are unusually large. As is typical of metal complexes in which tetraoxacyclododecane acts as a tetradentate ligand, the cation has the smallest vibrational amplitudes and is fairly isotropic and the ether oxygens exhibit less anisotropy than the ring carbons. The chlorine atom also displays very little anisotropy.

We thank T. P. Blumer for adapting the program *ORTEP* to the IBM 1130 computer and for preparing the stereo diagrams.

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