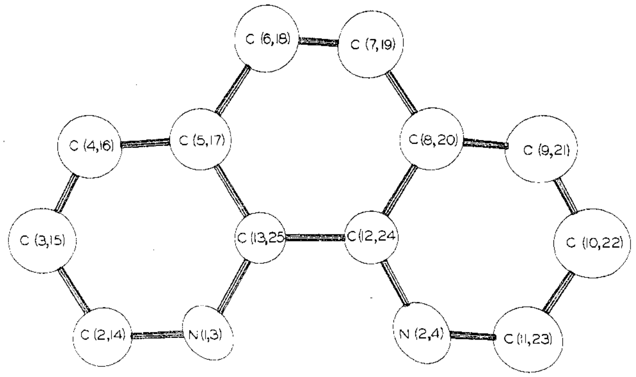

Figure 3. Numbering scheme for the phenanthroline ligands. Hydrogen atom numbers correspond to those of the carbon atoms to which they are bound.

$(NO_3)\cdot H_2O$ is, as was suggested earlier, very similar to that of the compound $[Cu(bipy)_2I]I$,[7] where bipy = 2,2'-bipyridine. In that five-coordinate complex, iodide ion was stabilized in bonding directly to copper(II) and occupied the equatorial position in the trigonal-bipyramidal coordination sphere. The structures observed to date thus suggest that stable bonding of reducing ligands such as cyanide ion and iodide ion to copper(II) is associated with the formation of the relatively rare trigonal-bipyramidal coordination geometry about the cupric ion.

Acknowledgment. Computing funds for this work were supplied by the University of Michigan and the University of Michigan Computing Center. The Syntex diffractometer was purchased through NSF Grant No. GP18277. The author thanks M. Strumpel for helpful discussions.

Registry No. $[Cu(phen)_2CN](NO_3)\cdot H_2O$, 53966-23-7.

Supplementary Material Available. Table VI, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W. Washington, D.C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number AIC40414F.

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Cyclomer Complexes. IV. Crystal Structure of a 1:1 Hexahydrate Complex of Magnesium Chloride with 1,4,7,10-Tetraoxacyclododecane

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The crystal structure of $Mg(H_2O)_6Cl_2\cdot C_8H_{16}O_4$, where $C_8H_{16}O_4$ is 1,4,7,10-tetraoxacyclododecane, has been determined by a single-crystal X-ray diffraction study. This complex crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 16.406 \pm 0.005$ Å, $b = 8.443 \pm 0.003$ Å, $c = 12.729 \pm 0.005$ Å, and $\beta = 93° 18' \pm 2'$, giving a calculated density of 1.432 g cm^{-3} for $Z = 4$. The intensities of 2006 independent reflections were measured using the θ–2θ scan mode of a Picker four-circle diffractometer and Mo Kα radiation. The structure was solved by Patterson and Fourier methods and all hydrogens were located. Full-matrix least-squares refinement, with the hydrogens assigned isotropic temperature factors and all heavier atoms anisotropic thermal parameters, converged to give an R factor of 3.5% for the 1646 reflections above background. The structure contains octahedral $Mg(H_2O)_6^{2+}$ units, very similar to those in $MgCl_2\cdot 6H_2O$, located on crystallographic twofold axes. The Mg–O distances range from 2.054 to 2.082 Å with errors of 0.001–0.002 Å. Eight of the twelve water hydrogens form hydrogen bonds to six different chloride ions, which are located in tetrahedral holes, while the remaining four hydrogens of the $Mg(H_2O)_6^{2+}$ unit form hydrogen bonds to ether oxygens from four different cyclomer molecules. The $Mg(H_2O)_6^{2+}$ units and the chloride ions form two-dimensional layers, as do the 12-membered rings. The tetraoxacyclododecane molecule is situated on a crystallographic center of symmetry and has normal bond distances and angles.

Introduction

As part of a systematic effort[1-4] to determine the nature of the complexes formed between 1,4,7,10-tetraoxacyclododecane ($C_8H_{16}O_4$) and inorganic salts, we have performed an X-ray diffraction study of a hexahydrate complex formed by this novel ligand with $MgCl_2$. Previous work[1,2] has established that in the compounds $Na(C_8H_{16}O_4)_2Cl\cdot 5H_2O$ and $Na(C_8H_{16}O_4)_2OH\cdot 8H_2O$ the heterocycle adopts a C_4 conformation to form 2:1 octacoordinate complexes of overall D_4 (square-antiprismatic) symmetry. X-Ray powder diffraction studies[5] indicate that KCl, RbCl, NaBr, KBr, and NaI form crystalline complexes isomorphous with $Na(C_8H_{16}O_4)_2Cl{\cdot}5H_2O$. In the crystal structure of $Ca(C_8H_{16}O_4)Cl_2{\cdot}8H_2O$ the ring again adopts the C_4 crown conformation[4] and the coordination polyhedron about Ca is also square antiprismatic, but four of the coordination sites are occupied by water oxygens. An entirely different ring geometry, of C_s symmetry, is found in the distorted octahedral $Cu(C_8H_{16}O_4)Cl_2$ complex.[3]

The Mg^{2+} ion has an ion radius approximately that of Cu^{2+} but also exhibits an affinity for water resulting in the formation of hexahydrate salts in which the water oxygens are octahedrally coordinated to the cation.[6] Thus, a crystal structure in which the tetraoxacyclododecane ligand might partially or completely displace water from the magnesium coordination sphere to form a complex analogous to those discussed above would be of considerable practical interest. The present study was carried out to explore this possibility and to determine the manner in which the cyclomer molecule was bound in the crystal lattice.

Experimental Section

The crystalline complex $MgCl_2{\cdot}6H_2O{\cdot}C_8H_{16}O_4$ is formed by a mildly exothermic process when $MgCl_2{\cdot}6H_2O$ is mixed with an excess of 1,4,7,10-tetraoxacyclododecane. The crystals are colorless needles elongated in the c direction.

Data were collected from a crystal of hexagonal cross section, with maximum diameter 0.20 mm and approximate length 1 mm, which was sealed in a thin-walled glass capillary tube to prevent loss of water of hydration. The reciprocal lattice levels $0kl$ and $h0l$ were surveyed on a precession camera and the $hk0$ and $hk1$ layers were recorded on Weissenberg photographs (Cu Kα radiation). The diffraction symmetry C_{2h} and the reflection conditions hkl, $h + k = 2n$, and $h0l$, $l = 2n$ ($h = 2n$), established the space group as either Cc ($C_s{}^4$) or $C2/c$ ($C_{2h}{}^6$). The crystal was then carefully centered on a Picker automatic four-circle diffractometer and aligned on the c axis by adjusting the arcs to bring the $hk0$ reciprocal lattice level into coincidence with the equatorial plane of the goniostat. Lattice constants were calculated from a least-squares refinement of the setting angles of 14 reflections with Mo Kα radiation (λ 0.71069 Å). The cell parameters $a = 16.406 \pm 0.005$ Å, $b = 8.443 \pm 0.003$ Å, $c = 12.729 \pm 0.005$ Å, and $\beta = 93° \ 18' \pm 2'$ give a unit cell volume of 1760.2 Å^3 and a calculated density $\rho = 1.432$ g cm^{-3} for FW 379.524 and $Z = 4$ at 25°. The precision of measurement of the lattice constants, as computed 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 4 formula units/cell imposes no symmetry requirements in space group Cc, but for $C2/c$ both the magnesium atom and the polyether ring must lie on either inversion centers or diads, whereas the chloride ions and the waters may occur either in general positions or in pairwise fashion on these symmetry elements.

The intensities of 2006 reflections were measured using the θ–2θ scan mode of the diffractometer and Mo Kα radiation selected by the (002) reflection of a highly oriented graphite crystal monochromator. The takeoff angle of the X-ray tube was 4°, and a counter aperture 6.0 × 6.0 mm was placed 30 cm from the crystal; 1.5-mm diameter incident- and exit-beam collimators were used to restrict stray radiation. The scan speed was 2°/min over 2θ angles of $2° + \Delta$, where Δ is the separation of the Kα doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Attenuators were used to prevent the count rate from exceeding 12,000/sec. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The data collected represent the unique reflections in the sphere $\sin\theta \leq 0.461$, equivalent to the complete Cu Kα sphere. A test reflection (133) monitored after every 50 measurements showed good stability; the root-mean-square deviation in its intensity was less than 1% and the maximum deviation was below 3%. An error $\sigma(I) = [(0.02I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_0 - kN_b$ in order to establish the weights $w = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement. Here N_0 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 by the expression $(Lp)^{-1} = 2(\sin 2\theta)(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m \cos^2 2\theta)$ where $2\theta_m$ is the monochromator setting angle.[18] The 360 reflections for which either $I < 0$ or $I/\sigma(I) < 3$ were denoted absent and were not used in the structure analysis. The linear absorption coefficient for this material is μ(Mo Kα) = 4.34 cm^{-1}. No absorption corrections were applied in view of the low absorption factors and the relatively uniform diameter of the crystal.

Solution and Refinement of the Structure

The solution of the structure required the location of half of the ring, one chlorine atom, one magnesium atom, and either three or four water oxygens. Examination of a three-dimensional Patterson function[7] $P(u, v, w)$ revealed the position of the chlorine atoms and the MgO_6 octahedron.

An electron density map phased on the six independent atoms—chlorine, magnesium, and four oxygens—showed the ring atoms about the inversion center at ($^1/_4$, $^1/_4$, $^1/_2$). A structure factor calculation based on the 12 independent atoms yielded a reliability factor $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.16. Full-matrix least-squares refinement[8,9] for the 12 atoms with isotropic thermal parameters converged at values of 0.118 for R_1 and 0.156 for $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$. One additional cycle of refinement[10a] with anisotropic thermal parameters lowered R_1 and R_2 to 0.071 and 0.111, respectively. The methylene hydrogen coordinates were now generated by calculation, and a check of a difference electron density map[10b] showed peaks, ranging from 0.58 to 0.76 e Å^{-3}, at each of their positions. The difference Fourier also revealed the locations of all of the water hydrogens, which had peak heights ranging from 0.52 to 0.66 e Å^{-3}. Inclusion of the 14 hydrogens in the structure factor calculation[11] reduced R_1 to 5.2% and R_2 to 7.0%; three cycles of least-squares assuming anisotropic temperature factors for the heavier atoms and isotropic temperature factors for hydrogen took R_1 and R_2 to their final values of 0.035 and 0.041, respectively, for the 1646 reflections above background. In the final cycle the mean parameter shift had been reduced to 0.01σ and no individual shift exceeded 0.10σ. A final difference Fourier[10b] contained no peaks greater than 0.24 e Å^{-3} and no negative regions less than -0.35 e Å^{-3}. The effects of secondary extinction on the intensity data appeared to be minor and no correction was applied. The corrections[9] to the scattering factors from anomalous dispersion do not exceed 0.2 e and were not used.

The final atomic parameters and their standard deviations as obtained from the least-squares refinement[10a] are given in Table I, and the table of observed and calculated structure factors is available on request.[12] Table II gives root-mean-square components of thermal displacement along the principal axes as defined by the anisotropic thermal parameters. The directions of these axes may be obtained by direct calculation or inferred from the computer-produced stereoview[10c] of the complex in Figure 1, where thermal motion is represented by 50% probability ellipsoids. Important interatomic distances and angles are listed in Table III. The standard deviations in Tables II and III were calculated from the variance–covariance matrix obtained in the final least-squares cycle.[10d]

Discussion

The results indicate that the cyclomer does not chelate the Mg^{2+} cation but is held instead in the lattice by hydrogen bonds. The ring conformation, of symmetry C_i, is unlike any previously found for complexes of 1,4,7,10-tetraoxacyclododecane.[1–4] The octahedral $Mg(H_2O)_6{}^{2+}$ structural unit found in $Mg(H_2O)_6Cl_2$ also occurs in the present structure, but the type of coordination about the chloride ions is significantly different. As in the alkali metal ion–cyclomer complexes, a separation into two-dimensional organic and aqueous layers takes place.

The Hydrogen-Bonded System. The inorganic layers in crystals of $Mg(H_2O)_6Cl_2{\cdot}C_8H_{16}O_4$ occur in the yz planes at $x = 0$ and $x = {}^1/_2$ and are comprised of hexahydrated magnesium ions (situated on the diads) and chloride ions. The structure of these layers is illustrated[10c] in Figure 2a. With respect to the water oxygens the chlorides occupy tetrahedral sites and form four hydrogen bonds, thus utilizing eight of the twelve available hydrogens from a $Mg(H_2O)_6{}^{2+}$ unit. By contrast, in $Mg(H_2O)_6Cl_2$ the chlorides are each held (Figure 2b) by six hydrogen bonds in octahedral fashion and thus utilize

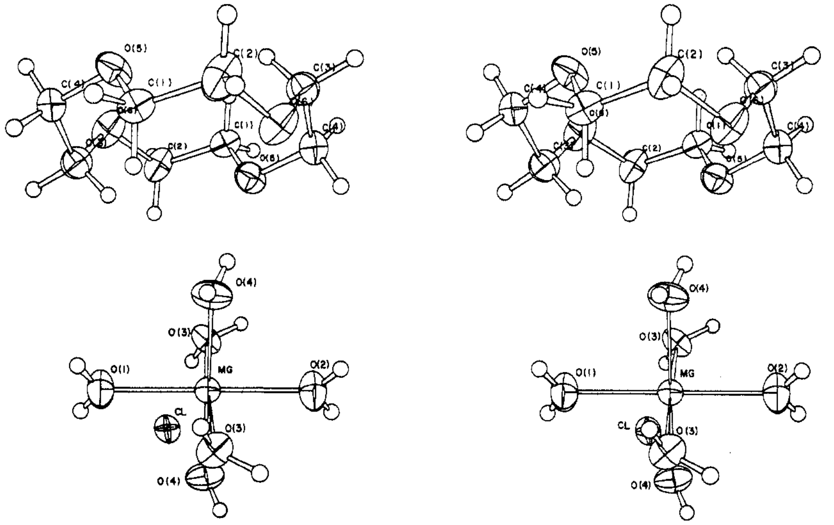

Figure 1. Three-dimensional view of the cation, $Mg(H_2O)_6^{2+}$, cyclomer, and chloride showing ellipsoids of thermal motion. The hydrogens are drawn at their observed positions with spheres of uniform radius. The unique orientation of the O(3) water molecule is evident.

Table I. Final Structure Parameters[a,b]

Atom	x/a	y/b	z/c	$10^5\beta_{11}$	$10^5\beta_{22}$ (or B^c for H)	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cl	0.45989 (3)	0.21064 (6)	0.07353 (3)	374 (2)	1128 (8)	325 (3)	31 (3)	4 (2)	69 (4)
Mg	0	0.20332 (9)	0.25	182 (3)	707 (10)	251 (4)	0	18 (3)	0
O(1)	0	0.44664 (22)	0.25	506 (10)	832 (27)	450 (13)	0	−43 (9)	0
O(2)	0	−0.04034 (22)	0.25	525 (10)	796 (27)	428 (12)	0	16 (9)	0
O(3)	0.09955 (8)	0.19849 (17)	0.15577 (10)	270 (5)	1162 (20)	388 (8)	90 (8)	74 (5)	91 (10)
O(4)	0.07503 (8)	0.20239 (19)	0.38531 (10)	240 (5)	1755 (26)	356 (8)	86 (10)	17 (5)	24 (12)
O(5)	0.23535 (7)	0.09629 (15)	0.39670 (10)	229 (5)	1172 (20)	502 (8)	1 (8)	35 (5)	224 (10)
O(6)	0.31204 (8)	0.42907 (16)	0.38601 (10)	338 (6)	1306 (23)	586 (10)	−209 (9)	141 (6)	−308 (12)
C(1)	0.31042 (11)	0.14546 (24)	0.35545 (15)	238 (7)	1162 (30)	377 (11)	−60 (12)	55 (7)	−51 (15)
C(2)	0.30169 (14)	0.30696 (24)	0.30791 (15)	402 (9)	1138 (30)	320 (10)	−195 (14)	115 (8)	−54 (15)
C(3)	0.23894 (12)	0.49488 (25)	0.42385 (15)	298 (8)	1024 (28)	423 (12)	−33 (12)	18 (7)	52 (15)
C(4)	0.25578 (12)	0.53940 (22)	0.53660 (15)	293 (8)	762 (24)	441 (11)	19 (11)	59 (7)	12 (14)
H(1A)	0.3283 (12)	0.0686 (24)	0.3047 (16)		3.31 (45)				
H(1B)	0.3532 (13)	0.1418 (26)	0.4126 (17)		3.59 (48)				
H(2A)	0.2459 (13)	0.3168 (23)	0.2688 (16)		3.14 (45)				
H(2B)	0.3438 (13)	0.3234 (24)	0.2586 (18)		3.69 (47)				
H(3A)	0.1960 (12)	0.4208 (23)	0.4188 (14)		2.53 (39)				
H(3B)	0.2224 (11)	0.5966 (27)	0.3808 (17)		3.57 (47)				
H(4A)	0.2107 (11)	0.6063 (23)	0.5566 (15)		2.58 (39)				
H(4B)	0.3049 (11)	0.5961 (22)	0.5464 (14)		2.09 (37)				
H(5)	−0.0132 (16)	0.4957 (29)	0.1996 (19)		5.28 (65)				
H(6)	−0.0120 (16)	−0.0940 (29)	0.1987 (19)		5.02 (64)				
H(7A)	0.1273 (15)	0.1080 (31)	0.1476 (20)		4.51 (57)				
H(7B)	0.0889 (16)	0.2303 (30)	0.0996 (22)		4.74 (65)				
H(8A)	0.1176 (13)	0.1671 (25)	0.3876 (18)		3.09 (54)				
H(8B)	0.0559 (17)	0.2163 (32)	0.4385 (21)		5.00 (69)				

[a] Standard errors are given in parentheses. [b] The anisotropic temperature factors are given by the expression $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Isotropic temperature factor in Å^2.

Table II. Root-Mean Square Components (Å) of Thermal Displacement along Principal Axes[a,b]

Atom	Axis 1	Axis 2	Axis 3
Cl	0.1598 (7)	0.2035 (7)	0.2267 (7)
Mg	0.1429 (13)	0.1576 (12)	0.1598 (12)
O(1)	0.173 (3)	0.188 (3)	0.266 (3)
O(2)	0.170 (3)	0.187 (3)	0.268 (3)
O(3)	0.166 (2)	0.183 (2)	0.221 (2)
O(4)	0.164 (2)	0.184 (2)	0.254 (2)
O(5)	0.169 (2)	0.178 (2)	0.232 (2)
O(6)	0.174 (2)	0.185 (2)	0.274 (2)
C(1)	0.165 (3)	0.181 (3)	0.211 (3)
C(2)	0.149 (3)	0.183 (3)	0.255 (3)
C(3)	0.180 (3)	0.194 (3)	0.205 (3)
C(4)	0.166 (3)	0.182 (3)	0.206 (3)

[a] Ordered on increasing magnitude. [b] Standard errors in parentheses were calculated from the variance-covariance matrix obtained in the final least-squares cycle.

all twelve hydrogen atoms.[6] The four remaining hydrogen atoms in the present structure are available to form hydrogen bonds to the four ether-type oxygens of the cyclomer. The C_i symmetry of the ring causes the hydrogen bonds to occur symmetrically in both positive and negative directions with respect to a. Because the hydrogen bonds to chloride occur in the yz planes, while the interlayer hydrogen bonds to the cyclomer oxygens are located very nearly in planes parallel to xy, a three-dimensional network is formed (Figure 3) that links the entire crystal lattice. Interlayer ties of the type found here were not observed in the alkali ion complexes.[1,2]

The tetrahedral array about a chloride is formed by four hydrogens from three different cations as shown in Figure 2a: from the chloride at (−0.04011, 0.28936, 0.57353) two bonds are formed to the cation unit centered at (0, 0.20333, $^1/_4$) and one bond each is formed to the cations at (0, −0.20333, $^3/_4$) and (0, 0.79667, $^3/_4$). The tetrahedron is oriented with one

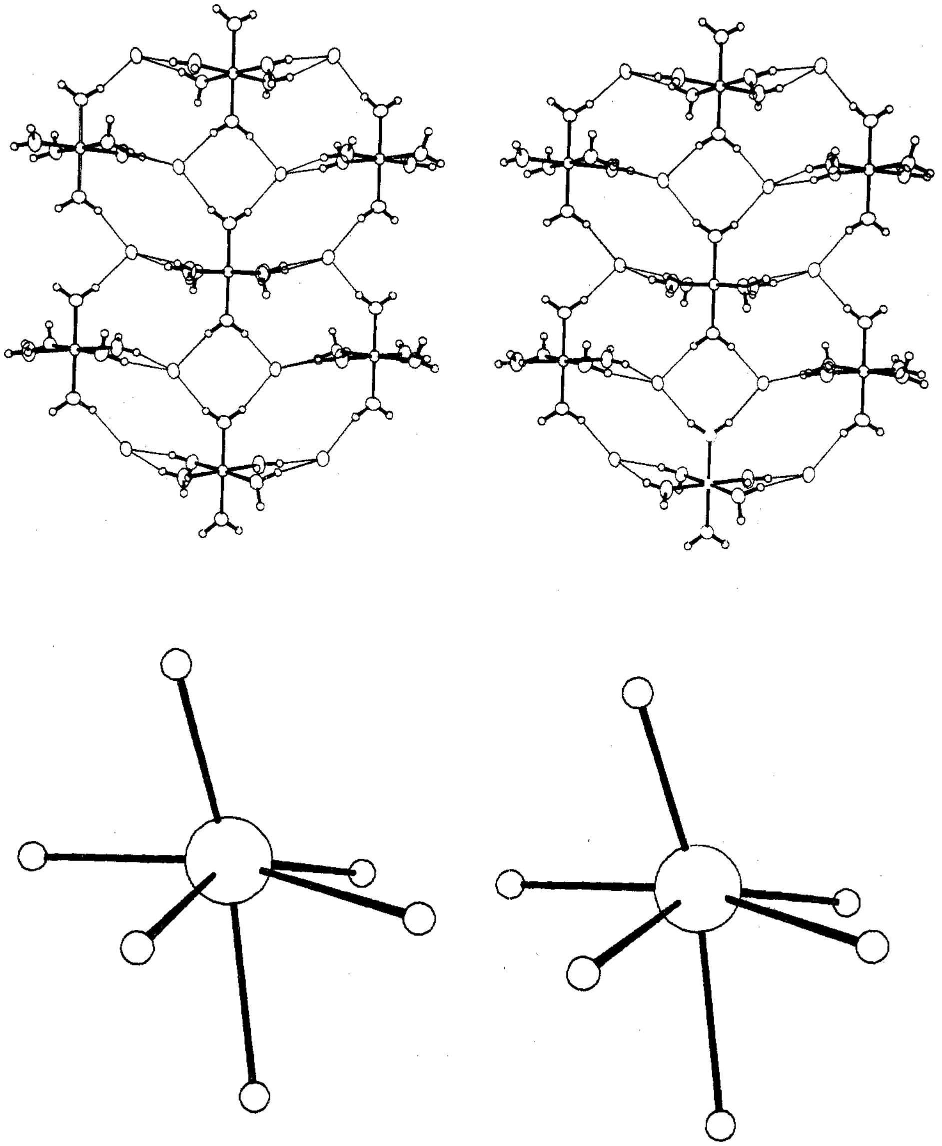

Figure 2. (a) Top: Three-dimensional view of the $Mg(H_2O)_6Cl_2$ layer in $Mg(H_2O)_6Cl_2 \cdot C_8H_{16}O_4$. The *y* axis is vertical and *z* is horizontal. Note the tetrahedral coordination about the chlorides. (b) Bottom: Coordination of six hydrogen atoms about chloride in $Mg(H_2O)_6Cl_2$.[6]

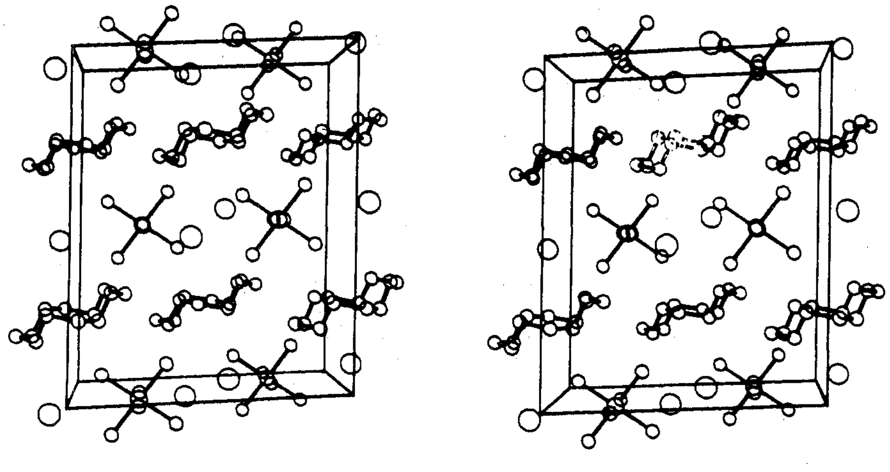

Figure 3. Three-dimensional diagram of the crystal structure of $Mg(H_2O)_6Cl_2 \cdot C_8H_{18}O_4$ viewed down the *y* axis. The *x* axis is vertical. The box delineates one unit cell.

edge approximately parallel and another approximately perpendicular to the *b* axis.

To give a more accurate picture of the geometry of the hydrogen-bonding system, it is useful to extrapolate the positions of the hydrogen nuclei. As is well-known the X-ray diffraction experiment yields the positions of maximum electron density resulting in a systematic shortening of the O–H bond lengths.[11] Further systematic shortening can occur as a consequence of thermal motion; unfortunately neither the riding model nor the independent atom model corrections are con-

Table III. Bond Distances and Angles[a,b]

Distances, Å

Mg-O(1)	2.054 (2)	O(5)-C(1)	1.428 (2)
Mg-O(2)	2.057 (2)	O(5)-C(4)′	1.428 (2)
Mg-O(3)	2.082 (1)	O(6)-C(2)	1.435 (2)
Mg-O(4)	2.059 (2)	O(6)-C(3)	1.430 (2)
C(1)-C(2)	1.495 (3)	C(3)-C(4)	1.494 (3)
C(1)-H(1A)	0.97 (2)	C(3)-H(3A)	0.94 (2)
C(1)-H(1B)	0.98 (2)	C(3)-H(3B)	1.05 (2)
C(2)-H(2A)	1.02 (2)	C(4)-H(4A)	0.98 (2)
C(2)-H(2B)	0.97 (2)	C(4)-H(4B)	0.94 (2)

Angles, Deg

Central atom	Atom 1	Atom 2	Angle	Central atom	Atom 1	Atom 2	Angle
Mg	O(1)	O(3)	91.12 (0.05)	O(5)	C(4)′	C(1)	113.02 (0.14)
	O(1)	O(4)	90.22 (0.05)	O(6)	C(2)	C(3)	116.38 (0.15)
	O(2)	O(3)	88.88 (0.05)				
	O(2)	O(4)	89.78 (0.05)				
	O(3)	O(4)	91.77 (0.05)				
	O(3)	O(4)′	88.23 (0.05)				
C(1)	O(5)	C(2)	110.45 (0.14)	C(2)	C(1)	O(6)	111.71 (0.16)
	O(5)	H(1A)	110.5 (1.2)		C(1)	H(2A)	109.5 (1.1)
	O(5)	H(1B)	108.3 (1.2)		C(1)	H(2B)	109.7 (1.2)
	C(2)	H(1A)	111.4 (1.2)		O(6)	H(2A)	110.3 (1.1)
	C(2)	H(1B)	112.1 (1.3)		O(6)	H(2B)	106.6 (1.2)
	H(1A)	H(1B)	103.9 (1.7)		H(2A)	H(2B)	109.0 (1.7)
C(3)	O(6)	C(4)	108.01 (0.15)	C(4)	C(3)	O(5)′	112.10 (0.16)
	O(6)	H(3A)	111.0 (1.2)		C(3)	H(4A)	107.2 (1.1)
	O(6)	H(3B)	109.9 (1.1)		C(3)	H(4B)	111.4 (1.2)
	C(4)	H(3A)	109.2 (1.1)		O(5)′	H(4A)	111.2 (1.1)
	C(4)	H(3B)	108.9 (1.2)		O(5)′	H(4B)	105.8 (1.1)
	H(3A)	H(3B)	109.8 (1.6)		H(4A)	H(4B)	109.1 (1.6)
O(1)	H(5)	H(5)″	116.2 (3.8)	O(2)	H(6)	H(6)″	111.9 (1.8)
	Mg	H(5)	121.9 (1.9)		Mg	H(6)	124.0 (1.8)
O(3)	H(7A)	H(7B)	106.0 (2.4)	O(4)	H(8A)	H(8B)	116.5 (2.6)
	Mg	H(7A)	120.2 (1.5)		Mg	H(8A)	122.6 (1.7)
	Mg	H(7B)	112.5 (2.0)		Mg	H(8B)	118.6 (2.0)

[a] Standard errors in parentheses were calculated from the variance-covariance matrix obtained in the final least-squares cycle. [b] Primed atoms are related by the center at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$); double-primed atoms by the diad at (0, y, $\frac{1}{4}$).

sidered reliable for O–H bonds.[13] In our experiment O–H bond lengths from 0.76 to 0.90 Å (±0.03 Å) were found, giving an average, when weighted for multiplicity, of 0.80 Å. This range is slightly shorter than the range 0.82–0.93 Å found in the X-ray structure of oxalic acid dihydrate.[14] To improve the hydrogen positions, we have modified the coordinates obtained by least-squares analysis in the following way. The neutron diffraction study[6] of $Mg(H_2O)_6Cl_2$ by Agron and Busing yielded an O–H bond length of 0.980 ± 0.003 Å and an H–O–H bond angle of 111.8°. The average H–O–H angle determined here, 112.3°, is in good agreement with their result. We have, therefore, maintained our O–H bond vectors as originally determined, but have set the O–H bond distances to 0.980 Å. The modified hydrogen fractional coordinates are given in Table IV and form the basis for all further discussion. A comparison of the hydrogen bond lengths and angles for the two sets of hydrogen positions (determined and calculated) is given in Table V.

The four hydrogen bonds to the chlorides are as follows: Cl···H(7B) $(-x, y, \frac{1}{2} - z)$, 2.15 Å; Cl···H(6) $(x, -y, \frac{1}{2} + z)$, 2.15 Å; Cl···H(5) $(x, 1 - y, \frac{1}{2} + z)$, 2.26 Å; Cl···H(8B), 2.27 Å, with estimated errors of the order of 0.03 Å. The range of values obtained by Agron and Busing is 2.206–2.500 Å for the six hydrogens (Figure 2b) coordinated to chloride, but for the coordination of four hydrogens about the chloride somewhat smaller interatomic distances might be expected. The H···Cl···H angles (Table VI) vary from 61.7 to 141.9°, indicating a high degree of distortion from tetrahedral symmetry. The O···Cl distances ranging between 3.119 and 3.220 Å are normal for this type of interaction.

Table IV. Modified Hydrogen Positions[a]

	x/a	y/b	z/c
H(5)	−0.017	0.508	0.187
H(6)	−0.015	−0.105	0.188
H(7A)	0.130	0.100	0.147
H(7B)	0.086	0.239	0.085
H(8A)	0.130	0.157	0.388
H(8B)	0.051	0.220	0.453

[a] The positions are obtained by setting the O–H bond lengths to 0.98 Å while maintaining the O–H bond vectors.

The hydrogen bonds all approximate linearity as indicated by the O–H···Cl angles, which range from 161.1 to 168.9°, for the assumed hydrogen positions. These values differ only slightly from those calculated from the atomic positions obtained in our refinement (Table V). In addition, the positions of H(5) and H(6) are extremely close to being coplanar with the four chlorides surrounding a $Mg(H_2O)_6^{2+}$ ion. Chlorides related by the twofold axis and the b translations (Figure 3) define an exact plane given by the equation[15] $0.9732x' - 0.2296z' = -0.910$; H(5) and H(6) are respectively 0.01 and 0.03 Å from this plane.

The hydrogen bonds to the ring oxygens have lengths of 1.79 Å for O(6)···H(7A) $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and 1.80 Å for O(5)–H(8A). These values are within the range of published O···H distances compiled from neutron diffraction studies by

Table V. Hydrogen-Bond Distances and Angles[a]

Hydrogen bond O–H···X	Symmetry transform for X	Measd H positions, Å			Assumed H positions, H···X, Å	Measd H positions, O–H···X, deg	Assumed H positions, O–H···X, deg
		O···X	O–H	H···X			
O(4)–H(8A)···O(5)	x, y, z	2.774 (2)	0.76 (2)	2.02 (2)	1.80	174.0 (2.3)	173.2
O(3)–H(7A)···O(6)	$^1/_2 - x, -^1/_2 + y, ^1/_2 - z$	2.766 (2)	0.90 (3)	1.87 (3)	1.79	172.9 (2.3)	172.5
O(1)–H(5)···Cl	$-^1/_2 + x, -^1/_2 + y, z$	3.206 (2)	0.78 (2)	2.45 (2)	2.26	163.8 (2.0)	162.4
O(2)–H(6)···Cl	$-^1/_2 + x, -^1/_2 + y, z$	3.119 (2)	0.81 (2)	2.32 (2)	2.15	168.7 (2.0)	167.8
O(3)–H(7B)···Cl	$^1/_2 - x, ^1/_2 - y, -z$	3.119 (2)	0.77 (3)	2.35 (3)	2.15	169.8 (2.0)	168.9
O(4)–H(8B)···Cl	$-^1/_2 + x, ^1/_2 - y, ^1/_2 + z$	3.220 (2)	0.77 (3)	2.48 (3)	2.27	162.7 (2.0)	161.1

Other angles	Assumed H positions, deg	Other angles	Assumed H positions, deg
H(5)–Cl–H(6)	95.5	C(1)–O(5)–H(8A)	137.8
H(5)–Cl–H(7B)	141.9	C(4)′–O(5)–H(8A)	109.1
H(5)–Cl–H(8B)	122.1	C(2)–O(6)–H(7A)	103.5
H(6)–Cl–H(7B)	122.2	C(3)–O(6)–H(7A)	117.4
H(6)–Cl–H(8B)	99.3		
H(7B)–Cl–H(8B)	61.7		

[a] Standard errors in parentheses were calculated from the variance–covariance matrix obtained in the last least-squares cycle.

Hamilton and Ibers,[16] although no values are cited for hydrogen···ether oxygen bonds. The O–H···O angles, 172.5 and 173.8°, are nearly linear.

Structure of the $Mg(H_2O)_6{}^{2+}$ Unit. The four independent Mg–O bond lengths determined here, 2.054 Å for O(1), 2.057 Å for O(2), 2.082 Å for O(3), and 2.059 Å for O(4), may be compared to the two independent values, 2.056 and 2.062 Å, measured by Agron and Busing.[6] In each study the standard deviation of the bond length is 0.002 Å, except for our Mg–O(3) where the value is 0.001 Å. The Mg–O(3) bond differs from all the other values by a statistically significant amount. It is difficult to propose a systematic error in the data at the present level of refinement (R_1 = 3.5%) which could account for an error in this one bond length. As determined in the least-square analysis[10a] no correlation coefficient for any O(3) parameter exceeds a value of 0.12, and no other chemically equivalent bonds differ by more than three standard deviations.

The source of this difference appears instead to be the unique manner in which the O(3) water molecule is bound to the cation: the angle between the vector normal to the plane of the water molecule and the Mg–O bond vector is quite different for O(3) when compared to the other water molecules of this structure or with those of $Mg(H_2O)_6Cl_2$.[6] For O(1) and O(2) symmetry requires that the vector normal to the water plane and the Mg–O vector form a 90° angle. For O(4) the calculated angle between the plane normal and the bond vector is 104.3°. The values obtained by Agron and Busing, 90 and 104.0°, are very similar. But for O(3) the calculated angle is a surprisingly large 132.3°. An intriguing possibility is that the Mg–O(3) bond is slightly weakened as the water molecule tilts to orient its two hydrogen atoms to form the hydrogen bonds to O(6) and Cl.

The O–Mg–O angles range from 88.23 to 91.77° (*cf.* 88.67 to 91.33° in $Mg(H_2O)_6Cl_2$), very close to the ideal octahedral angle of 90°.

Cyclomer Conformation. The $C_8H_{16}O_4$ ring contains a crystallographic center of symmetry; no further symmetry elements are present. This C_i geometry is quite different from those determined in metal ion complexes where the heterocycle acts as a tetradentate ligand,[1-4] specifically in $Na(C_8H_{16}O_4)_2Cl{\cdot}5H_2O$,[1] $Na(C_8H_{16}O_4)_2OH{\cdot}8H_2O$,[2] and $Ca(C_8H_{16}O_4)Cl_2{\cdot}8H_2O$,[3] where a C_4 conformation occurs, and in $Cu(C_8H_{16}O_4)Cl_2$[4] where a C_s geometry is obtained. The torsion angles[17] generating this C_i conformation are shown in Figure 4 and a good view of the ring geometry can be obtained in Figure 1. A distinguishing feature of the conformation is the coplanarity, within 0.01 Å, of the six atoms C(3), C(4), O(5), C(3)′, C(4)′, and O(5)′; the remaining six atoms of the ring fall into essentially parallel planes 1.30 Å displaced to either side of this central plane. (The primes designate atoms related by the center of symmetry.) These features can be seen quite clearly in Figure 3 and arise as a consequence of the near-right-angle turns made by the ring at the oxygen atoms and at C(1) and C(3). Interestingly, one of the C–C torsion angles, namely, C(1)–C(2) (−83.1°), shows the largest deviation from the staggered conformation yet found in any of the structures[1-4] containing the tetraoxacyclododecane molecule.

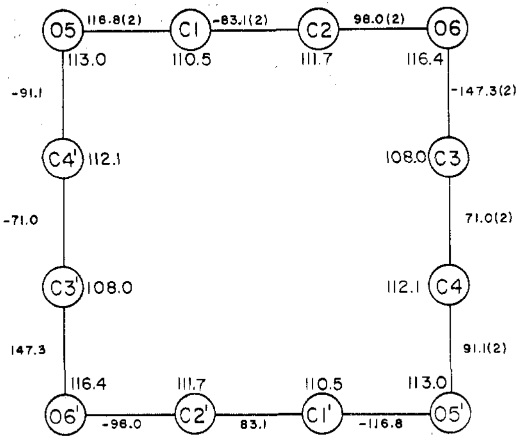

Figure 4. Torsion and internal bond angles for the C_i conformation of 1,4,7,10-tetraoxacyclododecane as found in $Mg(H_2O)_6Cl_2{\cdot}C_8H_{16}O_4$. The standard deviations of the torsion angles are given in parentheses.

The four oxygens form a rhombic figure with sides of 2.923 and 3.084 Å, for O(5)···O(6)′ and O(5)···O(6) respectively. The angles are 76.1° at O(5) and 103.9° at O(6). By comparison, in structures containing the C_4 conformation,[1-3] the oxygens form squares with sides of about 2.8 Å, or approximately twice the van der Waals radius of oxygen.

The ring located at ($^1/_4$, $^1/_4$, $^1/_2$) interacts with hydrogen atoms from hexahydrated cations on each of the four twofold axes passing through the unit cell: the four cation units which link to this ring are centered at (0, 0.20, $^1/_4$), (0, −0.20, $^3/_4$), ($^1/_2$, 0.70, $^1/_4$) and ($^1/_2$, 0.30, $^3/_4$). The C–O···H angles associated with the hydrogen bonds range from 103.5 to 137.8° (Table V), indicating that lone-pair orbitals on oxygens (assuming these to be tetrahedrally hybridized) point in the general direction of the hydrogen nuclei, but only in an approximate manner.

The internal angles in the ring show no evidence of being unusually strained. The angles at carbon, which vary in the present structure from 108.0 to 112.1° (Table III), are in the middle of the range 106.0–114.3° found for the other structures[1-4] containing this heterocycle and are very close to the tetrahedral angle. The range of C–O–C angles found previously[1-4] was 112.3–114.6°; one of our two C–O–C angles (113.0, 116.4°) falls slightly outside these limits. It is satisfying to note that the average C–O and C–C bond distances found here are precisely the same, 1.430 and 1.495 Å, respectively, as the respective averages of 36 determinations of the C–O distance and 18 determinations of the C–C distance in the previous four structures,[1-4] and that the individual values all fall within three standard deviations of these averages. The mean C–H bond distance, 0.98 Å, is as usual shorter than the true internuclear separation,[11] presumably about 1.09 Å, because of the bias of the electron density of the hydrogen atoms toward the bonding region. Some systematic errors in bond distances may occur because of thermal motion, but no correction for these was attempted.

The structure contains no atoms with unusually large thermal amplitudes (Table II and Figure 1). The oxygen atoms of the hexahydrated magnesium unit exhibit their largest components of thermal vibration in directions approximately perpendicular to the Mg–O bonds. The cation itself shows the smallest thermal amplitudes and is nearly isotropic. In contrast to those structures where the heterocycle functions as a tetradentate ligand,[1-4] the ring oxygens show considerable anisotropy.

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Registry No. $Mg(H_2O)_6Cl_2 \cdot C_8H_{16}O_4$, 53993-08-1.

Supplementary Material Available. A listing of calculated and observed structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40465C.

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Crystal Structure of Tetraphenylphosphonium Trithiocyanatomercurate(II)

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$[(C_6H_5)_4P][Hg(SCN)_3]$ crystallizes in the space group $P2_1/c$ with unit-cell parameters a = 11.574 (4) Å, b = 20.014 (8) Å, c = 12.144 (4) Å, β = 103.56 (3)°, and Z = 4. The structure was refined on 1899 independent observed reflections to an R factor of 0.039. The anionic part of the compound can be described as infinite chains of $[Hg(SCN)_3]^-$ ions, in which one of the SCN groups is bridging. The Hg–S bonds of the two nonbridging groups are of reasonable lengths (2.46 Å) for a basically three-coordinate species. For the bridging group, the Hg–S bond is much longer (2.59 Å) and nitrogen is close (2.40 Å) to the mercury atom of the next ion. As a result of this interionic Hg···N interaction, the metal is displaced by 0.45 Å from the trigonal plane toward the nitrogen atom and its overall coordination corresponds to a flattened tetrahedron of one nitrogen and three sulfur atoms. The $[[Hg(SCN)_3]^-]_n$ chains run parallel to the c axis and the space between the chains is filled with $[(C_6H_5)_4P]^+$ cations.

Introduction

Compounds of the type $MHgX_3$ are known for a variety of monovalent cations (M) and halide or pseudohalide anions (X).[1,2] Crystallographic studies have shown that chloro compounds with small cations (Na,[3] NH_4,[4] and Cs)[5] are double salts in which linear $HgCl_2$ molecules and chloride ions are packed in such a way that an approximate octahedral geometry is achieved around mercury. According to Zhdanov and Sanadze,[6] $KHg(SCN)_3$ and $NH_4Hg(SCN)_3$ are double salts as well. In those cases, the $Hg(SCN)_2$ molecule is bent at mercury and the metal is surrounded by a very distorted tetrahedron of sulfur atoms. Trigonal $[HgX_3]^-$ ions have been observed in crystals of $[(CH_3)_4N][HgBr_3]$[7] and $[(CH_3)_3S][HgI_3]$.[8]

The existence of discrete trihalogenomercurate anions in presence of larger cations prompted us to investigate similar systems with thiocyanate ions. The structure of the $[(C_6H_5)_4P]^+$ salt is reported here.

Experimental Section

Preparation. When KSCN and $[(C_6H_5)_4P]Cl$ both dissolved in