(Inoue's values in parentheses) are 1.48 (1.45), 1.38 (1.31), and 0.70 (0.70) BM/g-atom of copper, respectively. The moment at room temperature is considerably below the spin-only value for copper(II) but is well above the moment found for the strongly coupled planar dimers ($\mu_{eff} = ca.$ 0.5 BM). The observed value is indicative of weak antiferromagnetic coupling and, as the previous workers found, the variation of the magnetic susceptibility with temperature follows neither the theoretical prediction for isolated dinuclear units[3] nor the theoretical prediction for higher polymeric units.[16] Since the structure analysis has indicated dinuclear units, the discrepancy probably results from interactions between clusters.

Significant antiferromagnetic exchange has been found in copper(I) dimers having Cu–O···H···O–Cu[17] and Cu–C≡N···H···N≡C–Cu[18] hydrogen-bonded bridges. Weak antiferromagnetic behavior has long been observed in hydrated salts such as $MCl_2 \cdot 2H_2O$ (M = Fe, Co, Cu) and $MCl_2 \cdot 6H_2O$ (M = Co, Ni), with $2J$ values as great as -25 cm^{-1}.[19]

The principal antiferromagnetic coupling is undoubtedly related to superexchange within the four-membered Cu_2O_2

ring. The nonplanar nature of the ring should diminish markedly the importance of a potential π pathway[13] for superexchange. This structure, thus, provides additional evidence for superexchange through a σ pathway. The weak coupling in the present compound and the small Cu–O–Cu angle are also in line with recent geometric correlations for hydroxy-bridged complexes[20] and chloro-bridged complexes.[21]

Registry No. CuL·2H₂O, 51567-40-9.

Supplementary Material Available. Observed and calculated structure factors (in electrons) for $CuC_9H_{14}N_2O_4$ 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2067.

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Cyclomer Complexes. Crystal Structure of a 2:1 Pentahydrate Complex of 1,4,7,10-Tetraoxacyclododecane with Sodium Chloride [Na⁺(C₈H₁₆O₄)₂][Cl⁻·5H₂O]

F. P. van REMOORTERE* and F. P. BOER

The crystal structure of NaCl·2C₈H₁₆O₄·5H₂O, where C₈H₁₆O₄ is 1,4,7,10-tetraoxacyclododecane, has been determined by a single-crystal X-ray diffraction study. The complex crystallizes in space group *Pcca* with lattice parameters $a = 22.122 \pm 0.012$, $b = 9.544 \pm 0.004$, and $c = 12.082 \pm 0.006$ Å ($Z = 4$). The intensities of 2203 reflections were measured on a Picker automatic diffractometer (Cu Kα radiation) and the structure was solved by iterative application of Sayre's equation. All but water hydrogens were located by difference synthesis. Full-matrix least-squares refinement of atom positions, hydrogen isotropic thermal parameters, and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 7.6\%$ for 1948 reflections above background. The sodium ion forms an eight-coordinate sandwich complex of approximate D_4 symmetry with two polyether rings, each of which obeys approximate C_4 symmetry. The oxygen atoms are arranged at the corners of a square antiprism with Na–O distances ranging from 2.473 to 2.517 Å. The Na⁺ cation is in no way associated with either the chloride ion or the water molecules. The latter form rings consisting of six waters joined by hydrogen bonds which are linked by a spiro oxygen that is hydrogen bonded to four other oxygens to form infinite chains along c. The chloride ions are located between these chains and appear to be hydrogen bonded to four water molecules.

Introduction

Cyclomers of alkylene oxides are readily prepared[1] and constitute a remarkably versatile series of new ligands. The unique properties of these compounds and the unexpected and novel geometries of their complexes appear to be associated with their conformational flexibility and the presence of lone-pair electrons on the oxygen atoms. One of the most promising members of this series is 1,4,7,10-tetraoxacyclododecane, the cyclic tetramer of ethylene oxide. This report

describes the structure of an unusual eight-coordinate crystalline complex formed by this heterocycle, where the sodium cation lies sandwiched between eight oxygen atoms at the vertices of a square antiprism. This structural type seems to be of general significance since complexes formed by NaCl, KCl, RbCl, NaBr, KBr, and NaI have been shown to be isomorphous by X-ray powder diffraction.[2]

Although the affinity of ethers for alkali ions in solution is well-known[3] and a few crystalline complexes of linear

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polyethers have been reported,[4-7] interest in the complexes of cyclic polyethers is of recent origin.[8-17] Pedersen, in an important series of papers,[8,9] has prepared and identified numerous complexes of polyethers condensed from aromatic diols. A number of these "crown" ether complexes with alkali metal ions have now been described by Truter and coworkers.[12] Dietrich, Lehn, and Sauvage[13,14] have reported the synthesis of related diazapolyoxa macrocycles, which can chelate metal ions to form crystalline complexes with coordination numbers as high as 8, as shown in two recent structure determinations.[15,16] A particularly interesting complex of this general type is the structure communicated[18,19] by Dunitz, *et al.*, between KSCN and the antibiotic nonactin, which we believe to be the first example of cubic eight-coordination observed in a molecular species.[20,21] The nonactin and diazapolyoxa chelates are, however, not of the simple polyether type, since some of the coordination sites are carbonyl oxygens in the former compound and nitrogen atoms in the latter.

Experimental Section

Crystals of $NaCl \cdot 2C_8H_{16}O_4 \cdot 5H_2O$, obtained by adding 2 equiv of the cyclic ether to a saturated aqueous solution of NaCl, were supplied by E. C. Steiner. With care large colorless plates can be grown and these could be cleaved to produce rod-shaped fragments of fairly uniform cross section suitable for our experiments. The crystals were sealed in thin-walled Lindemann glass capillaries to prevent loss of water of hydration. The unit cell and space group were determined on a crystal mounted in a 0.2-mm capillary along the [001] axis. The diffraction symmetry D_{2h} and the systematic absence of the reflection classes $0kl$, $l = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, displayed on Weissenberg photographs, established the space group uniquely as *Pcca* (D_{2h}^8). The crystal was then carefully aligned on a Picker four-circle goniostat, and least-squares refinement of the setting angles of 12 reflections with Cu Kα radiation (λ 1.5418 Å) gave the dimensions of the orthorhombic cell. The lattice parameters $a = 22.122 \pm 0.012$, $b = 9.544 \pm 0.004$, and $c = 12.082 \pm 0.006$ Å are consistent with a calculated density 1.305 g cm^{-3} for mol wt 500.948 and $Z = 4$. The stoichiometry can only be accommodated in this space group by requiring that the sodium and chlorine atoms lie on inversion centers or diads and that at least one water molecule lies on a diad.

Intensity data were collected on a somewhat larger crystal

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Table I. Summary of Test Models

Model	Position	Atom	Multiplier	B,[a] Å^2	R_1[a]	R_2[a]
A	4d	Cl	0.25	2.0	0.17	0.24
	4e	Cl	0.25	5.7		
B	4d	Cl	0.50	3.2	0.29	0.38
	4e	Cl	0.00			
C	4d	Cl	0.00		0.42	0.81
	4e	Cl	0.50	2.0		
D	4d	Cl	0.30	3.0	0.15	0.20
	4e	Cl	0.20	4.3		
E	4d	Cl	0.50	5.0	0.14	0.20
	4e	O	0.50	2.7		

[a] The numbers indicated are after two cycles of full-matrix least-squares refinement and are believed to be close to the converged values in all cases.

mounted in a 0.3-mm capillary. This crystal was aligned with its [01$\bar{1}$] vector parallel to the φ axis of the goniostat. An independent set of lattice constants computed from the setting angles of 15 reflections for this crystal was within the standard deviations above. The intensities were measured using the θ–2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. The takeoff angle of the tube was 3°, 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° + Δ, where Δ is the separation of the Kα doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Two stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. Attenuators were used to prevent the count rate from exceeding 12,000/sec. The reciprocal lattice was recorded out to the instrumental limit (sin θ = 0.909) and a total of 2203 independent reflections was measured. In addition to the (611) reflection, monitored after every 50 measurements, ten other reflections recorded at 24-hr intervals showed good stability. An error $\sigma(I) = [(0.02I)^2 + N_0 + k^2 N_b]^{1/2}$ was assigned to the net intensity $I = N_0 - kN_b$ 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 $\Sigma w(|F_o| - |F_c|)^2$ was minimized. 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 terms are the intensities corrected for Lorentz and polarization effects. The 240 reflections for which $I < 0$ or $I/\sigma(I) < 2.0$ were denoted absent and were omitted from the refinement. The linear absorption coefficient for Cu Kα radiation is 20.1 cm^{-1}. No absorption corrections were made; transmission factors for this crystal were estimated to range from 0.55 to 0.74.

Solution and Refinement of the Structure

The signs of 311 reflections were determined by the Sayre equation[22] using the multiple-solution method of Long. An E map[23] revealed the ring atoms and two water oxygens in general positions. The peak at 4c was identified as the sodium ion from its position between the two polyether rings and its sharpness. The more diffuse peaks at 4d and 4e could be accounted for by (1) chloride ion disordered between the two sites, (2) chloride at one site and water at the other, and (3) disorder of water and chloride among both sites. The first hypothesis, which had the unattractive feature of failing to account for the stoichiometry indicated by the analysis, was thought to be unlikely, but was tested thoroughly in models A–D of Table I. In this table are listed the positions, atom types, and occupancy factors for these two sites, together with isotropic temperature factors and the R factors R_1 and R_2 after two cycles of full-matrix refinement of the model.[24,25] (R_1 and R_2 are defined as $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $\{\Sigma w(F_o - F_c)^2/\Sigma w F_o^2\}^{1/2}$, respectively.) Models B and

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Table II. Atomic Parameters and Standard Deviations[a,b]

Atom	x/a	y/b	z/c	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cl	0.25	0	0.0210 (2)	321 (5)	1428 (21)	1013 (15)	12 (8)	0	0
Na	0	0.2391 (2)	0.25	124 (4)	893 (21)	519 (13)	0	23 (5)	0
O(1)	0.0761 (1)	0.4337 (3)	0.2579 (2)	165 (6)	1106 (32)	748 (20)	−16 (11)	2 (9)	3 (21)
C(2)	0.0720 (2)	0.5150 (4)	0.1591 (4)	269 (10)	942 (45)	898 (36)	−67 (18)	1 (16)	159 (34)
C(3)	0.0754 (2)	0.4240 (5)	0.0568 (4)	281 (11)	1260 (55)	753 (33)	173 (21)	89 (16)	196 (35)
O(4)	0.0266 (1)	0.3270 (3)	0.0623 (2)	197 (6)	1056 (32)	654 (19)	29 (11)	33 (8)	50 (20)
C(5)	0.0326 (2)	0.2120 (5)	−0.0138 (3)	333 (13)	1338 (54)	458 (26)	11 (22)	11 (15)	42 (31)
C(6)	0.0737 (2)	0.1004 (5)	0.0308 (3)	275 (11)	1228 (52)	562 (27)	41 (20)	101 (15)	68 (31)
O(7)	0.0479 (1)	0.0520 (3)	0.1322 (2)	187 (5)	1036 (30)	530 (17)	17 (11)	19 (8)	26 (19)
C(8)	0.0892 (3)	−0.0265 (4)	0.1972 (4)	268 (11)	948 (50)	716 (35)	101 (19)	16 (16)	44 (31)
C(9)	0.1322 (2)	0.0632 (5)	0.2597 (4)	186 (9)	1283 (52)	771 (33)	154 (18)	−12 (14)	44 (35)
O(10)	0.0977 (1)	0.1579 (3)	0.3258 (2)	158 (5)	1078 (31)	630 (18)	47 (11)	2 (8)	94 (20)
C(11)	0.1318 (2)	0.2745 (5)	0.3677 (4)	189 (9)	1399 (56)	780 (34)	30 (19)	−130 (14)	−204 (35)
C(12)	0.1370 (2)	0.3897 (5)	0.2847 (4)	160 (8)	1255 (53)	1039 (39)	−65 (17)	−35 (15)	−87 (39)
W(1)	0.2996 (2)	0.2666 (4)	0.3924 (3)	293 (8)	1997 (53)	1063 (31)	−32 (18)	5 (13)	93 (34)
W(2)	0.2856 (19)	0.2690 (4)	0.1602 (3)	444 (12)	2143 (60)	1073 (33)	37 (22)	−133 (16)	−53 (36)
W(3)	0.25	0.5	0.0217 (3)	267 (9)	700 (34)	496 (24)	0 (15)	0	0

Atom	x/a	y/b	z/c	B, Å²	Atom	x/a	y/b	z/c	B, Å²
H(21)	0.121 (3)	0.599 (7)	0.157 (5)	10.5 (1.6)	H(81)	0.108 (2)	−0.093 (4)	0.144 (3)	3.2 (0.8)
H(22)	0.027 (2)	0.548 (5)	0.195 (4)	7.7 (1.2)	H(82)	0.087 (3)	−0.059 (7)	0.230 (5)	7.4 (1.8)
H(31)	0.136 (3)	0.373 (7)	0.047 (5)	10.1 (1.4)	H(91)	0.155 (2)	0.111 (5)	0.216 (3)	4.1 (1.1)
H(32)	0.080 (3)	0.473 (6)	−0.009 (5)	9.0 (1.6)	H(92)	0.147 (2)	−0.000 (5)	0.313 (4)	5.6 (1.0)
H(51)	0.041 (2)	0.226 (5)	−0.076 (5)	5.8 (1.1)	H(111)	0.169 (2)	−0.254 (5)	0.383 (4)	5.7 (1.2)
H(52)	−0.009 (3)	0.093 (7)	−0.019 (6)	10.4 (1.6)	H(112)	0.107 (2)	0.292 (5)	0.436 (5)	6.9 (1.3)
H(61)	0.113 (2)	0.133 (4)	0.039 (3)	4.2 (1.0)	H(121)	0.181 (3)	0.460 (10)	0.359 (7)	17.6 (3.0)
H(62)	0.069 (3)	0.017 (7)	−0.032 (5)	9.9 (1.5)	H(122)	0.164 (2)	0.352 (4)	0.214 (3)	4.4 (0.9)

[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 were included to test the possibility that one of these peaks might be spurious, but the high R values indicate that this hypothesis is to be rejected. We note that model D, in which the occupancies are proportional to the peak heights in the E map, gives lower R values than model A where equal Cl populations are assumed. However, an R factor still lower than those for A–D is yielded by model E, the only one consistent with the elemental analysis, although this model, which assumes an ordered chlorine at 4d and an ordered oxygen at 4e, is not completely satisfactory with respect to the peak heights at these sites in the E-map. Model E was used in subsequent refinement. This model corresponds to the second hypothesis above, but the third hypothesis which allows some exchange of O and Cl between 4d and 4e cannot be ruled out and in fact appears attractive in view of the E-map peak heights and the temperature factors. Although it is clear that chloride ions are located primarily at 4d, a meaningful determination of the relative occupancy factors is not feasible because of the interdependence of occupancy factors, scattering factors, and temperature parameters.

At this stage a difference electron density map was generated.[23] The 16 ether hydrogens appeared clearly, close to their calculated positions with peak heights ranging from 0.37 to 0.75 e Å⁻³ (average 0.50 e Å⁻³). The water hydrogens could not be located. Although four peaks between 0.38 and 0.60 e Å⁻³ were present near the waters in general positions, their locations did not appear chemically reasonable. One cycle of full-matrix least-squares refinement including the ether hydrogens[25] and assuming isotropic thermal motion for all atoms reduced R_1 from 0.130 to 0.123 and R_2 from 0.182 to 0.168. Anisotropic temperature factors were now introduced for the nonhydrogen atoms, and one further cycle of full-matrix least-squares gave R_1 and R_2 equal to 0.094 and 0.137, respectively. Fifteen strong low-order reflections that appeared to show severe secondary extinction were omitted from the reflection list at this time. After three more cycles, refinement converged at discrepancy indices $R_1 = 0.076$ and $R_2 = 0.101$ for 1948 reflections.

Atomic parameters and their estimated standard deviations[26] are given in Table II. A table of observed and calculated structure factors is available to the interested reader.[27] The root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table III. The directions of these components may be inferred from Fig-

Table III. Root-Mean-Square Thermal Displacements (Å) along Principal Axes[a,b]

Atom	Axis 1	Axis 2	Axis 3
Cl	0.256 (2)	0.274 (2)	0.283 (2)
Na	0.172 (3)	0.199 (3)	0.203 (3)
O(1)	0.202 (4)	0.227 (3)	0.235 (3)
C(2)	0.196 (5)	0.258 (5)	0.267 (5)
C(3)	0.181 (6)	0.259 (5)	0.289 (6)
O(4)	0.204 (4)	0.226 (3)	0.230 (3)
C(5)	0.183 (5)	0.249 (5)	0.288 (6)
C(6)	0.186 (5)	0.240 (5)	0.273 (5)
O(7)	0.195 (3)	0.215 (3)	0.222 (3)
C(8)	0.198 (6)	0.230 (6)	0.267 (6)
C(9)	0.187 (5)	0.237 (5)	0.267 (5)
O(10)	0.191 (3)	0.210 (3)	0.234 (3)
C(11)	0.182 (5)	0.237 (5)	0.282 (6)
C(12)	0.191 (5)	0.244 (5)	0.280 (5)
W(1)	0.268 (4)	0.278 (4)	0.307 (4)
W(2)	0.266 (4)	0.313 (4)	0.346 (5)
W(3)	0.180 (4)	0.192 (5)	0.257 (4)

	Hydrogen Displacements		
H(21)	0.365	H(81)	0.201
H(22)	0.312	H(82)	0.306
H(31)	0.358	H(91)	0.228
H(32)	0.338	H(92)	0.266
H(51)	0.271	H(111)	0.269
H(52)	0.363	H(112)	0.296
H(61)	0.231	H(121)	0.472
H(62)	0.354	H(122)	0.236

[a] Ordered on increasing magnitude. Hydrogen atoms are isotropic. [b] Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

ures 1, 3, and 7 where anisotropic motion is represented by ellipsoids of 50% probability.[28] Bond distances and angles are listed in Tables IV and V, respectively; the standard errors given in Tables III–V were computed from the variance–covariance matrix obtained in the final least-squares cycle.[26]

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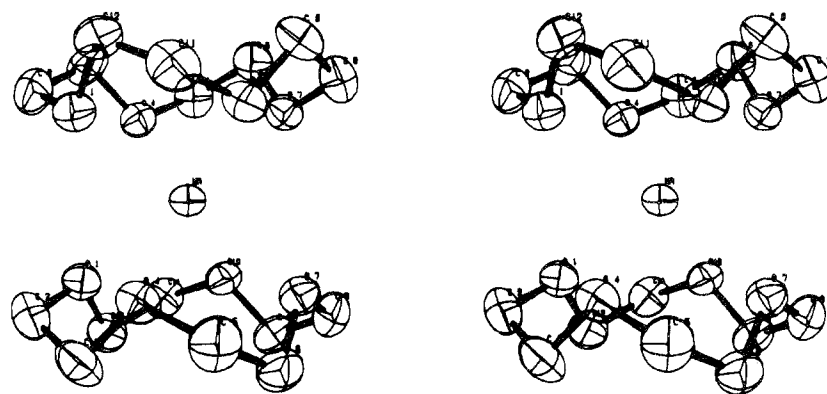
Figure 1. Three-dimensional view of the cyclomer–metal complex showing ellipsoids of thermal motion and the numbering system.

Table IV. Selected Interatomic Distances (Å)[a,b]

Sodium–Oxygen Distances		Carbon–Hydrogen Bonds	
Na–O(1)	2.508 (3)	C(2)–H(21)	1.34 (6)
Na–O(4)	2.488 (3)	C(2)–H(22)	1.13 (5)
Na–O(7)	2.517 (3)	C(3)–H(31)	1.43 (6)
Na–O(10)	2.473 (3)	C(3)–H(32)	0.93 (6)
		C(5)–H(51)	0.79 (5)
Carbon–Carbon Bonds		C(5)–H(52)	1.47 (7)
C(2)–C(3)	1.512 (6)	C(6)–H(61)	0.92 (4)
C(5)–C(6)	1.500 (6)	C(6)–H(62)	1.10 (7)
C(8)–C(9)	1.485 (7)	C(8)–H(81)	1.00 (4)
C(11)–C(12)	1.492 (7)	C(8)–H(82)	0.50 (6)
		C(9)–H(91)	0.86 (4)
Carbon–Oxygen Bonds		C(9)–H(92)	0.94 (5)
C(2)–O(1)	1.427 (5)	C(11)–H(11)	0.87 (5)
C(12)–O(1)	1.450 (5)	C(11)–H(112)	1.00 (6)
C(3)–O(4)	1.423 (5)	C(12)–H(121)	1.49 (8)
C(5)–O(4)	1.438 (5)	C(12)–H(122)	1.10 (4)
C(6)–O(7)	1.428 (5)		
C(8)–O(7)	1.419 (5)	Oxygen–Oxygen Inter-ring	
C(9)–O(10)	1.427 (5)	Distances	
C(11)–O(10)	1.436 (5)	O(1)–O(1)(I)	3.370 (5)
		O(1)–O(4)(I)	3.303 (4)
Sodium–Carbon Distances		O(4)–O(10)(I)	3.464 (4)
Na–C(2)	3.268 (4)	O(7)–O(7)(I)	3.549 (5)
Na–C(5)	3.277 (4)	O(7)–O(10)(I)	3.414 (4)
Na–C(8)	3.275 (5)		
Na–C(11)	3.261 (4)	Distances to Water Oxygens	
Na–C(3)	3.368 (4)	W(1)–W(2)	2.822 (6)
Na–C(6)	3.380 (4)	W(1)–W(3)(II)	2.934 (4)
Na–C(9)	3.374 (4)	W(2)–W(3)	2.878 (4)
Na–C(12)	3.381 (4)	W(1)–Cl(II)	3.177 (4)
		W(2)–Cl	3.169 (4)
Oxygen–Oxygen Intra-ring			
Distances		Sodium–Chlorine Distances	
O(1)–O(4)	2.796 (4)	Na–Cl	6.591 (3)
O(4)–O(7)	2.796 (4)	Na–Cl(II)	6.820 (3)
O(7)–O(10)	2.777 (4)		
O(10)–O(1)	2.799 (4)		

[a] Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.
[b] Roman numerals correspond to the symmetry transformations described in Table V.

Principal Structural Features

Our results establish that the sodium ion is complexed by two cyclomer molecules in a symmetrical sandwich-type configuration (Figure 1). Oxygen atoms from two ether rings surround the cation, which exhibits the unusual coordination number 8. The complex approximates D_4 symmetry, although only a C_2 axis, passing through the sodium atom at 0, y, $1/4$ and relating the two 12-membered rings, is imposed by the space group. The oxygen atoms are arranged at the vertices of a slightly distorted square antiprism (Figure 2) at distances from sodium averaging 2.496 Å.

The water molecules and chloride ions form an interesting network of hydrogen bonds based on six-membered rings
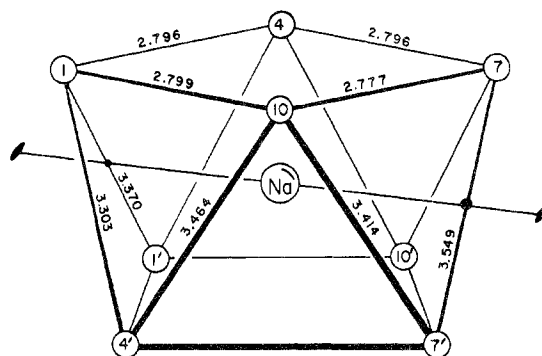

Figure 2. Square-antiprism arrangement of oxygen atoms around sodium indicating the inter-oxygen distances. The crystallographic twofold axis is shown.

(Figure 3) that extends in infinite layers parallel to the (100) plane. The ring comprised of six water molecules is situated on the 4e twofold axis. It consists of two W(3) oxygens, located on the diad at $1/4$, $1/2$, z and $1/4$, $1/2$, $1/2 + z$, plus pairs of water molecules, W(1) and W(2), related by this diad. The three unique distances in this ring, W(1)···W(2) = 2.822 ± 0.006 Å, W(1)···W(3) = 2.934 ± 0.004 Å, and W(2)···W(3) = 2.878 ± 0.004 Å, are in the normal range for hydrogen-bonded oxygens. Adjacent rings, related by the c glide, are connected through W(3) which acts as a spiro-type link to form infinite chains in the z direction. The angles internal to the rings at W(3) are W(1)–W(3)–W(1)′ = 115.6 ± 0.2° and W(2)–W(3)–W(2)′ = 108.9 ± 0.2°, and the remaining unique angles formed between W(1) and W(2) at W(3) are 80.2 ± 0.1 and 142.1 ± 0.1° (see Table V). That this configuration represents a large distortion from a tetrahedral geometry at W(3) can also be seen from the dihedral angle of 46.3° between two rings connected by this atom (compare 90° in a tetrahedron). The rings themselves are moderately nonplanar as evidenced by deviations of ±0.15 Å for W(1) and W(2) from the best planes[29] (which include the C_2 axis). The remaining internal angles in the six-membered rings are 118.8 ± 0.2° at W(1) and 127.9 ± 0.2° at W(2).

Parallel chains of water molecules related by the cell translations along b are interconnected by chloride ions on the 4d diad at $1/4$, 0, z and $1/4$, 0, $1/2 + z$ to form additional chains of six-membered rings spiro-linked along z by chloride ions. Four-membered rings are thus generated between the

(29) J. Gvildys, "Least-Squares Plane and Line Fitter," Program Library B-125, Argonne National Laboratory, Argonne, Ill., May 18, 1965; see V. Shomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

Table V. Selected Interatomic Angles[a]

Transformations

I	$-x$	y	$1/2 - z$
II	$1/2 - x$	y	$1/2 + z$
III	$1/2 - x$	y	$z - 1/2$
IV	x	$1 - y$	$z - 1/2$
V	$1/2 - x$	$1 - y$	z
VI	$1/2 - x$	$-y$	z
VII	x	$-y$	$z - 1/2$

Vertex	Atom 1	Atom 2	Angle, deg
Na	O(1)	O(4)	68.1 (0.1)
	O(1)	O(10)	68.4 (0.1)
	O(4)	O(7)	67.9 (0.1)
	O(7)	O(10)	67.6 (0.1)
	O(1)	O(1)(I)	84.4 (0.1)
	O(1)	O(4)(I)	82.8 (0.1)
	O(4)	O(10)(I)	88.6 (0.1)
	O(7)	O(7)(I)	89.6 (0.1)
	O(7)	O(10)(I)	86.3 (0.1)
	O(1)	O(7)	105.3 (0.1)
	O(4)	O(10)	103.7 (0.1)
	O(1)	O(7)(I)	141.8 (0.1)
	O(1)	O(10)(I)	146.4 (0.1)
	O(4)	O(4)(I)	140.6 (0.1)
	O(4)	O(7)(I)	148.7 (0.1)
	O(10)	O(10)(I)	143.4 (0.1)
O(1)	Na	C(12)	114.7 (0.1)
	Na	C(2)	109.2 (0.1)
O(4)	Na	C(3)	116.2 (0.1)
	Na	C(5)	110.3 (0.1)
Cl	W(2)	W(2)(VI)	115.9 (0.2)
	W(2)	W(1)(III)	72.3 (0.1)
	W(2)	W(1)(VII)	145.4 (0.1)
	W(1)(III)	W(1)(VII)	121.4 (0.1)
W(1)	W(2)	W(3)(II)	118.8 (0.2)
	W(2)	Cl(II)	117.1 (0.1)
	W(3)(II)	Cl(II)	102.6 (0.1)
O(1)	C(2)	C(12)	113.7 (0.3)
C(2)	O(1)	C(3)	111.6 (0.3)
	O(1)	H(21)	107 (3)
	O(1)	H(22)	83 (3)
	C(3)	H(21)	107 (3)
	C(3)	H(22)	121 (3)
	H(21)	H(22)	123 (4)
C(3)	C(2)	O(4)	107.4 (0.3)
	C(2)	H(31)	108 (2)
	C(2)	H(32)	115 (4)
	O(4)	H(31)	120 (3)
	O(4)	H(32)	116 (4)
	H(31)	H(32)	90 (4)
O(4)	C(3)	C(5)	113.4 (0.3)
C(5)	O(4)	C(6)	111.6 (0.3)
	O(4)	H(51)	120 (4)
	O(4)	H(52)	124 (3)
	C(6)	H(51)	108 (4)
	C(6)	H(52)	81 (2)
	H(51)	H(52)	104 (4)
C(6)	C(5)	O(7)	107.2 (0.3)
	C(5)	H(61)	111 (3)
	C(5)	H(62)	102 (3)
	O(7)	H(61)	113 (3)
	O(7)	H(62)	108 (3)
	H(61)	H(62)	114 (4)

Vertex	Atom 1	Atom 2	Angle, deg
O(7)	Na	C(6)	115.1 (0.1)
	Na	C(8)	109.4 (0.1)
O(10)	Na	C(9)	117.3 (0.1)
	Na	C(11)	110.3 (0.1)
O(1)	O(4)	O(10)	88.4 (0.1)
O(4)	O(1)	O(7)	91.2 (0.1)
O(7)	O(4)	O(10)	88.8 (0.1)
O(10)	O(1)	O(7)	91.5 (0.1)
C(2)	C(5)	C(11)	89.1 (0.1)
C(5)	C(2)	C(8)	90.7 (0.1)
C(8)	C(5)	C(11)	89.5 (0.1)
C(11)	C(2)	C(8)	90.7 (0.1)
C(3)	C(6)	C(12)	89.4 (0.1)
C(6)	C(3)	C(9)	91.1 (0.1)
C(9)	C(6)	C(12)	89.2 (0.1)
C(12)	C(3)	C(9)	90.2 (0.1)
W(2)	W(3)	W(1)	127.9 (0.2)
	W(3)	Cl	104.1 (0.1)
	W(1)	Cl	123.2 (0.2)
W(3)	W(2)	W(2)(V)	108.9 (0.2)
	W(2)	W(1)(III)	80.2 (0.1)
	W(2)	W(1)(IV)	142.1 (0.1)
	W(1)(III)	W(1)(IV)	115.6 (0.2)
O(7)	C(6)	C(8)	112.8 (0.3)
C(8)	O(7)	C(9)	112.9 (0.3)
	O(7)	H(81)	104 (2)
	O(7)	H(82)	135 (9)
	C(9)	H(81)	115 (2)
	C(9)	H(82)	90 (9)
	H(81)	H(82)	99 (8)
C(9)	C(8)	O(10)	107.9 (0.3)
	C(8)	H(91)	112 (3)
	C(8)	H(92)	101 (3)
	O(10)	H(91)	109 (3)
	O(10)	H(92)	102 (3)
	H(91)	H(92)	124 (4)
O(10)	C(9)	C(11)	114.1 (0.3)
C(11)	O(10)	C(12)	112.0 (0.3)
	O(10)	H(111)	114 (3)
	O(10)	H(112)	98 (3)
	C(12)	H(111)	103 (3)
	C(12)	H(112)	118 (3)
	H(111)	H(112)	112 (4)
C(12)	C(11)	O(1)	106.9 (0.3)
	C(11)	H(121)	89 (3)
	C(11)	H(122)	109 (2)
	O(1)	H(121)	128 (3)
	O(1)	H(122)	114 (2)
	H(121)	H(122)	105 (3)

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

six-membered rings and are spiro-linked along y alternately by water W(3) molecules and chloride ions. Both the six-membered ring containing chloride and the four-membered ring are again moderately nonplanar. The W(1) and W(2) oxygens deviate by ±0.13 and ±0.14 Å, respectively from the best plane[29] through the six atoms. Nonplanarity in the four-membered ring can be measured by the dihedral angle of 6.7° between planes[29] through the atoms {W(1), W(2), W(3)} and {W(1), W(2), Cl} or alternatively by the average deviation of 0.07 Å from the least-square plane[29] through all four atoms. The dihedral angle between six-membered rings linked by the chloride is 40.6°, and the dihedral angle be-
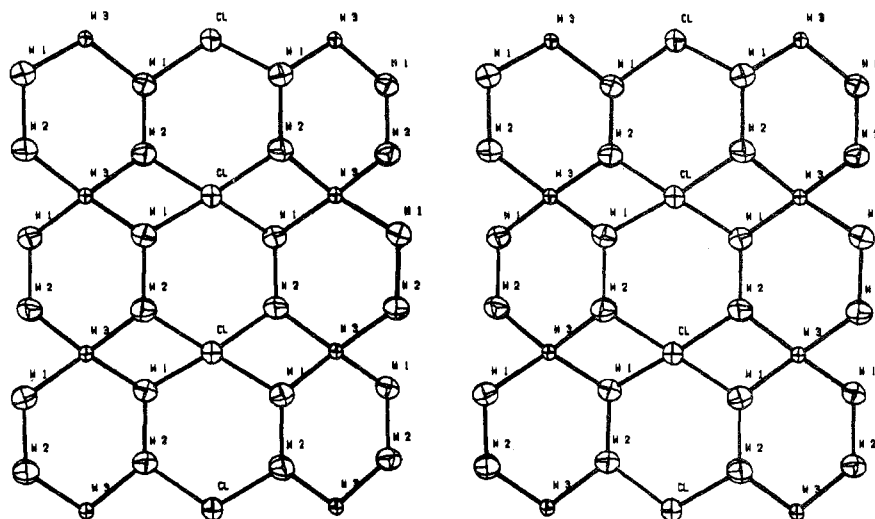
Figure 3. Three-dimensional view of the hydrogen-bonded network of water molecules and chloride ions at $x = {}^1/_4$. The z axis is vertical and y is horizontal; 1.5 unit cells are drawn in each direction.
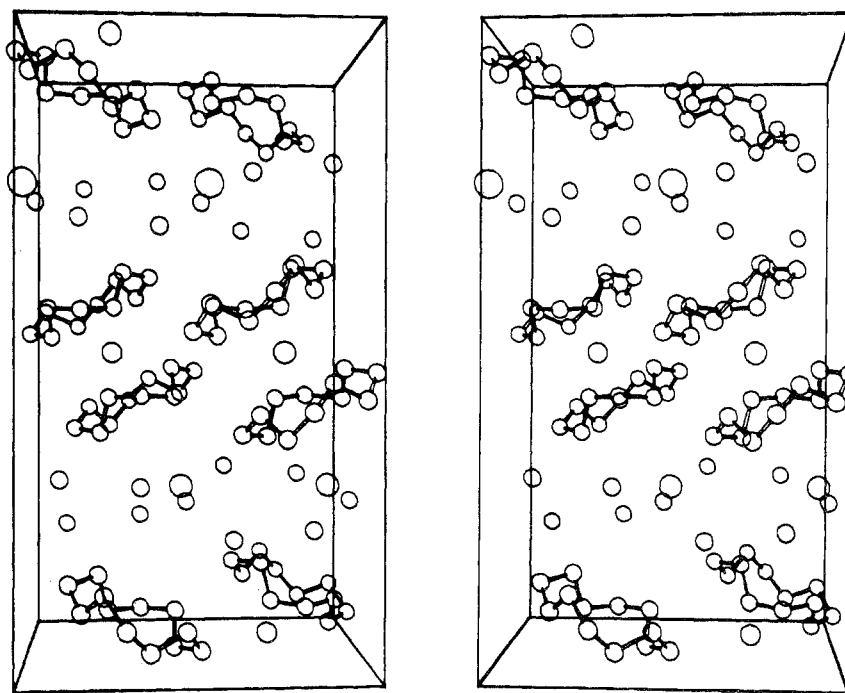

Figure 4. Three-dimensional diagram of the crystal structure in a unit cell of $[Na^+(C_8H_{16}O_4)_2][Cl^-\cdot 5H_2O]$ viewed down the y axis. The x axis is vertical and the z axis is horizontal. The origin is at the lower right front corner of the box.

tween adjacent six-membered rings sharing the W(1)-W(2) edge is 43.4°. The angles at chlorine internal to the six-membered rings are 121.4 ± 0.1° to W(1) and 115.9 ± 0.2° to W(2), and that internal to the four-membered ring is 72.3 ± 0.1°. The remaining unique angle at Cl is 145.4 ± 0.1° (Table V). The internal angles in the six-membered ring at W(1) and W(2) are 117.1 ± 0.1 and 123.2 ± 0.2°, respectively.

The water-chlorine distances W(1)· · ·Cl = 3.177 ± 0.004 Å and W(2)· · ·Cl = 3.169 ± 0.004 Å are typical of oxygen-chloride hydrogen-bond lengths.[30,31] This hydrogen-bonding scheme, as shown in Figure 3, would provide a functional role for all of the water hydrogen atoms with five crystal-

lographically unique protons available for five unique O-H· · ·O and O-H· · ·Cl⁻ interactions. The bond distances in this network also support our assignment of 4d positions to chloride and 4e positions to water.

An interesting feature of the crystal structure (Figures 4 and 5) is its separation into essentially organic and aqueous layers with the layer comprised of cyclomer complex presenting only methylene groups to the aqueous layer. None of the water molecules is closer than 3.63 Å to a carbon, well outside the van der Waals limit, while the shortest C· · ·Cl approach is 3.93 Å. No association of sodium with water or chloride occurs; the shortest Na· · ·Cl interionic distances are 6.591 ± 0.003 and 6.820 ± 0.003 Å (Table V). Thus, at $x = 0$ there is a layer of cyclomer complexes in which all of the 12-membered rings are essentially parallel. Packing within this layer occurs through the inversion centers and the cell translations along b. The network of water

(30) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **26**, 2200 (1957).
(31) W. C. Hamilton and S. J. La Placa, *Acta Crystallogr., Sect. B*, **24**, 1147 (1968).
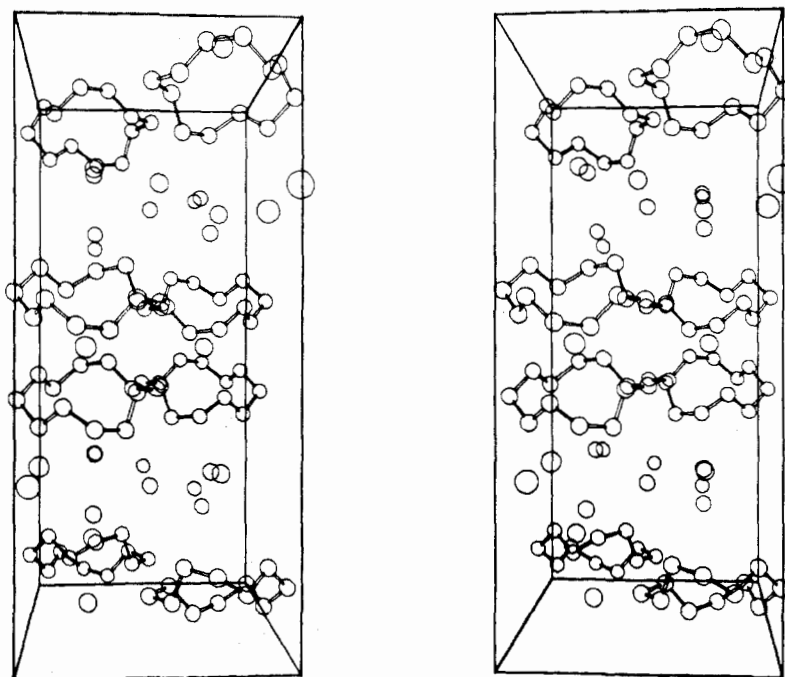
Figure 5. Three-dimensional diagram of the crystal structure in a unit cell of $[Na^+(C_8H_{16}O_4)_2][Cl^-\cdot5H_2O]$ viewed down the z axis. The x axis is vertical and the y axis is horizontal. The origin is at the lower left front corner of the box.

molecules and chloride ions described above is located at $x = {}^1/_4$. The next organic layer, related to the first by the screw diad along a, is found at $x = {}^1/_2$. Again the cyclomer rings within the layer remain parallel, but with a different spatial orientation with respect to those of the $x = 0$ layer.

Geometry of the Cyclomer–Metal Complex

The square antiprism defined by the eight oxygen atoms has an s/l ratio of 0.816. The symbol s represents the average $O\cdots O$ distance on the square faces of the antiprism, 2.792 Å, and l is the average $O\cdots O$ distance between squares, 3.420 Å. (See Figure 2.) The four unique distances on the square faces fall in a narrow range (2.777–2.799 Å) close to the lower limit for intramolecular contacts between oxygen atoms. However, the l values show a wide variation (3.303–3.549 Å) that results from a tilt of 3.0° between the plane[29] defined by O(1), O(4), O(7), O(10) and the corresponding plane related by the twofold axis. This tilt is the major source of deviation from ideal D_4 symmetry and may arise because the l distances, which are substantially longer than the sum (2.8 Å) of two oxygen van der Waals radii, are too great to provide steric resistance to packing forces tending to distort the symmetry. The equation of the least-squares plane[29] through the four atoms listed above is $19.940x + 0.248y - 5.223z = 0.282$. Individual oxygen atoms are displaced by only 0.0045 Å from this plane, and the sodium atom is removed by 1.528 Å along the normal.

The O–Na–O angles can be grouped according to four classes characteristic of a square antiprism. This is done in Table V. Their average values are 68.0, 86.3, 104.5, and 144.1°, but a substantial variation within classes results because of the tilt between rings described above. The Na–O–C angles in this complex range from 109.2 to 117.3° (Table V) and thus allow lone pair electrons from tetrahedrally hybridized oxygen atoms to be directed approximately toward the cation. Dunitz has reported[19] M⁺–O–C angles between 107 and 115° in the eight-coordinate K⁺-nonactin complex.
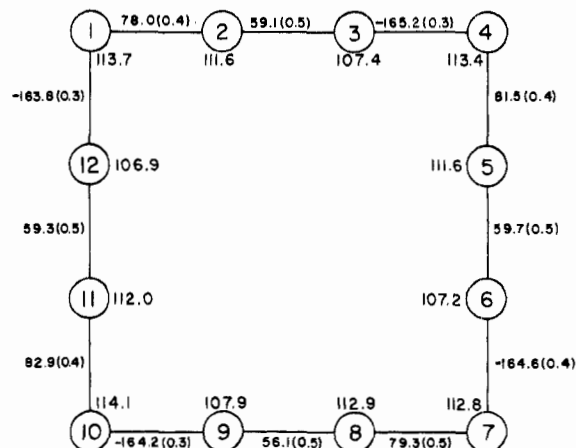
In discussing the significance of metal–oxygen distances

Figure 6. Torsion angles and internal bond angles in 1,4,7,10-tetraoxacyclododecane as found in $[Na^+(C_8H_{18}O_4)_2][Cl^-\cdot5H_2O]$. In parentheses are given the standard deviations[29] for the torsional angles. The sign convention is the one suggested by W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

in complexes with alkali ions, the sum $\Sigma r_i^M + r_{vdw}^O$ of the metal ion radius r_i^M and the oxygen van der Waals radius $r_{vdw}^O = 1.40$ Å would appear to be an attractive guidepost. For sodium ($r_i^{Na} = 0.95$ Å) this sum is 2.35 Å and is of the same magnitude as the shortest metal–oxygen distances in hydrated sodium salts,[32] where Na–O interactions range roughly from 2.3 to 2.7 Å. In the K⁺-nonactin complex,[19] the average M–O distance (2.81 Å) was found to be 0.08 Å longer than $\Sigma r_i^K + r_{vdw}^O$, and in each of two macrocyclic complexes with Rb⁺ the observed[12,15] M–O distances averaged 2.90 Å, a value only 0.02 Å longer than the sum $\Sigma r_i^{Rb} + r_{vdw}^O$. In the present structure, however, the average value (2.496 Å) of the four unique Na–O distances (2.473, 2.488, 2.508, and 2.517 Å, all ±0.003 Å) is 0.15 Å longer than

(32) R. W. G. Wyckoff, "Crystal Structures," Vol. III, 2nd ed, Interscience, New York, N. Y., 1965, Chapter X.
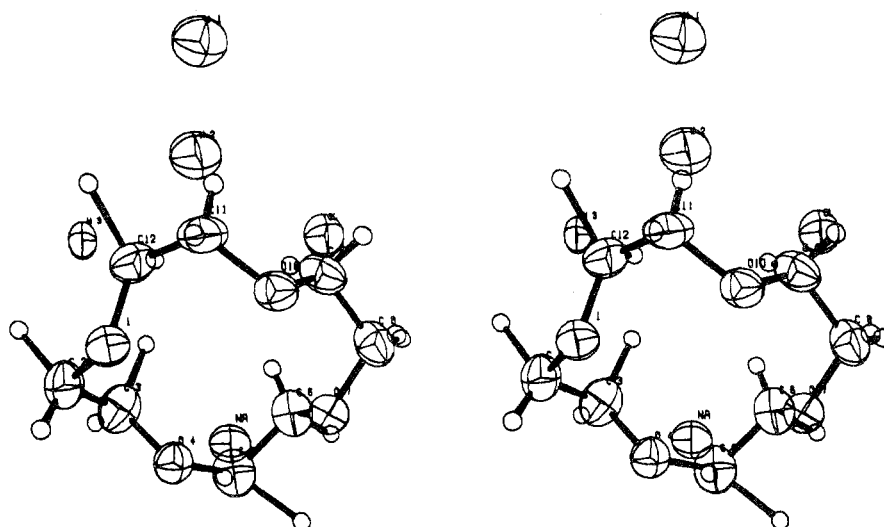
Figure 7. Three-dimensional view of the crystallographically independent atoms showing ellipsoids of thermal motion. The hydrogen atoms are drawn at their observed positions with spheres of uniform radius.

$\Sigma r_i^{Na} + r_{vdw}^O$. Here we should note that these distances do not appear to be restricted by steric repulsion in the square antiprism; if the inter-ring distance is decreased to the point where O· · ·O contacts are reduced to the van der Waals limit ($s = l = 2.80$ Å), a "minimum" permitted cation-oxygen distance of 2.30 Å is found. In our view, the observed Na-O separations may represent a compromise between an optimal "radial" distance, presumably lower than the actual distance, and the need to maintain a geometry where the oxygen lone-pair orbitals are directed to the positive charge center. The stability of particular complexes may then depend on the balance between these two factors. However, further structural investigations will be required to test this point.

The Tetraoxacyclododecane Ring

The 12-membered rings conform quite closely to the point group C_4. Accordingly, there are two distinct kinds of carbon atoms, which we label type α [C(2), C(5), C(8), C(11)] and type β [C(3), C(6), C(9), C(12)]. Significantly different internal angles occur at the two types of carbon atoms, averaging $112.0°$ for O-C(α)-C(β) and $107.4°$ for C(α)-C(β)-O. The average internal angle at oxygen is $113.5°$ (Table V). The Na· · ·C distances (Table IV) fall into narrow ranges, 3.261-3.277 Å for α and 3.368-3.381 Å for β, and the planes through sets of four symmetry-related carbon atoms are 2.00 and 2.57 Å from sodium along the respective normals. As in the case of the oxygen atoms, the squares formed by the carbon atoms are fairly regular, with sides varying between 3.639 and 3.672 Å for α and between 3.074 and 3.133 Å for β, the corners being within $1.1°$ of the right angle (Table V).

The torsional angles, shown in Figure 6, also display C_4 symmetry. These define a ring conformation that serves to stagger the methylene hydrogens as evidenced by the average torsional angle of $58.6°$ about the C-C bonds. We have seen that this geometry brings the four oxygen atoms into close proximity on one side of the ring in a manner that directs the lone-pair electrons toward the sodium atom, while

the methylene groups remain away from the cation on the back side of the molecule.

The four values for the C-C bonds average to 1.497 Å, while the mean C-O distance, an average of eight independent measurements, is 1.431 Å. No bond deviates from these average values by more than 0.02 Å. The hydrogen atoms did not behave well in the refinement and show anomalously large variations in temperature factors, bond lengths, and bond angles (see tables). Their positions can also be ascertained from Figure 7, which shows the ring from another angle.

Thermal Motion

Thermal motion in the heterocycle is distributed very uniformly around the ring (Table III, Figures 1 and 7). The oxygen atoms have lower thermal amplitudes and exhibit less anisotropy than the carbons (Table III). The sodium ion is also fairly isotropic and shows the smallest thermal amplitudes of any atom except W(3), where the results may be anomalous because of possible chloride substitution at this site. The thermal parameters of the oxygen atoms W(1) and W(2) are the largest in the structure and show moderate anisotropy (Figures 3 and 7).