

The Crystal Structure of the Complex of 1,4,7,10-Tetraoxacyclododecane with Copper(II) Chloride

By F. P. VAN REMOORTERE, F. P. BOER AND E. C. STEINER*

Dow Chemical U.S.A., Midland, Michigan 48640, U.S.A.

(Received 11 November 1974; accepted 13 January 1975)

The crystal structure of $C_8H_{16}O_4 \cdot CuCl_2$, the complex of 1,4,7,10-tetraoxacyclododecane with copper(II) chloride has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in the space group $P2_12_1$ with $a = 7.062$ (3), $b = 13.661$ (8), and $c = 12.337$ (7) Å ($Z = 4$). The intensities of 1565 unique reflections were measured on a Picker automatic diffractometer (Mo $K\alpha$ radiation) and the structure was solved by Patterson and Fourier methods. All hydrogen atoms were located. Full-matrix least-squares refinement of atom positions, hydrogen isotropic temperature factors and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 3.4\%$ for the 1038 reflections above background. The Cu(II) ion is hexacoordinate and its coordination geometry can be pictured as an elongated and distorted octahedron, where two *cis* sites are taken by chlorine atoms and the remaining vertices are occupied by the four oxygens of the macrocycle. The equatorial plane of the coordination polyhedron coincides with a non-crystallographic mirror plane and contains the copper atom, two chlorines and two oxygens in a square-planar pattern. The Cu–Cl bond lengths are 2.214 (2) and 2.228 (2) Å and the Cu–O distances are 2.128 (3) and 2.113 (3) Å. The apical Cu–O bonds are much longer, 2.343 (4) and 2.403 (3) Å respectively, and the angle between them is only 135.2° compared with 180° in an ideal octahedron.

Introduction

The preceding studies in this series have established that the 1,4,7,10-tetraoxacyclododecane ligand chelates the alkali metal ions Na, K, and Rb to form novel eight-coordinate species of 2:1 stoichiometry (van Remoortere & Boer, 1974; Boer, Neuman & van Remoortere, 1974). In these complexes the $[M^+(C_8H_{16}O_4)_2]$ units display approximate D_4 symmetry and the 12-membered rings adopt a conformation belonging to the subgroup C_4 . Two attractive properties are inherent in this geometry: a lone-pair orbital from each of the four oxygen atoms is oriented toward the central ion and the methylene hydrogens are staggered. An identical ring conformation is found (North, Steiner, van Remoortere & Boer, 1974) in the 1:1 adduct $CaCl_2 \cdot C_8H_{16}O_4 \cdot 8H_2O$. Although different stoichiometries are involved, all of these complexes are of the sandwich type and all contain a cation with an ion radius of at least 0.95 Å. Another common feature of these structures is the complete separation of the positive and negative charge centers.

A number of considerations led us to conjecture that, if the ion radius were decreased, the complexes formed might be governed by different structural principles. Indeed, the stabilities of macrocyclic complexes are believed to depend on the size of the metal ions relative to the dimensions of the cages in which they are bound (Pedersen, 1967). The abilities of the ligands to direct oxygen lone-pair orbitals toward the

charge center may be a second contributing factor. The square antiprism geometry has certain limitations in these respects, since the requirement that inter-ring O...O contacts should not penetrate two van der Waals radii imposes (van Remoortere & Boer, 1974) a minimum metal–oxygen distance of 2.30 Å. Short inter-ring separations will also give rise to a less favorable orientation of the lone-pair orbitals with respect to the cation. However, the flexibility of 1,4,7,10-tetraoxacyclododecane heterocycle suggests a potential to adapt its conformation to varied stereochemical requirements and thus lend itself to the formation of other coordination polyhedra. To test hypotheses, and to ascertain whether there exist similarities to 1:1 complexes of certain 18-membered macrocycles (Bright & Truter, 1970; Hecceg & Weiss, 1970) (in which the cations are held in the central cavities of the rings), we are undertaking the structure determination of complexes of 1,4,7,10-tetraoxacyclododecane with some small cations. A single-crystal X-ray diffraction study of an anhydrous 1:1 complex formed by this heterocycle with $CuCl_2$ is reported below.

Experimental

Crystals of $CuCl_2 \cdot C_8H_{16}O_4$ are deep green, form rectangular prisms elongated on *a*, and exhibit well developed faces. A crystal of dimensions $1.50 \times 0.26 \times 0.35$ mm (corresponding to *a*, *b* and *c*) was sealed in a thin-walled Lindemann-glass capillary and aligned along its *a* axis. The reciprocal lattice levels $0kl$ and $1kl$, and $h0l$ and $hk0$ were recorded on Weissenberg and precession photographs respectively. From the dif-

* The crystallographic work was carried out by F.V.R. and F.P.B.; E.C.S. synthesized the complex.

fraction symmetry D_{2h} and the systematic absence of $h00$ reflections for h odd, $0k0$ for k odd, and $00l$ for l odd, the space group could be assigned as $P2_12_12_1$ (No. 19, orthorhombic D_2^7). The crystal was then carefully centered on a Picker four-circle goniostat, and the lattice constants were calculated by least-squares refinement of the setting angles of ten reflections (Mo $K\alpha$ radiation, $\lambda=0.71069$ Å). The unit-cell dimensions, $a=7.062$ (3), $b=13.661$ (8), and $c=12.337$ (7) Å, give a calculated density of 1.734 g cm $^{-3}$ for M.W. 310.67 and $Z=4$. The estimated standard deviations of the lattice constants obtained from the least-squares analysis were a factor of ten better than the errors assigned, which are based on our experience in reproducing results with different crystals and/or orientations. The space group requires no molecular symmetry elements.

Intensity data were gathered using the $\theta-2\theta$ scan mode of the diffractometer and Mo $K\alpha$ radiation selected by the 0002 reflection of a highly-oriented graphite crystal monochromator. The take-off angle of the X-ray 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 restricted stray radiation. The scan speed was 2° min $^{-1}$ over 2θ angles of $2^\circ + \Delta$, where Δ is the separation of the $K\alpha$ doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Two stationary-crystal stationary-counter background counts of 10 s were taken at each end of the scan. The reciprocal lattice was recorded out to $\sin \theta=0.461$, equivalent to the Cu $K\alpha$ sphere. Attenuators were used to prevent counting rates in excess of 12000 s $^{-1}$. The 171 reflection monitored after every 50 measurements showed good stability ($\pm 1\%$) through 461 reflections. At this point a sudden loss of intensity of 4.5% was encountered, which could not be accounted for by a change in crystal alignment. When further loss of intensity occurred, a second crystal of dimensions $0.60 \times 0.14 \times 0.32$ mm (on a , b and c) was mounted and aligned. This crystal was

used to collect the remaining 1114 reflections (to a total of 1575), and during this period the test reflection remained stable within 1%. An overlapping set of ten widely separated reflections were measured to establish a preliminary scale factor for correlating the two portions of the data set. An error $\sigma(I)=[(0.02I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensity $I=N_0 - kN_b$ 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_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 (Azaroff, 1955). The 197 reflections for which $I/\sigma(I) < 3.3$ were denoted absent and omitted from the refinement. An absorption correction was applied to the data, using a linear absorption coefficient $\mu(\text{Mo } K\alpha)=22.99$ cm $^{-1}$. Transmission factors ranged between 0.480 and 0.630 for the first crystal, and between 0.482 and 0.726 for the second.

Solution and refinement of the structure

The position of the copper atom was deduced from the three largest peaks in a sharpened three-dimensional Patterson function. A combination of Patterson and Fourier methods then yielded the locations of the Cl, O, and C atoms in a straightforward manner. Full-matrix least-squares refinement of positions and isotropic temperature factors of the 15 heavier atoms converged to the R values $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.073$ and $R_2 = \sum \{w[F_o - F_c]^2 / \sum wF_o^2\}^{1/2} = 0.095$. The positions of the hydrogen atoms were calculated with a computer program written for this purpose. A difference Fourier confirmed the presence of peaks at or near all of the sites predicted for hydrogens, as well as numerous peaks of the same order of magnitude identified as anisotropic residuals. The hydrogen atoms were now included at their calculated positions, and their coor-

Table 1. Final structure parameters

The anisotropic thermal parameters are in the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. Hydrogen atoms have isotropic temperature factors. Estimated standard deviations are given in parentheses.

	x	y	z	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cu	-0.09125 (8)	0.51965 (4)	0.45760 (4)	1046 (15)	305 (4)	339 (5)	13 (6)	70 (6)	0 (3)
Cl(1)	0.05833 (21)	0.40073 (10)	0.36856 (10)	1905 (35)	449 (8)	521 (9)	231 (15)	174 (15)	-58 (7)
Cl(2)	-0.04441 (23)	0.63396 (10)	0.33327 (10)	2663 (41)	411 (8)	543 (10)	66 (16)	379 (16)	124 (7)
				$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(1)	-0.4125 (5)	0.4809 (2)	0.4374 (3)	145 (7)	46 (2)	55 (2)	-2 (4)	-1 (4)	-4 (2)
C(2)	-0.5021 (8)	0.5714 (5)	0.4605 (5)	131 (12)	58 (4)	62 (4)	22 (5)	4 (6)	-6 (4)
C(3)	-0.4338 (7)	0.6162 (5)	0.5636 (5)	118 (12)	62 (4)	57 (4)	13 (6)	17 (6)	-9 (3)
O(4)	-0.2297 (5)	0.6259 (3)	0.5557 (3)	142 (8)	49 (2)	50 (3)	-2 (4)	-1 (4)	-11 (2)
C(5)	-0.1452 (8)	0.6532 (5)	0.6568 (5)	179 (13)	53 (4)	55 (4)	0 (6)	-13 (6)	-20 (3)
C(6)	0.0691 (9)	0.6431 (4)	0.6421 (5)	191 (14)	48 (4)	68 (4)	-22 (7)	-4 (7)	-18 (3)
O(7)	0.1169 (5)	0.5465 (3)	0.6088 (3)	164 (8)	52 (2)	48 (2)	2 (4)	-4 (4)	4 (2)
C(8)	0.0925 (8)	0.4731 (4)	0.6908 (4)	187 (12)	71 (4)	40 (3)	19 (8)	6 (6)	6 (3)
C(9)	-0.0028 (8)	0.3847 (5)	0.6390 (5)	185 (14)	56 (4)	59 (4)	19 (6)	-7 (7)	15 (4)
O(10)	-0.1664 (5)	0.4218 (2)	0.5831 (3)	154 (8)	40 (2)	59 (2)	-15 (4)	-5 (4)	8 (2)
C(11)	-0.2956 (8)	0.3476 (4)	0.5547 (5)	212 (14)	43 (3)	73 (5)	-26 (6)	3 (8)	5 (4)
C(12)	-0.4696 (7)	0.4002 (3)	0.5087 (5)	180 (13)	50 (3)	52 (3)	-3 (7)	-12 (5)	6 (3)

Table 1 (cont.)

	x	y	z	B (Å ²)
H(21)	-0.640 (8)	0.567 (3)	0.467 (4)	-0.5 (1.0)
H(22)	-0.450 (7)	0.618 (3)	0.395 (4)	0.4 (1.1)
H(31)	-0.471 (7)	0.577 (4)	0.620 (4)	-0.1 (1.1)
H(32)	-0.478 (7)	0.690 (4)	0.561 (4)	1.6 (1.3)
H(51)	-0.212 (7)	0.614 (3)	0.718 (3)	-0.5 (1.0)
H(52)	-0.174 (9)	0.714 (4)	0.684 (4)	1.2 (1.0)
H(61)	0.153 (8)	0.657 (4)	0.718 (4)	2.6 (1.3)
H(62)	0.104 (7)	0.687 (4)	0.587 (4)	0.0 (1.1)
H(81)	0.030 (6)	0.499 (3)	0.748 (4)	0.2 (1.0)
H(82)	0.240 (7)	0.449 (4)	0.719 (4)	1.7 (1.2)
H(91)	-0.031 (6)	0.337 (3)	0.700 (4)	0.1 (1.0)
H(92)	0.076 (8)	0.355 (4)	0.584 (4)	1.3 (1.2)
H(111)	-0.292 (12)	0.293 (5)	0.604 (5)	5.4 (2.0)
H(112)	-0.218 (7)	0.305 (4)	0.475 (4)	1.4 (1.1)
H(121)	-0.563 (7)	0.353 (3)	0.463 (4)	0.7 (1.0)
H(122)	-0.529 (7)	0.419 (4)	0.573 (4)	0.8 (1.1)

ordinates and isotropic thermal parameters were allowed to vary for three additional cycles of refinement, during which R_1 was reduced from 0.066 to 0.064 and R_2 from 0.076 to 0.070. Although all hydrogen atoms remained in chemically reasonable positions, four assumed temperature factors (B) between 0 and 0.5 Å², while two had B values in excess of 10 Å². The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962); those for hydrogen were from Stewart, Davidson & Simpson (1965).

Anisotropic thermal parameters were now introduced for the non-hydrogen atoms, and one cycle of refinement lowered R_1 to 0.038 and R_2 to 0.042. However, after this cycle seven hydrogen atoms had negative B 's, including several whose B values had been fairly large at the end of the isotropic refinement. At this point, we applied a correction for secondary extinction to those strong low-order reflections that were systematically less intense than their calculated values. The corrected structure factors were obtained from the Zachariasen (1963) expression $F_o^{corr} = F_o[1 + \beta c I_{obs}]$ with $c = 0.5808 \times 10^{-6}$, where I_{obs} is the scaled observed inten-

sity and β is a geometrical factor. Four additional cycles of least-squares refinement were now performed during which negative B values were automatically reset to the arbitrary value of 0.1 Å². In the last cycle hydrogen B 's were not varied. The final $R_1 = 0.034$ and $R_2 = 0.037$ for the 1378 reflections above background. Sufficient convergence in the last cycle is indicated by values of $(\Delta/\sigma)_{max}$ of 0.12 for non-hydrogen atoms and 0.18 for hydrogens. Four hydrogen B values continued to refine to negative values (as low as -0.53 Å²) even in the last cycle, and several others had low positive values (Table 1). In view of the low overall temperature factor of the structure ($B_0 = 2.7$ Å² from a Wilson plot) and the fairly large standard deviations (1.0-1.1) on these parameters, the unusually low values may have arisen in part from random errors.* During the refinement separate scale factors were varied for the reflections from each of the two crystals, their final ratio differed by less than 0.5% from that assigned initially on the basis of overlapping reflections. A final difference synthesis showed no positive or negative density of magnitude in excess of 0.70 e Å⁻³.

The final positional and temperature parameters, and their standard deviations as calculated in the least-squares refinement, are listed in Table 1. Root-mean-square components of thermal displacement along the principal axes, derived from the anisotropic thermal parameters, are given in Table 2, and their directions may be inferred from Fig. 1, where the three-dimensional structure of the complex is shown using ellipsoids of 50% probability to represent the anisotropic thermal motion. In Tables 3 and 4 respectively we summarize bond distances and angles, together with their

* It was pointed out by a referee that the large crystal used for data collection may have caused the unusual behavior of the hydrogen temperature factors by its non-uniform exposure to the X-ray beam. The editor suggested that the Stewart, Davidson & Simpson (1965) scattering factors for hydrogen may also have contributed.

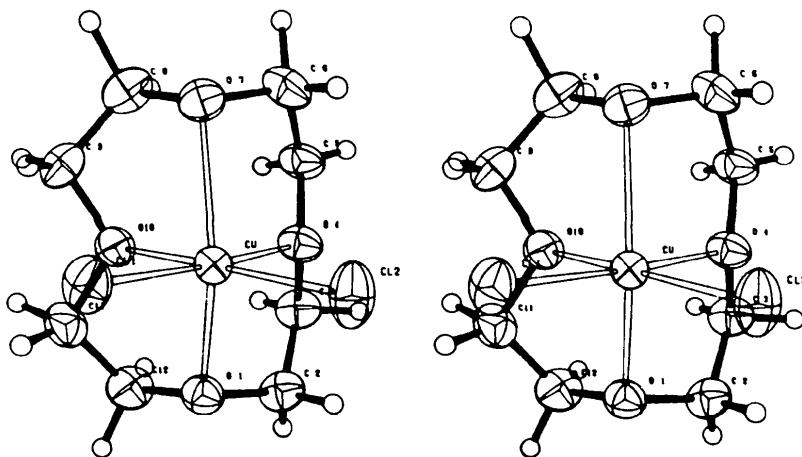


Fig. 1. Three-dimensional stereopair view of the CuCl₂ complex of 1,4,7,10-tetraoxacyclododecane. An approximate non-crystallographic mirror plane passes through Cu, Cl(1), Cl(2), O(4) and O(10). The ellipsoids represent amplitudes of thermal vibration at 50% probability.

standard errors. The errors listed in Tables 2, 3 and 4 were computed from the variance-covariance matrix obtained in the final least-squares cycle. Table 5 lists the structure factors.

Table 2. *Root-mean-square components of thermal motion along the principal axes (Å)**

	Axis 1	Axis 2	Axis 3
Cu	0.152 (1)	0.169 (1)	0.172 (1)
Cl(1)	0.166 (2)	0.214 (2)	0.240 (2)
Cl(2)	0.165 (2)	0.209 (2)	0.278 (2)
O(1)	0.191 (5)	0.200 (5)	0.215 (5)
C(2)	0.168 (9)	0.217 (8)	0.245 (8)
C(3)	0.155 (9)	0.214 (8)	0.250 (8)
O(4)	0.180 (6)	0.190 (5)	0.229 (5)
C(5)	0.165 (9)	0.214 (8)	0.254 (8)
C(6)	0.171 (9)	0.226 (9)	0.258 (8)
O(7)	0.191 (5)	0.205 (5)	0.222 (5)
C(8)	0.173 (7)	0.209 (9)	0.267 (8)
C(9)	0.178 (9)	0.222 (9)	0.254 (9)
O(10)	0.174 (6)	0.200 (6)	0.228 (5)
C(11)	0.178 (9)	0.238 (8)	0.248 (8)
C(12)	0.173 (9)	0.235 (8)	0.261 (8)

* Ordered on increasing magnitudes. The errors in parentheses were computed from the variance-covariance matrix obtained in the final least-squares cycle.

Table 3. *Selected interatomic distances (Å)*
Standard deviations calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

Cu—Cl(1)	2.228 (2)	C(2)—O(1)	1.418 (6)
Cu—Cl(2)	2.214 (2)	C(12)—O(1)	1.453 (7)
		C(3)—O(4)	1.451 (6)
Cu—O(1)	2.343 (4)	C(5)—O(4)	1.431 (6)
Cu—O(4)	2.128 (3)	C(6)—O(7)	1.423 (6)
Cu—O(7)	2.403 (3)	C(8)—O(7)	1.435 (6)
Cu—O(10)	2.113 (3)	C(9)—O(10)	1.438 (6)
		C(11)—O(10)	1.444 (6)
Cu—C(2)	2.987 (6)	C(2)—H(21)	0.98 (5)
Cu—C(3)	3.049 (6)	C(2)—H(22)	1.09 (5)
Cu—C(5)	3.084 (6)	C(3)—H(31)	0.92 (5)
Cu—C(6)	3.051 (6)	C(3)—H(32)	1.06 (6)
Cu—C(8)	3.219 (5)	C(5)—H(51)	1.04 (4)
Cu—C(9)	2.966 (6)	C(5)—H(52)	0.91 (5)
Cu—C(11)	2.960 (6)	C(6)—H(61)	1.12 (6)
Cu—C(12)	3.189 (6)	C(6)—H(62)	0.94 (6)
		C(8)—H(81)	0.91 (5)
C(2)—C(3)	1.492 (8)	C(8)—H(82)	1.15 (5)
C(5)—C(6)	1.530 (9)	C(9)—H(91)	1.02 (5)
C(8)—C(9)	1.523 (8)	C(9)—H(92)	0.97 (5)
C(11)—C(12)	1.500 (8)	C(11)—H(111)	1.05 (7)
		C(11)—H(112)	1.17 (5)
		C(12)—H(121)	1.08 (5)
		C(12)—H(122)	0.94 (5)

Table 4. *Selected interatomic angles (°)*

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

Vertex	Atom 1	Atom 2	Vertex	Atom 1	Atom 2				
Cu	Cl(1)	Cl(2)	95.85 (7)	C(5)	O(4)	C(6)	106.6 (4)		
	Cl(1)	O(1)	103.99 (9)		O(4)	H(51)	108 (2)		
	Cl(1)	O(4)	174.8 (1)		O(4)	H(52)	118 (3)		
	Cl(1)	O(7)	101.78 (9)		C(6)	H(51)	119 (3)		
	Cl(1)	O(10)	91.1 (1)		C(6)	H(52)	110 (4)		
	Cl(2)	O(1)	103.32 (9)		H(51)	H(52)	95 (4)		
	Cl(2)	O(4)	89.0 (1)		C(6)	C(5)	O(7)	110.6 (5)	
	Cl(2)	O(7)	109.8 (1)			C(5)	H(61)	114 (3)	
	Cl(2)	O(10)	172.5 (1)			C(5)	H(62)	107 (3)	
	O(1)	O(4)	76.7 (1)			O(7)	H(61)	106 (3)	
	O(1)	O(7)	135.2 (1)			O(7)	H(62)	109 (3)	
	O(1)	O(10)	72.1 (1)			H(61)	H(62)	111 (4)	
	O(4)	O(7)	74.6 (1)			C(8)	O(7)	C(9)	108.1 (4)
	O(4)	O(10)	84.2 (1)				O(7)	H(81)	109 (3)
O(7)	O(10)	71.4 (1)	O(7)	H(82)			108 (2)		
O(1)	C(2)	C(12)	114.4 (4)	C(9)			H(81)	115 (3)	
	Cu	C(2)	102.3 (3)	C(9)			H(82)	108 (3)	
	Cu	C(12)	112.1 (3)	H(81)			H(82)	109 (4)	
	O(4)	C(3)	C(5)	112.3 (4)			C(9)	C(8)	O(10)
Cu		C(3)	115.6 (3)	C(8)				H(91)	107 (2)
Cu		C(5)	118.8 (3)	C(8)	H(92)			112 (3)	
O(7)		C(6)	C(8)	114.6 (4)	O(10)			H(91)	115 (3)
	Cu	C(6)	102.8 (3)	O(10)	H(92)			106 (3)	
	Cu	C(8)	111.5 (3)	H(91)	H(92)			111 (4)	
	O(10)	C(9)	C(11)	114.6 (4)	C(11)			O(10)	C(12)
Cu		C(9)	111.9 (3)	O(10)				H(111)	105 (4)
Cu		C(11)	111.2 (3)	O(10)		H(112)		107 (3)	
C(2)		O(1)	C(3)	112.6 (5)		C(12)		H(111)	125 (5)
	O(1)	H(21)	114 (3)	C(12)		H(112)		114 (2)	
	O(1)	H(22)	102 (2)	H(111)		H(112)		99 (4)	
	C(3)	C(3)	H(21)	106 (3)		C(12)		C(11)	O(1)
C(3)		H(22)	106 (2)	C(11)				H(121)	111 (3)
H(21)		H(22)	116 (4)	C(11)			H(122)	103 (3)	
C(2)		C(2)	O(4)	107.6 (4)			O(1)	H(121)	109 (2)
		C(2)	H(31)	108 (3)			O(1)	H(122)	116 (3)
		C(2)	H(32)	106 (3)			H(121)	H(122)	109 (4)
		O(4)	H(31)	113 (3)					
O(4)		O(4)	H(32)	102 (3)					
	H(31)	H(32)	120 (4)						

Discussion

In the CuCl2 complex with 1,4,7,10-tetraoxacyclododecane the Cu(II) ion is hexacoordinate and the separation of positive and negative charge centers found (van Remoortere & Boer, 1974; North, Steiner, van Remoortere & Boer, 1974) in some alkali and alkaline earth halide complexes of this ligand does not occur. The coordination geometry can be pictured as a severely distorted octahedron where two cis sites are taken by chlorines and the remaining vertices are occupied by

the four oxygens of a single macrocycle. Although not imposed by the space group, the complex and the heterocyclic ligand approximate C2v symmetry.

The equatorial plane of the coordination polyhedron, which coincides with the plane of symmetry, contains the atoms Cu, Cl(1), Cl(2), O(4), and O(10) in the square planar pattern common among Cu(II) complexes. The equatorial Cu-O distances, of average length 2.12 Å, indicate that these bonds are much stronger than the apical Cu-O interactions, which average 2.37 Å. Within the square plane, the Cl-Cu-O

Table 5. Structure factor table for CuCl2 · C8H16O4 in e × 34-49

Table with multiple columns of numerical data representing structure factors for various h, k, l indices. The table is organized into several sections based on the indices.

angles deviate only about 1° from the right angle, while the positive and negative deviations of about 6° (Table 4) for the Cl–Cu–Cl and O–Cu–O angles respectively may be related to the relative size of chlorine and oxygen atoms.

The distortions of the octahedron apparently arise because the size of the heterocycle precludes the angle between the apical oxygen from reaching the ideal value of 180° , and an O(1)–Cu–O(7) angle of only 135.2° is actually attained. We note that Cu(II) structures of this distorted octahedral type, containing a closely held square-planar grouping plus longer bonds to irregular apical sites, have been observed previously (Freeman, Guss, Healy, Martin & Nockolds, 1969). The average Cu–Cl bond length in this structure, 2.221 \AA , is slightly shorter than the value of 2.242 \AA found in the square plane of glycyglycylglycinocopper(II) chloride sesquihydrate (Freeman, Robinson & Schoone, 1964) and substantially shorter than the distances 2.284 and 2.336 \AA reported in the Cu(II)

complex of tetraoxadiazacyclooctadecane (Herceg & Weiss, 1970). While Cu–O bond lengths between 1.90 and 2.00 are commonly reported in the literature, and our values are all fairly long compared with these, they are considerably shorter than the shortest Cu–O distances (2.708 and 2.756 \AA) found in the tetraoxadiazacyclooctadecane complex (Herceg & Weiss, 1970), where these interactions must be very weak.

The small differences among pairs of bond distances in the equatorial plane, 0.014 \AA for Cu–Cl and 0.015 \AA for Cu–O bond, appear to be insignificant. On the other hand, the large difference between the two apical Cu–O distances, 2.343 (4) \AA and 2.403 (3) \AA for O(1) and O(7) respectively, must be regarded as significant. This result is somewhat puzzling because O(1) and O(7) are related by the mirror plane of the complex and should have identical chemical roles. The only explanation we can venture at this time is that the apical interactions are fairly weak and hence more easily subject to distortion from crystal packing forces.

The conformation of the 12-membered ring can be readily seen in Fig. 1, and a schematic diagram summarizing its torsion angles is given in Fig. 2. This structure permits the heterocycle to act as a tetradentate ligand in a fundamentally different manner from that in the complexes where it adopts the C_4 conformation (van Remoortere & Boer, 1974; Boer, Neuman, van Remoortere & Steiner, 1974; North, Steiner, van Remoortere & Boer, 1974); in the latter compounds bonding to the metal occurs through four lone-pair orbitals from the same side of the ring (referred to a hypothetical planar conformation), but in the C_s geometry three lone pairs from one side of the ring [O(1), O(4) and O(7)] are used, and one lone pair from the opposite side [O(10)]. As Figs. 1 and 2 indicate, the equatorial mirror plane is followed quite faithfully, but important differences in structure exist across an imaginary plane passing through Cu, O(1), and O(7). One such difference is in the orientation of the equatorial oxygen atoms with respect to the cupric ion: for O(4) the C–O–Cu angles, 115.6° and 118.8° , differ significantly from the tetrahedral value of 109.5° , but for O(10) the angles, 111.2° and 111.9° , are quite close to tetrahedral. [For the apical oxygens, which are

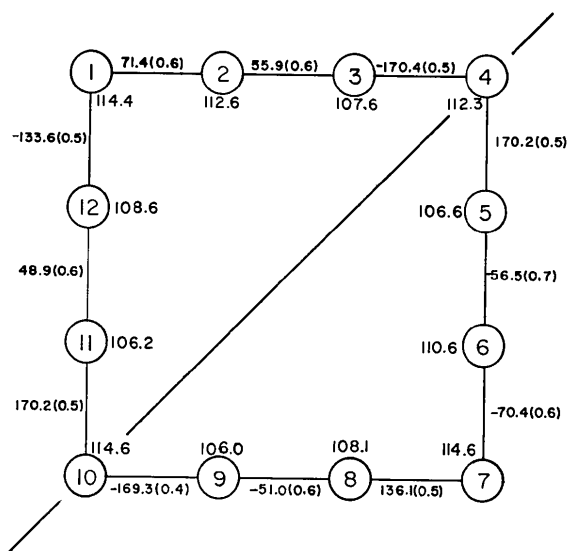


Fig. 2. Torsion angles and internal bond angles in 1,4,7,10-tetraoxacyclododecane as found in its CuCl_2 complex. The standard deviations for the torsion angles are given in parentheses.

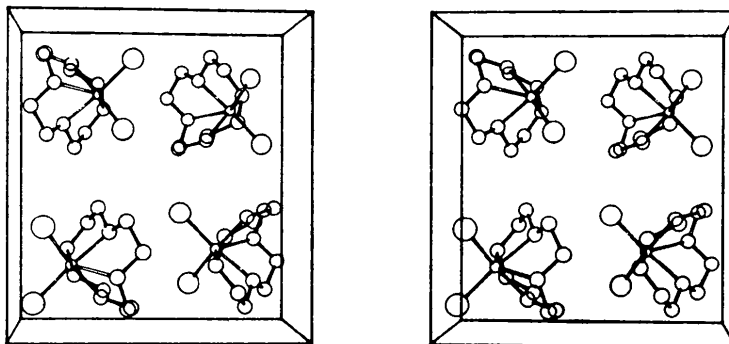


Fig. 3. Three-dimensional stereopair view of molecular packing in the CuCl_2 complex of 1,4,7,10-tetraoxacyclododecane down the a axis. The box represents the unit-cell outline with the b axis vertical and c horizontal. The origin of the box is at $0,0,0$.

related to each other by the approximate mirror, the corresponding angles are 102.3° and 112.1° at O(1) and 102.8° and 111.5° at O(7)]. Because the torsion angles about the four C–O bonds to the equatorial oxygens are all fairly close to 180° (Fig. 2), there exists in each half of the ring a chain of five approximately coplanar atoms; *i.e.*, atoms C(2) through C(6) and C(8) through C(12). However, the orientations of the planes through these groups of atoms relative to the [Cu, O(1), O(7)] plane are entirely different.

The ring conformation has a number of other noteworthy features. The methylene hydrogens are fairly well staggered as indicated by torsion angles of 55.9° , -56.5° , -51.0° , and 48.9° about the C–C bonds. By comparison, the average C–C torsion angle (van Remoortere & Boer, 1974) for the C_4 conformation in $[\text{Na}^+(\text{C}_8\text{H}_{16}\text{O}_4)_2][\text{Cl}^- \cdot 5\text{H}_2\text{O}]$ was 58.8° . The range of internal ring angles (112.3° to 114.6° at oxygen, 106.0° to 112.6° at carbon) is virtually the same as in the NaCl complex (van Remoortere & Boer, 1974) (112.8° to 114.1° at oxygen, 106.9° to 112.9° at carbon); some of the individual differences among these values are of course chemically and crystallographically significant.

The average values for the three types of bond distances in the macrocycle are 1.511 for C–C bond, 1.437 Å for C–O bonds, and 1.02 Å for C–H bonds. The last value is, of course, shorter than the true inter-nuclear separation, presumed to be about 1.09 Å, owing to the bias of the electron density of the hydrogen atom toward the bonding region. All individual bond distances in the ring (Table 3) are within three standard deviations of these average values. Bond angles involving hydrogen atoms have large random errors, ranging between 3 and 5° , and accordingly show a fairly wide scatter (Table 4). All values, however, are within about three standard deviations of the tetrahedral angle.

The structure contains some hints as to why this C_s conformation might have been adopted. A square-planar complex based on the C_4 conformation would give reasonable Cu–O distances but would not orient the lone-pair orbitals suitably and would also create certain problems as to the disposition of the two chlorides. [A *trans* octahedral configuration is prohibited because one site would be blocked by the methylene groups of the heterocycle (van Remoortere & Boer, 1974).] Hypothetical conformations of C_{2v} symmetry can be generated by reflecting either the left or right hand sides of Fig. 1 across an imaginary mirror plane passing through Cu, O(1), and O(7). Because of the favorable orientation of O(10) the structure based on the left hand unit would appear more attractive. However, an examination of Fig. 1, or of a model, shows that the creation of a mirror image would result in severely crowded contacts between hydrogen atoms on C(2) and C(6) and between those on C(8) and C(12). The C_s structure avoids these contacts while maintaining a favorable orientation for one equatorial

oxygen atom. An interesting question to be resolved by further studies is whether this conformation will recur for other small cations or is a result of the special affinity of Cu(II) for square planar structures.

The nature of the thermal motion in this structure is similar in most respects to other cyclomer complexes (van Remoortere & Boer, 1974; Boer, Neuman, van Remoortere & Steiner, 1974; North, Steiner, van Remoortere & Boer, 1974). The metal ion has the lowest vibrational amplitudes and exhibits the least anisotropy (Table 2 and Fig. 1). Thermal motion is distributed fairly uniformly over the 12 ring atoms with the oxygen atoms showing less anisotropy than the carbons. The chlorine atoms have the most anisotropy, with the largest components of thermal motion approximately perpendicular to the equatorial plane.

A three-dimensional view of the crystal structure is given in Fig. 3 and the shortest non-hydrogen intermolecular contacts are listed in Table 6. None of these are unusually short. The chlorine atoms form their closest intermolecular contacts with atoms of the heterocycle related by the screw diad along *c* while a number of contacts between atoms of adjacent rings are generated by the *a* translation.

Table 6. *Interatomic contacts below 3.80 Å*

		Transformation, second atom		
Cl(2)···O(10)	3.778 Å	$-\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
Cl(1)···C(8)	3.723	$-\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
Cl(1)···C(11)	3.704	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
Cl(1)···C(12)	3.747	$1+x$	y	z
Cl(2)···C(3)	3.725	$-\frac{1}{2}+x$	$1\frac{1}{2}-y$	$1-z$
Cl(2)···C(11)	3.744	$-\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
O(1)···C(8)	3.356	$-\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
O(7)···C(2)	3.272	$1+x$	y	z
O(7)···C(3)	3.360	$1+x$	y	z
O(7)···C(12)	3.748	$1+x$	y	z
C(2)···C(8)	3.442	$-\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
C(6)···C(3)	3.661	$1+x$	y	z

References

- AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701–704.
 BOER, F. P., NEUMAN, M. A., VAN REMOORTERE, F. P. & STEINER, E. C. (1974). *Inorg. Chem.* **13**, 2826–2834.
 BRIGHT, D. & TRUTER, M. R. (1970). *Nature, Lond.* **225**, 176–177.
 FREEMAN, H. C., GUSS, J. M., HEALY, M. J., MARTIN, R. P., & NOCKOLDS, C. E. (1969). *Chem. Commun.* pp. 225–226.
 FREEMAN, H. C., ROBINSON, G. & SCHOONE, J. C. (1964). *Acta Cryst.* **17**, 719–730.
 HERCEG, M. & WEISS, R. (1970). *Inorg. Nucl. Chem. Lett.* **6**, 435–437.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–209. Birmingham: Kynoch Press.
 NORTH, P. P., STEINER, E. C., VAN REMOORTERE, F. P. & BOER, F. P. (1975). *Inorg. Chem.* In the press.
 PEDERSEN, C. J. (1967). *J. Amer. Chem. Soc.* **89**, 7017–7036.
 REMOORTERE, F. P. VAN & BOER, F. P. (1974). *Inorg. Chem.* **13**, 2071–2078.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.