requirements: double-helical structures with N(3)—Ag bonding and stoichiometry of one uracil base per silver. The first three, (I)–(III), include two N(3)—Ag—O bonds and the second three, (IV)–(VI), include N(3)—Ag—N(3) and O—Ag—O bonds. In these structures, a marked tendency for Ag^+ to form an eight-membered chelate ring is completely fulfilled. If we neglect O(2) as a candidate for metal bonding because of its low basicity, structures (III) and (V) remain, which are identical with those presented by Guay & Beauchamp (1979). Moreover, there is a distinct possibility of slightly modified structures for (III) and (V), i.e. those with the metal-ion bridge between the stacked bases via additional Ag—O(4) bonds without major alternation of the stacking geometry, as shown in (1-methyl-thyminato)Ag, Ag(1-methylcytosine), and in the present complex.

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Structure of Tricarbonylbis(triphenylphosphine)ruthenium(0)–Tetrahydrofuran (2/1), octadecane-7,16-diacetatocopper(II) Methanol Solvate, [Cu(C₁₆H₂₈N₂O₈)].CuCl₂.CH₃OH

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Abstract. $M_r = 606.43$, monoclinic, $P2_1/n$, $a = 16.711$ (3), $b = 9.671$ (2), $c = 15.829$ (3) Å, $\beta = 111.00$ (2)°, $V = 2388.2$ (9) Å³, $Z = 4$, $D_x = 1.687$ (1) Mg m⁻³, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 4.715$ mm⁻¹, $F(000) = 1248$, $T = 293$ K. Final $R = 0.078$ for 1877 observed reflections. Both Cu atoms have coordination spheres of irregular octahedral shapes, the first (inside the ligand cavity) being coordinated symmetrically to pairs of N, ether O, and carbonyl O atoms, the second (of $CuCl_2$) to two Cl and four carbonyl O atoms of neighbouring ligands, thus joining the molecules into chains parallel to [101]. Additional complexation by $CuCl_2$ results in an inequality in N configurations and loss of symmetry in the ligand.

Introduction. The structure of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diacetatocopper(II)

Table 1. *Atomic fractional coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}*(Å^2)$
Cu(1)	2055 (1)	2385 (1)	−403 (1)	3·05 (5)
N(1)	1654 (5)	4088 (7)	115 (5)	3·0 (3)
C(2)	1407 (6)	5297 (9)	−545 (7)	3·1 (3)
C(3)	2011 (7)	5595 (10)	−1025 (7)	3·7 (4)
O(4)	2838 (4)	5955 (6)	−390 (5)	4·0 (3)
C(5)	3508 (7)	5845 (10)	−729 (7)	4·0 (4)
C(6)	3919 (6)	4420 (11)	−560 (8)	4·0 (4)
O(7)	3284 (4)	3433 (6)	−1038 (5)	3·8 (3)
C(8)	3658 (6)	2095 (10)	−1031 (8)	4·1 (4)
C(9)	2902 (6)	1168 (10)	−1545 (7)	3·6 (3)
N(10)	2400 (5)	702 (7)	−1000 (5)	2·8 (3)
C(11)	2859 (6)	−476 (9)	−393 (7)	3·5 (4)
C(12)	2568 (7)	781 (11)	356 (7)	4·1 (4)
O(13)	1691 (5)	−1155 (6)	45 (5)	4·4 (3)
C(14)	1290 (8)	−1159 (11)	682 (9)	4·9 (4)
C(15)	1346 (8)	187 (12)	1194 (7)	5·5 (5)
O(16)	1130 (4)	1300 (6)	528 (5)	4·3 (2)
C(17)	984 (7)	2532 (10)	943 (7)	3·8 (4)
C(18)	857 (6)	3705 (10)	284 (7)	3·5 (4)
C(19)	2360 (6)	4482 (8)	958 (6)	3·0 (3)
C(20)	3074 (6)	3411 (9)	1248 (7)	3·0 (3)
O(21)	3660 (4)	3533 (6)	1977 (4)	3·5 (2)
O(22)	3035 (4)	2440 (6)	679 (4)	3·4 (2)
C(23)	1565 (6)	163 (9)	−1667 (6)	3·3 (3)
C(24)	933 (6)	1384 (9)	−2006 (7)	3·4 (4)
O(25)	337 (4)	1297 (6)	−2739 (4)	3·6 (2)
O(26)	1063 (4)	2420 (6)	−1486 (4)	3·8 (2)
Cu(2)	4549 (1)	2115 (1)	2087 (1)	3·16 (4)
Cl(1)	3970 (2)	555 (3)	2718 (2)	4·9 (1)
Cl(2)	5223 (2)	780 (3)	1432 (2)	5·6 (1)
C(Me)	4456 (7)	2966 (11)	1901 (8)	5·8 (5)
O(Me)	5174 (5)	−2312 (8)	2544 (6)	7·0 (3)

* Calculated from the anisotropic thermal parameters as B_{eq}
$= 8\pi^2(U_1.U_2.U_3)^{1/3}$ where U_i are the eigenvalues of the U_{ij} matrix.

(ACCU) was recently reported twice independently (Uechi, Ueda, Tazaki, Takagi & Ueno, 1982; Gluziński, Krajewski, Urbańczyk-Lipkowska, Bleidelis & Mishnyov, 1982). The discussed ligand 7,16-diaza-18-crown-6-*N,N'*-diacetic acid seems to have a unique metal-selectivity for Cu^{II} (Uechi *et al.*, 1982) and was therefore the object of intensive investigations. In the course of these it was found recently (Koliński & Mroziński, 1983) that the above ligand when complexed in methanolic solution with an excess of copper(II) dichloride forms crystals of greater Cu content than the already known complex, until the $CuCl_2$ excess is exhausted. The results of an elemental analysis suggested the presence of one $CuCl_2$ molecule built in some way into the known ACCU complex $(ACCU.CuCl_2)$. The nature of coordination of this additional Cu atom and its influence on the ligand structure was not clear and therefore the present X-ray diffractometric investigation was undertaken on this new compound.

Experimental. Black crystal ($0.22 \times 0.25 \times 0.20$ mm) sealed in a Lindemann capillary tube. Siemens AED diffractometer, $Cu K\alpha$ radiation, $\omega/2\theta$ scan, $2\theta_{max} = 100°$, $hkl_{max} = 13, 16, 17$. Stability controlled on two reflections at every 25 reflection intervals, up to 36% loss of intensity. 2713 unique reflections collected, 1877 observed with $I > 2\sigma_I$; $R_{int} = 0.024$ from 90 pairs of

$hk0$ reflections. Cell constants refined against 20 reflections. Space group $P2_1/n$ (from absences). Lorentz and polarization but no absorption correction. Structure solved by heavy-atom method: positions of two Cu atoms in the asymmetric unit derived from three Cu–Cu vectors on three-dimensional Patterson projections (*SHELX*76, Sheldrick, 1976). Positional parameters of Cl and all non-H ligand atoms found from F_o Fourier synthesis. After refinement in anisotropic mode (full-matrix least-squares procedure in *SHELX*) one methanol molecule was located from the Fourier difference maps. Final refinement performed with all geometrically calculated positions of H atoms treated as rigid groups (except methanol hydroxyl). Hydroxyl H atom found from difference Fourier maps and refined separately (damping 0·2). Final $R = 0.078$, $R_w = 0.083$; $w = 3.1/(\sigma_F^2 + 0.003\,F^2)$. $(\Delta/\sigma)_{max} = 0.02$. Max. electron density on Fourier difference maps < 0.4 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations done on SEL minicomputer.

Discussion. The fractional atomic coordinates of all non-H atoms in the asymmetric unit and B_{eq} values are listed in Table 1.* Fig. 1 presents a projection of the molecule showing the coordination mode for both Cu atoms.
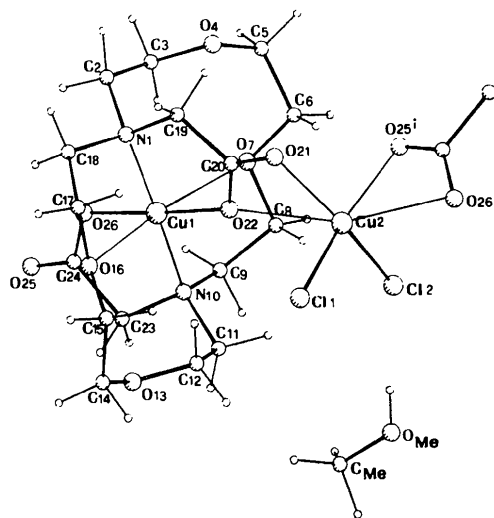
Fig. 1. Projection of ACCU.CuCl$_2$ on the *ab* plane with crystallographic labelling of atoms. Light lines are coordination bonds. A carboxyl group of the molecule at $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ is also shown.

Table 2. *Distances* (Å) *and angles* (°) *for the ligand molecule and the* Cu *coordination spheres* (e.s.d.'s *in parentheses*)

N(1)-C(2)	1·523 (12)	C(8)-C(9)	1·525 (13)	C(15)-O(16)	1·459 (13)	C(20) O(22)	1·287 (12)
C(2)-C(3)	1·493 (17)	C(9)-N(10)	1·473 (15)	O(16)-C(17)	1·423 (13)	N(10) C(23)	1·509 (10)
C(3)-O(4)	1·430 (11)	N(10)-C(11)	1·510 (11)	C(17)-C(18)	1·504 (14)	C(23) C(24)	1·546 (12)
O(4)-C(5)	1·408 (16)	C(11)-C(12)	1·464 (18)	C(18)-N(1)	1·496 (15)	C(24) O(25)	1·232 (10)
C(5)-C(6)	1·520 (14)	C(12)-O(13)	1·416 (14)	N(1)-C(19)	1·480 (10)	C(24)-O(26)	1·265 (11)
C(6)-O(7)	1·426 (11)	O(13)-C(14)	1·396 (18)	C(19)-C(20)	1·521 (12)	O(Me) C(Me)	1·414 (12)
O(7)-C(8)	1·435 (12)	C(14)-C(15)	1·518 (16)	C(20)-O(21)	1·223 (10)		

C(2)-N(1)-C(18)	105·8 (7)	C(8)-C(9)-N(10)	113·8 (9)	C(12)-O(13)-C(14)	117·0 (8)
C(2)-N(1)-C(19)	110·7 (6)	N(1)-C(19)-C(20)	112·5 (7)	O(13)-C(14)-C(15)	115·4 (10)
C(18)-N(1)-C(19)	112·1 (8)	C(19)-C(20)-O(21)	119·7 (8)	C(14)-C(15)-O(16)	107·2 (9)
N(1)-C(2)-C(3)	115·5 (8)	C(19)-C(20)-O(22)	116·6 (7)	C(15)-O(16)-C(17)	108·9 (8)
C(2)-C(3)-O(4)	110·4 (8)	O(21)-C(20)-O(22)	123·6 (8)	O(16)-C(17)-C(18)	108·4 (9)
C(3)-O(4)-C(5)	114·4 (8)	C(9)-N(10)-C(11)	109·7 (8)	C(17)-C(18)- N(1)	113·4 (8)
O(4)-C(5)-C(6)	111·9 (9)	C(9)-N(10)-C(23)	105·9 (7)	N(10)-C(23)-C(24)	108·9 (7)
C(5)-C(6)-O(7)	108·1 (7)	C(11)-N(10)-C(23)	108·4 (6)	C(23)-C(24)-O(25)	119·7 (8)
C(6)-O(7)-C(8)	111·1 (7)	N(10)-C(11)-C(12)	115·3 (9)	C(23)-C(24)-O(26)	116·2 (7)
O(7)-C(8)-C(9)	104·5 (7)	C(11)-C(12)-O(13)	111·9 (8)	O(25)-C(24)-O(26)	124·0 (8)
Cu(1)-O(22)-C(20)	117·6 (5)	Cu(1)-O(26)-C(24)	117·5 (5)		

Cu(1)-N(1)	2·056 (8)	Cu(1)-O(16)	2·701 (8)	Cu(2)-Cl(1)	2·214 (3)	Cu(2) O(22)	2·725 (5)
Cu(1)-O(7)	2·781 (8)	Cu(1)-O(22)	1·899 (5)	Cu(2)-Cl(2)	2·202 (4)	Cu(2) O(25')	1·977 (6)
Cu(1)-N(10)	2·065 (8)	Cu(1)-O(26)	1·911 (6)	Cu(2)-O(21)	1·983 (6)	Cu(2) O(26')	2·759 (6)

N(1)-Cu(1)-O(7)	103·9 (3)	O(16)-Cu(1)-O(22)	89·8 (3)	Cl(2)-Cu(2) O(25')	95·4 (2)
N(1)-Cu(1)-O(16)	76·2 (3)	O(16)-Cu(1)-O(26)	90·8 (3)	Cl(2)-Cu(2)-O(26')	90·4 (2)
N(1)-Cu(1)-O(22)	85·2 (3)	N(1)-Cu(1)-N(10)	176·5 (3)	O(21)-Cu(2)-O(22)	53·2 (2)
N(1)-Cu(1)-O(26)	92·4 (3)	O(7)-Cu(1)-O(16)	168·5 (2)	O(21)-Cu(2)-O(25')	85·2 (3)
O(7)-Cu(1)-N(10)	76·0 (3)	O(22)-Cu(1)-O(26)	177·3 (2)	O(21)-Cu(2)- O(26')	113·4 (2)
O(7)-Cu(1)-O(22)	78·8 (3)	Cl(1)-Cu(2)-Cl(2)	101·1 (1)	O(22)-Cu(2)-O(25')	113·7 (2)
O(7)-Cu(1)-O(26)	100·7 (3)	Cl(1)-Cu(2)-O(21)	94·4 (2)	O(25')-Cu(2)-O(26')	52·4 (2)
N(10)-Cu(1)-O(16)	104·6 (3)	Cl(1)-Cu(2)-O(22)	91·1 (2)	Cl(1)-Cu(2)-O(25')	147·5 (2)
N(10)-Cu(1)-O(22)	98·2 (3)	Cl(1)-Cu(2)-O(26')	99·4 (2)	Cl(2)-Cu(2)-O(21)	149·1 (2)
N(10)-Cu(1)-O(26)	84·2 (3)	Cl(2)-Cu(2)-O(22)	99·5 (2)	O(22)-Cu(2)-O(26')	164·0 (2)

Symmetry code: (i) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

The bond lengths and angles in the ligand molecule (Table 2) do not reveal any points of particular interest except some N—C bonds which are significantly longer than usually observed for tertiary amino N. This was observed similarly for ACCU (Gluziński *et al.*, 1982; Uechi *et al.*, 1982) as well as for other 7,16-diaza-18-crown-6 complexes with Pb or Cu salts (Metz & Weiss, 1973; Herceg & Weiss, 1973*a,b*) but not for uncomplexed 7,16-diaza-18-crown-6 (Herceg & Weiss, 1972) or for the KNCS complex (Moras, Metz, Herceg & Weiss, 1972). It seems, therefore, that the presence of a heavy metal coordinated to the ring N atoms has a loosening influence on the N—C bonds in the discussed ligand.

The ligand in the title compound does not have any exact or approximate symmetry elements contrary to that of ACCU as well as of 7,16-diaza-18-crown-6-N,N'-dipropionatocopper(II) (PRCU) (Krajewski, Gluziński, Urbańczyk-Lipkowska & Dobler, 1983) which are both of exact C_i symmetry. This loss of symmetry as a result of further complexation with CuCl$_2$ may be seen when one considers the differences in the 18-membered heteroring conformations. A convenient method for comparison of conformations of macrocyclic rings consists of the consideration of the sequence of torsion angles (*cf.* Urbańczyk-Lipkowska, Krajewski, Gluziński, Andreetti & Bocelli, 1981) indicating the mutual configuration of the 1,4-atoms involved. Thus, an *anti* position (*a*) may be defined by

the angle $|\theta| > 150°$, and a *gauche* position (*g*) by the angle $|\theta| < 75°$. An asterisk at these indices denotes a strong deviation ($\Delta|\theta| \sim 25$-30°) from the ideal 180 or 60° values. In this convention the following configuration sequence in ACCU.CuCl$_2$ may be established [starting from the N(1)—C(2) bond towards increasing label numbers]: |-a-g-a-g*-g-a-a-g-g-a-g-a-g-g*-a-a-g-a-|. Similarly, the configuration sequence for ACCU or PRCU is (-a-g-a*-g*-g-a-a-g-g*-)(×2). The substantial difference in these sequences involves the bonding modes of N atoms which are asymmetrical in ACCU.CuCl$_2$ (-g-a- and -a-a-) and symmetrical in ACCU or PRCU (-g*-a-).

In ACCU.CuCl$_2$ the Cu(1) atom placed inside the ligand cavity is coordinated to N(1), N(10), O(7), O(16), O(22) and O(26). The coordination distances to N(1), N(10), O(22) and O(26) are considerably shorter (about 2 Å) than those to O(7) and O(16) (2·7-2·8 Å). Thus, the coordination-sphere polyhedron of Cu(1) is an irregular octahedron (Fig. 2*a*). The atoms N(1), N(10), O(22) and O(26) are coplanar, the mean deviation of these atoms from the least-squares plane defined by them being ±0·002 (7) Å. Cu(1) lies 0·018 (2) Å out of this plane. The atoms O(7), Cu(1) and O(16) are not collinear [angle at Cu(1) is 168·5 (1)°; angles of Cu(1)—O(7) and Cu(1)—O(16) to the normal of the plane are 18·8 (2) and 14·2 (2)° respectively]. Nevertheless, this coordination polyhedron is similar in its shape to that found in ACCU.
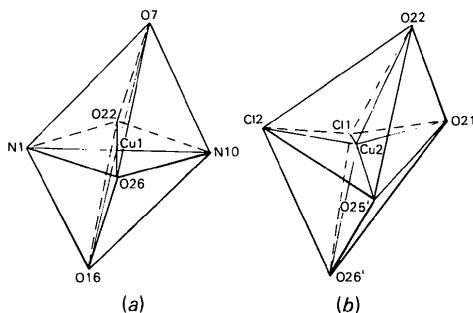
Fig. 2. Shapes of coordination polyhedra for (a) Cu(1), and (b) Cu(2). For atomic labelling see Table 1. For symmetry code see Table 2.

The Cu(2) atom of the CuCl$_2$ molecule is coordinated to four carboxylic O atoms of two neighbouring molecules of the ligand. The coordination distances are comparable to those of Cu(1) (two short, two elongated) (Table 2). Taking into account the two Cl atoms, the coordination sphere for Cu(2) is a completely irregular octahedron where Cl—Cl forms an edge (Fig. 2b). The volumes of both polyhedra despite differing geometry and coordinating elements are very close [V = 13·68 (4) and 13·38 (3) Å^3 for Cu(1) and Cu(2) respectively].

The common O(22) and O(26) atoms of the two coordination spheres cause the molecules of the complex to be joined forming chains parallel to [101]. The Cu(1)⋯Cu(2) and Cu(2)⋯Cu(1^i) distances are 4·604 (2) and 4·651 (2) Å respectively; their angles at

Cu(1) and Cu(2) are 177·28 (3) and 170·78 (3)° respectively.

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The Structures of the Lanthanide Ethyl Sulfate Enneahydrates, $M(C_2H_5SO_4)_3.9H_2O$ [M = La—Lu (except Pm)], at 171 K

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Abstract. M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. Isomorphous, hexagonal $P6_3/m$, $Z = 2$, $\lambda(Mo\ K\bar{\alpha}) = 0·71069$ Å. M = La: M_r = 676·40, a = 14·045 (1), c = 7·0996 (5) Å, V = 1212·8 (2) Å^3, D_x = 1·852 g cm^{-3}, μ = 20·97 cm^{-1}, $F(000)$ = 684, R = 0·020, 1560 reflections. M = Lu: M_r = 712·46, a = 13·834 (1), c = 6·9612 (8) Å, V = 1153·8 (3) Å^3, D_x = 2·051 g cm^{-3}, μ = 46·30 cm^{-1}, $F(000)$ = 712, R = 0·020, 1438 reflections. The lanthanide ions are coordinated by nine water molecules, with the coordination polyhedron having $\bar{6}$ (C_{3h}) symmetry. The metal–oxygen distances decrease with increasing atomic number, and correlate well with the ionic radius of the metal. The ethyl sulfate ions are hydrogen-bonded to the water molecules coordinating the metal ion. Probability-plot analysis shows that the geometry of the ethyl sulfate ion is independent of both the structure and the temperature in the range 171–298 K. Hydrogen atoms were located using difference Fourier syntheses, and were successfully refined.