Structure of Dichloro(5,6,8,9,11,12,14,15-octahydro-2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene)copper(II)* Chloroform Solvate, [Cu(C$_{14}$H$_{20}$O$_{5}$)Cl$_{2}$].CHCl$_{3}$, a Cu^{II}—Crown-Ether Complex with Pentagonal-Bipyramidal Geometry

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Abstract. $M_r = 522 \cdot 12$, monoclinic, $P2_1/c$, $a = 14 \cdot 650$ (5), $b = 11 \cdot 268$ (7), $c = 13 \cdot 623$ (4) Å, $\beta = 106 \cdot 94$ (3)°, $U = 2151$ (2) Å^3, $Z = 4$, $D_m = 1 \cdot 65$, $D_x = 1 \cdot 612$ (2) Mg m^{-3}, $T = 296$ K, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å, $\mu = 1 \cdot 666$ mm^{-1}, $R = 5 \cdot 1\%$ for 2796 independent reflections. The Cu^{II} ion is situated in the central cavity of the benzo-15-crown-5 ligand, and the complex has pentagonal-bipyramidal geometry with the two Cl$^-$ anions axially coordinated. This is the first example of a seven-coordinated Cu^{II} complex.

Introduction. In our previous paper, anisotropic inversion of the *g* factors ($g_{||} < g_{\perp}$) with respect to the $3d_{z^2}$ ground-state doublet was reported for the Cu^{II} complex of a five-O-atom-containing crown ether in solution (Ishizu, Haruta, Nakai, Miyoshi & Sugiura, 1978). An important aspect of the structure proposed is that it is seven coordinate with pentagonal-bipyramidal geometry and with the five O atoms in the equatorial plane and the two Cl$^-$ anions at the apical positions. It was also shown that introduction of the fused benzene ring to the macrocycle enhanced the $3d_{z^2}$ character in the ground state of the complex (Ishizu, Haruta, Kohno, Mukai, Miyoshi & Sugiura, 1980). In order to visualize the structure of these complexes, an X-ray

diffraction study was carried out for the Cu^{II} complex of benzo-15-crown-5.

Experimental. Commercial anhydrous CuCl$_2$ (0·04 mmol) dried at 383 K was placed in the reaction tube equipped with a side-arm tube containing the ligand (0·4 mmol), about 4 ml of dry chloroform was brought into the reaction tube and the reaction mixture was sealed under vacuum, wine-red crystals grew in the side-arm tube; analytical data (%): found: C 35·19, H 4·21, O 15·04, Cu 12·32, calculated: C 34·59, H 4·05, O 15·32, Cu 12·17, $F(000) = 1060$; crystal 0·3 × 0·3 × 0·4 mm coated with plastic, Rigaku automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, three standard reflections (400, 600 and 555) measured every 150 reflections, $2\theta \leq 60°$, 3047 reflections with $|F_o| > 3 \sigma (F_o)$ measured, intensities corrected for Lorentz and polarization effects and reduced to 2796 independent reflections, 3710 unobserved reflections; heavy-atom method, positions of H atoms calculated from those of the non-hydrogen atoms; all coordinates, anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for H refined by the block-diagonal least-squares procedure based on $|F_o|$; unit weights; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); final $wR = 5 \cdot 7\%$; calculations performed on a FACOM M-200 computer at this Institute using the *UNICS* III program system (Sakurai & Kobayashi, 1979).

Discussion. The atomic parameters are given in Table 1.* A stereoscopic drawing of the complex and the bond parameters are shown in Figs. 1 and 2. The complex possesses an approximate mirror plane through Cu^{II} and O(10) perpendicular to the benzene ring. In agreement with the structure proposed previously, the seven-coordinate Cu^{II} ion is situated on a slightly distorted pentagonal plane of O atoms and the two Cl^- anions are at the apexes.

Upon complex formation, the 15-membered ring of the free ligand, which takes a rectangular-type conformation (Hanson, 1978), changes to a pentagonal form. One can see that the molecular structure of this complex is very similar to that of the Mg^{II} complex of benzo-15-crown-5 or the Co^{II} complex of 15-crown-5, $[Co^{II}(H_2O)_2$ (15-crown-5)] $(NO_3)_2$, where the cation is coordinated to seven atoms, that is, to the five crown O atoms and the two N of isothiocyanate (NCS) anions in the former (Owen, 1978), and to the five crown O atoms and the two water O atoms in the latter (Holt, Alcock, Hendrixson, Malpass, Ghirardelli & Palmer, 1981).

The 15-membered ring has a crown conformation and the five ether O atoms are nearly planar. O(7) and O(13) deviate by 0·345 (8) and 0·313 (8) Å, respec-
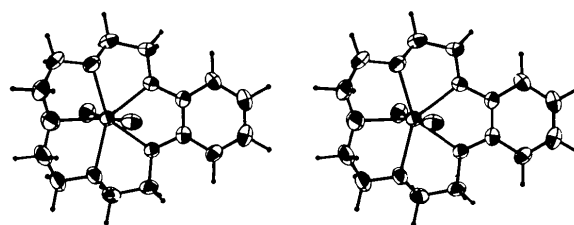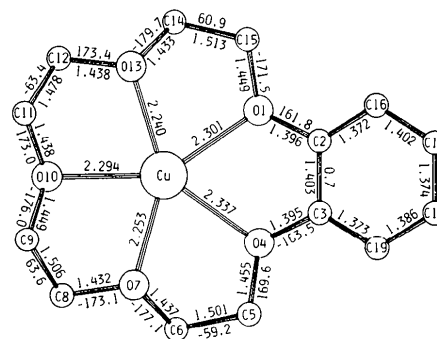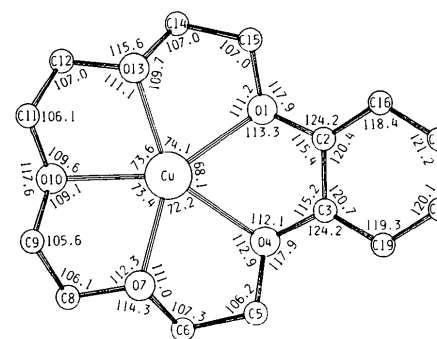
* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38181 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters*

Positional parameters are multiplied by 10^4. The equivalent isotropic temperature factor is defined by $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$. The numbering of the atoms is given in Figs. 2 and 3.

	x	y	z	$B_{eq}(\text{Å}^2)$
Cu	2479 (1)	322 (1)	−60 (1)	2·84 (0·02)
Cl(1)	1881 (1)	−1172 (2)	663 (1)	3·59 (0·05)
Cl(2)	3133 (1)	1850 (2)	−667 (1)	4·2 (0·1)
Cl(3)	3016 (2)	−4586 (2)	378 (2)	5·9 (0·1)
Cl(4)	1950 (2)	−3903 (2)	−1685 (2)	6·1 (0·1)
Cl(5)	971 (2)	−4462 (3)	−172 (2)	7·7 (0·1)
O(1)	3285 (3)	1002 (4)	1552 (3)	3·0 (0·1)
O(4)	4014 (3)	−477 (4)	528 (3)	3·1 (0·1)
O(7)	2650 (3)	−994 (5)	−1239 (3)	3·8 (0·1)
O(10)	1191 (3)	575 (5)	−1481 (4)	5·2 (0·2)
O(13)	1443 (3)	1472 (4)	430 (4)	4·0 (0·1)
C(2)	3914 (4)	168 (6)	2143 (5)	2·9 (0·2)
C(3)	4304 (4)	−637 (6)	1590 (5)	3·0 (0·2)
C(5)	4172 (5)	−1447 (6)	−109 (5)	3·5 (0·2)
C(6)	3637 (5)	−1129 (7)	−1194 (5)	3·9 (0·2)
C(8)	2031 (6)	−743 (8)	−2244 (5)	4·9 (0·3)
C(9)	1065 (5)	−485 (9)	−2110 (6)	5·4 (0·3)
C(11)	386 (5)	983 (9)	−1173 (6)	5·4 (0·3)
C(12)	743 (5)	1967 (8)	−443 (6)	5·0 (0·3)
C(14)	1952 (5)	2312 (6)	1181 (6)	4·0 (0·2)
C(15)	2648 (5)	1613 (6)	2021 (5)	3·8 (0·2)
C(16)	4156 (5)	106 (6)	3193 (5)	3·4 (0·2)
C(17)	4793 (5)	−782 (7)	3692 (5)	3·9 (0·2)
C(18)	5171 (5)	−1574 (7)	3149 (6)	3·9 (0·2)
C(19)	4931 (4)	1498 (6)	2089 (5)	3·6 (0·2)
C(20)	2000 (5)	−3830 (7)	−382 (6)	4·4 (0·2)

Fig. 1. A stereoscopic drawing of the molecule.

(a)

(b)

Fig. 2. The bond parameters. (*a*) Bond lengths (Å) and torsion angles (°). Torsion angles around the 15-membered ring are expressed by the figures outside the ring. (*b*) Bond angles (°). The standard deviations are: bond lengths: Cu—O 0·005, O—C 0·009, C—C 0·010, C—C (in the benzo group) 0·010 Å; torsion angles: 0·6°; bond angles: O—C—O 0·2, in the ring 0·5, in the benzo group 0·6°.

tively, toward Cl(1) from the plane of O(1), O(4) and O(10). The Cu^{II} ion is situated in the same plane with a deviation of 0·144 (3) Å. The line connecting Cl(1), Cu and Cl(2) is essentially straight, deviating only by 4·06 (7)°. The benzene ring, O(1) and O(4) are nearly in a plane, and the dihedral angle between this plane and the above-mentioned plane [O(1), O(4) and O(10)] is 29·1 (1)°.

The apical Cu—Cl distances [2·254 (2) and 2·242 (2) Å] of the present bipyramidal complex are very close to the equatorial Cu—Cl distances [2·228 (2) and 2·214 (2) Å] of the octahedral Cu^{II}–12-crown-4 complex (van Remoortere, Boer & Steiner, 1975). The equatorial Cu—O distances observed (2·240–2·337 Å) are much longer than those [2·113 (3) and 2·128 (3) Å] of the octahedral complex, and rather similar to those of the apical Cu—O distances [2·343 (4) and 2·403 (3) Å] in the octahedral complex. These observations are consistent with previous proposals derived from ESR studies, that is, the ground state of the present complex is $3d_{z^2}$ and that of the octahedral complex is $3d_{x^2-y^2}$ or $3d_{xy}$ (Ishizu et al., 1980).

The effective radii of Mg^{II} (0·86 Å), Co^{II} (0·88 Å) and Cu^{II} (0·87 Å) for octahedral coordination are very similar (Shannon & Prewitt, 1969). These values indicate that these ions fit the cavity (diameter: 1·7–2·2 Å) of this crown ring well. Therefore, similar radii will also be maintained for the pentagonal-bipyramidal coordination.

The molecular packing between Cl(1) and carbon in $CHCl_3$ [3·343 (8) Å] is slightly closer than the sum of the ordinary van der Waals radii (Fig. 3).
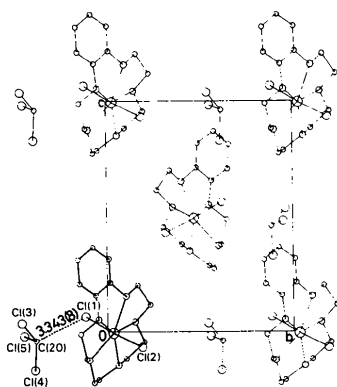

Fig. 3. The crystal structure projected along the a axis. The projection is limited between $x = 0$ and 0·52.

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Structure of cis-Bis(acetylacetonato)diaquacalcium Monohydrate, [Ca(C5H7O2)2(H2O)2].H2O

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Abstract. $M_r = 292·34$, Pbnb, $a = 5·260 (2)$, $b = 13·683 (3)$, $c = 20·062 (7)$ Å, $V = 1443·8 (9)$ Å^3, $Z = 4$, $D_m (295 K) = 1·33$, $D_x (85 K) = 1·34$ g cm^{-3}, Mo Kα radiation, $\lambda = 0·71069$ Å, $\mu = 4·30$ cm^{-1}, $T = 85$ K, $R = 0·048$, 1290 unique observed reflections, recrystallized from water. The complex possesses twofold symmetry and cis coordination of the two water molecules with Ca—O 2·356 (2) Å. Two bidentate acetylacetonate ligands complete the octahedral coordination about the Ca^{2+} ion with Ca—O 2·336 (2) and 2·320 (2) Å. An additional water molecule is also present in the lattice and is hydrogen bonded to the complexes.

Introduction. During our study of the electronic, vibrational, and magnetic-resonance spectra of various closed-shell metal acetylacetonate (acac) complexes, we found it necessary to obtain the crystal and molecular structure of the title compound. Solution of this structure adds another member to the diverse group of structures found for $[M^{II}(acac)_2L_n]$ compounds.

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