$(Cl_2CHCOO)_2$ fragment with the longer Cu—Cu distance the axial Cu—O(ethanolato) distances are elongated to 2·858 Å and the Cu—O(carboxylate) distances shortened to 2·517 Å. In the other $Cu_2(Me_2NCH_2CH_2O)_2(Cl_2CHCOO)_2$ fragment the axial Cu—O(ethanolato) distances are shortened to 2·633 Å and the Cu—O(carboxylate) distances elongated to 3·063 Å. A similar situation has also been observed in $[Cu(Et_2NCH_2CH_2O)(Cl_2CHCOO)]_4$ which has pseudo $C_2$ symmetry. The molecular symmetry of $[Cu(Et_2NCH_2CH_2O)(Cl_3CCOO)]_4$ and $[Cu(Bu_2NCH_2CH_2O)(Cl_2CHCOO)]_4$ is $C_1$, the long Cu–Cu distances being 3·619–3·996 Å, the axial Cu–O(ethanolato) distances ranging from 2·52 to 3·01 Å and the Cu–O(carboxylate) distances from 2·43 to 2·74 Å. In both complexes one Cu atom is five-coordinate, the apical site of the square-pyramidal coordination being occupied by an ethanolato O atom (2·52–2·60 Å). The sixth octahedral site is blocked by an alkyl substituent of the aminoethanolato ligand. Thus, steric hindrances and packing effects due to the size of substituents have a greater influence on the molecular symmetry and structure than does the basicity of the carboxylate ligand.

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# Structure of the Copper(II) Complex of 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-diacetic Acid

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## Abstract

The title compound, $[Cu(C_{16}H_{28}N_2O_8)]$, $M_r = 439\cdot95$, crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions $a = 7\cdot608\ (3)$, $b = 9\cdot064\ (2)$, $c = 7\cdot000\ (2)$ Å, $\alpha = 109\cdot51\ (3)$, $\beta = 93\cdot67\ (3)$ and $\gamma = 81\cdot32\ (3)°$; $V = 449\cdot7\ (3)$ Å$^3$, $D_m = 1\cdot619$, $D_x = 1\cdot624$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 1·26 mm$^{-1}$. The structure was solved by a Patterson function and refined by block-diagonal least-squares procedures to give a final $R$ value of 0·022 for 1967 reflections with measurable intensities collected on a four-circle diffractometer. The complex is centrosymmetric, with the Cu atom situated at the center of the aza crown-ether ring cavity. The Cu atom is coordinated to the two ring N atoms and the two O atoms of the two acetic acid

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moieties in a *trans* square-planar configuration with Cu—N and Cu—O distances of 2·045 (1) and 1·935 (1) Å respectively. The crown-ether O atoms, on either side of the coordination plane at a Cu—O distance of 2·636 (2) Å, are weakly bonded to the Cu atom to complete the elongated rhombic-octahedral coordination with the two five- and one eight-membered chelate rings alternating. This folded coordination structure well represents the characteristic complexing behavior associated with both crown-ether and complexane structures.

## Introduction

In the course of our investigations on the development of a complexane-type chelating agent (Takagi, Tazaki & Ueno, 1978) the title ligand, consisting of an 18-membered macrocycle with two acetic acid moieties attached to the two ring N atoms, was synthesized as a new complexane, and the interaction with the metal was examined in aqueous solution (Tazaki, Takagi & Ueno, 1981). This chelating agent has an ability to complex with divalent cations of alkaline-earth and first-row transition metals. The complex with $Cu^{II}$ is by far the most stable, having $10^6$ times the estimated stability constant of the next stable complex with $Zn^{II}$. This behavior is very unusual for complexane-type ligands (Sillen & Martell, 1964, 1971; Perrin, 1979). In complexation the title ligand seemed to exhibit a unique metal-selectivity associated with both crown-ether and complexane structures. Therefore, the X-ray structural determination of the complex with $Cu^{II}$ was carried out in order to reveal the coordination structure and to understand the high selectivity toward $Cu^{II}$.

## Experimental

The ligand was synthesized by cyanomethylating the two amino N atoms of commercially available 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix 22, E. Merck), followed by the hydrolysis of nitrile to carboxylic acid. Single crystals of the $Cu^{II}$ complex were prepared by mixing the ligand and copper(II) acetate in an aqueous solution and then evaporating the water.

Preliminary X-ray photographs obtained by the Weissenberg technique showed the crystals to be triclinic. The unit-cell parameters and intensity data were measured on a Syntex $P\bar{1}$ automated four-circle X-ray diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0·71073$ Å) at room temperature. The unit-cell parameters were determined by a least-squares procedure using 15 centered reflections. The crystal used for X-ray work was ground to a sphere 0·33 mm in diameter. The density was measured by flotation in aqueous KI solution. The crystal data are given in the *Abstract*.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters with e.s.d.'s in parentheses*

For non-hydrogen atoms $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}/B$ (Å$^2$) |
|---|---|---|---|---|
| Cu | 0 | 0 | 0 | 1·59 (0) |
| O(1) | 0·1212 (1) | 0·0703 (1) | 0·2594 (2) | 2·24 (2) |
| C(1) | 0·1848 (2) | 0·2011 (2) | 0·3006 (2) | 1·95 (4) |
| O(2) | 0·2707 (2) | 0·2607 (2) | 0·4531 (2) | 3·14 (3) |
| C(2) | 0·1391 (2) | 0·2878 (2) | 0·1478 (2) | 1·96 (4) |
| N | 0·1073 (1) | 0·1745 (1) | −0·0571 (2) | 1·60 (2) |
| C(3) | −0·0069 (2) | 0·2541 (2) | −0·1864 (2) | 1·96 (4) |
| C(4) | −0·2011 (2) | 0·2951 (2) | −0·1315 (2) | 2·13 (4) |
| O(3) | −0·2260 (1) | 0·4228 (1) | 0·0558 (2) | 2·27 (2) |
| C(5) | −0·3710 (2) | 0·4204 (2) | 0·1725 (2) | 2·34 (4) |
| C(6) | −0·3262 (2) | 0·3211 (2) | 0·3089 (2) | 2·45 (4) |
| O(4) | −0·2938 (2) | 0·1579 (1) | 0·1894 (2) | 2·43 (2) |
| C(7) | −0·2947 (2) | 0·0541 (2) | 0·3047 (2) | 2·32 (4) |
| C(8) | −0·2850 (2) | −0·1105 (2) | 0·1558 (2) | 2·13 (4) |
| †H(2)1 | 0·030 (2) | 0·361 (2) | 0·191 (3) | 2·2 (3) |
| H(2)2 | 0·233 (3) | 0·350 (2) | 0·141 (3) | 2·9 (4) |
| H(3)1 | 0·042 (2) | 0·350 (2) | −0·178 (3) | 2·2 (3) |
| H(3)2 | −0·001 (2) | 0·186 (2) | −0·321 (3) | 1·9 (3) |
| H(4)1 | −0·247 (2) | 0·204 (2) | −0·128 (3) | 2·0 (3) |
| H(4)2 | −0·262 (2) | 0·328 (2) | −0·242 (3) | 2·5 (4) |
| H(5)1 | −0·470 (2) | 0·384 (2) | 0·084 (3) | 2·6 (4) |
| H(5)2 | −0·407 (3) | 0·523 (2) | 0·253 (3) | 3·0 (4) |
| H(6)1 | −0·426 (3) | 0·340 (2) | 0·396 (3) | 2·7 (4) |
| H(6)2 | −0·223 (3) | 0·352 (2) | 0·387 (3) | 3·0 (4) |
| H(7)1 | −0·402 (3) | 0·083 (2) | 0·382 (3) | 3·1 (4) |
| H(7)2 | −0·198 (2) | 0·067 (2) | 0·400 (3) | 2·6 (4) |
| H(8)1 | −0·368 (2) | −0·108 (2) | 0·049 (3) | 2·1 (3) |
| H(8)2 | −0·310 (2) | −0·183 (2) | 0·219 (3) | 2·5 (3) |

† The H atoms are labelled in terms of the C atoms to which they are attached.

Intensity data of 2074 independent reflections within a range of $2\theta < 55°$ were collected by the $\theta$–$2\theta$ scan technique with a variable scan rate of 4·0 to 24·0° min$^{-1}$. Of these, intensities of 1967 reflections were larger than $3\sigma(I)$, and only these reflections were used in the least-squares refinement. The intensity data were corrected for Lorentz and polarization effects, but no corrections for absorption or extinction were made because of the low absorption coefficient and the small size of the crystal. The preliminary scale and overall temperature factors were estimated by Wilson statistics. The statistical distribution of the normalized structure factors strongly favored the centrosymmetric space group, which was subsequently confirmed by successful refinement.

## Structure determination and refinement

The Cu atom was assigned the position (0,0,0) since there is one molecule in a triclinic unit cell. The positions of all the non-hydrogen atoms were readily deduced from a Patterson function. Refinement was carried out by the block-diagonal least-squares method in which the function minimized was $\sum w(|F_o| - |F_c|)^2$ where initially equal weights and later Cruickshank's (1965) weighting scheme were adopted. After several cycles of refinement with anisotropic thermal parameters, the positions of all the H atoms were revealed from a difference Fourier synthesis. Refinement including these H atoms was terminated when all shift/e.s.d. ratios for the non-hydrogen atoms became less than 0·02. The final conventional $R$ index was 0·022 for 1967 measurable reflections. The final difference Fourier synthesis showed no significant features in the undulations within $\pm 0·3$ e Å$^{-3}$. The atomic scattering factors for $Cu^{2+}$, O, N and $C_{cov}$, and also the anomalous-dispersion correction for the Cu atom were taken from *International Tables for X-ray Crystallography* (1974). Those for the H atoms were adopted from the table of Stewart, Davidson & Simpson (1965). All calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University, mainly by the use of the *UNICS* II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The drawings were made with *ORTEP* (Johnson, 1965). The final atomic parameters are listed in Table 1 where the equivalent isotropic thermal parameters are given for the non-hydrogen atoms.*

## Results and discussion

A projection of the molecular structure onto the *ab* plane is shown in Fig. 1 with the atomic nomenclature scheme, and a stereoscopic illustration of the molecular structure is shown in Fig. 2. The bond distances, bond angles and torsion angles are listed in Table 2.

The complex is centrosymmetric, with the Cu atom situated at the center of the crown-ring cavity. The Cu atom is coordinated to the two ring N atoms and to the two O atoms of the two acetic acid moieties to form two glycine five-membered chelate rings. The coordinated N and O atoms are in a *trans* square-planar position (equatorial plane), with Cu–N and Cu–O bond distances of 2·045 (1) and 1·935 (1) Å, respectively. The Cu atom is also weakly coordinated to

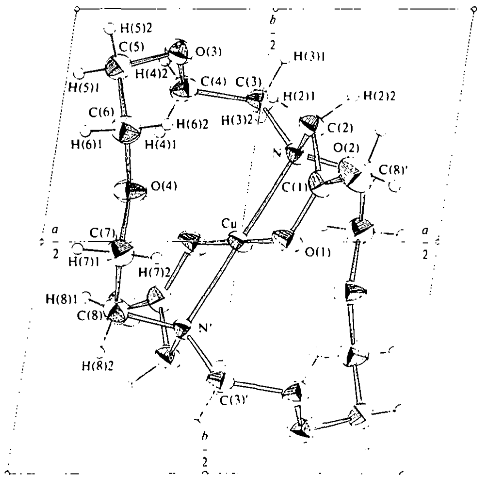

Fig. 1. A projection of the molecular structure onto the *ab* plane.

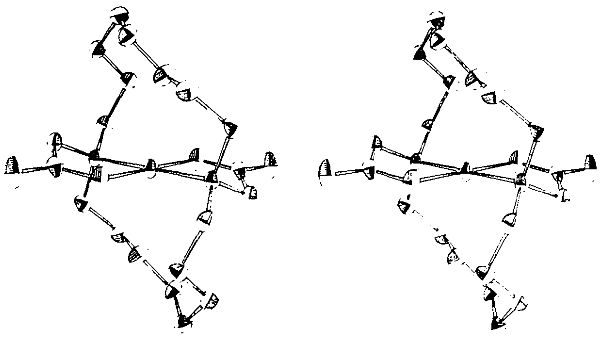

Fig. 2. A stereoview of the molecular structure.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

(*a*) Bond distances and angles involving the Cu atom

| | | | |
|---|---|---|---|
| Cu–N | 2·045 (1) | Cu–O(4) | 2·636 (2) |
| Cu–O(1) | 1·935 (1) | | |
| N–Cu–O(1) | 84·37 (6) | Cu–N–C(2) | 104·13 (11) |
| N–Cu–O(4) | 101·60 (4) | Cu–N–C(3) | 114·61 (9) |
| O(1)–Cu–O(4) | 86·92 (5) | Cu–N–C(8)′ | 110·42 (9) |
| Cu–O(1)–C(1) | 115·84 (11) | Cu–O(4)–C(6) | 127·88 (11) |
| | | Cu–O(4)–C(7) | 93·06 (8) |

(*b*) Bond distances and angles of the glycine moiety

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·284 (2) | C(1)–C(2) | 1·521 (3) |
| C(1)–O(2) | 1·221 (2) | C(2)–N | 1·489 (2) |
| O(1)–C(1)–O(2) | 125·1 (2) | C(1)–C(2)–N | 110·6 (1) |
| O(1)–C(1)–C(2) | 115·4 (1) | C(2)–N–C(3) | 111·5 (1) |
| O(2)–C(1)–C(2) | 119·5 (2) | C(2)–N–C(8)′ | 107·4 (1) |

(*c*) Bond distances, bond angles and torsion angles of the crown ring

| 1 | 2 | 3 | 4 | 1–2 | 1–2–3 | 1–2–3–4 |
|---|---|---|---|---|---|---|
| C(8)′ | N | C(3) | C(4) | 1·502 (2) | 108·5 (1) | 168·0 (1) |
| N | C(3) | C(4) | O(3) | 1·497 (2) | 114·9 (1) | 71·4 (2) |
| C(3) | C(4) | O(3) | C(5) | 1·510 (2) | 110·7 (1) | −149·3 (1) |
| C(4) | O(3) | C(5) | C(6) | 1·431 (2) | 115·0 (1) | 85·7 (2) |
| O(3) | C(5) | C(6) | O(4) | 1·421 (2) | 114·1 (1) | −68·7 (2) |
| C(5) | C(6) | O(4) | C(7) | 1·509 (3) | 109·8 (1) | −165·2 (1) |
| C(6) | O(4) | C(7) | C(8) | 1·428 (2) | 113·2 (1) | 172·2 (1) |
| O(4) | C(7) | C(8) | N′ | 1·431 (2) | 106·9 (1) | 71·4 (2) |
| C(7) | C(8) | N′ | C(3)′ | 1·502 (2) | 114·1 (1) | 88·7 (2) |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36337 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the crown-ether O atoms on either side of the equatorial plane at a Cu—O distance of 2·636 (2) Å. The direction of the weak Cu—O interaction makes an angle of 12·4 (2)° with the normal to the equatorial plane with the equation $0{\cdot}7398u - 0{\cdot}4380v - 0{\cdot}2220w = 0$, where $u$, $v$ and $w$ are in Å referred to the $a$, $b$ and $c$ axes respectively. The environment about the central Cu atom can be described as an elongated rhombic octahedron with two five- and one eight-membered chelate rings alternating. This folded coordination structure well represents the characteristic complexing behavior associated with both crown-ether and complexane structures. It seems that the extraordinary stability of the present complex is attributable to the ability of this ligand to form an elongated octahedral coordination. This type of 4 + 2 coordination and the dimensions involved are common in $Cu^{II}$ complexes (Hathaway & Billing, 1970). A somewhat similar coordination geometry has been found in $CuCl_2$–$C_{12}H_{26}N_2O_4$, where the Cu atom is situated at the center of the diaza-18-crown-6 to be strongly coordinated to the two N and two Cl atoms and weakly coordinated to the two O atoms (Herceg & Weiss, 1973).

The C—C bonds [1·510 (2), 1·509 (3), 1·502 (2) Å] in the crown ring are somewhat shorter than a normal $C(sp^3)$—$C(sp^3)$ bond of 1·534 Å. This shortening, even when allowing for a reasonable thermal correction, has been observed in crown-type polyethers (Dalley, 1978). The C—O bond distances [1·431 (2), 1·421 (2), 1·428 (2), 1·431 (2) Å] in the same portion are close to the expected value of 1·42–1·43 Å, while the N—C bonds [1·489 (2), 1·497 (2), 1·502 (2) Å] are longer than the accepted value of 1·479 (5) Å for a four-covalent nitrogen bond (Sutton, 1965). The C—O bonds of the carboxyl group have double-bond character. This group is planar within the maximum deviation of 0·014 (3) Å from its least-squares plane, which is tilted by an angle of 14·5 (2)° in relation to the equatorial plane. The torsion angles about C—C bonds in the crown ring are nearly 70°, corresponding to the synclinal conformation which has been observed in most parts of other crown-type compounds. The two moieties C(8)′—N—C(3)—C(4) and C(6)—O(4)—C(7)—C(8) have antiplanar arrangements, to be connected to —O(3)—C(5)H— with a torsion angle of 85·7 (2)°. These conformations are reflected in the football-like molecular shape. The C—H bond distances are in the range 0·92 to 0·99 Å with an average of 0·96 (2) Å, and the H—C—H bond angles are reasonable. These bond distances and angles have been omitted in Table 2, since H atoms were unlikely to play a role except in crystal packing.

There are no intermolecular close contacts, the molecular packing being due to van der Waals forces only.

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