

# The Crystal and Molecular Structure of Bis(chloroacetato)- (*N,N,N',N'*-tetramethylethylenediamine)copper(II), $\text{Cu}(\text{C}_6\text{H}_{16}\text{N}_2)(\text{ClC}_2\text{H}_2\text{O}_2)_2$

MARKKU AHLGRÉN, REIJO HÄMÄLÄINEN and URHO TURPEINEN

Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data. The blue crystals belong to the monoclinic space group  $P2_1$  with  $a=7.266(3)$  Å,  $b=14.846(7)$  Å,  $c=7.260(2)$  Å,  $\beta=103.41(3)^\circ$  and  $Z=2$ . The structure was solved by direct and Fourier methods and refined by block-diagonal least-squares procedures to an  $R$  value of 0.022 for 1981 independent reflections having  $I > 3\sigma(I)$ . The structure is built-up from discrete  $\text{Cu}(\text{C}_6\text{H}_{16}\text{N}_2)(\text{ClC}_2\text{H}_2\text{O}_2)_2$  molecules and the copper(II) ion is surrounded by four atoms in a distorted square-planar arrangement with two Cu–N bonds, 2.039(3) and 2.037(3) Å, from the diamine ligand and two Cu–O bonds, 1.977(3) and 1.975(3) Å, from the chloroacetate groups. The two remaining oxygen atoms of the chloroacetate groups are at distances of 2.627(3) and 2.624(3) Å from the Cu atom. The angles between the “out-of-plane”  $\text{Cu}\cdots\text{O}$  directions and the normal to the “square-plane” are 25.7 and 25.6°, respectively, with the  $\text{O}\cdots\text{Cu}\cdots\text{O}$  angle 140.3(1)°.

Nickel(II) salts of simple aliphatic monocarboxylic acids form 1:1 complexes with *N,N,N',N'*-tetramethylethylenediamine.<sup>1</sup> These complexes are dimeric, with nickel(II) atoms joined by one water molecule and two carboxylate ions. The bridging carboxylate ligands have a *syn-syn* configuration as in most binuclear copper(II) carboxylate complexes, but the Ni–Ni distances are much longer ( $\sim 3.55$  Å) than in copper(II) complexes ( $\sim 2.62$  Å)<sup>2</sup> indicating that no metal-metal bonding occurs. The present work was undertaken in order to elucidate the structural changes that occur when copper(II) replaces nickel(II) in the system.

## EXPERIMENTAL

*Preparation and analyses.* The compound was prepared by adding 0.05 mol of *N,N,N',N'*-tetramethylethylenediamine (Fluka AG) to a methanol solution containing 0.05 mol of copper(II) chloroacetate, which was prepared from copper(II) carbonate (J. T. Baker) and chloroacetic acid (BDH). Propanol was added and the solution was allowed to evaporate at room temperature. After several days the product crystallized in the form of blue plates.

Copper was analyzed electrolytically. Calc. for  $\text{Cu}(\text{C}_6\text{H}_{16}\text{N}_2)(\text{ClC}_2\text{H}_2\text{O}_2)_2$ : Cu 17.33%. Found: Cu 17.24%. A density of 1.607 g/cm<sup>3</sup> was determined by the flotation method using carbon tetrachloride and methyl iodide. The calculated value with  $Z=2$  is 1.599 g/cm<sup>3</sup>.

*Space group, unit cell and intensity data.* Preliminary rotation and Weissenberg photographs taken with  $\text{CuK}\alpha$  radiation showed that the crystals belong to the monoclinic system, and systematic absences were recognized for the reflections  $0k0$ , when  $k$  odd. This indicated that the space group is  $P2_1$  (No. 4) or  $P2_1/m$  (No. 11). The centrosymmetric space group  $P2_1/m$  could be excluded because in that space group the copper(II) ions would be in a special position, introducing too high symmetry requirements for the complex molecule.

Lattice parameters  $a=7.266(3)$  Å,  $b=14.846(7)$  Å,  $c=7.260(2)$  Å and  $\beta=103.41(3)^\circ$  were obtained from a least-squares refinement of twelve well-centered reflections on a Syntex  $P2_1$  automatic diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda=0.71069$  Å). The crystal selected for X-ray intensity measurement was approximately  $0.40 \times 0.45 \times 0.50$  mm<sup>3</sup>. Intensity data were collected ( $5^\circ < 2\theta < 60^\circ$ ) at room temperature using the  $\omega$ -scan technique and the scan rate varying from 2.02 to

29.3° min<sup>-1</sup> depending upon the peak intensity. The intensity of one standard reflection, recorded after every 99 measurements to monitor the crystal stability, remained essentially constant throughout the data collection. Out of 2320 measured intensities 1981 were observed on the basis of  $I > 3\sigma(I)$ . The data were corrected for Lorentz and polarization factors and for absorption ( $\mu(\text{MoK}\alpha) = 18.5 \text{ cm}^{-1}$ ) from  $\phi$ -scan data.

## STRUCTURE DETERMINATION AND REFINEMENT

The MULTAN program system<sup>3</sup> was used to calculate phases for the 250 greatest  $|E|$ 's. Eight reflections were used in the starting set. The phase set with the highest combined figure of merit yielded an  $E$ -map from which the coordination sphere of the copper(II) ion could be found. The other non-hydrogen atoms were located by three-dimensional Fourier synthesis using the X-RAY 76 program system.<sup>4</sup>

Block-diagonal least-squares refinement was carried out on  $F$ . The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$  with the weighting scheme  $w = 1/(45.0 + |F_o| + 0.005|F_o|^2)$ . Scattering factors for Cu, Cl, O, N, and C were those tabulated by Cromer

and Mann<sup>5</sup> and for H atoms those of Stewart, Davidson and Simpson.<sup>6</sup> The effect of anomalous dispersion was taken into account in the structure factor calculation, using the values of  $\Delta f'$  and  $\Delta f''$  for Cu and Cl given in International Tables for X-Ray Crystallography.<sup>7</sup> Refinement of a model including all non-hydrogen atoms with individual isotropic thermal parameters led to an  $R$  value of 0.073 ( $R = \Sigma \|F_o\| - |F_c| / \Sigma \|F_o\|$ ). Further refinement with anisotropic thermal parameters reduced the  $R$  factor to 0.038. At this point all of the hydrogen atoms were located from a difference Fourier map. Five more least-squares cycles were then computed, in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters. After the last cycle the final  $R$  value was 0.022 for the 1981 observed reflections.

The final atomic coordinates and thermal parameters together with their estimated standard deviations are given for non-hydrogen atoms in Table 1 and for hydrogen atoms in Table 2. A list of observed and calculated structure factors is obtainable on request from the authors.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and anisotropic thermal parameters<sup>a</sup> ( $\times 10^3$ ) for non-hydrogen atoms. Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	1030(1)	4743(1)	-1030(1)	26(0.1)	24(0.1)	26(0.1)	2(0.2)	8(0.1)	2(0.2)
N1	-1693(4)	4363(2)	-1156(4)	25(1)	30(1)	27(1)	2(1)	5(1)	-1(1)
C1	-2195(4)	4783(4)	524(4)	27(1)	44(2)	33(1)	2(2)	11(1)	-2(2)
C2	-523(4)	4705(4)	2194(4)	35(1)	43(2)	27(1)	-4(2)	11(1)	1(2)
C3	-1953(6)	3375(3)	-1126(6)	43(2)	32(2)	49(2)	-7(1)	11(2)	-3(2)
C4	-2904(4)	4731(4)	-2919(4)	37(1)	51(2)	35(1)	3(2)	0(1)	-3(2)
C5	2922(4)	4756(5)	2903(4)	36(1)	53(2)	37(1)	-2(2)	-1(1)	7(2)
C6	1113(6)	6112(3)	1956(5)	51(2)	32(2)	42(2)	-4(2)	14(2)	-8(1)
N2	1161(4)	5124(2)	1693(4)	29(1)	29(1)	26(1)	-3(1)	6(1)	1(1)
O1	1172(4)	4006(2)	-3261(3)	47(1)	31(1)	34(1)	10(1)	15(1)	1(1)
C7	2133(5)	3312(2)	-2558(4)	35(2)	31(2)	32(2)	6(1)	13(1)	0(1)
C8	2380(5)	2650(2)	-4088(5)	50(2)	32(2)	37(2)	11(1)	16(1)	0(1)
C11	3670(1)	1664(1)	-3162(2)	48(1)	35(1)	62(1)	13(1)	16(1)	4(1)
O2	2774(4)	3185(2)	-858(4)	64(2)	58(2)	32(1)	21(2)	5(1)	-1(1)
O3	3258(3)	5478(2)	-1172(4)	34(1)	32(1)	46(1)	1(1)	15(1)	10(1)
C9	2557(4)	6173(2)	-2125(5)	32(1)	31(2)	33(1)	-1(1)	13(1)	3(1)
C10	4079(5)	6838(3)	-2387(5)	40(2)	34(2)	45(2)	2(1)	15(1)	11(1)
C12	3160(2)	7820(1)	-3671(1)	64(1)	33(1)	48(1)	3(1)	17(1)	12(1)
O4	856(4)	6303(2)	-2761(4)	34(1)	56(2)	63(2)	-1(1)	6(1)	20(2)

<sup>a</sup> The anisotropic thermal parameters are of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ .



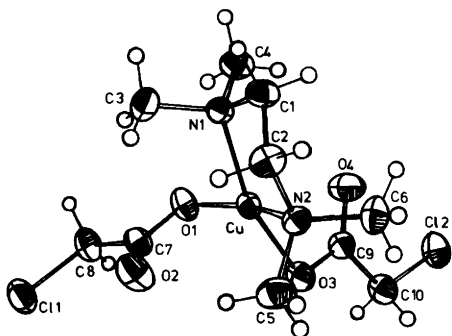


Fig. 1. A view of the complex molecule. Thermal ellipsoids are scaled to enclose 50 % probability.

The copper(II) ion is surrounded by four atoms in a distorted square-planar arrangement forming two Cu—O bonds of lengths 1.977(3) and 1.975(3) Å, and two Cu—N bonds of lengths 2.039(3) and 2.037(3) Å. The distortion is tetrahedral with N1 and O3 0.319 and 0.310 Å above the least-squares plane through N1, N2, O1 and O3, and with N2 and O1 0.319 and 0.309 Å below this plane, *cf.* Table 4. The degree of distortion is more clearly expressed by the dihedral angle of 25.6° between the Cu, N1, N2 and Cu, O1, O3 planes; the ideal value for square-planar arrangement is 0° and for tetrahedral arrangement 90°. The two remaining oxygen atoms O2 and O4 of the chloroacetate groups are at Cu—O distances of 2.627(3) and 2.624(3) Å, respectively. If the normal to the N1, N2, O1, O3 plane is considered as the “tetragonal axis” of the complex, the angles between the “out-of-plane” Cu···O directions and the “tetragonal axis” are 25.7 and 25.6°, respectively; the O2—Cu—O4 angle is 140.3(1)°.

The stereochemistry of the copper(II) complex may be considered as distorted square-planar or tetragonally distorted octahedral, depending upon whether or not the “out-of-plane” oxygen atoms

are considered to be bonded to Cu. Since the “in-plane” copper-ligand distances are not as short as those generally found for square-planar copper(II) complexes,<sup>8</sup> some interaction between the copper(II) and the “out-of-plane” oxygen atoms may exist, so that the environment of the copper(II) ion is best described as extremely tetragonally distorted octahedral, like that in  $\text{Cu}(\text{ClCH}_2\text{COO})_2(\alpha\text{-picoline})_2$ .<sup>9</sup>

The dimensions and angles of the diamine ligand are as expected. The diamine chelate ring is practically in symmetric *gauche* configuration. The ring carbon atoms lie 0.356 and 0.355 Å above and below the plane defined by Cu, N1, N2. In substituted ethylenediamine ligands the largest deviations are found in the ring carbon-carbon bond length. In this compound the C1—C2 length of 1.509(4) Å agrees quite well with those of 1.523(14) and 1.497(9) Å found in  $\text{Cu}(\text{CH}_3\text{CHOHCOO})_2(\text{tmen})$ <sup>10</sup> and  $\text{Ni}(\text{CH}_3\text{CHOHCOO})_2(\text{tmen})$ <sup>11</sup> but is somewhat shorter than the normal carbon-carbon single bond distance of 1.54 Å.<sup>12</sup> One possible explanation for this difference from the carbon-carbon single bond value is to be found in Maslen and Waters' suggestion that the ring C—C bond length in complexes ethylenediamine is somewhat flexible and responsive to the demands of the chemical system in which it finds itself.<sup>13</sup>

The C—H distances lie in the range 0.88–1.07 Å, with estimated standard deviations of about 0.05 Å. The acetate groups are planar and the copper(II) ion is only slightly displaced from these planes, as are the chlorine atoms, *cf.* Table 4. The dihedral angles between planes C, C, O, O and C, C, Cl are 1.0 and 0.8°. The O—C—O angles of 124.6(3)° agree well with the previously reported values of 123.8–125.4° found in  $\text{Cu}(\text{ClCH}_2\text{COO})_2(\alpha\text{-picoline})_2$ ,<sup>9</sup>  $\text{NH}_4\text{H}(\text{ClCH}_2\text{COO})_2$ ,<sup>14</sup> and two forms of  $\text{ClCH}_2\text{COOH}$ ,<sup>15,16</sup> but seem to be slightly smaller than those of 126.6–129.0° in  $[\text{Cu}(\text{ClCH}_2\text{COO})_2(\alpha\text{-picoline})]_2$ <sup>17</sup> and  $[\text{Ni}_2(\text{ClCH}_2\text{COO})_4(\text{tmen})_2]$

Table 4. Deviations (Å) of atoms from least-squares planes.

Plane I:	N1, N2, O1, O3										
N1	0.319	N2	-0.319	O1	-0.309	O3	0.310	0.000			
Plane II:	O1, O2, C7, C8										
O1	-0.001	O2	-0.001	C7	0.002	C8	-0.001	Cu	-0.013	Cl1	-0.031
Plane III:	O3, O4, C9, C10										
O3	0.001	O4	0.001	C9	-0.001	C10	0.000	Cu	0.007	Cl2	0.025

The angles between the planes: I, II = 85.9°; I, III = 86.1°; III = 86.2°

$\text{H}_2\text{O}$ ].<sup>1a</sup> The C—O bond lengths of 1.229–1.230(4) and 1.282–1.280(4) Å are significantly different, as are the C—C—O angles of 111.9–112.3(3)° and 123.5–123.1(3)°, cf. Table 3. From a chemical point of view the longer C—O bond length of each chloroacetate group would be expected to belong to the oxygen atom that is more strongly coordinated to the copper(II) ion and this is consistent with the observed Cu—O distances. These facts indicate that the carboxyl groups in the present compound are neither fully ionized or neutral in character.

## REFERENCES

1. a. Turpeinen, U. *Finn. Chem. Lett.* (1976) 173; b. *Ibid.* (1977) 36; c. *Ibid.* (1977) 123; d. Turpeinen, U., Ahlgrén, M. and Hämäläinen, R. *Ibid.* (1977) 246.
2. Doedens, R. J. *Prog. Inorg. Chem.* 21 (1976) 227.
3. Main, P., Woolfson, M. M., Lessinger, L., Germain, G. and Declercq, J.-P. *MULTAN 74, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data.*
4. Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park.
5. Cromer, D. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 149.
8. Hathaway, B. J. and Billing, D. E. *Coord. Chem. Rev.* 5 (1970) 143.
9. Davey, G. and Stephens, F. S. *J. Chem. Soc. A* (1971) 1917.
10. Ahlgrén, M., Hämäläinen, R. and Pajunen, A. *Finn. Chem. Lett.* (1977) 3.
11. Ahlgrén, M. and Turpeinen, U. *Finn. Chem. Lett.* (1977) 129.
12. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca 1960, p. 222.
13. Maslen, H. S. and Waters, T. N. *Coord. Chem. Rev.* 17 (1975) 158.
14. Ichikawa, M. *Acta Crystallogr. B* 28 (1972) 755.
15. Kanters, J. A. and Roelofsen, G. *Acta Crystallogr. B* 32 (1976) 3328.
16. Kanters, J. A., Roelofsen, G. and Feenstra, T. *Acta Crystallogr. B* 32 (1976) 3331.
17. Davey, G. and Stephens, F. S. *J. Chem. Soc. A* (1970) 2803.

Received September 5, 1977.