

The Crystal and Molecular Structure of Bis(chloroacetato)- (*N,N,N',N'*-tetraethylethylenediamine)copper(II), $\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_2)(\text{ClC}_2\text{H}_2\text{O}_2)_2$

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The crystal structure of the title compound has been determined from three-dimensional X-ray data and refined by full-matrix least-squares methods to an *R* value of 0.044 for 1596 independent reflections. The dark blue crystals belong to the orthorhombic space group *Pccn* with $a = 13.013(3)$, $b = 19.182(12)$, $c = 15.372(5)$ Å and $Z = 8$. The two independent complex molecules in the structure possess C_2 symmetry, and their corresponding bond lengths and angles are closely similar. Each copper(II) ion has a very distorted octahedral environment. The diamine nitrogen atoms and two carboxyl oxygen atoms occupy the equatorial sites at copper–ligand distances of about 2.0 Å and the axial sites are occupied by the second carboxyl oxygen atoms with Cu–O distances of about 2.7 Å.

The present structure determination is part of an investigation into the chemistry of copper(II) complexes formed by substituted ethylenediamines and haloacetates. The crystal structures of bis(chloroacetato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II)¹ and bis(trichloroacetato)aqua(*N,N,N',N'*-tetramethylethylenediamine)copper(II)² have already been published. These two compounds are different. In the trichloroacetato complex the copper(II) ion has a square-pyramidal environment, the carboxylate ligands being monodentately coordinated to the metal ion. In the chloroacetato complex the copper(II) ion has a distorted octahedral environment, the carboxylate ligands being unsymmetrically chelated.

EXPERIMENTAL

Dark blue crystals of bis(chloroacetato)-(*N,N,N',N'*-tetraethylethylenediamine)copper(II) were obtained by slow evaporation of an ethanol solution containing copper(II) chloroacetate and *N,N,N',N'*-tetraethylethylenediamine in the molar ratio 1:1.

Preliminary photographic work showed the crystals to be orthorhombic and the space group, on the basis of systematic absences, to be *Pccn*. Accurate cell dimensions were obtained by refining 19 reflections measured with a Syntex P2₁ diffractometer. The crystal data for $\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_2)(\text{ClC}_2\text{H}_2\text{O}_2)_2$ are:

$a = 13.013(3)$ Å	$F.W. = 422.84$
$b = 19.182(12)$ Å	$D_{\text{obs}} = 1.463 \text{ g cm}^{-3}$
$c = 15.372(5)$ Å	$D_{\text{calc}} = 1.464 \text{ g cm}^{-3}$
$V = 3837$ Å ³	$Z = 8$
Space group <i>Pccn</i> (No. 56)	$\mu(\text{MoK}\alpha) = 14.8 \text{ cm}^{-1}$

The crystal used for data collection had approximate dimensions of $0.2 \times 0.4 \times 0.5$ mm. The reflections were recorded in the range $3^\circ < 2\theta < 52^\circ$ at a variable scan rate from 2.5 to $30^\circ \text{ min}^{-1}$ by ω -scan technique and with Mo radiation (MoK α , $\lambda = 0.71069$ Å). A reference reflection, recorded after every 99 measurements, showed no significant variation in intensity during the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption from ϕ -scan data. Only the 1596 reflections with $F_o > 5\sigma(F_o)$ were used in subsequent calculations.

The structure was solved by direct and Fourier methods. The refinement was carried out by full-matrix least-squares calculations with the non-hydrogen atoms refined anisotropically. The hydrogen atoms were included in calculated positions

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters^a ($\times 10^3$) for non-hydrogen atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule A									
Cu	2500	2500	3232(1)	33(1)	42(1)	36(1)	4(1)	0	0
O1	1965(5)	1867(3)	2330(3)	46(4)	61(4)	42(4)	-7(3)	2(3)	-11(3)
O2	537(4)	2361(3)	2822(4)	54(3)	53(5)	57(4)	16(3)	-1(3)	-10(3)
C1	1004(7)	1940(4)	2355(5)	43(5)	40(5)	32(5)	-5(5)	1(4)	9(4)
C2	358(7)	1499(4)	1744(6)	49(5)	50(5)	58(5)	-1(5)	0(5)	-9(5)
Cl	857(2)	660(1)	1538(2)	90(2)	48(1)	98(2)	0(1)	-21(2)	-11(1)
N	2579(7)	1753(3)	4191(4)	54(4)	42(3)	36(3)	-1(5)	-5(5)	4(3)
C3	2790(8)	2180(5)	4980(5)	96(10)	62(5)	42(5)	-17(5)	-14(5)	13(4)
C4	3528(8)	1323(6)	4062(7)	39(5)	77(7)	83(8)	17(5)	-3(5)	29(6)
C5	3488(9)	834(6)	3313(8)	82(8)	93(9)	98(9)	51(7)	35(7)	10(7)
C6	1655(7)	1326(5)	4254(6)	46(5)	51(5)	48(5)	13(5)	7(5)	10(4)
C7	1641(8)	745(5)	4945(6)	66(6)	56(6)	74(7)	-1(5)	13(6)	13(5)
Molecule B									
Cu	7500	2500	4898(1)	31(1)	38(1)	35(1)	3(1)	0	0
O1	8037(4)	1872(3)	5806(3)	39(4)	52(4)	44(4)	6(3)	-6(3)	7(3)
O2	9475(5)	2352(3)	5346(4)	69(4)	60(5)	49(4)	-14(3)	-6(3)	11(3)
C1	9006(8)	1952(5)	5816(5)	56(7)	44(6)	39(5)	-3(5)	-3(4)	-10(4)
C2	9598(7)	1507(5)	6452(5)	54(5)	61(6)	46(5)	3(5)	-12(4)	5(5)
Cl	9088(2)	667(1)	6628(2)	107(2)	47(1)	77(2)	6(1)	-15(2)	10(1)
N	7550(7)	1755(3)	3923(4)	49(4)	38(3)	42(3)	-7(5)	4(5)	-4(3)
C3	7793(6)	2163(4)	3109(5)	47(5)	55(5)	38(4)	5(4)	7(4)	-3(4)
C4	6519(8)	1445(5)	3913(6)	47(5)	58(6)	55(6)	15(5)	-4(5)	-10(5)
C5	6279(6)	999(5)	4719(7)	38(5)	64(6)	80(7)	-13(4)	8(5)	-17(5)
C6	8377(7)	1225(5)	4013(6)	35(5)	47(5)	64(6)	2(4)	9(5)	-9(5)
C7	8366(8)	645(5)	3322(6)	70(6)	47(5)	71(7)	2(5)	15(5)	-9(5)

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

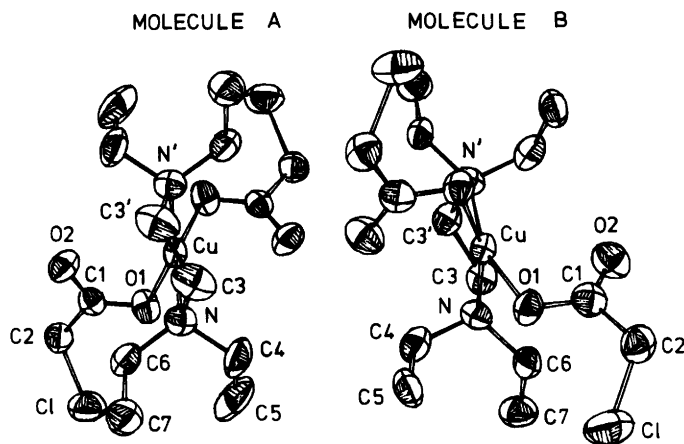


Fig. 1. A view of the molecules A and B along z axis.

($\text{C}-\text{H}=1.00 \text{ \AA}$) and not refined. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w=1/(1 + ((F_o - 85.0)/45.0)^2)$. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann³ and those for H from Stewart *et al.*⁴ An anomalous dispersion correction was included for the Cu and Cl atoms.⁵ Refinement of the model led to the final R value of 0.044 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$).

The computations were performed on a Univac 1108 computer with the X-RAY 76 program system.⁶

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters with standard deviations are given in Table 1. A list of the observed and calculated structure factors is obtainable on request from the authors.

In the unit cell there are two independent complex molecules (Fig. 1) with essentially similar corresponding bond lengths and angles, as can be seen from Table 2. The molecules have C_2 symmetry and are held in the crystal lattice by van der Waals' forces. With the exception of the contacts $\text{O}(2\text{A}) \cdots \text{C}(2\text{B})^i = 3.262(10) \text{ \AA}$ and $\text{C}(2\text{A}) \cdots \text{O}(2\text{B})^i =$

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with standard deviations in parentheses.

Molecule A	B		A	B		A	B	
The copper(II) environment								
Cu-N	2.059(6)	2.071(6)	N-Cu-N ⁱ	88.5(2)	87.4(2)	O2-Cu-O2 ⁱ	152.4(2)	150.1(2)
Cu-O1	1.970(6)	1.973(6)	O1-Cu-N	95.3(2)	94.6(2)	O2-Cu-O1	55.2(2)	54.0(2)
Cu-O2	2.645(5)	2.676(6)	O1-Cu-O1 ⁱ	90.6(2)	89.8(2)	O2-Cu-O1 ⁱ	103.7(2)	102.9(2)
			O1-Cu-N ⁱ	156.2(3)	160.8(3)	O2-Cu-N	98.6(3)	94.8(3)
						O2-Cu-N ⁱ	101.1(3)	106.8(3)
The diamine ligand								
N-C3	1.489(10)	1.510(10)	Cu-N-C3	102.1(4)	104.4(4)	N-C3-C3 ⁱ	111.9(7)	109.9(6)
N-C4	1.498(13)	1.468(13)	Cu-N-C4	109.2(6)	105.0(6)	N-C4-C5	114.9(9)	113.7(8)
N-C6	1.458(12)	1.487(12)	Cu-N-C6	113.4(6)	115.3(5)	N-C6-C7	117.5(8)	115.1(7)
C3-C3 ⁱ	1.442(13)	1.500(11)	C3-N-C4	105.0(8)	113.1(7)			
C4-C5	1.486(16)	1.537(14)	C3-N-C6	114.0(7)	106.2(7)			
C6-C7	1.540(13)	1.537(13)	C4-N-C6	112.3(7)	112.6(6)			
The chloroacetate ligand								
O1-C1	1.259(11)	1.270(11)	Cu-O1-C1	105.1(5)	106.7(5)	O1-C1-O2	125.3(8)	124.5(8)
O2-C1	1.239(10)	1.218(11)	Cu-O2-C1	74.3(5)	74.8(5)	O1-C1-C2	118.0(7)	116.5(8)
C1-C2	1.518(12)	1.509(13)				O2-C1-C2	116.7(8)	119.0(9)
C2-C1	1.764(9)	1.764(9)				C1-C2-C1	114.6(6)	115.1(7)

ⁱ Refers to equivalent position $1/2-x, 1/2-y, z$ in the molecule A and to $3/2-x, 1/2-y, z$ in the molecule B.

Table 3. Deviations (\AA) of selected atoms from least-squares planes.

Molecule A				Molecule B			
Plane IA: N, N ⁱ , O1, O1 ⁱ				Plane IB: N, N ⁱ , O1, O1 ⁱ			
N	.407	O1	-.421	N	-.331	O1	.341
N ⁱ	-.407	O1 ⁱ	.421	N ⁱ	.331	O1 ⁱ	-.341
Plane IIA: O1, O2, C1, C2				Plane IIB: O1, O2, C1, C2			
O1	.004	C2	.003	O1	-.001	C2	-.001
O2	.004	Cu	-.079	O2	-.001	Cu	-.041
C1	-.011	Cl	-.858	C1	.004	Cl	-.909

ⁱ Refers to equivalent position $1/2-x, 1/2-y, z$ in the molecule A and to $3/2-x, 1/2-y, z$ in the molecule B.

3.285(10) Å where equivalent position $I=(x-1, -y+1/2, z-1/2)$, all intermolecular distances are greater than 3.6 Å.

The coordination octahedron around the copper ions in the present compound is nearly identical with the coordination octahedron found in bis-(chloroacetato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II), $\text{Cu}(\text{tmen})(\text{ClAc})_2$.¹ Both are constituted of four oxygen atoms and two nitrogen atoms, and the corresponding bond lengths and angles agree closely. The marked distortion from true octahedron, which can be seen from Tables 2 and 3, can be attributed to the fact that the copper(II) ion exhibits Jahn-Teller distortion and that the chloroacetate ligands form four-membered chelate rings.

The bond lengths and angles of the diamine ligand are as expected. The diamine chelate rings are in symmetric *gauche* configuration. In the complex molecule A the ring carbon atoms lie 0.332 Å above and below the plane defined by the copper and the nitrogen atoms of the diamine ligand, in the complex B 0.352 Å.

The bond lengths of the chloroacetate ligands (Table 2) compare well with those found in $\text{Cu}(\text{tmen})(\text{ClAc})_2$.¹ However the conformation of this ligand is different in the two compounds due to packing effects. In $\text{Cu}(\text{tmen})(\text{ClAc})_2$ the chlorine atom of the chloroacetate ligand is nearly in the acetate plane (0.03 Å off the plane) and is nearer the carboxyl oxygen atom weakly bonded to the copper ion. In the present compound the chlorine atom deviates 0.86 Å in the molecule A and 0.91 Å in the molecule B from the acetate plane (Table 3) and is nearer the carboxyl oxygen atom strongly bonded to the copper ion. Obviously the deviation of the chlorine atom from the acetate plane is reflected in the O-C-C angles. In $\text{Cu}(\text{tmen})(\text{ClAc})_2$ the difference between the angles O1-C1-C2 and O2-C1-C2 is 11°, which is near the value of 12° found in the β -form of monochloroacetic acid,⁷ whereas in the present compound the angles are equal within 3σ .

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Received June 29, 1979.