

# The Crystal Structure of 2-Diethylaminoethanolato(trichloroacetato)copper(II) Tetramer, $C_{32}H_{56}Cl_{12}Cu_4N_4O_{12}$

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## Abstract

$Cu_4(C_2Cl_3O_2)_4(C_6H_{14}NO)_4$  is monoclinic, space group  $P2_1/n$ , with  $a = 14.772$  (7),  $b = 19.442$  (8),  $c = 20.085$  (8) Å,  $\beta = 106.87$  (3)°,  $Z = 4$ . The structure was refined to  $R = 0.083$ . The Cu and bridging ethanolato O atoms form an eight-membered  $Cu_4O_4$  ring, folded in a boat-like conformation, and forming a cubane-type structure through two pairs of long Cu–O distances perpendicular to each other. The Cu–Cu distances range from 3.094 (4) to 3.996 (4) Å. Each of the four crystallographically independent  $Cu^{II}$  atoms is surrounded by two ethanolato O atoms, a carboxyl O atom and an amino N atom in a distorted square-planar arrangement, with Cu–O distances of 1.93 (1)–1.98 (1) Å and Cu–N distances of 2.04 (2)–2.11 (2) Å. Around Cu(1), Cu(2) and Cu(4) there are two longer out-of-plane Cu–O distances of 2.44 (1)–2.60 (1) and 2.84 (1)–3.01 (1) Å formed with carboxyl and ethanolato O atoms, respectively. The fifth coordination site around Cu(3) is occupied by an ethanolato O atom at a distance of 2.52 (1) Å; the sixth site is blocked by an ethyl group of the 2-diethylaminoethanolato ligand, the terminal ethyl C atom lying 3.20 (3) Å from the Cu atom. Three of the four trichloroacetate groups are bidentate, bridging in *syn-syn* configuration from a basal coordination site of one Cu atom to an apical site of another; the fourth trichloroacetate group is monodentate.

## Introduction

Alkoxo-bridged  $Cu^{II}$  complexes of 2-dialkylaminoethanol with the general formula  $[Cu(R_2NCH_2CH_2O)X]_n$  ( $R = CH_3, C_2H_5, C_3H_7, C_4H_9$ ;  $X = Cl^-, Br^-, NCS^-, NCO^-$ ) have been investigated by a number of researchers (Hein & Beerstechen, 1955; Uhlig & Staiger, 1968; Pajunen & Lehtonen, 1971; Pajunen & Smolander, 1974; Estes & Hodgson, 1975; Matsumoto, Ueda, Nishida & Kida, 1976;

Mergehenn, Haase & Allmann, 1975; Merz & Haase, 1978) and been shown to be built up of dimeric, tetrameric and polymeric structures in the solid state. Recently, we began investigating complexes where  $X$  is acetate or haloacetate ( $R = CH_3, C_2H_5, C_3H_7, C_4H_9$ ). An acetate member possesses a hexameric structure and gives rise to a new type of  $Cu^{II}$  complex with 2-diethylaminoethanol (Ahlgrén, Smolander & Turpeinen, 1979). Haloacetate members possess a tetrameric cubane-like structure (Smolander, Turpeinen & Ahlgrén, 1978; Turpeinen, Hämäläinen, Ahlgrén & Smolander, 1979). In this study, we report the structure of 2-diethylaminoethanolato(trichloroacetato)-copper(II) tetramer.

## Experimental

The complex was prepared by dissolving  $Cu^{II}$  trichloroacetate in ethanol and adding an equimolar amount of 2-diethylaminoethanol. The resulting blue product was collected by filtration and recrystallized from chloroform.

The space group was determined from Weissenberg photographs as  $P2_1/n$ . The density was measured by flotation in a mixture of carbon tetrachloride and methyl iodide. Cell dimensions were determined by least squares from the setting angles of 16 reflections measured on a Syntex  $P2_1$  diffractometer. The crystal data are shown in Table 1.

The crystal used for data collection was  $0.20 \times 0.25 \times 0.30$  mm. Intensities were collected ( $5 < 2\theta < 45^\circ$ ) at room temperature on a Syntex  $P2_1$  diffractometer

Table 1. *Crystal data*

$C_{32}H_{56}Cl_{12}Cu_4N_4O_{12}$	FW	= 1368.4
Monoclinic $P2_1/n$	Z	= 4
$a = 14.772$ (7) Å	$D_m$	= 1.67 Mg m <sup>-3</sup>
$b = 19.442$ (8)	$D_c$	= 1.646
$c = 20.085$ (8)	$\lambda$ (Mo $K\alpha$ )	= 0.71069 Å
$\beta = 106.87$ (3)°	$\mu$ (Mo $K\alpha$ )	= 2.21 mm <sup>-1</sup>

with graphite-monochromatized Mo  $K\alpha$  radiation. The  $\omega$ -scan technique was employed with a scan range of  $1.0^\circ$ . The scan rate varied from  $2.55$  to  $29.3^\circ \text{ min}^{-1}$ , depending on the number of counts accumulated in a preliminary scan. Background measurements were taken at both ends of the scan with  $\omega$  displaced by  $1.0^\circ$  from the  $K\alpha$  peak; each background was measured for half the scan time. The intensity of a standard reflexion, recorded after every 99 measurements, remained essentially constant. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical  $\phi$ -scan data. Of the 7185 reflexions collected, 2780 had  $F_o > 4\sigma(F_o)$  and were used in subsequent calculations.

### Structure determination

The positions of the Cu atoms were derived from a sharpened Patterson map. All remaining non-hydrogen atoms were located on subsequent Fourier maps. Isotropic refinement of all non-hydrogen atoms converged at  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.143$ . Further refinement of anisotropic temperature factors for Cu, O and N and isotropic for Cl and C atoms improved  $R$  to  $0.123$ . Considerable electron density was observed near the Cl atoms, indicating either librational motion or rotational disorder of the trichloromethyl groups on the carboxylate ligands. Attempts to provide for rotational disorder in the trichloromethyl groups failed, so the Cl atom thermal parameters were allowed to vary anisotropically for the remainder of the refinement. In the last cycle the shifts in parameters were  $< 0.036\sigma$  and the final  $R$  was  $0.083$ . The largest peak on a final difference map had a density of  $1.1 \text{ e } \text{Å}^{-3}$  and was in the region of Cl(1), Cl(2) and Cl(3) belonging to the most disordered trichloromethyl group. A search for electron density in the expected H atom positions revealed several peaks of approximately  $0.5 \text{ e } \text{Å}^{-3}$ , but since a number of the H atoms could not be located, none was included in the final structure factor calculation.

The scattering factors of Cromer & Mann (1968) were used for Cu, Cl, O, N and C. Corrections for anomalous dispersion were applied to Cu and Cl (*International Tables for X-ray Crystallography*, 1974). The quantity minimized in the refinement was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/(60 + |F_o| + 0.003|F_o|^2)$ . The calculations were performed on a Univac 1108 computer with programs of the XRAY 76 system (Stewart, 1976).

Final atomic positional parameters are given in Table 2, bond distances and angles in Tables 3 and 4.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34541 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

	x	y	z
Cu(1)	2383 (2)	1345 (1)	-649 (1)
Cu(2)	3625 (2)	2744 (1)	-374 (1)
Cu(3)	2171 (2)	2796 (1)	467 (1)
Cu(4)	3381 (2)	1330 (2)	1007 (1)
Cl(11)	2020 (16)	-1074 (5)	-848 (7)
Cl(12)	923 (13)	-801 (10)	-37 (13)
Cl(13)	2629 (17)	-1224 (6)	573 (9)
Cl(21)	3726 (7)	1383 (5)	-2828 (4)
Cl(22)	5207 (8)	2284 (7)	-2115 (6)
Cl(23)	3394 (15)	2795 (7)	-2767 (6)
Cl(31)	796 (6)	4911 (5)	-616 (10)
Cl(32)	2445 (7)	5240 (4)	-985 (4)
Cl(33)	2481 (9)	5230 (5)	415 (5)
Cl(41)	2043 (7)	1116 (7)	2871 (5)
Cl(42)	4019 (7)	1154 (5)	3584 (4)
Cl(43)	2883 (10)	2368 (6)	3458 (5)
O(11)	2346 (10)	2355 (7)	-670 (6)
O(12)	2255 (11)	352 (8)	-559 (8)
O(13)	2455 (17)	273 (9)	586 (9)
O(21)	3529 (9)	2797 (7)	567 (7)
O(22)	3878 (13)	2578 (9)	-1255 (9)
O(23)	3439 (12)	1477 (9)	-1475 (7)
O(31)	2160 (11)	1821 (7)	644 (8)
O(32)	1917 (11)	3729 (7)	98 (8)
O(33)	2820 (11)	3855 (7)	-596 (8)
O(41)	3577 (9)	1368 (7)	93 (7)
O(42)	3206 (12)	1274 (10)	1937 (8)
O(43)	3679 (12)	2308 (9)	2269 (9)
N(1)	1098 (12)	1382 (10)	-1460 (9)
N(2)	4946 (13)	3199 (10)	59 (10)
N(3)	1009 (11)	2846 (9)	822 (9)
N(4)	4712 (14)	851 (9)	1344 (10)
C(11)	1682 (16)	2583 (11)	-1288 (11)
C(12)	806 (19)	2106 (14)	-1458 (14)
C(13)	396 (21)	880 (15)	-1338 (15)
C(14)	-623 (23)	952 (17)	-1915 (16)
C(15)	1276 (22)	1218 (16)	-2189 (16)
C(16)	1579 (24)	458 (18)	-2271 (17)
C(17)	2237 (17)	72 (13)	-12 (13)
C(18)	2024 (19)	-750 (13)	-125 (13)
C(21)	4137 (17)	3299 (12)	957 (12)
C(22)	5114 (18)	3159 (13)	832 (13)
C(23)	5717 (19)	2763 (15)	-133 (14)
C(24)	6752 (24)	2956 (17)	217 (18)
C(25)	5010 (19)	3950 (14)	-130 (14)
C(26)	4870 (21)	4053 (15)	-929 (15)
C(27)	3705 (17)	2024 (12)	-1622 (13)
C(28)	3986 (19)	2124 (14)	-2313 (14)
C(31)	1391 (16)	1594 (12)	854 (12)
C(32)	1050 (18)	2212 (14)	1241 (13)
C(33)	125 (17)	2904 (12)	219 (12)
C(34)	-799 (19)	2959 (13)	406 (14)
C(35)	1059 (20)	3494 (15)	1269 (14)
C(36)	2001 (19)	3672 (14)	1774 (14)
C(37)	2272 (15)	4044 (11)	-279 (11)
C(38)	2014 (19)	4821 (14)	-370 (13)
C(41)	4347 (17)	930 (13)	54 (12)
C(42)	5093 (17)	965 (12)	754 (12)
C(43)	4637 (21)	63 (16)	1406 (16)
C(44)	4223 (24)	-151 (18)	2002 (18)
C(45)	5319 (17)	1170 (13)	2018 (13)
C(46)	6387 (27)	877 (20)	2263 (19)
C(47)	3371 (16)	1813 (12)	2335 (11)
C(48)	3075 (21)	1599 (15)	3024 (15)

Table 3. *Interatomic distances (Å) with e.s.d.'s in parentheses*

	<i>m</i> = 1 <i>n</i> = 2 <i>p</i> = 3 <i>q</i> = 4	<i>m</i> = 2 <i>n</i> = 3 <i>p</i> = 4 <i>q</i> = 1	<i>m</i> = 3 <i>n</i> = 4 <i>p</i> = 1 <i>q</i> = 2	<i>m</i> = 4 <i>n</i> = 1 <i>p</i> = 2 <i>q</i> = 3
Cu( <i>m</i> )—N( <i>m</i> )	2.11 (2)	2.09 (2)	2.04 (2)	2.10 (2)
Cu( <i>m</i> )—O( <i>m</i> 1)	1.96 (1)	1.94 (2)	1.93 (1)	1.94 (2)
Cu( <i>m</i> )—O( <i>m</i> 2)	1.95 (2)	1.94 (2)	1.95 (1)	1.96 (2)
Cu( <i>m</i> )—O( <i>q</i> 1)	1.95 (1)	1.96 (1)	1.96 (1)	1.98 (1)
Cu( <i>m</i> )—O( <i>p</i> 1)	2.86 (2)	2.84 (1)	2.52 (1)	3.01 (1)
Cu( <i>m</i> )—O( <i>n</i> 3)	2.60 (2)	2.44 (1)		2.48 (2)
O( <i>m</i> 1)—C( <i>m</i> 1)	1.41 (2)	1.40 (3)	1.39 (3)	1.44 (3)
C( <i>m</i> 1)—C( <i>m</i> 2)	1.55 (3)	1.56 (4)	1.59 (4)	1.51 (3)
C( <i>m</i> 2)—N( <i>m</i> )	1.47 (3)	1.50 (3)	1.49 (3)	1.47 (3)
C( <i>m</i> 3)—N( <i>m</i> )	1.50 (4)	1.55 (4)	1.50 (3)	1.54 (4)
C( <i>m</i> 3)—C( <i>m</i> 4)	1.62 (4)	1.53 (4)	1.52 (4)	1.55 (5)
C( <i>m</i> 5)—N( <i>m</i> )	1.59 (4)	1.52 (3)	1.54 (3)	1.52 (3)
C( <i>m</i> 5)—C( <i>m</i> 6)	1.57 (5)	1.57 (4)	1.51 (3)	1.61 (5)
C( <i>m</i> 7)—O( <i>m</i> 2)	1.23 (3)	1.29 (3)	1.21 (3)	1.30 (3)
C( <i>m</i> 7)—O( <i>m</i> 3)	1.21 (3)	1.20 (3)	1.22 (3)	1.09 (3)
C( <i>m</i> 7)—C( <i>m</i> 8)	1.63 (4)	1.57 (4)	1.56 (3)	1.62 (4)
C( <i>m</i> 8)—Cl( <i>m</i> 1)	1.58 (3)	1.75 (3)	1.73 (3)	1.74 (3)
C( <i>m</i> 8)—Cl( <i>m</i> 2)	1.69 (4)	1.76 (3)	1.75 (3)	1.75 (3)
C( <i>m</i> 8)—Cl( <i>m</i> 3)	1.70 (3)	1.68 (3)	1.72 (3)	1.79 (3)

### Description of the structure and discussion

The unit cell contains four discrete tetranuclear molecules. The closest intermolecular contacts are between the Cl atoms of the trichloroacetate groups of neighbouring complexes and the shortest of these are 3.36 (1) Å between Cl(42<sup>ii</sup>) and Cl(31) and 3.35 (1) Å between Cl(32<sup>i</sup>) and Cl(21). These values may be in error, since the Cl atoms display a high degree of thermal motion. The other intermolecular separations below 3.9 Å are given in Table 5 and are consistent with van der Waals contacts (Bondi, 1964).

A stereoscopic view of the molecule is presented in Fig. 1. The Cu and bridging ethanolato O atoms form an eight-membered Cu<sub>4</sub>O<sub>4</sub> ring, folded in a boat-like conformation. One may consider the ring as derived from an idealized Cu<sub>4</sub>O<sub>4</sub> cube by stretching four edges in pairs, with two of the stretched distances approximately perpendicular to the other two (Fig. 2). The intramolecular Cu—Cu distances vary from 3.094 (4) to 3.996 (4) Å (Table 6).

The four nearest atoms around the Cu atoms, two ethanolato O atoms, a carboxyl O atom and an amino N atom, are arranged in a nearly square-planar coordination, except around Cu(3) where there is a marked tetrahedral distortion (Table 7). The fifth and sixth octahedral sites around Cu(1), Cu(2) and Cu(4) are occupied by the carboxyl O(*n*3) and the ethanolato O(*p*1), with Cu—O distances of 2.44 (1)—2.60 (1) and 2.84 (1)—3.01 (1) Å, respectively. The latter distances indicate only weak interactions between the out-of-

Table 4. *Interatomic angles (°) with e.s.d.'s in parentheses*

	<i>m</i> = 1 <i>n</i> = 2 <i>p</i> = 3 <i>q</i> = 4	<i>m</i> = 2 <i>n</i> = 3 <i>p</i> = 4 <i>q</i> = 1	<i>m</i> = 3 <i>n</i> = 4 <i>p</i> = 1 <i>q</i> = 2	<i>m</i> = 4 <i>n</i> = 1 <i>p</i> = 2 <i>q</i> = 3
O( <i>m</i> 2)—Cu( <i>m</i> )—O( <i>q</i> 1)	92.4 (6)	94.7 (7)	96.7 (7)	91.1 (7)
O( <i>m</i> 2)—Cu( <i>m</i> )—N( <i>m</i> )	90.9 (7)	92.6 (8)	89.9 (7)	92.2 (7)
O( <i>m</i> 1)—Cu( <i>m</i> )—N( <i>m</i> )	86.3 (7)	84.0 (7)	86.0 (7)	86.5 (7)
O( <i>m</i> 1)—Cu( <i>m</i> )—O( <i>q</i> 1)	90.4 (5)	88.8 (6)	92.6 (6)	90.2 (6)
O( <i>m</i> 1)—Cu( <i>m</i> )—O( <i>m</i> 2)	170.7 (7)	170.6 (7)	166.2 (6)	178.7 (7)
O( <i>q</i> 1)—Cu( <i>m</i> )—N( <i>m</i> )	176.7 (7)	172.6 (8)	154.6 (6)	176.0 (8)
O( <i>p</i> 1)—Cu( <i>m</i> )—O( <i>m</i> 1)	71.7 (5)	73.3 (5)	80.9 (6)	69.1 (5)
O( <i>p</i> 1)—Cu( <i>m</i> )—O( <i>m</i> 2)	101.3 (6)	100.0 (6)	91.8 (6)	111.8 (6)
O( <i>p</i> 1)—Cu( <i>m</i> )—O( <i>q</i> 1)	67.4 (5)	67.8 (4)	73.9 (5)	64.6 (5)
O( <i>p</i> 1)—Cu( <i>m</i> )—N( <i>m</i> )	111.9 (6)	111.7 (6)	130.5 (6)	111.9 (6)
O( <i>p</i> 1)—Cu( <i>m</i> )—O( <i>n</i> 3)	142.7 (5)	146.6 (5)		139.9 (5)
O( <i>n</i> 3)—Cu( <i>m</i> )—O( <i>m</i> 1)	84.6 (6)	87.8 (6)		85.9 (6)
O( <i>n</i> 3)—Cu( <i>m</i> )—O( <i>m</i> 2)	104.4 (7)	101.2 (6)		93.8 (7)
O( <i>n</i> 3)—Cu( <i>m</i> )—O( <i>q</i> 1)	84.8 (6)	84.9 (5)		85.4 (7)
O( <i>n</i> 3)—Cu( <i>m</i> )—N( <i>m</i> )	94.3 (7)	92.8 (6)		96.6 (7)
Cu( <i>m</i> )—O( <i>m</i> 1)—Cu( <i>n</i> )	111.1 (7)	105.2 (6)	119.1 (8)	111.8 (7)
Cu( <i>m</i> )—O( <i>m</i> 1)—Cu( <i>p</i> )	109.2 (6)	105.6 (5)	98.1 (6)	111.9 (6)
Cu( <i>n</i> )—O( <i>m</i> 1)—Cu( <i>p</i> )	86.4 (4)	82.5 (5)	81.2 (6)	82.7 (4)
Cu( <i>m</i> )—O( <i>m</i> 1)—C( <i>m</i> 1)	110 (1)	111 (1)	115 (1)	111 (1)
Cu( <i>n</i> )—O( <i>m</i> 1)—C( <i>m</i> 1)	121 (1)	122 (1)	118 (1)	120 (1)
Cu( <i>p</i> )—O( <i>m</i> 1)—C( <i>m</i> 1)	118 (1)	126 (1)	119 (1)	116 (1)
O( <i>m</i> 1)—C( <i>m</i> 1)—C( <i>m</i> 2)	109 (2)	105 (2)	108 (2)	107 (2)
C( <i>m</i> 1)—C( <i>m</i> 2)—N( <i>m</i> )	110 (2)	106 (2)	108 (2)	113 (2)
C( <i>m</i> 2)—N( <i>m</i> )—Cu( <i>m</i> )	103 (1)	105 (1)	105 (1)	102 (1)
C( <i>m</i> 2)—N( <i>m</i> )—C( <i>m</i> 3)	114 (2)	108 (2)	114 (2)	106 (2)
C( <i>m</i> 2)—N( <i>m</i> )—C( <i>m</i> 5)	109 (2)	108 (2)	111 (2)	113 (2)
C( <i>m</i> 3)—N( <i>m</i> )—Cu( <i>m</i> )	111 (1)	109 (1)	110 (2)	113 (2)
C( <i>m</i> 3)—N( <i>m</i> )—C( <i>m</i> 5)	109 (2)	111 (2)	107 (2)	112 (2)
C( <i>m</i> 5)—N( <i>m</i> )—Cu( <i>m</i> )	110 (1)	115 (1)	110 (1)	111 (1)
C( <i>m</i> 4)—C( <i>m</i> 3)—N( <i>m</i> )	112 (2)	117 (2)	116 (2)	113 (3)
C( <i>m</i> 6)—C( <i>m</i> 5)—N( <i>m</i> )	115 (2)	112 (2)	117 (2)	113 (2)
Cu( <i>m</i> )—O( <i>m</i> 2)—C( <i>m</i> 7)	123 (2)	127 (2)	130 (3)	119 (2)
Cu( <i>q</i> )—O( <i>m</i> 3)—C( <i>m</i> 7)	124 (2)	123 (2)	122 (1)	
O( <i>m</i> 2)—C( <i>m</i> 7)—O( <i>m</i> 3)	132 (2)	129 (3)	130 (2)	130 (3)
O( <i>m</i> 2)—C( <i>m</i> 7)—C( <i>m</i> 8)	111 (2)	110 (2)	115 (2)	106 (2)
O( <i>m</i> 3)—C( <i>m</i> 7)—C( <i>m</i> 8)	116 (2)	121 (2)	114 (2)	124 (2)
C( <i>m</i> 7)—C( <i>m</i> 8)—Cl( <i>m</i> 1)	118 (2)	111 (2)	109 (2)	115 (2)
C( <i>m</i> 7)—C( <i>m</i> 8)—Cl( <i>m</i> 2)	101 (2)	110 (2)	114 (2)	108 (2)
C( <i>m</i> 7)—C( <i>m</i> 8)—Cl( <i>m</i> 3)	112 (2)	110 (2)	109 (2)	109 (2)
Cl( <i>m</i> 1)—C( <i>m</i> 8)—Cl( <i>m</i> 2)	109 (2)	108 (2)	108 (1)	110 (2)
Cl( <i>m</i> 1)—C( <i>m</i> 8)—Cl( <i>m</i> 3)	114 (2)	109 (1)	109 (2)	106 (2)
Cl( <i>m</i> 2)—C( <i>m</i> 8)—Cl( <i>m</i> 3)	100 (2)	109 (2)	108 (1)	108 (1)

Table 5. *Intermolecular contacts <3.9 Å with e.s.d.'s in parentheses*

Cl(11)⋯Cl(23 <sup>i</sup> )	3.46 (2)	C(24)⋯Cl(32 <sup>iv</sup> )	3.88 (3)
Cl(21)⋯Cl(32 <sup>i</sup> )	3.35 (1)	C(13)⋯Cl(12 <sup>v</sup> )	3.82 (4)
Cl(31)⋯Cl(42 <sup>ii</sup> )	3.36 (1)	C(31)⋯Cl(12 <sup>v</sup> )	3.67 (3)
C(33)⋯Cl(42 <sup>ii</sup> )	3.70 (2)	C(44)⋯Cl(21 <sup>vi</sup> )	3.84 (3)
C(34)⋯Cl(43 <sup>iii</sup> )	3.88 (3)	Cl(31)⋯Cl(31 <sup>vii</sup> )	3.89 (3)
C(12)⋯O(43 <sup>iii</sup> )	3.61 (3)	Cl(22)⋯Cl(43 <sup>viii</sup> )	3.84 (2)
C(14)⋯O(43 <sup>ii</sup> )	3.77 (4)	Cl(43)⋯Cl(13 <sup>ix</sup> )	3.57 (2)
C(14)⋯C(36 <sup>ii</sup> )	3.80 (4)	Cl(33)⋯Cl(41 <sup>ix</sup> )	3.73 (1)
C(24)⋯C(34 <sup>iii</sup> )	3.53 (5)	Cl(33)⋯Cl(42 <sup>ix</sup> )	3.84 (2)

### Symmetry code

(i)	$-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$	(vi)	$-x + 1, -y, -z$
(ii)	$x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$	(vii)	$-x, -y + 1, -z$
(iii)	$x + 1, y, z$	(viii)	$x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$
(iv)	$-x + 1, -y + 1, -z$	(ix)	$-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$
(v)	$-x, -y, -z$		

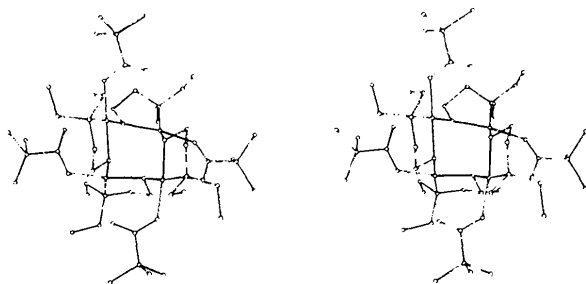


Fig. 1. Stereoview of the tetrameric unit  $[\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{Cl}_3\text{CCOO})_4]_1$ .

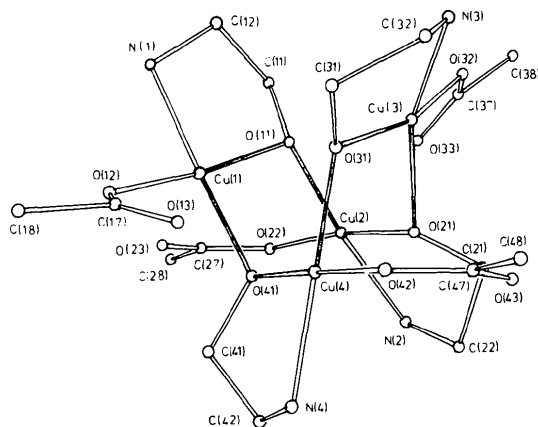


Fig. 2. View of the tetrameric array and atom-numbering scheme. The ethyl groups of the 2-diethylaminoethanolato ligands and the chlorine atoms of the trichloroacetate groups have been omitted for clarity.

Table 6. Cu—Cu distances (Å) with *e.s.d.*'s in parentheses

Cu(1)···Cu(2)	3.238 (4)	Cu(2)···Cu(3)	3.094 (4)
Cu(1)···Cu(3)	3.672 (4)	Cu(2)···Cu(4)	3.996 (4)
Cu(1)···Cu(4)	3.224 (4)	Cu(3)···Cu(4)	3.372 (4)

plane ethanolato O atoms and the Cu atoms, as do the angles  $\text{O}(p1)\text{—Cu}(m)\text{—}X$  [ $X = \text{O}(m1), \text{O}(q1), \text{O}(m2), \text{N}(m)$ ], which range from  $64.6$  to  $111.9^\circ$ . The fifth coordination site around Cu(3) is occupied by the ethanolato O(11) with  $\text{Cu}(3)\text{—O}(11) = 2.52(1)$  Å; filling of the sixth site is prevented by an ethyl group of the 2-diethylaminoethanolato ligand, the terminal ethyl C(36) lying  $3.20(3)$  Å from Cu(3). A similar non-bonded Cu—C distance was reported for bis(*N,N*-diethyl- $\alpha$ -alaninato)copper(II) (Nash & Schaefer, 1969).

The bond lengths and angles of the 2-diethylaminoethanolato ligands are as expected. Three of the four trichloroacetate groups are bidentate, forming triatomic bridges from a basal coordination site of one Cu atom

Table 7. Least-squares planes and deviations (Å) of some atoms of interest from the planes

(a) Plane defined by O(41), O(11), O(12), N(1)  
 $(-10.824x + 1.475y + 17.269z = -3.429)$

O(41)	-0.08	Cu(1)	-0.07
O(11)	0.08	O(23)	-2.62
O(12)	0.08	O(31)	2.47
N(1)	-0.08		

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.02 Å

(b) Plane defined by O(11), O(21), O(22), N(2)  
 $(-4.852x + 17.644y - 3.115z = 3.139)$

O(11)	0.09	Cu(2)	0.06
O(21)	-0.09	O(33)	2.48
O(22)	-0.08	O(41)	-2.49
N(2)	0.09		

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.02 Å

(c) Plane defined by O(21), O(31), O(32), N(3)  
 $(1.795x + 5.414y + 17.604z = 2.840)$

O(21)	0.31	Cu(3)	-0.11
O(31)	-0.33	O(11)	-2.32
O(32)	-0.30	C(36)	2.63
N(3)	0.33		

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.03 Å

(d) Plane defined by O(31), O(41), O(42), N(4)  
 $(5.967x + 17.208y + 2.087z = 4.533)$

O(31)	0.02	Cu(4)	-0.02
O(41)	-0.02	O(13)	-2.48
O(42)	-0.02	O(21)	2.50
N(4)	0.02		

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.02 Å

(e) Plane defined by O(12), O(13), C(17), C(18)  
 $(14.283x - 4.021y - 2.764z = 3.216)$

O(12)	0.02	C(18)	0.01
O(13)	0.02	Cu(1)	-0.17
C(17)	-0.05	Cu(4)	0.80

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.03 Å

(f) Plane defined by O(22), O(23), C(27), C(28)  
 $(12.446x - 5.732y + 3.752z = 2.869)$

O(22)	0.01	C(28)	0.01
O(23)	0.01	Cu(2)	-0.07
C(27)	-0.03	Cu(1)	-0.92

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.03 Å

(g) Plane defined by O(32), O(33), C(37), C(38)  
 $(8.481x + 4.230y + 11.806z = 3.343)$

O(32)	0.00	C(38)	0.00
O(33)	0.00	Cu(3)	0.25
C(37)	-0.01	Cu(2)	0.47

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.03 Å

(h) Plane defined by O(42), O(43), C(47), C(48)  
 $(12.292x - 6.725y + 3.482z = 3.753)$

O(42)	0.00	C(48)	0.00
O(43)	0.01	Cu(4)	-0.14
C(47)	-0.02	Cu(3)	-2.80

The *e.s.d.*'s ( $\sigma$ ) of the above deviations are 0.01–0.03 Å

to an apical site of another; the fourth group is monodentate. The CuOC(C)OCu groupings are not planar; rather the metal atoms are displaced 0.07–0.92 Å from

the planes defined by the carboxylate C and O atoms (Table 7). The Cl atoms display a high degree of anisotropic thermal motion, particularly marked for the Cl atoms attached to C(18). A similar situation has been observed in other structures containing trihalomethyl groups (Cotton & Winquist, 1969; Beltrán, Capilla & Aranda, 1978; Moreland & Doedens, 1978; Kalyanaraman, Kispert & Atwood, 1978).

A cubane-type structure very similar to that of the present complex has been found in the related complexes  $\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{Cl}_2\text{CHCOO})_4$  (Smolander, Turpeinen & Ahlgrén, 1978) and  $\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{ClCH}_2\text{COO})_4$  (Turpeinen, Hämäläinen, Ahlgrén & Smolander, 1979). The symmetry of the clusters decreases from  $S_4$  (via pseudo  $C_2$ ) to  $C_1$  on going from the chloroacetate complex to the dichloroacetate and trichloroacetate complexes, apparently owing to less favourable packing effects. The difference between the longest and shortest intramolecular Cu—Cu distances increases with increasing number of chloro substituents, being 0.546 Å in  $\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{ClCH}_2\text{COO})_4$ , 0.848 Å in  $\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{Cl}_2\text{CHCOO})_4$  and 0.902 Å in  $\text{Cu}_4(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})_4(\text{Cl}_3\text{CCOO})_4$ . The in-plane copper—ligand distances of these complexes are comparable but the out-of-plane copper—ligand distances are noticeably different. In the chloroacetate complex each Cu atom has a distorted octahedral environment, the out-of-plane Cu—O distances being nearly equal [Cu—O(carboxylate) = 2.663 (10) and Cu—O(ethanolato) = 2.720 (6) Å]. In the dichloroacetate complex one out-of-plane Cu—O distance around each Cu atom is elongated to 2.90–3.26 Å, while the other is unchanged with respect to the chloroacetate complex. In the present trichloroacetate complex, on the other hand, around three of the Cu atoms the out-of-plane Cu—O(ethanolato) distance is elongated to 2.84–3.01 Å and the out-of-plane Cu—O(carboxylate) distance is shortened to 2.44–2.60 Å; around the fourth Cu atom the out-of-plane Cu—O(ethanolato) distance is shortened to 2.52 Å, while the formation of the out-of-plane Cu—O(carboxylate) bond is prevented by an ethyl group of the 2-diethylaminoethanolato ligand.

Several halogeno- and pseudohalogeno(2-dialkylaminoethanolato)copper(II) complexes (Mergehenn & Haase, 1977) have a  $\text{Cu}_4\text{O}_4$  core like the present complex and have been classified on the basis of the distortion from the idealized cube (Merz & Haase, 1978). There are two extreme types, distinguished by the arrangement of the Cu—Cu and Cu—O distances. In type (I) there are two short ( $\sim 2.92$  Å) and four long ( $\sim 3.44$  Å) and in type (II) four short ( $\sim 3.18$  Å) and two long ( $\sim 3.45$  Å) intramolecular Cu—Cu separations. The present complex and the two other

haloacetate complexes we have studied contain two long and four short Cu—Cu distances as in type (II), but because the Cu—Cu distances range from 3.09 to 4.02 Å they stand as new examples of the variability of the  $\text{Cu}_4\text{O}_4$  core. Furthermore, the coordination around the Cu atoms is distorted octahedral or square-pyramidal in the haloacetate complexes, but distorted square-pyramidal or trigonal bipyramidal in the halogeno- and pseudohalogeno(2-dialkylaminoethanolato)copper(II) tetramer complexes.

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