

also seems to be applicable in interpreting the distortions of the coordination polyhedron. As the increasing hardness of the base can be interpreted in terms of increasing ionic character of the bond between the base itself and the hard acid  $\text{Re}^V$ , it may be expected that the harder atom ligands gain steric hindrance (increase their van der Waals radius) as a consequence of the higher population of their orbitals, in keeping with the observed deviations from the ideal octahedral geometry.

The authors thank Professor L. Magon, University of Ferrara, Italy, for helpful discussions and Mr G. Bertocchi for technical assistance. This work has been financially supported by the CNR (Rome).

### References

- BOMBIERI, G., MAZZI, U., GILLI, G. & HERNÁNDEZ-CANO, F. (1978). *J. Organomet. Chem.* **159**, 53–62.  
 BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 COTTON, F. A. & LIPPARD, S. J. (1965). *Inorg. Chem.* **4**, 1621–1629.  
 COTTON, F. A. & LIPPARD, S. J. (1966). *Inorg. Chem.* **5**, 416–423.

- DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*. Ithaca and London: Cornell Univ. Press.  
 GIGLIO, E. (1969). *Nature (London)*, **222**, 339–341.  
 GILLI, G., SACERDOTI, M., BERTOLASI, V. & ROSSI, R. (1982). *Acta Cryst.* **B38**, 100–104.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HURSTHOUSE, M. B., JAYAWERA, S. A. A. & QUICK, A. (1979). *J. Chem. Soc. Dalton Trans.* pp. 279–282.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.  
 KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York and London: Academic Press.  
 LOCK, C. J. L. & CHENG WAN (1975). *Can. J. Chem.* **53**, 1548–1553.  
 MAZZI, U., RONCARI, E., ROSSI, R., BERTOLASI, V., TRAVERSO, O. & MAGON, L. (1980). *Transition Met. Chem.* **5**, 289–293.  
 MAZZI, U., RONCARI, E., ROSSI, R., DUATTI, A. & MAGON, L. (1981). *Transition Met. Chem.* **6**, 169–173.  
 PEARSON, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3533–3539.  
 PEARSON, R. G. & SONGSTAD, J. (1967). *J. Am. Chem. Soc.* **89**, 1827–1836.  
 SHELDRIK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1982). **B38**, 429–433

## The Structure of (2-Dimethylaminoethanolato)(trifluoroacetato)copper(II) Tetramer

BY MARKKU AHLGRÉN, URHO TURPEINEN AND REIJO HÄMÄLÄINEN

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

(Received 24 March 1981; accepted 6 July 1981)

### Abstract

$[\text{Cu}_4(\text{C}_2\text{F}_3\text{O}_2)_4(\text{C}_4\text{H}_{10}\text{NO})_4]$ ,  $\text{C}_{24}\text{H}_{40}\text{Cu}_4\text{F}_{12}\text{N}_4\text{O}_{12}$ ,  $M_r = 1058.8$ , monoclinic,  $P2_1/c$ ,  $a = 14.073$  (3),  $b = 21.379$  (5),  $c = 14.201$  (3) Å,  $\beta = 104.65$  (2)°,  $Z = 4$ ,  $D_m = 1.70$ ,  $D_c = 1.701$  Mg m $^{-3}$ ,  $\mu$  (Mo  $K\alpha$ ) = 2.22 mm $^{-1}$ . Final  $R = 0.087$  for 3584 reflections. The Cu and bridging ethanolato O atoms form a cubane-type  $\text{Cu}_4\text{O}_4$  core in which the short Cu–O(ethanolato) bonds form an eight-membered ring folded in a boat-like conformation. The Cu–Cu distances range from 3.154 (2) to 3.813 (2) Å. Each Cu<sup>II</sup> atom has a distorted octahedral environment; two ethanolato O atoms, a carboxyl O atom and an amino N atom form the equatorial coordination plane with Cu–O bonds of 1.914 (9)–1.968 (9) Å and a Cu–N bond of

2.052 (12)–2.062 (13) Å. The axial sites are occupied by a carboxyl O atom and an ethanolato O atom with Cu–O distances of 2.663 (11)–2.847 (11) Å. The trifluoroacetate groups are bidentate, bridging in a *syn-syn* configuration from an equatorial coordination site of one Cu atom to an axial site of another.

### Introduction

As part of our studies on the effects of halogeno substitution of the carboxylate ligand on structures of transition-metal complexes we have prepared several copper(II) carboxylate complexes with 2-dialkylaminoethanols. Copper(II) acetate forms with 2-diethylaminoethanol a novel centrosymmetric hexa-

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) with *e.s.d.*'s in parentheses, the equivalent isotropic temperature factors (Hamilton, 1959) for Cu, O and N atoms and isotropic ones for F and C atoms

	x	y	z	B ( $\text{\AA}^2$ )
Cu(1)	514 (1)	752 (1)	2341 (1)	3.6 (1)
Cu(2)	1942 (1)	-239 (1)	3611 (1)	4.1 (1)
Cu(3)	2978 (1)	1087 (1)	4131 (1)	3.8 (1)
Cu(4)	2640 (1)	860 (1)	1876 (1)	4.1 (1)
O(11)	1174 (6)	499 (4)	3652 (6)	3.4 (5)
O(12)	-186 (7)	1140 (5)	1102 (6)	5.2 (6)
O(13)	1090 (10)	1595 (5)	726 (8)	7.4 (8)
O(21)	3074 (6)	258 (4)	3618 (6)	3.4 (5)
O(22)	849 (7)	-823 (5)	3471 (8)	6.3 (6)
O(23)	-241 (7)	-396 (5)	2208 (7)	5.6 (6)
O(31)	2328 (6)	1387 (4)	2859 (6)	3.8 (5)
O(32)	3487 (8)	850 (5)	5479 (6)	5.6 (6)
O(33)	2551 (9)	50 (6)	5632 (8)	6.9 (7)
O(41)	1513 (6)	351 (4)	1854 (6)	3.9 (5)
O(42)	3882 (8)	1276 (6)	1895 (7)	6.6 (7)
O(43)	4611 (8)	1271 (5)	3487 (9)	7.0 (7)
N(1)	-557 (9)	1119 (6)	2937 (8)	4.8 (7)
N(2)	2886 (9)	-991 (6)	3772 (10)	5.7 (8)
N(3)	2972 (10)	2008 (6)	4541 (8)	5.2 (7)
N(4)	2803 (10)	351 (6)	696 (8)	4.9 (7)
F(11)	-457 (19)	2455 (10)	37 (17)	10.7 (6)
F(12)	-1490 (14)	1716 (10)	-228 (15)	9.1 (5)
F(13)	-353 (16)	1772 (10)	-999 (14)	9.8 (5)
F(111)	-1176 (25)	2254 (16)	224 (22)	10.1 (8)
F(121)	-1017 (19)	1574 (11)	-837 (17)	5.7 (5)
F(131)	5 (21)	2311 (14)	-449 (22)	8.6 (8)
F(21)	-1346 (9)	-1391 (6)	2123 (9)	11.7 (4)
F(22)	-989 (10)	-1313 (6)	3556 (10)	12.8 (4)
F(23)	-147 (9)	-1875 (6)	2920 (9)	12.1 (4)
F(31)	2949 (15)	592 (11)	7476 (14)	9.4 (6)
F(32)	4337 (12)	811 (9)	7327 (10)	6.3 (4)
F(33)	3903 (16)	-147 (11)	7332 (14)	10.4 (6)
F(311)	3041 (16)	155 (12)	7566 (15)	4.8 (5)
F(321)	3605 (23)	1096 (14)	7378 (19)	9.0 (7)
F(331)	4429 (20)	255 (16)	7320 (19)	8.0 (7)
F(41)	6301 (12)	1617 (9)	3024 (12)	6.6 (4)
F(42)	5179 (12)	2352 (8)	2282 (13)	7.8 (4)
F(43)	5581 (14)	1490 (10)	1485 (14)	8.8 (5)
F(411)	6069 (38)	1279 (25)	2318 (43)	19.2 (17)
F(421)	5928 (23)	2050 (15)	3235 (21)	9.9 (8)
F(431)	5413 (16)	1974 (12)	1696 (16)	5.3 (5)
C(11)	533 (12)	538 (7)	4263 (11)	4.6 (4)
C(12)	-85 (15)	1118 (11)	4055 (15)	2.9 (5)
C(121)	-386 (32)	654 (21)	3924 (31)	6.0 (10)
C(13)	-1528 (14)	776 (9)	2514 (13)	7.4 (5)
C(14)	-790 (13)	1788 (9)	2756 (13)	7.1 (5)
C(15)	240 (14)	1511 (9)	656 (13)	5.2 (4)
C(16)	-581 (14)	1883 (9)	-118 (14)	8.1 (5)
C(21)	3965 (12)	-89 (8)	3932 (11)	5.3 (4)
C(22)	3796 (16)	-753 (11)	3560 (17)	4.1 (5)
C(221)	3865 (30)	-636 (20)	4312 (32)	6.2 (11)
C(23)	2860 (13)	-1340 (9)	4714 (13)	7.2 (5)
C(24)	2577 (13)	-1484 (9)	2983 (13)	7.6 (5)
C(25)	76 (13)	-787 (8)	2808 (12)	4.9 (4)
C(26)	-595 (15)	-1359 (10)	2851 (15)	9.5 (6)
C(31)	2315 (12)	2049 (8)	2767 (11)	5.6 (4)
C(32)	2286 (21)	2323 (13)	3732 (19)	5.4 (7)
C(321)	2956 (30)	2363 (18)	3524 (27)	4.9 (10)
C(33)	3967 (14)	2247 (9)	4957 (13)	7.1 (5)
C(34)	2439 (18)	2104 (11)	5323 (18)	11.6 (7)
C(35)	3134 (13)	450 (9)	5908 (12)	4.6 (4)
C(36)	3607 (13)	466 (9)	7105 (13)	7.3 (5)
C(41)	1205 (12)	16 (8)	935 (12)	5.5 (4)

Table 1 (cont.)

	x	y	z	B ( $\text{\AA}^2$ )
C(42)	2046 (16)	-173 (10)	567 (15)	9.4 (6)
C(43)	2640 (13)	783 (9)	-164 (14)	7.7 (5)
C(44)	3768 (16)	35 (10)	815 (15)	9.0 (6)
C(45)	4550 (14)	1364 (8)	2629 (15)	5.4 (4)
C(46)	5465 (15)	1797 (10)	2416 (15)	9.1 (6)

Population parameters: 0.6 for F(*ij*) (*i* = 1, 3, 4; *j* = 1, 2, 3) and for C(*i2*) (*i* = 1, 2, 3); 0.4 for F(*ij1*) (*i* = 1, 3, 4; *j* = 1, 2, 3) and C(*i21*) (*i* = 1, 2, 3).

nuclear structure in which the  $\text{Cu}^{\text{II}}$  atoms are linked by triply bridging  $\text{OH}^-$  ions and ethanolato O atoms, and by water, carboxylate and ethanolato O bridges (Ahlgrén, Turpeinen & Smolander, 1980). In all the other complexes we studied there is a tetranuclear cubane-like structure (Ahlgrén, Hämäläinen, Turpeinen & Smolander, 1979; Turpeinen, Hämäläinen & Ahlgrén, 1980, 1981) where overall ferromagnetic spin coupling is to be expected (Mergenhenn, Merz & Haase, 1980).

Blue crystals of the title compound were obtained by slow evaporation of an ethanol solution containing copper(II) trifluoroacetate and 2-dimethylamino-ethanol in molar ratio 1:1. The density was measured by flotation in a mixture of carbon tetrachloride and methyl iodide. The space group was determined from Weissenberg photographs as  $P2_1/c$ . The crystal used for data collection was  $0.30 \times 0.30 \times 0.45$  mm. Cell dimensions were determined by the least-squares method from 25 reflections measured on a Syntex  $P2_1$  diffractometer. Intensities were collected ( $5 < 2\theta < 50^\circ$ ) at room temperature with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The  $\omega$ -scan technique was employed with a variable scan rate from  $2.55$  to  $29.3^\circ \text{ min}^{-1}$  and a scan range of  $1.0^\circ$ . Background measurements were taken at both ends of the scan with  $\omega$  displaced by  $1.0^\circ$  from the  $K\alpha$  peak. The intensities of two standard reflections, recorded after every 98 measurements, remained essentially constant. The intensities were corrected for Lorentz and polarization effects. Of the 7589 reflections collected, 3584 had  $F_o > 4\sigma(F_o)$  and were used in subsequent calculations.

The structure was solved by a combination of direct and Fourier methods and refined by full-matrix least-squares techniques. The function minimized was  $\sum w (|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(F_o)$ . Scattering factors for neutral atoms were taken from Cromer & Mann (1968). Anomalous-dispersion corrections were included for Cu (Cromer & Liberman, 1970). Isotropic refinement of a model led to an  $R$  value of 0.144 ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ). Refinement with anisotropic temperature factors for non-hydrogen atoms gave  $R = 0.084$ . The thermal parameters of the F atoms of three carboxylate groups and one C atom of

Table 2. 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> )	2.062 (13)	2.061 (12)	2.052 (12)	2.058 (13)
Cu( <i>m</i> )-O( <i>m</i> 1)	1.936 (8)	1.914 (9)	1.917 (8)	1.917 (9)
Cu( <i>m</i> )-O( <i>m</i> 2)	1.968 (9)	1.950 (11)	1.934 (9)	1.955 (12)
Cu( <i>m</i> )-O( <i>q</i> 1)	1.919 (10)	1.921 (9)	1.936 (9)	1.929 (9)
Cu( <i>m</i> )-O( <i>p</i> 1)	2.819 (9)	2.724 (8)	2.760 (8)	2.717 (8)
Cu( <i>m</i> )-O( <i>n</i> 3)	2.663 (11)	2.847 (11)	2.708 (12)	2.845 (12)
Cu( <i>m</i> )-Cu( <i>p</i> )	3.813 (2)	3.713 (3)		
Cu( <i>m</i> )-Cu( <i>n</i> )	3.155 (2)	3.189 (3)	3.154 (2)	3.231 (3)
O( <i>m</i> 1)-C( <i>m</i> 1)	1.40 (2)	1.43 (2)	1.42 (2)	1.45 (2)
C( <i>m</i> 1)-C( <i>m</i> 2)	1.50 (3)	1.51 (3)	1.50 (3)	1.47 (3)
C( <i>m</i> 1)-C( <i>m</i> 21)	1.28 (4)	1.31 (5)	1.39 (4)	
N( <i>m</i> )-C( <i>m</i> 2)	1.56 (2)	1.48 (3)	1.46 (3)	1.52 (3)
N( <i>m</i> )-C( <i>m</i> 21)	1.69 (5)	1.59 (4)	1.63 (4)	
N( <i>m</i> )-C( <i>m</i> 3)	1.53 (2)	1.54 (2)	1.47 (2)	1.50 (2)
N( <i>m</i> )-C( <i>m</i> 4)	1.47 (2)	1.52 (2)	1.50 (3)	1.49 (3)
C( <i>m</i> 5)-O( <i>m</i> 2)	1.26 (2)	1.25 (2)	1.23 (2)	1.23 (2)
C( <i>m</i> 5)-O( <i>m</i> 3)	1.19 (2)	1.20 (2)	1.18 (2)	1.22 (2)
C( <i>m</i> 5)-C( <i>m</i> 6)	1.59 (2)	1.56 (3)	1.66 (2)	1.68 (3)
C( <i>m</i> 6)-F( <i>m</i> 1)	1.25 (3)	1.28 (2)	1.21 (3)	1.33 (2)
C( <i>m</i> 6)-F( <i>m</i> 2)	1.30 (3)	1.26 (3)	1.24 (2)	1.25 (3)
C( <i>m</i> 6)-F( <i>m</i> 3)	1.39 (3)	1.26 (3)	1.39 (3)	1.52 (3)
C( <i>m</i> 6)-F( <i>m</i> 11)	1.33 (4)		1.33 (3)	1.42 (6)
C( <i>m</i> 6)-F( <i>m</i> 21)	1.24 (3)		1.40 (4)	1.30 (3)
C( <i>m</i> 6)-F( <i>m</i> 31)	1.39 (4)		1.21 (3)	1.08 (3)

three aminoethanolato chelate rings showed disorder. These atoms were omitted, and after one cycle of refinement a difference synthesis was computed. Two positions were assigned to each of the omitted atoms with site occupancies 0.6 and 0.4. The concluding refinement with anisotropic thermal parameters for Cu, O and N atoms and with isotropic thermal parameters for C and F atoms reduced *R* to 0.087.\* The largest parameter shift in the last cycle of refinement was 0.9σ and the average shift/error ratio was 0.05. A difference map was then computed but attempts to locate H atoms failed. The largest residual peak, with a height of 1.1 e Å<sup>-3</sup>, was very near to the F(22) atom.

The calculations were performed on a Univac 1108 computer with programs MULTAN 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and XRAY 76 (Stewart, 1976). Final atomic positional parameters with isotropic temperature factors are given in Table 1, and bond distances and angles in Tables 2 and 3 respectively.

### Discussion

The structure is composed of cubane-like tetramers packing with van der Waals separations (Fig. 1). The

\* Lists of structure factors, thermal parameters, intermolecular contacts <3.4 Å and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36218 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. 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)	96.5 (4)	95.4 (4)	95.1 (4)	95.2 (4)
O( <i>m</i> 2)-Cu( <i>m</i> )-N( <i>m</i> )	87.4 (4)	89.0 (5)	89.9 (4)	88.2 (5)
O( <i>m</i> 1)-Cu( <i>m</i> )-N( <i>m</i> )	86.2 (4)	85.4 (4)	84.9 (4)	87.1 (5)
O( <i>m</i> 1)-Cu( <i>m</i> )-O( <i>q</i> 1)	90.2 (4)	91.0 (4)	90.8 (4)	90.3 (4)
O( <i>m</i> 1)-Cu( <i>m</i> )-O( <i>m</i> 2)	170.8 (4)	171.7 (4)	171.6 (5)	172.5 (4)
O( <i>q</i> 1)-Cu( <i>m</i> )-N( <i>m</i> )	175.2 (4)	171.4 (4)	172.3 (5)	172.0 (4)
O( <i>p</i> 1)-Cu( <i>m</i> )-O( <i>m</i> 1)	72.6 (3)	74.8 (3)	74.3 (3)	75.0 (3)
O( <i>p</i> 1)-Cu( <i>m</i> )-O( <i>m</i> 2)	104.3 (4)	102.5 (4)	102.2 (4)	102.0 (3)
O( <i>p</i> 1)-Cu( <i>m</i> )-O( <i>q</i> 1)	67.2 (3)	69.6 (3)	68.7 (3)	70.0 (3)
O( <i>p</i> 1)-Cu( <i>m</i> )-N( <i>m</i> )	114.7 (4)	116.7 (5)	116.0 (4)	116.4 (4)
O( <i>p</i> 1)-Cu( <i>m</i> )-O( <i>n</i> 3)	141.4 (3)	139.7 (3)	142.1 (3)	138.4 (3)
O( <i>n</i> 3)-Cu( <i>m</i> )-O( <i>m</i> 1)	84.0 (3)	80.6 (4)	82.9 (4)	78.1 (4)
O( <i>n</i> 3)-Cu( <i>m</i> )-O( <i>m</i> 2)	102.9 (4)	105.7 (4)	103.8 (4)	108.0 (4)
O( <i>n</i> 3)-Cu( <i>m</i> )-O( <i>q</i> 1)	83.0 (4)	79.6 (3)	81.9 (4)	79.1 (3)
O( <i>n</i> 3)-Cu( <i>m</i> )-N( <i>m</i> )	93.4 (4)	92.1 (5)	91.2 (5)	93.0 (4)
Cu( <i>m</i> )-O( <i>m</i> 1)-Cu( <i>n</i> )	109.7 (4)	111.9 (5)	110.2 (4)	114.7 (4)
Cu( <i>m</i> )-O( <i>m</i> 1)-Cu( <i>p</i> )	107.3 (4)	105.3 (3)	105.7 (4)	104.9 (3)
Cu( <i>m</i> )-O( <i>m</i> 1)-Cu( <i>n</i> )	83.9 (3)	83.5 (3)	83.5 (3)	83.7 (3)
Cu( <i>m</i> )-O( <i>m</i> 1)-C( <i>m</i> 1)	110.6 (7)	112.2 (8)	114.3 (8)	110.6 (9)
Cu( <i>m</i> )-O( <i>m</i> 1)-C( <i>m</i> 1)	121.4 (8)	119.8 (8)	121.0 (9)	117.6 (8)
Cu( <i>p</i> )-O( <i>m</i> 1)-C( <i>m</i> 1)	121.0 (7)	120.6 (8)	117.7 (8)	122.7 (8)
O( <i>m</i> 1)-C( <i>m</i> 1)-C( <i>m</i> 2)	111 (1)	109 (1)	108 (2)	112 (1)
O( <i>m</i> 1)-C( <i>m</i> 1)-C( <i>m</i> 21)	121 (2)	115 (2)	115 (2)	
C( <i>m</i> 1)-C( <i>m</i> 2)-N( <i>m</i> )	106 (2)	109 (2)	112 (2)	111 (2)
C( <i>m</i> 1)-C( <i>m</i> 21)-N( <i>m</i> )	110 (3)	113 (3)	109 (3)	
Cu( <i>m</i> )-N( <i>m</i> )-C( <i>m</i> 2)	105 (1)	106 (1)	106 (1)	106 (1)
Cu( <i>m</i> )-N( <i>m</i> )-C( <i>m</i> 21)	99 (2)	98 (2)	101 (2)	
Cu( <i>m</i> )-N( <i>m</i> )-C( <i>m</i> 3)	109 (1)	109 (1)	112 (1)	108 (1)
Cu( <i>m</i> )-N( <i>m</i> )-C( <i>m</i> 4)	117 (1)	114 (1)	112 (1)	116 (1)
C( <i>m</i> 2)-N( <i>m</i> )-C( <i>m</i> 3)	120 (1)	124 (1)	122 (2)	113 (1)
C( <i>m</i> 2)-N( <i>m</i> )-C( <i>m</i> 4)	101 (1)	101 (2)	99 (2)	106 (1)
C( <i>m</i> 21)-N( <i>m</i> )-C( <i>m</i> 3)	88 (2)	91 (2)	90 (2)	
C( <i>m</i> 21)-N( <i>m</i> )-C( <i>m</i> 4)	134 (2)	138 (2)	134 (2)	
C( <i>m</i> 3)-N( <i>m</i> )-C( <i>m</i> 4)	105 (1)	104 (1)	105 (1)	109 (1)
Cu( <i>m</i> )-O( <i>m</i> 2)-C( <i>m</i> 5)	121 (1)	123 (1)	126 (1)	125 (1)
O( <i>m</i> 2)-C( <i>m</i> 5)-O( <i>m</i> 3)	131 (2)	133 (2)	132 (2)	132 (2)
O( <i>m</i> 2)-C( <i>m</i> 5)-C( <i>m</i> 6)	108 (2)	110 (1)	113 (1)	113 (1)
O( <i>m</i> 3)-C( <i>m</i> 5)-C( <i>m</i> 6)	121 (2)	117 (1)	115 (2)	114 (1)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 1)	109 (2)	113 (2)	107 (2)	109 (2)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 2)	118 (2)	111 (2)	111 (2)	109 (2)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 3)	104 (2)	113 (2)	104 (2)	100 (2)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 11)	117 (2)		111 (1)	95 (3)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 21)	115 (2)		106 (2)	108 (2)
C( <i>m</i> 5)-C( <i>m</i> 6)-F( <i>m</i> 31)	100 (2)		111 (2)	120 (2)
F( <i>m</i> 1)-C( <i>m</i> 6)-F( <i>m</i> 2)	112 (2)	102 (2)	116 (2)	125 (2)
F( <i>m</i> 1)-C( <i>m</i> 6)-F( <i>m</i> 3)	106 (2)	108 (2)	109 (2)	100 (2)
F( <i>m</i> 2)-C( <i>m</i> 6)-F( <i>m</i> 3)	107 (2)	108 (2)	109 (2)	112 (2)
F( <i>m</i> 11)-C( <i>m</i> 6)-F( <i>m</i> 21)	113 (2)		108 (2)	104 (3)
F( <i>m</i> 11)-C( <i>m</i> 6)-F( <i>m</i> 31)	102 (2)		110 (2)	95 (3)
F( <i>m</i> 21)-C( <i>m</i> 6)-F( <i>m</i> 31)	107 (2)		111 (2)	127 (3)

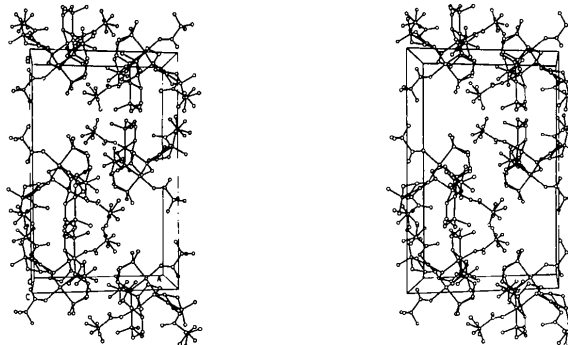


Fig. 1. A stereoview of the molecular packing.

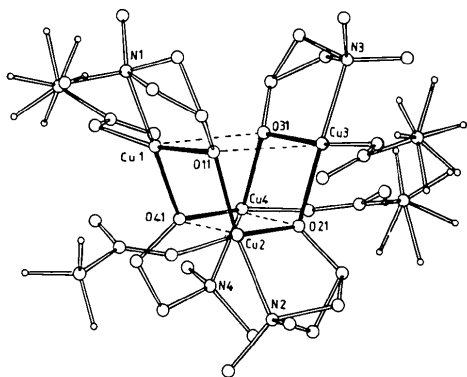


Fig. 2. A perspective drawing of the complex molecule.

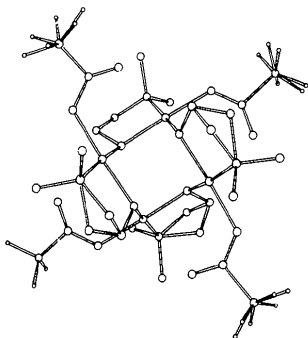


Fig. 3. A drawing of the complex molecule along the pseudo  $S_4$  axis.

shortest intermolecular distances are 2.47 (6) Å between F(33) and F(411<sup>i</sup>) ( $i = 1 - x, -y, 1 - z$ ) and 2.90 (3) Å between C(13) and F(311<sup>ii</sup>) ( $ii = -x, -y, 1 - z$ ), which indicate that the disordered sites of F and C atoms depend to some extent on each other. The other intermolecular contacts are normal (Bondi, 1964; Nahrngbauer, Lundgren & Andersen, 1979).

The structure of the molecule is shown in Figs. 2 and 3. The molecule is built up of four  $\text{Cu}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})(\text{F}_3\text{Ac})$  units which are joined together by the ethanolato O atom and carboxylate bridges. Three of the four aminoethanolato and carboxylate ligands are disordered. Within the  $\text{Cu}_4\text{O}_4$  core the long Cu—Cu distances are 3.713 (3) and 3.813 (2) Å and the four short Cu—Cu distances range from 3.154 (2) to 3.231 (3) Å.

The coordination of the  $\text{Cu}^{\text{II}}$  atoms is distorted octahedral (4 + 2). The four equatorial bonds are directed towards two ethanolato O atoms, an amino N atom and a carboxyl O atom with mean values of 1.92, 2.06 and 1.95 Å, respectively. The axial bonds are directed towards an ethanolato O atom and a carboxyl O atom with mean values of 2.76 and 2.77 Å, respectively. The major distortion of the coordination polyhedra of the Cu atoms is reflected in the angle (138.4–142.1°) between axial bonds.

The aminoethanolato O and N atoms are tetra-coordinate but the disorder of the N-bonded C atoms of three of the aminoethanolato chelate rings results in a rather bad description of these molecular fragments. Therefore, the observed N—C and C—C bond distances as well as the corresponding angles are far from normal.

The trifluoroacetate groups are bidentate, forming unsymmetrical triatomic bridges between Cu atoms which deviate 0.144 (2)–1.070 (2) Å from  $\text{C}_2\text{O}_2$  planes. The C—O bond distances range from 1.18 (2) to 1.26 (2) Å. In each carboxylate group the longer C—O bond involves the O atom coordinated in an equatorial Cu coordination site as expected, though the differences are only marginally significant. The F atoms of three of the trifluoroacetate groups are rotationally disordered, so two sets (with population parameters 0.6 and 0.4) rotated 60° to each other about the C—C axes were selected. Because of the disorder the bond distances and angles of the  $\text{CF}_3$  groups range widely and differ from more accurately determined values (Nahrngbauer, Lundgren & Andersen, 1979; Bullivant, Dove & Haley, 1980).

A cubane-type structure similar to that of the present complex has been found in the related complexes  $[\text{Cu}(\text{R}_2\text{NCH}_2\text{CH}_2\text{O})(\text{ClCH}_2\text{COO})]_4$  ( $\text{R} = \text{Me, Et; Turpeinen, Ahlgrén \& Hämäläinen, 1979; Turpeinen, Hämäläinen, Ahlgrén \& Smolander, 1979}$ ),  $[\text{Cu}(\text{R}_2\text{NCH}_2\text{CH}_2\text{O})(\text{Cl}_2\text{CHCOO})]_4$  ( $\text{R} = \text{Me, Bu, Et; Turpeinen, Hämäläinen \& Ahlgrén, 1980, 1981; Smolander, Turpeinen \& Ahlgrén, 1978}$ ) and  $[\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})(\text{Cl}_3\text{CCOO})]_4$  (Ahlgrén, Hämäläinen, Turpeinen & Smolander, 1979). The average equatorial Cu—O(carboxylate) (~1.95 Å) and Cu—O(ethanolato) (~1.94 Å) bond distances in the complexes are comparable and so show no noticeable variation with change of the substituents of the carboxylate and/or aminoethanolato ligand. On the other hand, the Cu—N distances seem to increase slightly with the size of the N substituent, being 2.06 Å in 2-dimethylaminoethanolato complexes, 2.09 Å in 2-diethylaminoethanolato complexes and 2.12 Å in the 2-dibutylaminoethanolato complex. The main differences occur in the Cu—Cu and axial Cu—O distances. In  $[\text{Cu}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})(\text{ClCH}_2\text{COO})]_4$  and  $[\text{Cu}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{O})(\text{ClCH}_2\text{COO})]_4$  which possess  $S_4$  molecular symmetry, and in the present complex in which the molecular symmetry is close to  $S_4$ , the averages of two long and four short Cu—Cu distances are 3.76 and 3.19 Å, respectively, and the axial Cu—O distances are nearly equal (~2.7 Å). In  $[\text{Cu}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})(\text{Cl}_2\text{CHCOO})]_4$ , which possesses  $C_2$  molecular symmetry, one of the long Cu—Cu distances is elongated about 0.15 Å with respect to the three above-mentioned complexes and the other shortened by the same amount. These changes are reflected in the axial Cu—O distances. In the  $\text{Cu}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2$ -

(Cl<sub>2</sub>CHCOO)<sub>2</sub> 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<sub>2</sub>(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>(Cl<sub>2</sub>CHCOO)<sub>2</sub> 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<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)(Cl<sub>2</sub>CHCOO)]<sub>4</sub> which has pseudo C<sub>2</sub> symmetry. The molecular symmetry of [Cu(Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)(Cl<sub>3</sub>CCOO)]<sub>4</sub> and [Cu(Bu<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)(Cl<sub>2</sub>CHCOO)]<sub>4</sub> is C<sub>1</sub>, 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.

#### References

AHLGRÉN, M., HÄMÄLÄINEN, R., TURPEINEN, U. & SMOLANDER, K. (1979). *Acta Cryst.* **B35**, 2870–2874.

*Acta Cryst.* (1982). **B38**, 433–436

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

BY TETSUO UECHI AND IKUHIKO UEDA

*College of General Education, Kyushu University 01, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan*

AND MASATO TAZAKI, MAKOTO TAKAGI AND KEIHEI UENO

*Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan*

(Received 20 April 1981; accepted 13 July 1981)

#### Abstract

The title compound, [Cu(C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>)], *M<sub>r</sub>* = 439.95, crystallizes in the triclinic space group *P*1 with one molecule in a unit cell of dimensions *a* = 7.608 (3), *b* = 9.064 (2), *c* = 7.000 (2) Å, *α* = 109.51 (3), *β* = 93.67 (3) and *γ* = 81.32 (3)°; *V* = 449.7 (3) Å<sup>3</sup>, *D<sub>m</sub>* = 1.619, *D<sub>x</sub>* = 1.624 Mg m<sup>-3</sup>, *μ*(Mo Kα) = 1.26 mm<sup>-1</sup>.

0567-7408/82/020433-04\$01.00

- AHLGRÉN, M., TURPEINEN, U. & SMOLANDER, K. (1980). *Acta Cryst.* **B36**, 1091–1095.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- BULLIVANT, D. P., DOVE, M. F. A. & HALEY, M. J. (1980). *J. Chem. Soc. Dalton Trans.* pp. 105–108.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MERGEHENN, R., MERZ, L. & HAASE, W. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1703–1709.
- NAHRINGBAUER, I., LUNDGREN, J.-O. & ANDERSEN, E. K. (1979). *Acta Cryst.* **B35**, 508–510.
- SMOLANDER, K., TURPEINEN, U. & AHLGRÉN, M. (1978). *Finn. Chem. Lett.* pp. 195–198.
- STEWART, J. M. (1976). The XRAY 76 System. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TURPEINEN, U., AHLGRÉN, M. & HÄMÄLÄINEN, R. (1979). *Acta Chem. Scand. Ser. A*, **33**, 593–596.
- TURPEINEN, U., HÄMÄLÄINEN, R. & AHLGRÉN, M. (1980). *Acta Cryst.* **B36**, 927–930.
- TURPEINEN, U., HÄMÄLÄINEN, R. & AHLGRÉN, M. (1981). *Cryst. Struct. Commun.* **10**, 179–186.
- TURPEINEN, U., HÄMÄLÄINEN, R., AHLGRÉN, M. & SMOLANDER, K. (1979). *Finn. Chem. Lett.* pp. 108–111.

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

© 1982 International Union of Crystallography