Uncertainty in the positions of the atoms in the trifluoromethanesulfonate counterion required the use of bond-length restraints in the refinement of the crystal structure. Ideal values were obtained from a search for ordered trifluoromethanesulfonate ions in the Cambridge Structural Database (Allen *et al.*, 1979). The average values from 131 structures with *R* values less than 0.10 are C—S 1.79, C—F 1.31 and S—O 1.42 Å.

Data collection: Enraf–Nonius CAD-4*F* diffractometer software. Data reduction: *Xtal*3.0 *ADDREF SORTRF* (Hall & Stewart, 1990). Program(s) used to solve structure: *Xtal*3.0 *FOURR*. Program(s) used to refine structure: *Xtal*3.0 *CRYLSQ*. Molecular graphics: *ORTEP* (Johnson, 1965) and *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *Xtal*3.0 *BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichlorobis(1-methylcytosine)copper(II)

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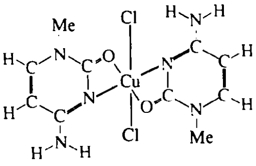
Abstract

The structure of bis[4-amino-1-methyl-2(1*H*)-pyrimidinone]dichlorocopper(II) consists of discrete $[CuCl_2(C_5H_7N_3O)_2]$ units. The coordination about the Cu^{II} ion is distorted 4 + 2 octahedral. The non-equivalent 1-methylcytosine ligands are bonded to the metal through N(3) and more weakly through O(2). The average N—Cu—Cl *trans* angle is 159.9 (1)°.

Comment

The compound bis(1-methylcytosinium) tetrachlorocuprate(II) has been described previously (Valle, Ettorre & Peruzzo, 1995). The structure of the title compound, (I), consists of discrete $[CuCl_2(C_5H_7N_3O)_2]$ units containing non-equivalent 1-methylcytosine and chloride ligands. The coordination about the Cu^{II} ion is distorted 4 + 2 octahedral. The Cu—N(3), Cu—N(3′), Cu—Cl(1) and Cu—Cl(2) bonds are normal. The difference in the length between the Cu—Cl(1) and Cu—Cl(2) bonds may be accounted for by the difference in the geometry between the Cl(1)···N(4)(x, $1 - y$, $z + \frac{1}{2}$) and Cl(2)···N(4)(x, $1 - y$, $z + \frac{1}{2}$) hydrogen bonds.



(I)

The Cu—O(2) and Cu—O(2′) contacts can be considered as weak bonds, which result in the Cu—N(3)—C(4) and Cu—N(3′)—C(4′) angles being larger than the Cu—N(3)—C(2) and Cu—N(3′)—C(2′) angles. There is an intramolecular hydrogen bond between N(4′) and O(2). Each molecule is linked to four neighbouring units by hydrogen bonds through its N(4), N(4′), O(2′), Cl(1) and Cl(2) atoms. In the related complex $[CuCl_2(C_4H_5N_3O)_2]$, (II), cytosine ligands are also co-

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† Deceased.

ordinated through their N(3) and O(2) atoms (Sundaralingam & Carrabine, 1971). However, the configuration of (II), unlike that of (I), is all *trans*, with angles N(3)—Cu—N(3′) 161.4 (5), Cl(1)—Cu—Cl(2) 165.7 (2), O(2)—Cu—O(2′) 158.9 (6). The coordination bond lengths for (II) are Cu—N 1.945 (12) and 1.966 (12) Å, Cu—Cl 2.265 (5) and 2.307 (5) Å, Cu—O 2.740 (8) and 2.876 (10) Å. The N(1) atoms in (II) are hydrogen bonded to either O(2) or to Cl atoms, the N(4) atoms to both O(2) and to Cl atoms. The N(4) atoms in (I) are hydrogen bonded to either O(2) or to Cl atoms. The difference in the configuration between (I) and (II) can be attributed to the difference in the hydrogen-bonding patterns of 1-methylcytosine and cytosine.

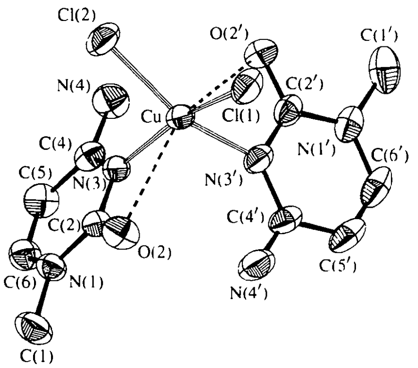

Fig. 1. *ORTEP*II (Johnson, 1976) plot of the $[CuCl_2(C_5H_7N_3O)_2]$ molecule. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals were obtained by slow evaporation of a 1:2 mixture of $CuCl_2$ and 1-methylcytosine in water.

Crystal data

$[CuCl_2(C_5H_7N_3O)_2]$
$M_r = 384.7$
Monoclinic
$C2/c$
$a = 31.328\ (2)$ Å
$b = 7.236\ (1)$ Å
$c = 13.216\ (2)$ Å
$\beta = 97.8\ (1)°$
$V = 2968.2\ (10)$ Å^3
$Z = 8$
$D_x = 1.72$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 7–12°$
$\mu = 1.85$ mm^{-1}
Room temperature
Needle
0.3 × 0.2 × 0.2 mm
Blue

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3736 measured reflections
3586 independent reflections
2457 observed reflections $[F > 3\sigma(F)]$

$R_{int} = 0.013$
$\theta_{max} = 28°$
$h = -41 \rightarrow 40$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.054$
$S = 1.14$
2457 reflections
246 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F) + 0.0015F^2]$

$(\Delta/\sigma)_{max} = 0.531$
$\Delta\rho_{max} = 0.482$ e Å^{-3}
$\Delta\rho_{min} = -0.825$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.37105 (2)	0.22242 (7)	0.92160 (4)	0.0337 (2)
Cl(1)	0.39476 (4)	0.2047 (2)	1.09150 (8)	0.0501 (3)
Cl(2)	0.32243 (4)	0.4409 (2)	0.9392 (1)	0.0663 (5)
O(2)	0.3224 (1)	−0.0767 (4)	0.8720 (2)	0.048 (1)
N(1)	0.2966 (1)	−0.0727 (5)	0.7014 (3)	0.038 (1)
N(3)	0.3425 (1)	0.1624 (5)	0.7784 (2)	0.033 (1)
N(4)	0.3617 (1)	0.4091 (5)	0.6859 (3)	0.050 (1)
C(1)	0.2747 (2)	−0.2506 (7)	0.7106 (4)	0.057 (2)
C(2)	0.3204 (1)	0.0010 (5)	0.7871 (3)	0.033 (1)
C(4)	0.3395 (1)	0.2520 (6)	0.6890 (3)	0.036 (1)
C(5)	0.3140 (2)	0.1790 (7)	0.6020 (3)	0.045 (2)
C(6)	0.2938 (1)	0.0174 (7)	0.6109 (3)	0.044 (1)
O(2′)	0.4432 (1)	0.4196 (4)	0.8794 (3)	0.047 (1)
N(1′)	0.4982 (1)	0.2125 (6)	0.8752 (3)	0.043 (1)
N(3′)	0.4272 (1)	0.1148 (5)	0.8889 (3)	0.037 (1)
N(4′)	0.4113 (1)	−0.1957 (5)	0.8968 (3)	0.055 (2)
C(1′)	0.5298 (2)	0.3623 (9)	0.8776 (4)	0.060 (2)
C(2′)	0.4556 (1)	0.2548 (6)	0.8813 (3)	0.038 (1)
C(4′)	0.4393 (1)	−0.0633 (6)	0.8866 (3)	0.041 (1)
C(5′)	0.4832 (2)	−0.1078 (7)	0.8771 (3)	0.051 (2)
C(6′)	0.5106 (1)	0.0325 (8)	0.8727 (3)	0.053 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cu—Cl(1)	2.271 (2)	Cu—Cl(2)	2.229 (2)
Cu—N(3)	2.028 (3)	Cu—N(3′)	2.022 (4)
N(3)—Cu—N(3′)	90.3 (2)	Cl(2)—Cu—N(3′)	157.1 (1)
Cl(2)—Cu—N(3)	91.6 (1)	Cl(1)—Cu—N(3′)	90.7 (1)
Cl(1)—Cu—N(3)	162.7 (1)	Cl(1)—Cu—Cl(2)	94.2 (1)
O(2)—Cu—O(2′)	144.4 (2)	N(3)—Cu—O(2)	55.5 (1)
Cl(1)—Cu—O(2)	107.2 (1)	N(3′)—Cu—O(2)	96.8 (1)
Cl(2)—Cu—O(2)	103.0 (1)	N(3)—Cu—O(2′)	100.9 (1)
Cl(1)—Cu—O(2′)	93.5 (1)	N(3′)—Cu—O(2′)	53.4 (1)
Cl(2)—Cu—O(2′)	104.0 (1)	Cu—N(3)—C(2)	105.5 (3)
Cu—N(3′)—C(2′)	109.0 (3)	Cu—N(3)—C(4)	133.5 (3)
Cu—N(3′)—C(4′)	129.1 (3)		
Cu···O(2)	2.677 (3)	Cu···O(2′)	2.793 (3)

D—H···A	H···A	D···A	D—H···A
N(4)—H(4B)···Cl(1^{i})	2.67 (5)	3.285 (4)	123 (3)
N(4)—H(4B)···Cl(2^{i})	2.59 (4)	3.498 (5)	158 (4)
N(4′)—H(4′A)···O(2)	2.23 (4)	2.890 (5)	160 (4)
N(4′)—H(4′B)···O(2′^{ii})	2.02 (14)	2.978 (5)	163 (9)

Symmetry codes: (i) $x, 1 - y, z - \frac{1}{2}$; (ii) $x, y - 1, z$.

The structure was phased by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined with full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Other calculations were performed using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, hydrogen bonds and complete geometry have been deposited with the IUCr (Reference: NA1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 628–630

A Dimeric Copper(II) Complex of an α-Hydroxylated Acid: [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2.2C_3H_7NO.2H_2O$

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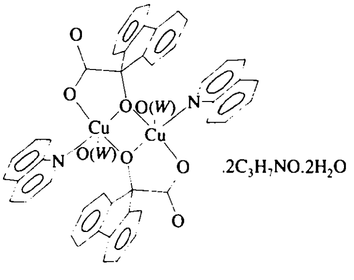
Abstract

The structure of bis[μ-(9-hydroxy-1:2κ^2O)-9-fluorenecarboxylato(2−)]-1κO;2κO-bis[aqua(quinoline-κN)copper(II)] bis(dimethylformamide) dihydrate has been determined by single-crystal X-ray diffraction. The binuclear Cu^{II} unit comprises a pair of Cu atoms linked by two hydroxy O-atom bridges. The coordination polyhedron around each Cu atom is a distorted square pyramid, the basal plane consisting of one N atom from the quinoline ligand, one carboxy O atom and two bridging O atoms from two α-hydroxylated acid ligands, while the axial coordination site is occupied by an O atom of the coordinated water molecule with a Cu—O bond length of 2.424 (4) Å.

Comment

There are two structure types in copper complexes of α-hydroxylated acid: mononuclear structures (Prout *et al.*, 1968; Bkouche-Waksman, 1994) and binuclear structures with a Cu_2O_2 core (Liu, 1992; Liu & Yu, 1992). This work is a part of our study on copper complexes of α-hydroxylated acid. The title compound, (I), is composed of one [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2$ binuclear unit, two DMF solvent molecules and two uncoordinated water molecules. The molecular configuration is shown in Fig. 1; atoms labelled *a* are related by the centre of inversion to those listed in Table 1. Therefore, the binuclear unit with a Cu_2O_2 core possesses a centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with a Cu(1)···Cu(1*a*) distance of 3.007 (4) Å and Cu(1)—O(1)—Cu(1*a*) angle of 103.1 (1)°. The Cu atom is coordinated by two bridging hydroxy O atoms [O(1) and O(1*a*)] of two acid ligands, one carboxy O atom [O(3)], one N atom [N(1)] of the quinoline ligand, and one O atom [O(5)] of one coordinated water molecule, to form a distorted square-pyramidal polyhedron; the Cu(1) atom is shifted 0.183 Å out of the basal plane of O_3N towards the axial atom, O(5). The most distorted bond angles are 76.9 (1), 166.6 (2) and 159.2 (1)° in the square pyramid; the Cu—O(1*a*) bond of 1.936 (3) Å is 0.03 Å longer than Cu—O(1) [1.904 (3) Å]. These structural characteristics are seen in some other copper complexes of α-hydroxylated acids (Liu, 1992; Liu & Yu, 1992).



(I)

The axial Cu(1)—O(5)(water) bond length of 2.424 (4) Å is in good agreement with the usual Cu–

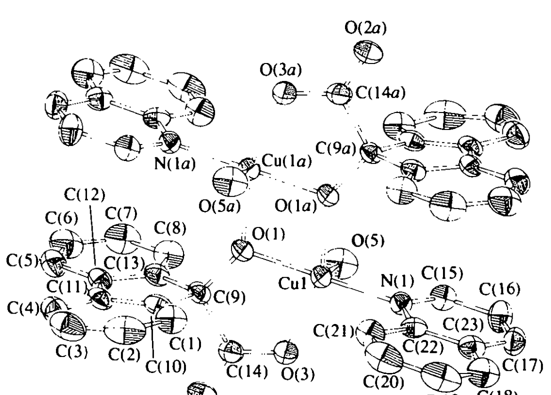


Fig. 1. A view of the binuclear unit [$Cu(C_{14}H_8O_3)(C_9H_7N)(H_2O)]_2$ showing the atom numbering and 30% probability displacement ellipsoids.