$S = 1.087$
4081 reflections
328 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 0.6103P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Sb1—N1	2.265 (2)	Sb1—O3	2.198 (2)
Sb1—N2	2.507 (2)	Sb1—O5	2.543 (2)
Sb1—O1	2.144 (1)	Sb1—O7	2.254 (1)
N1—Sb1—N2	74.7 (1)	N2—Sb1—O7	70.0 (1)
N1—Sb1—O1	78.2 (1)	O1—Sb1—O3	76.2 (1)
N1—Sb1—O3	74.3 (1)	O1—Sb1—O5	146.1 (1)
N1—Sb1—O5	86.3 (1)	O1—Sb1—O7	73.1 (1)
N1—Sb1—O7	82.4 (1)	O3—Sb1—O5	70.7 (1)
N2—Sb1—O5	64.8 (1)	O3—Sb1—O7	144.5 (1)
N2—Sb1—O1	136.4 (1)	O5—Sb1—O7	134.7 (1)
N2—Sb1—O3	126.4 (1)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6A···O8[i]	0.89 (3)	2.34 (3)	3.119 (3)	146 (3)
N3—H3B···O8[ii]	0.86 (4)	2.01 (4)	2.860 (3)	170 (3)
N6—H6B···O2[ii]	0.87 (3)	2.29 (3)	3.107 (3)	157 (3)
N4—H4B···O9	0.84 (3)	2.04 (3)	2.804 (3)	150 (3)
N5—H5···O7[ii]	0.87 (3)	2.29 (3)	3.117 (3)	160 (3)
N3—H3A···O6	0.82 (3)	2.05 (3)	2.848 (3)	166 (3)
N4—H4A···O5	0.83 (3)	2.27 (3)	3.081 (2)	168 (3)
O9—H9A···O6[iii]	0.85 (4)	1.90 (4)	2.741 (3)	172 (4)
O9—H9B···O4	0.97 (5)	2.06 (5)	2.947 (3)	151 (5)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, y, z - 1$; (iii) $x - 1, y, z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different ψ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set was over 99% complete. Crystal decay, monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, was found to be negligible.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997b). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97 and *PARST*96 (Nardelli, 1995).

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Diclofenac interactions: tetrakis[μ-2-(2,6-dichloroanilino)phenylacetato]-1:2κ8O:O′-diacetone-1κO,2κO-dicopper(II)(Cu—Cu) acetaldehyde solvate

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Abstract

The structure of the centrosymmetric dimeric copper(II) title compound, $[Cu_2(C_{14}H_{10}Cl_2NO_2)_4(C_3H_6O)_2]\cdot C_2H_4O$, has been determined and compared with the structures of analogous O-bridged Cu^{II} dimers. Polarographic experiments on aqueous solutions containing a mixture

of the Cu^{II} ion and diclofenac have been used to determine both the formation constant $[1\,(1) \times 10^8]$ and the solubility product $[2\,(1) \times 10^{-12}]$ of the complex.

Comment

In previous papers, we have investigated the structures of several salts of [2-(2,6-dichloroanilino)phenyl]acetic acid (diclofenac, hereinafter D; Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997, 1998). There is evidence that the anti-inflammatory activity of diclofenac is related to a competitive binding of the carboxyl group with a component of the prostaglandin synthetase system. However, carboxylate groups may interact as bridging ligands with divalent transition metals present in the biological environment, thereby altering the bioavailability of the drug. Moreover, it is well known that many complexes of divalent transition metals are capable of catalyzing the hydrolysis of RNA (Stern *et al.*, 1990; Kimura, 1994).

Thus, structural studies on diclofenac–metal interactions may prove of biological interest. However, only a few studies on diclofenac–metal interactions have been published. Two of these seem especially relevant to the present work, since they include the spectrophotometric determination of a 2:1 D–Cu^{II} complex (Agatonović-Kustrin *et al.*, 1991) and a spectral analysis of the complexes $D_2Zn^{II}·H_2O$, D_2Hg^{II} and $D_2Cd^{II}·H_2O$ (Kovala-Demertzi *et al.*, 1993). The latter work also describes the crystal structure of the complex $D_2(C_2H_5OH)_2Cd^{II}·H_2O$, which was formed by slow evaporation from a solution of $D_2Cd^{II}·H_2O$ in ethanol. This crystal structure apparently represents the only example of D acting as a ligand.
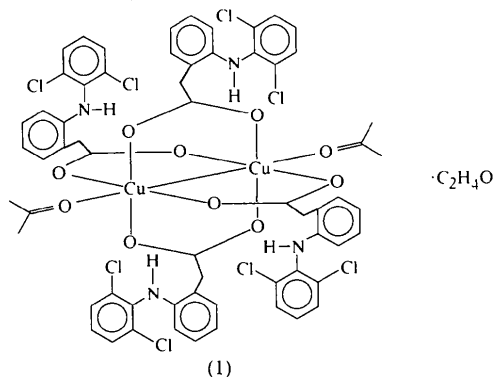
In this paper, we describe the crystal structure of a dinuclear complex obtained by reaction of sodium [2-(2,6-dichloroanilino)phenyl]acetate (NaD) with copper(II) nitrate (see *Experimental*), and examine the role of D as a ligand. The molecular geometry of the title compound is illustrated in Fig. 1 and listed in Table 1. The $[D_4(acetone)_2Cu^{II}_2]$ complex, (1), lies across a crystallographic centre of symmetry which coincides with the midpoint of the Cu—Cu vector.

(1)

The acetaldehyde solvate molecule is statistically disordered over two sites related by inversion. The two Cu^{II} ions are bridged by four carboxylate groups acting as bidentate ligands [Cu—O1(carboxylate) = 1.973 (2) and 1.968 (2) Å for molecules A and B, respectively]. Four carboxylate O atoms define each equatorial coordination plane. Two acetone molecules are bonded in axial sites [Cu—O(acetone) 2.177 (2) Å]. The Cu—Cu distance of 2.610 (1) Å and the magnetic moment of 1.37 BM both indicate the formation of a dinuclear species. In particular, the value of the magnetic moment, being lower than the spin-only value (1.73 BM) indicates spin pairing of the two paramagnetic Cu atoms. A distorted octahedral arrangement is found around each Cu^{II} ion, which is displaced by 0.1906 (9) Å from the equatorial plane in the direction of the axial ligand. This geometry is typical of oxo-bridged dinuclear Cr^{II}, Cu^{II}, Mo^{II} and Rh^{II} compounds. In particular, the structural characteristics of (1) are close to the mean values calculated for 31 dinuclear Cu^{II}–acetate compounds (Hoang *et al.*, 1993), *i.e.* Cu—Cu 2.621 (8), Cu—O(equatorial) 1.976 (5), Cu—N,O(apical) 2.16 (2) and Cu···equatorial plane 0.221 (9) Å. The occurrence of acetone as the apical ligand is unusual in dinuclear Cu^{II} chemistry, the only reported case being the adduct of Cu^{II} with (2,4-dichloro-5-methylphenylthio)-acetate [Cu(DCMPTA)₂] (Smith *et al.*, 1985).

The bond distances and angles involving the acetone molecule are comparable with those found in [Cu(DCMPTA)₂]. In particular, the value of the Cu—O3—C15 angle [134.8 (2)°], which is close to the value found in [Cu(DCMPTA)₂] [132.9 (4)°], confirms that the O3 atom coordinates to the Cu^{II} centre through one of its two lone pairs of electrons.

The Cu—Cu and Cu—O(acetone) distances in [Cu(DCMPTA)₂] of 2.646 (1) and 2.206 (3) Å, respectively, are slightly longer than the analogous distances in (1). These differences probably stem from the different natures of the equatorial ligand. In fact, a correlation between the strength of the carboxylic acid and some structural features of the dinuclear complexes has been proposed (Melník, 1982). However, a comparison between the structural characteristics of (1) and those of a copper(II)–acetate hydrate complex [Cu—Cu 2.616 (1), Cu—O(equatorial) 1.969 (3), Cu—O(apical) 2.156 (4) and Cu···equatorial plane 0.19 Å; Meester *et al.*, 1973] shows a substantial coincidence of these geometrical details in spite of diclofenac being a stronger acid than acetic acid (pK_a 3.8 *versus* 4.76).

The conformations of the two independent D anions in (1) are slightly different. The dihedral angles between the two phenyl rings are 74.5 (1) and 67.2 (1)° for molecules A and B, respectively. The C—O distances of the carboxylate groups are similar [1.256 (3) and 1.254 (3) Å for A, and 1.261 (3) and 1.250 (3) Å for B] and suggest complete charge delocalization. Two intramolecular hydrogen bonds are observed in each molecule; N1···O1

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the unit cell of (1). Non-H atoms are represented by displacement ellipsoids at 50% probability and H atoms are shown as spheres of arbitrary size. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

3.112 (4) and 3.063 (3) Å, and N1$\cdots$Cl1 2.988 (3) and 2.959 (3) Å for molecules *A* and *B*, respectively. No strong hydrogen bond is involved in the packing.

The behaviour of (1) in aqueous solution was tested by recording the polarographic current voltage curves for the reduction of a constant amount of Cu^{II} ions (5 × 10^{-5} mol dm^{-3}) as a function of an increasing concentration of D. The results were analysed by logarithmically plotting both the *il/id* ratio and the $-\Delta E_{1/2}$ (mV) *versus* the concentration of D (mol dm^{-3}). The *il* and *id* values are the limiting currents of the reduction of Cu^{II} ion in the presence and absence of D, respectively. $\Delta E_{1/2}$ is the difference between the half-wave potentials of the reduction of the Cu^{II} ion in the presence and absence of D. The resulting plot can be divided into three regions. At concentrations of D from 1 × 10^{-5} to 1 × 10^{-4} mol dm^{-3} (region I), both *il/id* and $-\Delta E_{1/2}$ have constant values. At concentrations of D from 1 × 10^{-4} to 1 × 10^{-3} mol dm^{-3} (region II), *il/id* decreases gradually while $-\Delta E_{1/2}$ increases linearly. Between 1 × 10^{-3} and 1 × 10^{-2} mol dm^{-3} D (region III), *il/id* still decreases whereas $-\Delta E_{1/2}$ maintains a constant value of −150 (5) mV. A possible effect of electrode passivation induced by aggregates of D was excluded by means

of polarographic measurements on solutions of Tl^{I} ions and D (Feroci *et al.*, 1992).

The polarographic data from the Cu^{II} solutions can be explained as follows: in region I, only a very small amount of complex is formed; in region II, the shift in the potential suggests the formation of a complex between Cu^{II} and D, and the gradual decrease in *il/id* seems to indicate that the complex has a limited solubility or that its dissociation at equilibrium is slow; in region III, the addition of D does not increase the concentration of the complex, but leads rather to the formation of 'micelles', as was confirmed by the observation that within this range, turbidity occurs and the solutions show a Tyndall effect (Hiemenz, 1977). The polarographic experiments allow the computation of a molar ratio of D to the Cu^{II} ion of 2:1. The formation constant of the complex was found to be 1 (1) × 10^8 (Heyrovsky & Kuta, 1965). Finally, from the *il/id* ratio, a value of 2 (1) × 10^{-12} was obtained for the solubility product of complex (1).

Experimental

Copper(II) nitrate hydrate (4.0 mmol) was dissolved in water and added to an aqueous solution of the sodium salt of

diclofenac (2.0 mmol). The reaction mixture was shaken gently for several minutes. The green microcrystalline precipitate was filtered off and subsequently redissolved in acetone. After evaporation of the solvent, grey–blue crystals were obtained. An attempt was made to measure the density of the crystal by flotation, but the accuracy was severely limited by the solubility of the crystals in all solvents employed. The magnetic susceptibility (400×10^{-6} erg G^{-2} mol^{-1}) was measured at 301 K using an Evans balance and was corrected for the diamagnetism of all atoms. Polarographic experiments were performed using an AME 466 polarograph equipped with an electrolytic cell. The reference electrode was a saturated calomel electrode and the working electrode was a dropping mercury electrode. A platinum wire was used as counter-electrode.

Crystal data
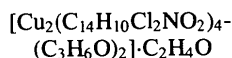
$[Cu_2(C_{14}H_{10}Cl_2NO_2)_4-$
$(C_3H_6O)_2]\cdot C_2H_4O$
$M_r = 1467.80$
Triclinic
$P\bar{1}$
$a = 11.148\,(2)$ Å
$b = 14.47\,(1)$ Å
$c = 11.08\,(1)$ Å
$\alpha = 110.13\,(6)°$
$\beta = 96.85\,(3)°$
$\gamma = 81.97\,(4)°$
$V = 1657\,(2)$ Å^3
$Z = 1$
$D_x = 1.471$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.13–15.55°$
$\mu = 1.025$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.25 \times 0.18 \times 0.15$ mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: empirical via ψ scan (North et al., 1968)
$T_{min} = 0.772$, $T_{max} = 0.857$
10 052 measured reflections
9621 independent reflections

4100 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 29.96°$
$h = -15 \rightarrow 15$
$k = -20 \rightarrow 19$
$l = 0 \rightarrow 15$
3 standard reflections frequency: 160 min intensity decay: 4.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 0.902$
9621 reflections
428 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.2788P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—Cu	2.6103 (13)	O1B—C14B	1.261 (3)
Cu—O1A	1.973 (2)	O2B—C14B	1.250 (3)
Cu—O1B	1.968 (2)	O3—C15	1.214 (4)
Cu—O3	2.177 (2)	C15—C17	1.480 (5)
O1A—C14A	1.256 (3)	C15—C16	1.481 (6)
O2A—C14A	1.254 (3)		
O1B—Cu—O1A	93.29 (10)	O3—C15—C17	120.5 (4)
O1B—Cu—O3	94.75 (9)	O3—C15—C16	123.0 (3)
O1A—Cu—O3	92.70 (9)	C17—C15—C16	116.5 (4)
C15—O3—Cu	134.8 (2)		

The amine H atoms were located by a difference Fourier synthesis and were refined isotropically. The remaining H atoms were placed in calculated positions and refined riding on their parent atoms, except that the torsion angles of the methyl groups were defined locating one H atom for each group on the difference Fourier maps.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976).

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