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# Structures of Binuclear Copper(II) Chloroacetate Complexes: Tetrakis-($\mu$-monochloroacetato-*O,O'*)-bis[(3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione)copper(II)], $[Cu_2(C_2H_2ClO_2)_4(C_8H_{10}N_4O_2)_2]$

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**Abstract.** $M_r = 889\cdot4$, triclinic, $P\bar{1}$, $a = 7\cdot932$ (2), $b = 12\cdot798$ (2), $c = 9\cdot078$ (5) Å, $\alpha = 93\cdot19$ (6), $\beta = 109\cdot95$ (3), $\gamma = 96\cdot92$ (6)°, $V = 855\cdot3$ Å$^3$, $Z = 1$, $D_x = 1\cdot73$, $D_m = 1\cdot74$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 16\cdot8$ cm$^{-1}$, $F(000) = 450$, $T = 300$ K, final $R = 0\cdot067$ for 1405 observed reflections. The Cu atoms are bridged in pairs by four monochloroacetate groups to form centrosymmetric binuclear molecules: [Cu(chloroacetate)$_2$(caffeine)]$_2$. The Cu atom lies 0·236 (1) Å from the plane of the four bonded O atoms [mean Cu—O 1·97 (4) Å] towards the N atom of the caffeine, Cu—N 2·23 (4) Å. The distorted octahedral environment around Cu is completed by the second Cu atom [Cu···Cu 2·711 (3) Å].

**Introduction.** The interaction of nucleic acids and their constituents with a metal atom has been extensively studied by Hodgson (1977). Caffeine (3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione) is a purine alkaloid possessing pharmacological properties as a therapeutic agent with analeptic activity.

Several crystal structures of caffeine with organic substrates have been determined: with barbital (Craven & Gartland, 1974), with 5-chlorosalicylic acid (Shefter, 1968) and as the hydrochloride dihydrate (Mercer & Trotter, 1978). In these structures the caffeine molecule shows significant deviations from planarity.

Only a few crystal structures of Cu$^{II}$ compounds with caffeine have been described. In triaqua(caffeine)nitratocopper(II) nitrate (Biagini Cingi, Chiesi Villa, Gaetani Manfredotti & Guastini, 1972), Cu is pentacoordinated, in square-pyramidal geometry, the base consisting of two molecules of water, nitrate ion and caffeine imidazole N atom. The Cu atom is situated 0·13 Å above the basal plane. The caffeine molecule is approximately planar in this structure. In aqua(caffeine)dichlorocopper(II) (Bandoli, Biagini Cingi, Clemente & Rizzardi, 1976) the geometry around Cu$^{II}$ is tetragonal-pyramidal, distorted towards trigonal-bipyramidal with the chromophore CuCl$_3$ON, containing a puckered basal plane.

To our knowledge, copper(II) carboxylates with caffeine as a ligand have not been previously studied by X-ray analysis. One of us (Melník, 1981) prepared and studied the electronic, IR and EPR spectra and magnetic susceptibilities of the title compound over a range of temperature. A binuclear structure was proposed, similar to that of copper(II) acetate monohydrate (Van Niekerk & Schoening, 1953). The X-ray analysis reported here confirms this conclusion.

**Experimental.** Preparation following Melník (1981). Green prismatic crystal 0·05 × 0·1 × 0·15 mm. $D_m$ by flotation in CHBr$_3$/CCl$_4$. Weissenberg photographs indicated a triclinic space group. Cell parameters refined on a Syntex $P2_1$ computer-controlled four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation by least squares from the angles of 10 selected reflections. Two standard reflections (001 and 100) remeasured after every 98 reflections, variations 1·70 and 1·20% respectively. 2438 reflections measured, $2\theta_{max} = 45°$, 1405 [$I > 1\cdot96\sigma(I)$] observed; index range $h$ 0 to 10, $k \pm 13$, $l \pm 9$. Intensities corrected for Lorentz–polarization factors; absorption ignored. Positions of non-H atoms determined from the $E$ map obtained with *MULTAN*80 (Main *et al.*, 1980), using molecular scattering factors for the calculation of the $E$ values, and Karle's (1968) recycling procedure. Anisotropic least-squares refinement (on $F$) in block-diagonal approximation with *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972); subsequent difference Fourier maps revealed positions for 4 H atoms in the caffeine molecule [at C(8), C(14), C(10) and C(12)]; remaining H atoms in calculated positions; temperature parameters of the H atoms set at 4·0 Å$^2$ and not refined; H-atom coordinates refined; final $R = 0\cdot067$, $wR = 0\cdot080$ and $S = 2\cdot8$; $\sqrt{w} = 1$ for $|F| < 15\cdot5$, $\sqrt{w} = 15\cdot5/|F|$ for $|F| \geq 15\cdot5$ (Hughes, 1941); in the final least-squares cycle $(\Delta/\sigma)_{max} = 0\cdot173$; atomic scattering factors from Cromer & Waber (1965); max. and min. values of the residual difference electron density map 0·3 and −0·4 e Å$^{-3}$.

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**Discussion.** Final atomic parameters are in Table 1.*

The structure consists of centrosymmetric units of [$(ClCH_2COO)_4Cu_2(C_8H_{10}N_4O_2)_2$] (see Fig. 1). Fig. 2 illustrates the packing of these units in the unit cell. Each Cu atom is coordinated by four O atoms from chloroacetate groups and one N atom of the caffeine ligand situated at the vertices of a weakly deformed tetragonal pyramid. The N atom is in the apical position and the displacement of the Cu atom from the basal plane is 0·236 (1) Å. The distance between the Cu atoms, 2·711 (3) Å, indicates an intermetallic interaction (Melník, 1982). The bond lengths and angles are listed in Table 2.

The bridging C atoms of the chloroacetate groups [C(17), C(18)] are $sp^2$ hybridized [the sum of bond angles at both these atoms is 360 (1)°]. The caffeine ligand is significantly non-planar, the dihedral angle between the pyrimidine and imidazole rings being 1 (1)°. The least-squares plane for the non-hydrogen atoms of the caffeine ligand forms an angle of 73 (1)° with the basal plane [O(15), O(16), O(19′), O(20′)].

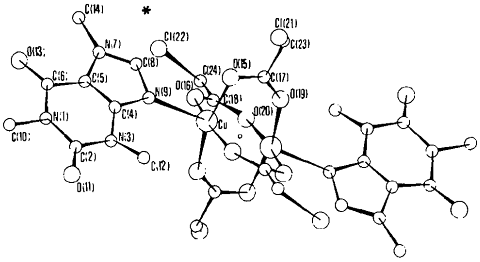

Fig. 1. Structure of the title compound showing the atomic numbering.

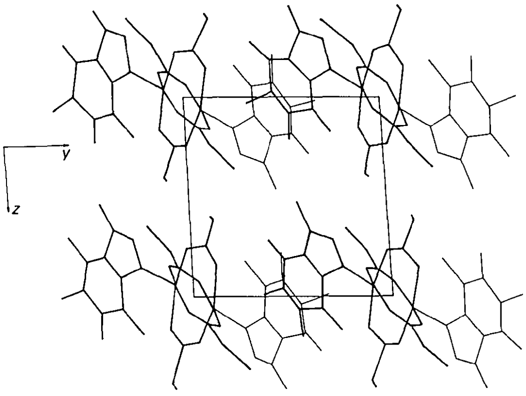

Fig. 2. Projection of the crystal structure on (100).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Cu | 0·0489 (2) | 0·9099 (1) | 0·9517 (1) | 2·93 (3) |
| N(1) | 0·222 (1) | 0·4609 (7) | 0·959 (1) | 3·5 (3) |
| C(2) | 0·309 (1) | 0·5428 (9) | 1·076 (1) | 3·3 (3) |
| N(3) | 0·259 (1) | 0·6420 (7) | 1·047 (1) | 3·1 (3) |
| C(4) | 0·128 (2) | 0·6549 (8) | 0·908 (1) | 2·9 (3) |
| C(5) | 0·040 (2) | 0·5714 (9) | 0·797 (1) | 3·1 (3) |
| C(6) | 0·083 (2) | 0·4662 (9) | 0·815 (1) | 3·4 (3) |
| N(7) | −0·084 (1) | 0·6116 (8) | 0·676 (1) | 3·7 (3) |
| C(8) | −0·063 (2) | 0·7155 (9) | 0·722 (1) | 3·8 (3) |
| N(9) | 0·065 (1) | 0·7469 (8) | 0·863 (1) | 3·6 (3) |
| C(10) | 0·282 (2) | 0·356 (1) | 0·993 (2) | 5·4 (5) |
| O(11) | 0·428 (1) | 0·5303 (7) | 1·197 (1) | 4·6 (3) |
| C(12) | 0·341 (2) | 0·733 (1) | 1·169 (2) | 4·9 (4) |
| O(13) | 0·013 (1) | 0·3885 (6) | 0·718 (1) | 5·3 (3) |
| C(14) | −0·227 (2) | 0·554 (1) | 0·537 (2) | 5·5 (4) |
| O(15) | 0·064 (1) | 0·9816 (6) | 0·769 (1) | 4·4 (3) |
| O(16) | −0·220 (1) | 0·8783 (6) | 0·850 (1) | 4·1 (2) |
| C(17) | 0·025 (2) | 1·0743 (9) | 0·756 (1) | 3·2 (3) |
| C(18) | −0·335 (2) | 0·934 (1) | 0·860 (2) | 4·2 (4) |
| O(19) | −0·026 (1) | 1·1274 (5) | 0·8492 (9) | 4·2 (2) |
| O(20) | −0·301 (1) | 1·0262 (6) | 0·932 (1) | 3·8 (2) |
| Cl(21) | 0·2498 (5) | 1·1206 (4) | 0·5927 (5) | 6·0 (1) |
| Cl(22) | −0·5854 (6) | 0·7775 (4) | 0·6530 (7) | 7·9 (2) |
| C(23) | 0·040 (2) | 1·130 (1) | 0·614 (2) | 4·3 (4) |
| C(24) | −0·537 (2) | 0·893 (1) | 0·780 (2) | 5·9 (5) |

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A prime indicates an atom at $-x, 2-y, 2-z$.

| | | | |
|---|---|---|---|
| Cu—N(9) | 2·23 (4) | C(6)—C(5) | 1·43 (3) |
| Cu—O(15) | 1·97 (4) | N(7)—C(5) | 1·37 (4) |
| Cu—O(16) | 1·99 (4) | N(7)—C(14) | 1·46 (6) |
| N(1)—C(2) | 1·38 (6) | N(7)—C(8) | 1·35 (3) |
| N(1)—C(6) | 1·41 (3) | C(8)—N(9) | 1·34 (4) |
| N(1)—C(10) | 1·49 (3) | Cl(21)—C(23) | 1·76 (2) |
| C(2)—N(3) | 1·39 (3) | C(17)—O(15) | 1·26 (2) |
| C(2)—O(11) | 1·21 (3) | C(17)—O(19) | 1·26 (2) |
| N(3)—C(4) | 1·37 (3) | C(17)—C(23) | 1·54 (4) |
| N(3)—C(12) | 1·49 (6) | Cl(22)—C(24) | 1·75 (6) |
| C(4)—C(5) | 1·36 (5) | C(18)—O(16) | 1·25 (4) |
| C(4)—N(9) | 1·36 (4) | C(18)—O(20) | 1·26 (4) |
| C(6)—O(13) | 1·22 (5) | C(18)—C(24) | 1·53 (5) |
| Cu—O(19′) | 1·96 (4) | Cu—O(20′) | 1·96 (4) |
| N(9)—Cu—O(15) | 97·8 (4) | C(5)—C(6)—N(1) | 111·7 (9) |
| N(9)—Cu—O(16) | 88·5 (4) | C(5)—C(6)—O(13) | 126 (1) |
| O(15)—Cu—O(16) | 90·1 (4) | N(1)—C(6)—O(13) | 122 (1) |
| C(6)—N(1)—C(10) | 117·7 (9) | C(5)—N(7)—C(8) | 105·0 (9) |
| C(6)—N(1)—C(2) | 127·0 (9) | C(5)—N(7)—C(14) | 129 (1) |
| C(10)—N(1)—C(2) | 115·3 (9) | C(8)—N(7)—C(14) | 126 (1) |
| N(1)—C(2)—O(11) | 122 (1) | N(7)—C(8)—N(9) | 114 (1) |
| N(1)—C(2)—N(3) | 116·8 (9) | C(4)—N(9)—C(8) | 102·3 (9) |
| N(3)—C(2)—O(11) | 121 (1) | C(23)—C(17)—O(15) | 119 (1) |
| C(4)—N(3)—C(2) | 120·1 (9) | C(23)—C(17)—O(19) | 115 (1) |
| C(4)—N(3)—C(12) | 119·9 (9) | O(15)—C(17)—O(19) | 126 (1) |
| C(2)—N(3)—C(12) | 120·0 (9) | Cl(21)—C(23)—C(17) | 110·7 (9) |
| N(9)—C(4)—N(3) | 126·5 (9) | Cu—O(15)—C(17) | 119 (1) |
| N(9)—C(4)—C(5) | 112·0 (9) | C(24)—C(18)—O(16) | 120 (1) |
| N(3)—C(4)—C(5) | 121 (1) | C(24)—C(18)—O(20) | 114 (1) |
| C(4)—C(5)—N(7) | 106 (1) | O(16)—C(18)—O(20) | 126 (1) |
| C(4)—C(5)—C(6) | 123 (1) | Cl(22)—C(24)—C(18) | 114 (1) |
| N(7)—C(5)—C(6) | 131 (1) | Cu—O(16)—C(18) | 127·7 (7) |
| N(9)—Cu—O(19′) | 96·1 (4) | O(16)—Cu—O(19′) | 89·2 (4) |
| N(9)—Cu—O(20′) | 105·2 (4) | O(16)—Cu—O(20′) | 166·2 (4) |
| O(15)—Cu—O(19′) | 166·1 (4) | O(19′)—Cu—O(20′) | 89·0 (4) |
| O(15)—Cu—O(20′) | 88·3 (4) | | |

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42112 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Geometrical data for binuclear copper*(II) *chloroacetate complexes*

| Ligand | Urea, $OC(NH_2)_2$ | Quinoline $NC_9H_7$ | 2-Picoline, $NC_5H_4CH_3$ | 3-Picoline $NC_5H_4CH_3$ | Caffeine, $C_8H_{10}N_4O_2$ | Mean value |
|---|---|---|---|---|---|---|
| Cu···Cu (Å) | 2·65 | 2·72 | 2·75 | 2·69 | 2·71 | 2·70 ±0·04 |
| Basal plane–basal plane (Å) | 2·23 | 2·23 | 2·23 | 2·23 | 2·23 | 2·23 ±0·00 |
| Cu–basal plane (Å) | 0·21 | 0·25 | 0·26 | 0·23 | 0·24 | 0·24 ±0·02 |
| Sum of bond lengths Cu–O–C–O–Cu (Å)* | 6·49 | 6·44 | 6·44 | 6·43 | 6·46 | 6·45 ±0·02 |
| Sum of bond angles Cu–O–C–O–Cu (°)* | 375·0 | 374·3 | 374·9 | 374·3 | 374·0 | 374·5 ±0·4 |
| Cu–O (Å)* | 1·97 | 1·973 | 1·974 | 1·974 | 1·97 | 1·974 ±0·004 |
| Cu–N (Å) | 2·10 | 2·211 | 2·161 | 2·269 | 2·23 | 2·19 ±0·07 |
| Reference | (*a*) | (*b*) | (*c*) | (*d*) | (*e*) | |

References: (*a*) Ivanov, Simonov, Ablov & Milkova (1974); (*b*) Simonov, Ivanov, Ablov, Milkova & Malinovskii (1976*a*); (*c*) Davey & Stephens (1970); (*d*) Simonov, Milkova, Ablov & Malinovskii (1976*b*); (*e*) present work.

* Where more than one chemically equivalent distance or angle is present, the mean value is tabulated.

In Table 3 are compared some geometric parameters of binuclear complexes of the $(ClCH_2COO)_4Cu_2(L)_2$ type ($L$ = neutral ligand). It is evident that the differences in these geometric parameters are not significant, and thus we can consider these to be constant characteristics of such binuclear complexes.

In the title complex, the caffeine N(9) atom is 0·13 (3) Å out of the Cu, C(4), C(8) plane, indicating a slight deviation from $sp^2$ hybridization. If the Cu—N(9) bond length is compared with Cu—$L$ bond lengths according to Melník (1982), no effect of the ligand geometry on this bond is observed.

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# Tetracarbonyl(tri-*tert*-butylstibine)iron, $[Fe(CO)_4\{Sb(C_4H_9)_3\}]$

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**Abstract.** $M_r$ = 460·98, orthorhombic, $P2_12_12_1$, $a$ = 10·135 (3), $b$ = 10·209 (3), $c$ = 19·224 (5) Å, $U$ = 1989·1 (10) Å$^3$, $Z$ = 4, $D_x$ = 1·539 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu$ = 21·15 cm$^{-1}$, $F(000)$ = 928, $T$ = 293 K, $R$ = 0·032 for 1992 observed reflections. The tri-*tert*-butylstibine molecule occupies an axial position in the trigonal-bipyramidal complex. The axial–axial angle, Sb—Fe—C, is 175·9 (2)°; the average equatorial–equatorial angle is 120·0°; and the average axial–equatorial angle is 90·0°.

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