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Unusual *O*-coordination of caffeine in tetrakis(μ-3,5-dinitrobenzoato-κ^2O:O')bis[(caffeine-κO)copper(II)]

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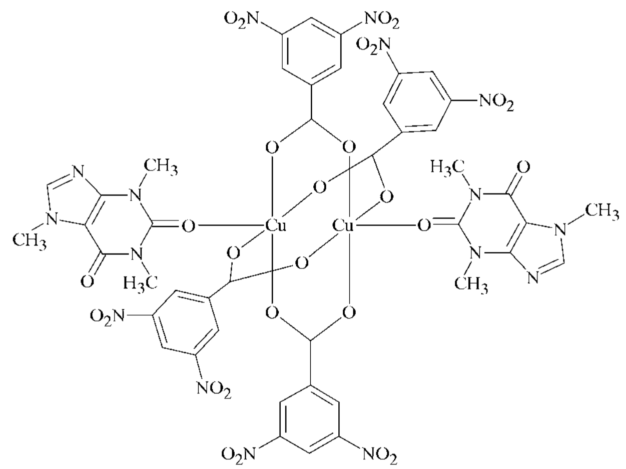
The title compound {systematic name: tetrakis(μ-3,5-dinitrobenzoato-κ^2O:O')bis[(3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione-κO^2)copper(II)]}, $[Cu_2(C_7H_3N_2O_6)_4(C_8H_{10}N_4O_2)_2]$, consists of paddle-wheel dimeric tetrakis(μ-3,5-dinitrobenzoato-κ^2O:O')dicopper(II) units with *O*-coordinated caffeine molecules in both apical positions. The entire dimeric molecule lies on a tetragonal inversion $\overline{4}$ axis, and thus one nitrobenzoate anion with one Cu atom in a special position belong to the independent part of the molecule. The caffeine ligand bonded to the Cu atom is disordered on a local twofold non-crystallographic axis coincident with the $\overline{4}$ axis. A π–π stacking interaction is observed between the caffeine rings and adjacent symmetry-related benzene rings of the 3,5-dinitrobenzoate anions.

Comment

Benzoates, especially salicylates and fenamates, are known to play an important role in human medicine. The preparation of new nitro-substituted benzoato–copper complexes with different biologically active ligands, the study of their composition, stereochemistry, structure and spectroscopic properties, and of course the study of their biological activity, are the basis of our approach to analyzing these compounds.

The complex molecule of the title compound, (I) (Fig. 1), is located on a $\overline{4}$ inversion axis, with both Cu atoms and atoms O7, C8 and C10 of the caffeine ligand on a twofold axis. Each Cu atom in the dimeric structure has a tetragonal–pyramidal coordination, with four carboxylate O atoms (O1, O2 and their symmetry equivalents) in equatorial positions [Cu—O1 = 1.933 (2) Å and Cu—O2 = 1.983 (2) Å] and caffeine atom O7 in the apical position [Cu—O7 = 2.180 (3) Å]. The Cu$\cdots$Cu^{ii} separation is 2.661 (3) Å [symmetry code: (ii) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{5}{4} - z$], which is close to the Cu$\cdots$Cu distance in $[Cu_3(C_7H_3N_2O_6)_6(CH_3OH)_2]_n$ (Hökelek *et al.*, 1998). The Cu atoms are slightly displaced from the basal plane by 0.200 (1) Å toward the apical O7 atom, and the τ parameter (Addison *et al.*, 1984) of 0.16 implies tetragonal geometry.



(I)

The caffeine molecules are significantly planar; the dihedral angle between the pyrimidine and imidazole rings is 0°. These dihedral angles in other complexes with caffeine are in the range 0–5°. The dihedral angle is 0° only for $[Cu_2(\mu\text{-flufenamato-}\kappa^2O{:}O')_4(\text{caffeine-}\kappa N)(H_2O)]$ (Melník *et al.*, 1998) and $[Cu_2(\mu\text{-}CCl_3CO_2\text{-}\kappa^2O{:}O')_4(\text{caffeine-}\kappa N)_2]\cdot C_6H_6$ (Horie *et al.*, 1986).

There are π–π stacking interactions (Fig. 2) (Janiak, 2000) between the caffeine rings and adjacent symmetry-related benzene rings of the 3,5-dinitrobenzoate anions at ($-x$, $-y$, $-z + 1$) and (x, $y + \frac{1}{2}$, $-z + 1$); the distances between the caffeine and benzene planes are in the range 3.28–3.52 Å.

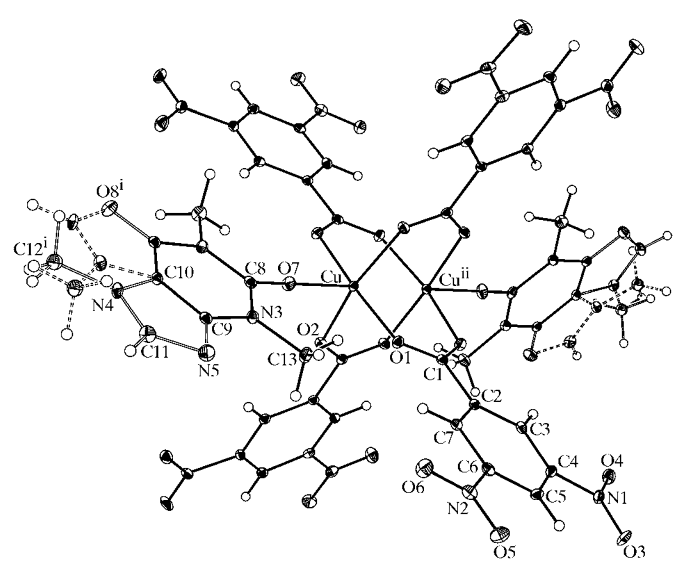


Figure 1
A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For disorder information, see *Experimental*. [Symmetry codes: (i) $-x, \frac{1}{2} - y, z$; (ii) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{5}{4} - z$.]

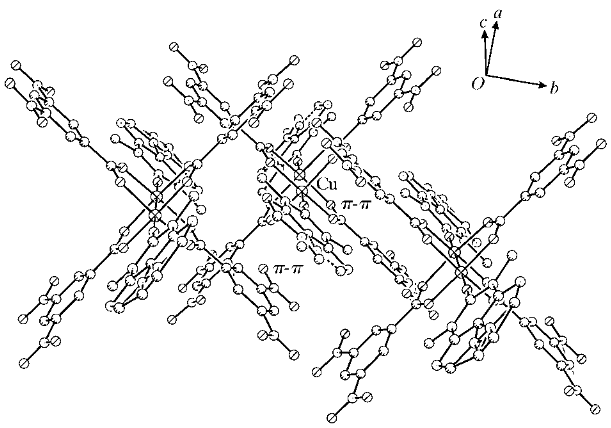


Figure 2
The π–π stacking interactions (dashed lines) in the crystal structure of (I).

As a ligand, caffeine usually prefers an N atom as the donor atom, *e.g.* in the copper(II) carboxylate complexes [Cu_2(μ-flufenamato-κ^2O:O')$_4$(caffeine-κN)(H_2O)] (Melník *et al.*, 1998) or [Cu_2(μ-RCO_2-κ^2O:O')$_4$(caffeine-κN)$_2$], where RCO_2^- is the benzoate anion (Kawata *et al.*, 1992), the naproxenate anion (Koman *et al.*, 2000), the chloroacetate anion (Koreň *et al.*, 1985), the *o*-iodobenzoate anion (Valach *et al.*, 2001), the benzoylformate anion (Harada *et al.*, 1997) or the trichloroacetate anion (Horie *et al.*, 1986). The Cu$\cdots$Cu separations and Cu—N_{ap}(caffeine) bond distances in these complexes are in the ranges 2.633–2.852 and 2.239–2.116 Å, respectively. The O atom was found to participate in co-ordination only in {[Cu_2(μ-CCl_3CO_2-κ^2O:O')$_4$(μ-caffeine-κ^2N:O)]·2$PhCH_3$}$_n$, which contains caffeine as a bridging ligand (Uekusa *et al.*, 1992). It is interesting that the bonding of caffeine *via* an O atom in the title compound results in a smaller distance from the Cu atom to the basal plane compared with those compounds with caffeine as an *N*-donor ligand [0.223 (Melník *et al.*, 1998), 0.204 (Kawata *et al.*, 1992), 0.217 (Koman *et al.*, 2000), 0.236 (Koreň *et al.*, 1985), 0.236 (Valach *et al.*, 2001), 0.259 (Harada *et al.*, 1997) or 0.315 Å (Horie *et al.*, 1986)].

Complex (I) is also unusual for the manner of bonding adopted by the 3,5-dinitrobenzoate anion. This anion prefers a monodentate or ionic bonding manner, and there is only one example of a bidentate bridging mode forming copper(II) acetate-like dimers, *viz.* [$Cu_3(C_7H_3N_2O_6)_6(CH_3OH)_2$]$_n$ (Hökelek *et al.*, 1998), and in this case (*O*-donor apical ligand), the Cu atom is displaced from the basal plane by 0.195 Å.

Experimental

Caffeine (0.5 mmol) was added to copper(II) acetate (1 mmol) in an aqueous solution (50 ml). 3,5-Dinitrobenzoic acid (2 mmol) was then added. The powdery blue product was filtered off, washed with water and dried at room temperature. Blue crystals of (I) suitable for X-ray analysis were obtained from the mother liquor after a few weeks by slow room-temperature crystallization.

Crystal data

[$Cu_2(C_7H_3N_2O_6)_4(C_8H_{10}N_4O_2)_2$]
M_r = 1359.96
Tetragonal, $I4_1/a$
a = 12.900 (5) Å
c = 30.33 (3) Å
V = 5047 (3) Å^3
Z = 4
D_x = 1.790 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 100 (2) K
Tetragonal plate, blue
0.24 × 0.12 × 0.11 mm

Data collection

Kuma KM-4-CCD area-detector diffractometer
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
T_{min} = 0.826, T_{max} = 0.908
19901 measured reflections
5131 independent reflections
2721 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 35.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.078
S = 1.01
5131 reflections
216 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1^i	1.933 (2)	Cu—O2^i	1.983 (2)
Cu—O1	1.933 (2)	Cu—O7	2.180 (3)
Cu—O2	1.983 (2)	Cu$\cdots$Cu^{ii}	2.661 (3)
O1^i—Cu—O1	173.16 (8)	O1^i—Cu—O7	93.42 (4)
O1^i—Cu—O2	88.75 (6)	O1—Cu—O7	93.42 (4)
O1—Cu—O2	90.27 (6)	O2—Cu—O7	98.21 (4)
O1—Cu—O2^i	88.75 (6)	O2^i—Cu—O7	98.21 (4)
O2—Cu—O2^i	163.57 (8)		

Symmetry codes: (i) $-x, -y + \frac{1}{2}, z$; (ii) $y - \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{5}{4}$.

Discrete positional disorder of the caffeine ligands is observed. Molecules of (I) lie around a $\overline{4}$ inversion axis. Atoms Cu, O7, C8 and C10 lie on special positions on the twofold rotation axis and have occupancy factors of 0.5 in the asymmetric unit. In Fig. 1, atoms which have full occupancy in complete molecules are drawn with solid lines. Atoms which have 0.5 occupancy in parts *A* or *B* alongside the twofold rotation axis are drawn with open or open dashed lines. Atom N5 from the caffeine ligand in part *A* and atom O8 from the caffeine ligand in mirror part *B* lie in the same positions and were constrained by EXYZ and EADP (*SHELXL97*; Sheldrick, 1997) with occupancy factors of 0.5. In part *A*, the full caffeine ligand consists of atoms O7, C8, C9, N3, N4, N5, C11 and C13, atoms in inversion C9^i, N3^i, C13^i, C12^i and O8^i [symmetry code: (i) $-x, -y + \frac{1}{2}, z$], and their parent H atoms. In part *B*, the full molecule consists of atoms O7, C8, C9, N3, C12, O8 and C13, atoms in inversion C9^i, N3^i, C13^i, N4^i, N5^i and C11^i, and their parent H atoms. The remaining H atoms were positioned geometically, with C—H = 0.95 and 0.98 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3010). Services for accessing these data are described at the back of the journal.

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