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## Key indicators

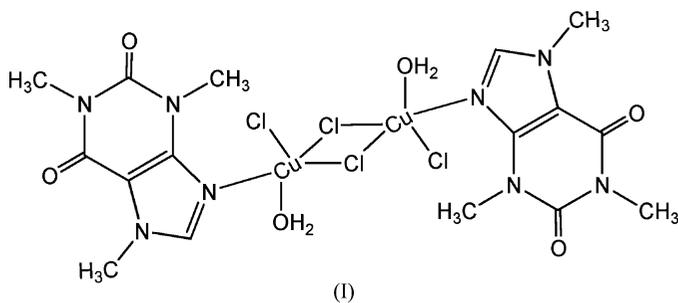
Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.030  
 $wR$  factor = 0.060  
Data-to-parameter ratio = 13.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Di- $\mu$ -chloro-bis[aqua(caffeine)chlorocopper(II)]

The title compound, di- $\mu$ -chloro-bis[aquachloro(3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione)copper(II)],  $[\text{Cu}_2\text{Cl}_4(\text{C}_8\text{H}_{10}\text{N}_3\text{O}_2)_2(\text{H}_2\text{O})_2]$ , has the same chemical empirical formula as another compound [Bandoli *et al.* (1976). *Inorg. Chim. Acta*, **20**, 71–78]. However, the title compound is a dimer arranged around an inversion centre, whereas Bandoli's compound is a chiral polymer. In the title compound, the  $\text{Cu}^{\text{II}}$  atom has a distorted tetragonal pyramidal coordination, formed by three Cl atoms, one N atom of the caffeine ligand and one O atom of a water molecule.

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## Comment

Caffeine (3,7-dihydro-1,3,7-trimethyl-1,4-purine-2,6-dione) is a purine alkaloid possessing pharmacological properties as a therapeutic agent with analeptic activity. Recently, the title compound, (I), has been synthesized. Among the 13 copper(II)–caffeine structures deposited in the Cambridge Structural Database (CONQUEST, Version 1.7; Allen, 2002), another compound (Bandoli *et al.*, 1976) has the same chemical empirical formula but with a different structure from (I). This prompted us to carry out the present structural study.



The asymmetric unit consists of one-half of the dinuclear complex, (I), which is arranged around an inversion centre (Fig. 1). The  $\text{Cu}^{\text{II}}$  atom is pentacoordinated by atom N1 from

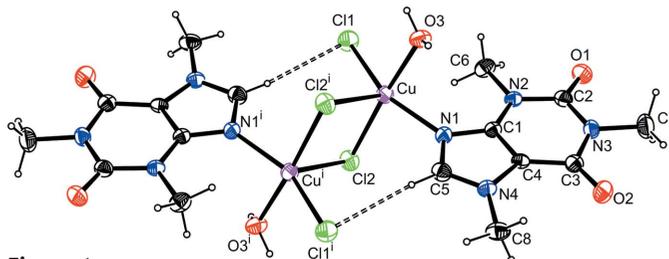
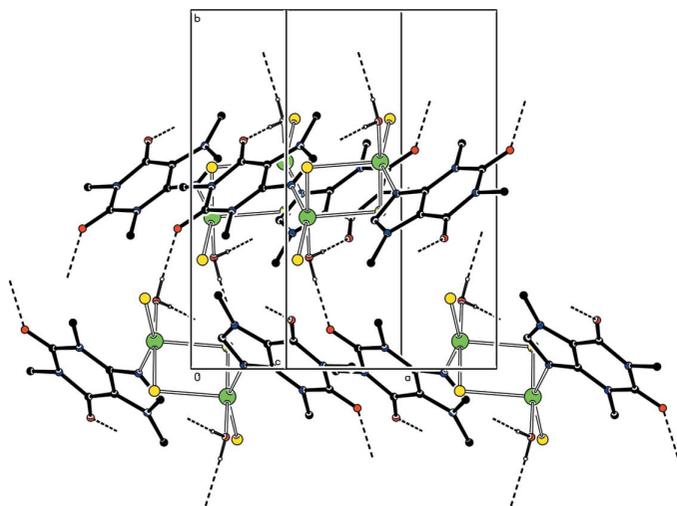


Figure 1

The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ ]. Hydrogen bonds are shown as dashed lines.


**Figure 2**

A packing diagram for (I), showing the hydrogen-bonding network. Hydrogen bonds are depicted by dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

the caffeine ligand, atom O3 from the H<sub>2</sub>O molecule, and atoms Cl1, Cl2 and the symmetry-related Cl2<sup>i</sup> [symmetry code: (i) 1 - x, 1 - y, 1 - z]. In (I), atoms Cl1 and Cl2 are *cis* to each other and two Cu<sup>II</sup> atoms are linked by double Cl bridges, Cl2 and Cl2<sup>i</sup>, to form a dimer, whereas in Bandoli's compound, two Cl atoms are *trans* to each other and the pentacoordinated Cu<sup>II</sup> atoms are linked by a single Cl bridge to form chiral polymeric chains.

The coordination polyhedron around the Cu<sup>II</sup> atom may be described as a distorted tetragonal pyramid. The caffeine imidazole atom N1, atom O3 from the water molecule, and atoms Cl1 and Cl2 lie in the basal plane, while atom Cl2<sup>i</sup> is located at the apex. The dihedral angle between the mean basal plane and the caffeine plane is 60.0 (4)°. This value is much less than in related copper(II)-purine compounds (Sletten, 1969; De Meester & Skapski, 1971; Biagini Cingi *et al.*, 1972; Bandoli *et al.*, 1976), where the corresponding dihedral angles are approximately 90°. This may be related to the occurrence of a weak C5-H5...Cl1<sup>i</sup> intramolecular hydrogen-bond interaction (Table 1). The Cu-Cl2<sup>i</sup> bond distance [2.6504 (11) Å] is obviously shorter than that observed in Bandoli's compound (Bandoli *et al.*, 1976), while the Cu-N1 and Cu-O3 bonds are slightly longer. The geometry of the caffeine ligand is consistent with our previous study (Jin *et al.*, 2005).

The crystal packing of (I) is stabilized by O-H...O hydrogen bonds which build up a three-dimensional network (Table 1 and Fig. 2).

## Experimental

Caffeine and CuCl<sub>2</sub>·4H<sub>2</sub>O in a molar ratio of 1:1 were mixed and dissolved in sufficient water by heating to 353 K, when a clear solution resulted. Crystals of (I) were formed by gradual evaporation of water over a period of one week at 293 K.

## Crystal data

[Cu<sub>2</sub>Cl<sub>4</sub>(C<sub>8</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 693.33  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 9.761 (2) Å  
*b* = 12.891 (3) Å  
*c* = 10.901 (2) Å  
 β = 110.64 (2)°  
*V* = 1283.6 (5) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.794 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 34 reflections  
 θ = 6.1–14.3°  
 μ = 2.12 mm<sup>-1</sup>  
*T* = 296 (2) K  
 Prism, green  
 0.32 × 0.30 × 0.30 mm

## Data collection

Siemens P4 diffractometer  
 ω scans  
 Absorption correction: ψ scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.504, *T<sub>max</sub>* = 0.536  
 2763 measured reflections  
 2393 independent reflections  
 1569 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.050  
 θ<sub>max</sub> = 25.5°  
*h* = 0 → 11  
*k* = 0 → 15  
*l* = -13 → 12  
 3 standard reflections  
 every 97 reflections  
 intensity decay: 0.5%

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030  
*wR* (*F*<sup>2</sup>) = 0.060  
*S* = 0.80  
 2392 reflections  
 172 parameters

H atoms treated by a mixture of independent and constrained refinement  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0292*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δσ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.30 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.33 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> -H... <i>A</i>
C5-H5...Cl1 <sup>i</sup>	0.93	2.62	3.544 (3)	172
O3-H3A...O2 <sup>ii</sup>	0.84 (1)	1.92 (1)	2.758 (3)	175 (3)
O3-H3B...O1 <sup>iii</sup>	0.85 (1)	1.90 (2)	2.708 (3)	159 (3)

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 1, -y + 1, -z + 2; (iii) x - ½, -y + ½, z - ½.

The H atoms of the water molecule were located in a difference Fourier map and incorporated in the refinement with O-H distances restrained to 0.85 (1) Å and H...H distances restrained to 1.39 (2) Å. H atoms attached to C atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of C-H = 0.96 (C<sub>methyl</sub>) or 0.93 Å (C<sub>aromatic</sub>), with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C<sub>aromatic</sub>) or 1.5*U*<sub>eq</sub>(C<sub>methyl</sub>).

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: SHELXTL; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1998).

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Bandoli, G., Cingibiagini, M., Clemente, D. A. & Rizzardi, G. (1976). *Inorg. Chim. Acta*, **20**, 71–78.  
 Biagini Cingi, M., Chiesi Villa, A., Gaetani Manfredotti, A. & Guastini, C. (1972). *Cryst. Struct. Commun.* **1**, 363–366.  
 Bruker (1998). SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Burnett, M. N. & Johnson, C. K. (1996). ORTEPIII. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

- De Meester, P. & Skapski, A. C. (1971). *J. Chem. Soc. A*, pp. 2167–2170.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Jin, Z.-M., Li, L., Hu, M.-L., Su, H. & Tong, C.-X. (2005). *Acta Cryst.* **E61**, m1849–m1851.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sletten, E. (1969). *Acta Cryst.* **B25**, 1480–1491.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.