

## A tetranuclear copper(II) cluster: bis( $\mu$ -4-chlorobenzoato- $\kappa^2$ O: $O'$ )- (4-chlorobenzoato- $\kappa^2$ O, $O'$ )(4-chloro- benzoato- $\kappa$ O)tetrakis( $\mu_3$ -2-pyridyl- methanolato- $\kappa^4$ N, $O$ : $O$ : $O$ )tetra- copper(II)

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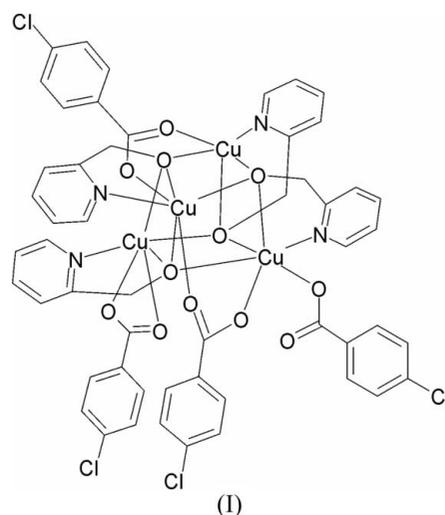
The title compound,  $[\text{Cu}_4(\text{C}_7\text{H}_4\text{ClO}_2)_4(\text{C}_6\text{H}_6\text{NO})_4]$ , consists of isolated tetranuclear clusters, where the  $\text{Cu}^{2+}$  cations are five- and sixfold coordinated by O atoms from the 4-chlorobenzoate anions and by pyridine N and methanolate O atoms from bidentate 2-pyridylmethanolate ligands. While three Cu atoms are six-coordinated by an  $\text{NO}_5$  donor set forming distorted octahedra, the fourth Cu atom is five-coordinated by an  $\text{NO}_4$  donor set forming a distorted tetragonal-pyramidal coordination around the Cu atom. The nucleus is a deformed cubane-like  $\text{Cu}_4\text{O}_4$  structure, with  $\text{Cu}\cdots\text{Cu}$  distances in the range 3.0266 (11)–3.5144 (13) Å.

### Comment

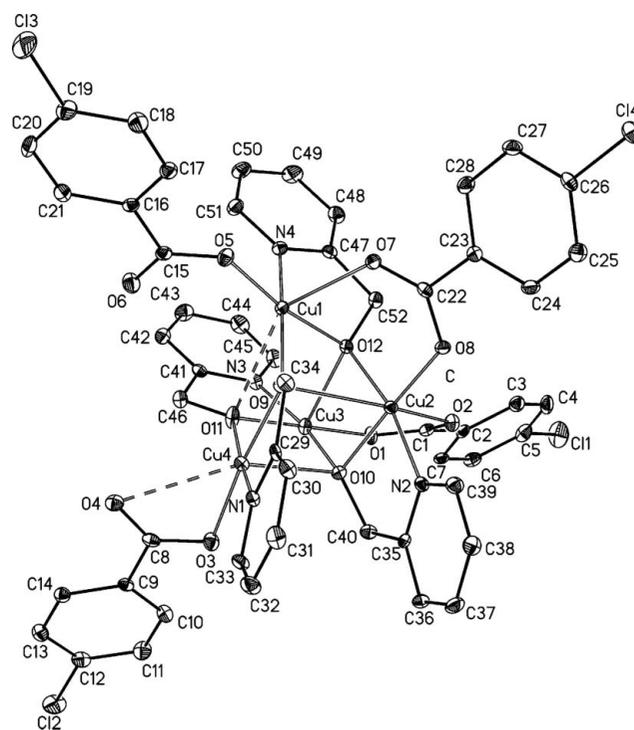
Much attention has been devoted in the past 20 years to the preparation and characterization of multinuclear metal complexes (Oshio & Ichida, 1995). These metal complexes have been prepared with the aim of providing new functional materials such as single-molecule magnets or catalysts (Sessoli *et al.*, 1993). In these complexes, the bridging ligands may provide superexchange pathways between the metal centres. Several tetrameric transition metal complexes with  $\mu_3$ -bridging 2-pyridylmethanolate anions have been crystallographically studied. These complexes form cubane-like core structures (Clemente-Juan *et al.*, 2000, 2002; Efthymiou *et al.*, 2009; Escuer *et al.*, 1999; Lecren *et al.*, 2008; Wang *et al.*, 2010; Yang *et al.*, 2003, 2005, 2006; Zhang *et al.*, 2010).

In this paper, we present an interesting structure, a tetrameric copper(II) complex, namely bis( $\mu$ -4-chlorobenzoato)(4-chlorobenzoato)(4-chlorobenzoato)tetrakis( $\mu_3$ -2-pyridyl-

methanolato)tetracopper(II), (I). The full tetranuclear molecule defining the asymmetric unit is shown in Fig. 1. The four  $\text{Cu}^{2+}$  cations and four  $\mu_3$ -bridging methanolate O atoms of the 2-pyridylmethanolate ligands form a deformed cubane-like  $\text{Cu}_4\text{O}_4$  core (Fig. 2). The distances between pairs of  $\text{Cu}^{2+}$  cations are in the range 3.0266 (11)–3.5144 (13) Å. Each pair of Cu atoms ( $\text{Cu1}\cdots\text{Cu2}$  and  $\text{Cu2}\cdots\text{Cu3}$ ) is also bridged by one carboxylate group of a 4-chlorobenzoate ligand (Fig. 2). Each  $\text{Cu}^{2+}$  ion is coordinated in a different coordination environment.

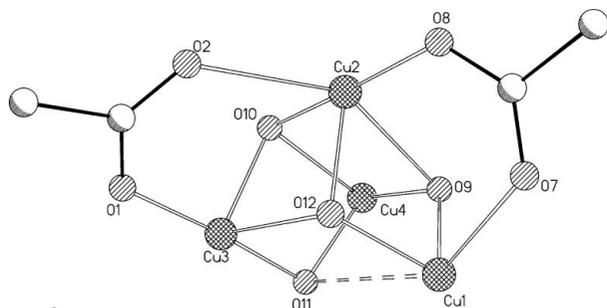


The Cu1 cation is six-coordinated by O and N atoms from chelating ligands and lies in the centre of a [4+1+1] coordi-



**Figure 1**

A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. The Cu4–O4 and Cu1–O11 semicoordinated bonds are drawn as dashed lines.



**Figure 2**  
The structure of the cubane-like core of tetrameric complex (I)

ation polyhedron. The axial Cu1–O11 semicoordination bond distance is 2.873 (2) Å. The tetragonal plane is formed by one pyridine N and one methanolate O atom from a chelating 2-pyridylmethanolate anion [Cu1–N4 = 1.988 (2) Å and Cu1–O12 = 1.974 (2) Å], one carboxylate O atom from a monodentate 4-chlorobenzoate anion [Cu1–O5 = 1.919 (2) Å] and one methanolate O atom from a neighbouring bridging 2-pyridylmethanolate anion [Cu1–O9 = 1.945 (2) Å]. The axial positions of the coordination polyhedron are occupied by one carboxylate O atom from a bridging 4-chlorobenzoate anion [Cu1–O7 = 2.385 (2) Å] and one methanolate O atom from a second neighbouring bridging 2-pyridylmethanolate anion [Cu1–O11 = 2.873 (2) Å].

The Cu2 atom has a tetragonal–bipyramidal [4+2] coordination environment. The tetragonal plane is built up by one pyridine N and one methanolate O atom from a chelating 2-pyridylmethanolate anion [Cu2–N2 = 1.998 (2) Å and Cu2–O10 = 1.957 (2) Å], one carboxylate O atom from a bridging 4-chlorobenzoate anion [Cu2–O8 = 1.932 (2) Å] and one methanolate O atom from a neighbouring bridging 2-pyridylmethanolate anion [Cu2–O12 = 1.965 (2) Å]. The axial positions of the tetragonal bipyramid are occupied by one carboxylate O atom from a second bridging 4-chlorobenzoate anion [Cu2–O7 = 2.607 (2) Å] and one methanolate O atom from a second neighbouring bridging 2-pyridylmethanolate anion [Cu2–O9 = 2.545 (2) Å].

The Cu3 cation is coordinated in a tetragonal–pyramidal [4+1] geometry. The tetragonal plane is formed by one pyridine N and one methanolate O atom from a chelating 2-pyridylmethanolate anion [Cu3–N3 = 2.008 (2) Å and Cu3–O11 = 1.913 (2) Å], one carboxylate O atom from a bridging 4-chlorobenzoate anion [Cu3–O1 = 1.918 (2) Å] and one methanolate O atom from a neighbouring bridging 2-pyridylmethanolate anion [Cu3–O10 = 1.955 (2) Å]. The axial position is occupied by one methanolate O atom from a second neighbouring bridging 2-pyridylmethanolate anion [Cu3–O12 = 2.303 (2) Å]. For this type of five-coordinate structure, the parameter  $\tau$  [ $\tau = (\alpha - \beta)/60$ , where  $\alpha$  and  $\beta$  are the equatorial angles] was introduced by Addison *et al.* (1984). The value of  $\tau$  ranges from 0 for perfectly tetragonal–pyramidal geometry to 1 for perfectly trigonal–bipyramidal geometry. In this case,  $\tau = 0.14$ , which favours the description as a tetragonal–pyramidal geometry.

The coordination polyhedron around Cu4 has [4+1+1] geometry. The Cu4 cation is coordinated by one pyridine N

and one methanolate O atom from a chelating 2-pyridylmethanolate anion [Cu4–N1 = 1.984 (2) Å and Cu4–O9 = 1.954 (2) Å], one carboxylate O atom from a chelating 4-chlorobenzoate anion [Cu4–O3 = 1.937 (2) Å] and one methanolate O atom from a neighbouring bridging 2-pyridylmethanolate anion [Cu4–O11 = 1.942 (2) Å] in the equatorial plane. The next two positions of the coordination polyhedron are occupied by one methanolate O atom from a neighbouring bridging 2-pyridylmethanolate anion [Cu4–O10 = 2.396 (2) Å] and one carboxylate O atom from a chelating 4-chlorobenzoate anion [Cu4–O4 = 2.811 (2) Å].

The packing in (I) is rather complex; the crystal structure does not contain medium–strong hydrogen bonds but the molecules are linked through weak C–H···O and C–H···Cl hydrogen-bonding interactions (Gilli & Gilli, 2009). There are three weak intramolecular C–H···O hydrogen bonds (entries 1–3 in Table 1). These complex molecules are in turn connected through weak intermolecular C–H···O hydrogen bonds (entries 4–7 in Table 1) and weak C–H···Cl hydrogen bonds (entries 8–9 in Table 1). These weak contacts are further reinforced by a C–H··· $\pi$  interaction (Suezawa *et al.* 2002), *viz.* C28–H28···Cg1<sup>vi</sup> [Cg1 is the centroid of the C2–C7 ring; symmetry code: (vi)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ], with H28···Cg1 = 2.62 Å and a shortest distance of H28···C4<sup>vi</sup> = 2.79 Å.

This communication reports the second known example of a tetragonal cubane-like copper(II) complex with  $\mu_3$ -bridging 2-pyridylmethanolate anions, the first being that reported by Ang *et al.* (2004). However, while in this latter complex all four Cu<sup>2+</sup> cations show the same type of coordination polyhedra, the title compound, as already described, does not. Examples of both types can be found among the reports in the literature dealing with cubane-like tetramers of different transition metals (nickel, iron and zinc) and  $\mu_3$ -bridging 2-pyridylmethanolate anions. Thus, in the two cubane-like tetrameric nickel(II) complexes reported by Zhang *et al.* (2010) and Efthymiou *et al.* (2009), all the Ni<sup>II</sup> cations have a similar coordination, with the metal centres being connected *via* four  $\mu_3$ -bridging 2-pyridylmethanolate anions. Different coordination geometries, on the other hand, can be found in the nickel(II) complex reported by Clemente-Juan *et al.* (2000) and the two iron(II) complexes reported by Clemente-Juan *et al.* (2002), where only one  $\mu_3$ -bridging 2-pyridylmethanolate anion connects three of the four metal centres; the remaining bridges linking the metal ions are provided by different ligands.

All the cases discussed so far correspond to cubane-like complexes without internal crystallographic symmetry, but there are, in addition, reported examples of tetranuclear cubane-like metal complexes presenting a higher degree of symmetry in tetragonal space groups where only one-quarter of the molecule is independent, such as those presented by Wang *et al.* (2010), Yang *et al.* (2003, 2005, 2006) and Escuer *et al.* (1999).

Since the bridging ligands in cubane-like complexes may provide superexchange pathways between the metal centres, magnetic susceptibility measurements in (I) are underway.

## Experimental

For the preparation of the title compound,  $\text{Cu}(\text{4-ClC}_6\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$  (0.001 mol, 0.411 g) was dissolved in methanol (50 ml) and treated with 2-pyridylmethanol (0.001 mol, 0.10 ml) in a 1:1 molar ratio. The mixture was stirred and left to stand at room temperature, giving crystals of (I) suitable for X-ray analysis (yield 85%). Analysis found: C 52.45, H 3.71, N 4.68, Cu 10.78%; calculated: C 52.67, H 3.74, N 4.73, Cu 10.72%.

### Crystal data

$[\text{Cu}_4(\text{C}_7\text{H}_4\text{ClO}_2)_4(\text{C}_6\text{H}_6\text{NO})_4]$	$V = 10541(6) \text{ \AA}^3$
$M_r = 1308.84$	$Z = 8$
Monoclinic, $I2/a$	Mo $K\alpha$ radiation
$a = 20.326(6) \text{ \AA}$	$\mu = 1.86 \text{ mm}^{-1}$
$b = 14.184(4) \text{ \AA}$	$T = 100 \text{ K}$
$c = 36.696(13) \text{ \AA}$	$0.45 \times 0.35 \times 0.25 \text{ mm}$
$\beta = 94.89(3)^\circ$	

### Data collection

Kuma KM-4 CCD area-detector diffractometer	36942 measured reflections
Absorption correction: analytical <i>CrysAlis RED</i> (Agilent, 2011)	12348 independent reflections
$T_{\min} = 0.467$ , $T_{\max} = 0.659$	8586 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	685 parameters
$wR(F^2) = 0.069$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
12348 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C34—H34A $\cdots$ O5	0.99	2.59	3.116 (3)	114
C39—H39 $\cdots$ O8	0.95	2.55	3.034 (3)	112
C46—H46A $\cdots$ O6	0.99	2.52	3.462 (3)	158
C33—H33 $\cdots$ O4 <sup>i</sup>	0.95	2.46	3.010 (3)	117
C36—H36 $\cdots$ O6 <sup>ii</sup>	0.95	2.41	3.221 (3)	143
C37—H37 $\cdots$ O4 <sup>ii</sup>	0.95	2.46	3.279 (3)	145
C48—H48 $\cdots$ O8 <sup>iii</sup>	0.95	2.53	3.401 (3)	152
C30—H30 $\cdots$ Cl3 <sup>iv</sup>	0.95	2.78	3.501 (3)	134
C34—H34A $\cdots$ Cl2 <sup>v</sup>	0.99	2.75	3.337 (3)	118

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

The structure was refined in the nonconventional monoclinic space group  $I2/a$ , a variant of  $C2/c$ . H atoms were positioned in ideal positions, with  $C-H = 0.95 \text{ \AA}$  for aromatic H atoms and  $C-H = 0.99 \text{ \AA}$  for methylene H atoms, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrysAlis CCD* (Agilent, 2011); cell refinement: *CrysAlis RED* (Agilent, 2011); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3141). Services for accessing these data are described at the back of the journal.

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