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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.031
 wR factor = 0.081
Data-to-parameter ratio = 19.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis(μ -2-nitrobenzoato- $\kappa^2\text{O}:\text{O}'$)bis[aqua-
copper(II)] ethanol disolvate

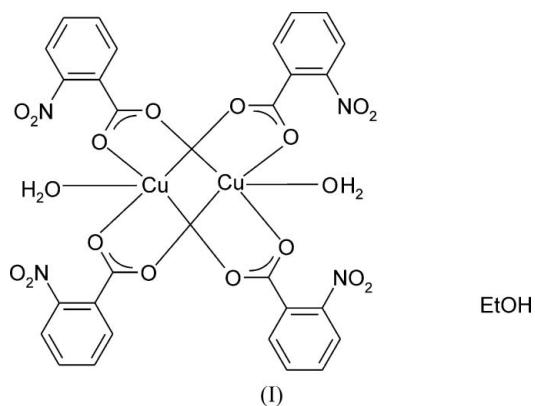
The title complex, $[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{C}_2\text{H}_6\text{O}$, forms a dimer of the paddle-wheel type located on a crystallographic inversion center. The two Cu^{2+} cations [$\text{Cu} \cdots \text{Cu} = 2.6543(10)$ Å] are connected by four 2-nitrobenzoate ligands. The apical positions of the square-pyramidal copper coordination polyhedra are occupied by the water O atoms. The two ethanol solvent molecules are linked to complex molecules *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, which create one-dimensional chains of $R_2^2(13)$ and $R_4^4(12)$ rings. A π - π stacking interaction is observed between symmetry-related benzene rings of the 2-nitrobenzoate anions.

Received 21 October 2006

Accepted 29 October 2006

Comment

Different benzoates, especially salicylates and fenamates, are known to play an important role in human medicine (Sorenson, 1976; Weder *et al.*, 2002). Our effort in this field has been targeted to substituted benzoate complexes. Some papers dealing with mononuclear or binuclear copper(II) 2-nitrobenzoate complexes have been published recently (Chi *et al.*, 2006; Stachová, Melník *et al.*, 2006; Stachová, Korabik *et al.*, 2006; Deutsch *et al.*, 2006; Stachová *et al.*, 2004) and they confirm an interesting range of bonding versatility of the 2-nitrobenzoate ligand. Moreover, the co-occurrence of different polymorphic structures was confirmed (Deutsch *et al.*, 2006). We present here a new centrosymmetric binuclear 2-nitrobenzoate-copper(II) complex with water molecules as ligands and ethanol as solvent, $[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{C}_2\text{H}_6\text{O}$ (I) (Fig. 1).



The Cu^{2+} cation is coordinated by four carboxylate O atoms from four 2-nitrobenzoate anions and one water O atom in a square-pyramidal geometry; the Cu^{2+} cations are bridged by four 2-nitrobenzoate anions. The distance between the two Cu^{2+} cations is 2.6543(10) Å, which is similar to that in related Cu^{2+} complexes: two forms of $[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{H}_2\text{O})_2]$, (II)

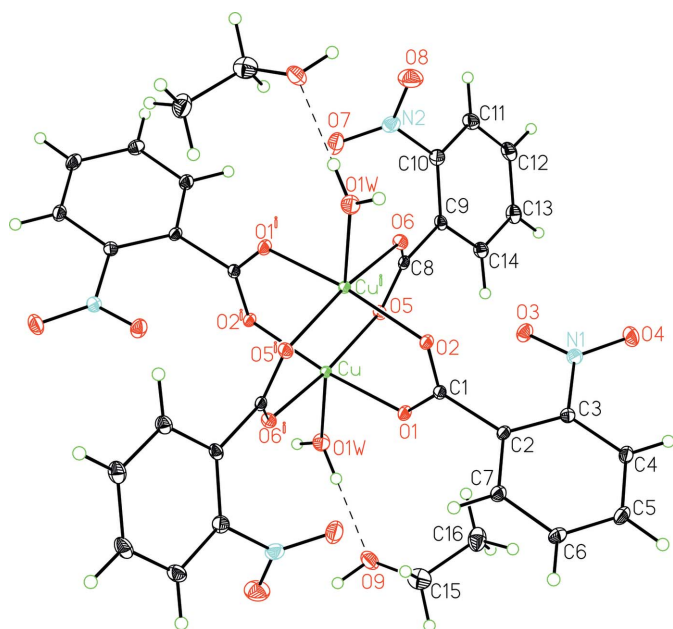


Figure 1
The molecular structure of (I), with the atom numbering scheme [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. Displacement ellipsoids are drawn at the 30% probability level.

and (III) (Deutsch *et al.* 2006), and $[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, (IV) (Stachová *et al.* 2004). The Cu^{2+} atoms in (I) are each displaced towards their bound water O atom from the $\text{O1/O2}^i/\text{O5/O6}^i$ [symmetry code: (i) $1 - x, 1 - y, 1 - z$] plane by 0.198 (1) Å. The $\text{Cu}-\text{O}(\text{carboxyl})$ bond distances [1.9657 (12)–1.9922 (12) Å] are shorter than the $\text{Cu}-\text{O1W}$ bond length [2.1331 (15) Å] in (I), and they are similar to $\text{Cu}-\text{O}(\text{carboxylate})$ and $\text{Cu}-\text{O}(\text{water})$ bond lengths in (II)–(IV).

Within each stack of the title compound, a one-dimensional chain of $R_2^3(13)$ and $R_4^4(12)$ (Bernstein *et al.*, 1995) rings parallel to the bc direction is present; the two rings are connected *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds (Fig. 2). Details of the hydrogen-bonding geometry are given in Table 2.

$\pi-\pi$ stacking interactions (Janiak, 2000) are also present between two symmetry-related adjacent benzene rings (C9–C14) of the 2-nitrobenzoate anions [$Cg \cdots Cg^{\text{iii}} = 3.69$ Å, where Cg is the centroid of the benzene ring; symmetry code: (iii) $-x, -y + 1, -z$; distance between two benzene ring planes is 3.40 Å], similar to those in diaquatetrakis(4-nitrobenzoato- O, O')dicopper(II) acetone disolvate (Kristiansson & Tergenius, 2001).

This structure is completely different from that of (IV) and it is very similar to one of polymorphic pair (II) (Deutsch *et al.* 2006). Owing to the presence of ethanol within channels along the c axis, the shortest $\text{Cu} \cdots \text{Cu}$ interdimer distance in (I) is 5.933 (1) Å, while in (II) it is 5.25 Å. Similarity was also found in the relative orientation of the benzene rings and the carboxylate groups expressed by the angle φ_{rot} (Kawata *et al.* 1992). The φ_{rot} angles for (I) are 82.9 (1) and 41.8 (1)°, and for (II) they are 84.7 and 46.5°.

Experimental

An ethanol solution of copper(II) acetate (1 mmol in *ca* 15 ml of ethanol) was stirred with 3-pyridylmethanol (3-pyme, 1 mmol). 2-Nitrobenzoic acid (2 mmol) was then added. The reaction mixture was stirred until the precipitation of a light blue powder product had finished. The product $[\text{Cu}(\text{C}_7\text{H}_4\text{NO}_4)_2(3\text{-pyme})_2]$ was filtered off and dried at ambient temperature and a turquoise mother liquid was left for crystallization. A mixture of green and blue crystals was obtained from the mother liquid. The green crystals were separated by hand and used for X-ray structure determination.

Crystal data

$[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{C}_2\text{H}_6\text{O}$	$Z = 2$
$M_r = 919.72$	$D_x = 1.711 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.326$ (3) Å	$\mu = 1.29 \text{ mm}^{-1}$
$b = 20.028$ (6) Å	$T = 100$ (2) K
$c = 10.803$ (3) Å	Block, green
$\beta = 97.77$ (3)°	$0.59 \times 0.55 \times 0.48 \text{ mm}$
$V = 1784.9$ (10) Å ³	

Data collection

Kuma KM-4 CCD diffractometer	22049 measured reflections
ω scans	5144 independent reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2003)	4424 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.494, T_{\text{max}} = 0.636$	$R_{\text{int}} = 0.027$
	$\theta_{\text{max}} = 30.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.2345P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.62 \text{ e } \text{Å}^{-3}$
5144 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{Å}^{-3}$
270 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

$\text{Cu}-\text{O1W}$	2.1331 (15)	$\text{Cu}-\text{O5}$	1.9664 (12)
$\text{Cu}-\text{O1}$	1.9746 (12)	$\text{Cu}-\text{O6}^i$	1.9657 (12)
$\text{Cu}-\text{O2}^i$	1.9922 (12)	$\text{Cu}-\text{Cu}^i$	2.6543 (10)
$\text{O1}-\text{Cu}-\text{O1W}$	91.37 (5)	$\text{O1}-\text{Cu}-\text{O5}$	90.28 (5)
$\text{O2}^i-\text{Cu}-\text{O1W}$	100.11 (5)	$\text{O1}-\text{Cu}-\text{O6}^i$	90.04 (5)
$\text{O5}-\text{Cu}-\text{O1W}$	97.18 (6)	$\text{O2}^i-\text{Cu}-\text{O5}$	89.56 (5)
$\text{O6}^i-\text{Cu}-\text{O1W}$	94.38 (6)	$\text{O2}^i-\text{Cu}-\text{O6}^i$	87.82 (5)
$\text{O1}-\text{Cu}-\text{O2}^i$	168.45 (5)	$\text{O5}-\text{Cu}-\text{O6}^i$	168.42 (5)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O9}-\text{H9O} \cdots \text{O2}^{\text{ii}}$	0.84	2.10	2.852 (2)	149
$\text{O1W}-\text{H1W} \cdots \text{O9}$	0.84 (1)	1.88 (1)	2.715 (2)	178 (2)
$\text{O1W}-\text{H2W} \cdots \text{O8}^{\text{ii}}$	0.84 (1)	2.29 (1)	2.991 (2)	141 (2)

Symmetry code: (ii) $x + 1, y, z$.

All H atoms of C–H (aromatic, methylene and methyl) bonds were placed in calculated positions (0.95, 0.99 and 0.98 Å, respectively) and refined using a riding model; isotropic displacement parameters were fixed [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic or methylene C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{methyl C})$]. The hydroxyl H atom was placed in a calculated position (O–H = 0.84 Å); $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$. The water H atoms were located in a difference map and refined with the O–H distances restrained to 0.84 (1) Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

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).

We thank the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences for financial support (1/2452/05), and the Research and Development Support Agency for financial support (APVT-20-005504).

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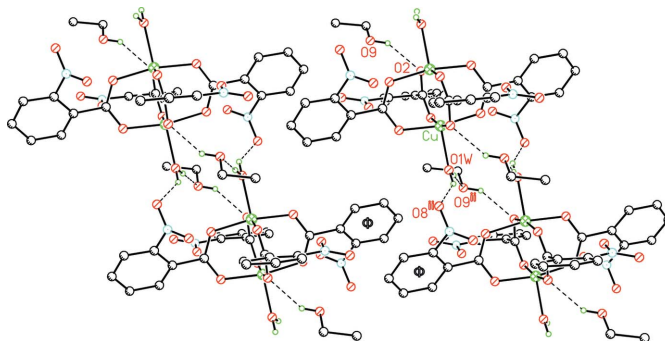


Figure 2

The O–H...O hydrogen bonds (dashed lines) and π – π stacking interaction in the packing of (I), viewed approximately along the *a* axis [symmetry code: (ii) $x + 1, y, z$].