

Bis[μ -3-phosphonopropionato(2-)]bis[aqua-(1,10-phenanthroline)copper(II)]

Xian-Ming Zhang,^a Rui-Qin Fang,^a Hai-Shun Wu^a and Seik Weng Ng^{b*}

^aSchool of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, People's Republic of China, and ^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.048

wR factor = 0.133

Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Each Cu atom in the centrosymmetric dinuclear title compound, $[\text{Cu}_2(\text{C}_3\text{H}_5\text{O}_5\text{P})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$, is chelated by an *N*-heterocycle and is also coordinated by a molecule of water. The two Cu atoms are bridged by the 3-phosphonopropionato(2-) unit, giving rise to a square-pyramidal geometry for the metal centre. The molecules are linked by hydrogen bonds into a layer structure.

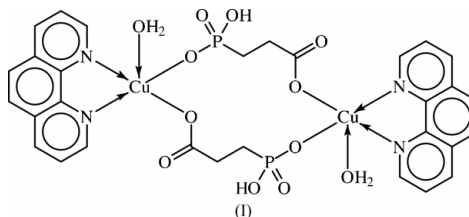
Received 4 November 2003

Accepted 17 November 2003

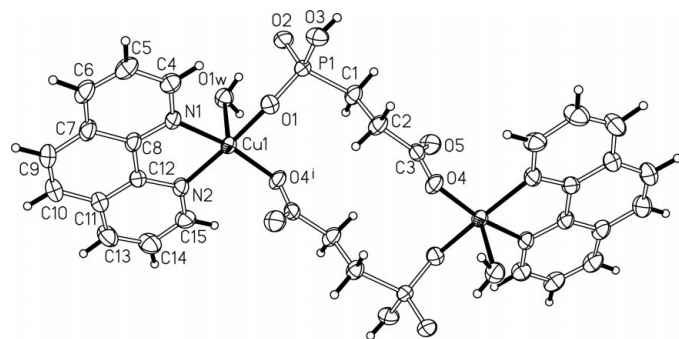
Online 22 November 2003

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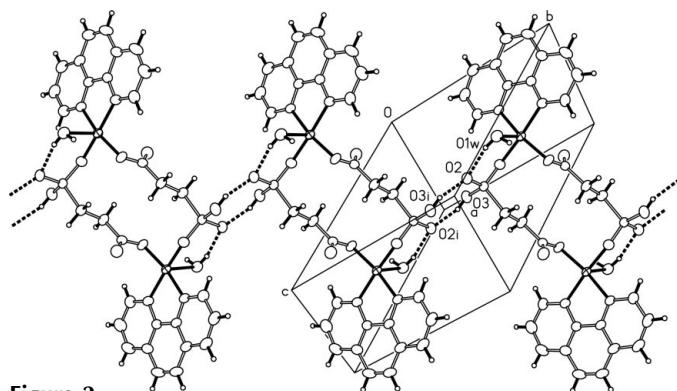
Whereas metal phosphonates, which have a variety of applications (Clearfield, 1998; Zhu *et al.*, 2000), have been well studied, only a few metal derivatives of the phosphonocarboxylic acids, such as phosphonoacetic acid and 3-phosphonopropionic acid, have been characterized to date (Stock *et al.*, 2000). The phosphonoacetate homologue was first crystallographically authenticated in the salt $\text{K}_4[\text{Cu}(\text{O}_2\text{CCH}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}] \cdot 6\text{H}_2\text{O}$ (Afonin *et al.*, 1998). The Cu 3-propionato(3-) analogue has also been authenticated, in $[\text{Cu}_3(\text{O}_2\text{CCH}_2\text{CH}_2\text{PO}_3)_2] \cdot 8\text{H}_2\text{O}$ (Britel *et al.*, 1985). The present Cu complex was synthesized by reacting a copper salt with trimethyl 3-phosphonopropionate under hydrothermal conditions; the ester underwent cleavage of the three ester bonds to yield the title aquacopper derivative, (I), which crystallizes as a centrosymmetric dimer.



The Cu atoms in (I) are each chelated by an *N*-heterocycle. The two Cu atoms are bridged by the 3-phosphonopropionato(2-) unit and they are also each coordinated by one water molecule, giving rise to a square-pyramidal geometry for the metal atom (Fig. 1, Table 1). The molecules are linked by hydrogen bonds (Table 2) into a layer structure. The interdimer hydrogen bond involving the $-\text{PO}_3$ unit $[\text{O}3 \cdots \text{O}2^i 2.569(4)\text{ \AA}$; symmetry code: (i) $1 - x, 1 - y, 1 - z$] is particularly short and leads to the formation of a linear chain (Fig. 2). The doubly bonded O atom is also involved in an intradimer hydrogen bond to the water molecule $[\text{O}1\text{W} \cdots \text{O}2 2.732(4)\text{ \AA}]$. The interchain interaction $\text{O}1\text{W} \cdots \text{O}4^{ii}$ $[2.789(4)\text{ \AA}$; symmetry code: (ii) $x - 1, y, z$] gives rise to a layer structure. The bond dimensions within the anionic ligand of (I) are comparable with those found in ammonium salts of the parent acid (Bowes *et al.*, 2003).


Figure 1

A view of the dimer of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $2 - x, 2 - y, 1 - z$].


Figure 2

A view of the linear chain structure in (I) arising from the short interdimer hydrogen bond [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

Experimental

Copper diacetate dihydrate (0.20 g, 1 mmol), trimethyl 3-phosphonopropionate (0.23 g, 1 mmol), 1,10-phenanthroline (0.20 g, 1 mmol) and water (7 ml) were placed in a 15 ml Teflon-lined stainless-steel bomb, which was then heated at 433 K for 120 h. The bomb was cooled slowly to room temperature and blue needle-shaped crystals of (I) were isolated in about 50% yield. A block was cut from a needle for the diffraction measurements. CHN analysis found: C 43.50, H 3.69, N 6.72%; calculated for $C_{30}H_{30}Cu_2N_4O_{12}$: C 43.54, H 3.65, N 6.77%.

Crystal data

$[Cu_2(C_3H_5O_5P)_2(C_{12}H_8N_2)_2(H_2O)_2]$	$Z = 1$
$M_r = 827.60$	$D_x = 1.706 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.948 (1) \text{ \AA}$	Cell parameters from 1568 reflections
$b = 10.384 (2) \text{ \AA}$	$\theta = 2.8\text{--}25.7^\circ$
$c = 11.625 (2) \text{ \AA}$	$\mu = 1.49 \text{ mm}^{-1}$
$\alpha = 111.707 (2)^\circ$	$T = 298 (2) \text{ K}$
$\beta = 96.514 (2)^\circ$	Block, blue
$\gamma = 109.965 (2)^\circ$	$0.28 \times 0.24 \times 0.22 \text{ mm}$
$V = 805.6 (2) \text{ \AA}^3$	

Data collection

Bruker APEX area-detector diffractometer	3338 independent reflections
φ and ω scans	2651 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.027$
$T_{\text{min}} = 0.539, T_{\text{max}} = 0.735$	$\theta_{\text{max}} = 27.0^\circ$
4524 measured reflections	$h = -10 \rightarrow 9$
	$k = -13 \rightarrow 11$
	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.133$
 $S = 1.05$
 3338 reflections
 235 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0715P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1—O1	1.940 (2)	Cu1—N1	2.021 (3)
Cu1—O4 ⁱ	1.947 (2)	Cu1—N2	2.029 (3)
Cu1—O1w	2.287 (3)		
O1—Cu1—O4 ⁱ	93.8 (1)	O4 ⁱ —Cu1—N1	167.9 (1)
O1—Cu1—O1w	92.6 (1)	O4 ⁱ —Cu1—N2	93.4 (1)
O1—Cu1—N1	90.2 (1)	O1w—Cu1—N1	96.5 (1)
O1—Cu1—N2	169.6 (1)	O1w—Cu1—N2	94.2 (1)
O4 ⁱ —Cu1—O1w	94.7 (1)	N1—Cu1—N2	81.3 (1)

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

Table 2

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

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1w—H1w1 \cdots O2	0.84 (1)	1.91 (1)	2.732 (4)	167 (4)
O1w—H1w2 \cdots O4 ⁱ	0.83 (1)	2.19 (3)	2.789 (4)	129 (4)
O3—H3O \cdots O2 ⁱⁱ	0.84 (1)	1.76 (2)	2.569 (4)	162 (4)

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 1 - y, 1 - z$.

The water H atoms and the H atom belonging to the PO_3 group were located and refined, with distance restraints of $O\text{—}H = 0.85 (1)$ and $H\cdots H = 1.38 (1) \text{ \AA}$. The aliphatic and aromatic H atoms were placed in calculated positions and refined using a riding model, with C—H distances of 0.97 (aliphatic) and 0.93 \AA (aromatic), and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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