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Di-μ-phosphonomethylcarboxylato-bis-[(1,10-phenanthroline)copper(II)] dihydrate

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Key indicators

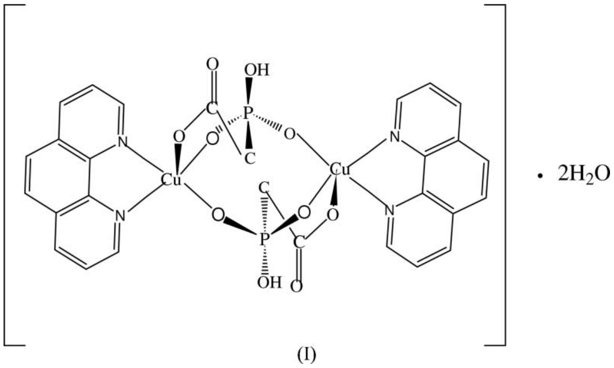
Single-crystal X-ray study
T = 288 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.078
Data-to-parameter ratio = 15.8

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

In the title dinuclear complex, $[Cu_2(C_2H_3O_5P)_2(C_{12}H_{10}N_2)_2]\cdot 2H_2O$, the unique Cu^{II} atom is coordinated in the basal plane by two N atoms from a 1,10-phenanthroline ligand and two (P—O) O atoms from a phosphonocarboxylate ligand, while the distorted square-pyramidal coordination is completed by the apical coordination of a (C—O) O atom from a phosphonocarboxylate ligand. The phosphonocarboxylate system acts as a tribidendate bridging ligand, forming a centrosymmetric dimer. In the crystal structure, molecules are linked *via* O—H···O hydrogen bonds to form a two-dimensional framework. In addition, significant π–π stacking interactions contribute to the stabilization of the structure.

Comment

Metal phosphonates are important in science and industry (Cheetham *et al.*, 1999), having applications such as catalysis, adsorption and separation (Bhardwaj *et al.*, 1993; Alberti *et al.*, 1996), and the study of dinuclear complexes of copper(II) is a very active research field (Melnik *et al.*, 1998). Organophosphonate anions have several potential donor atoms and thus can act as polyfunctional ligands, connecting inorganic frameworks (Maeda, 2004). Depending on the metal ion, this anion can coordinate in three different modes, *viz.* O_{POH}, O_{PO} and O_{CO}. The first structure determination of a phosphonoacetic acid complex was $K_4[Cu(O_3PCH_2COO)_2(H_2O)]\cdot 6H_2O$ (Afonin *et al.*, 1998). Since then, several other structures have been reported, *e.g.* $[Al(O_3PCH_2COO)]\cdot 3H_2O$ (Hix *et al.*, 1998) and a series of isostructural mononuclear phosphonoacetic acid complexes with Mg^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+} and Cu^{2+} (Slepokura *et al.*, 2002).



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1 and selected geometric parameters are given in Table 1. In the centrosymmetric dinuclear complex, the phosphonocarboxylate ligands act as tribidentate bridges,

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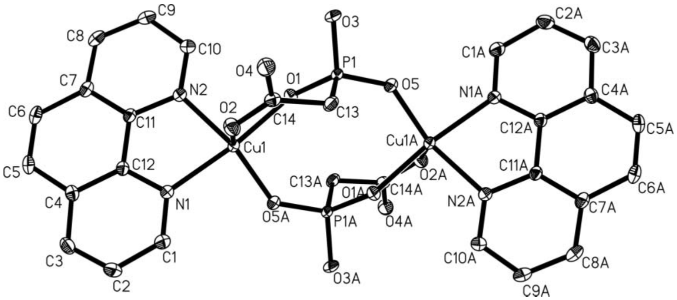

Figure 1
View of (I), showing displacement ellipsoids drawn at the 30% probabilty level. H atoms have been omitted for clarity. The suffix A indicates the symmetry position ($1 - x, 1 - y, 2 - z$).

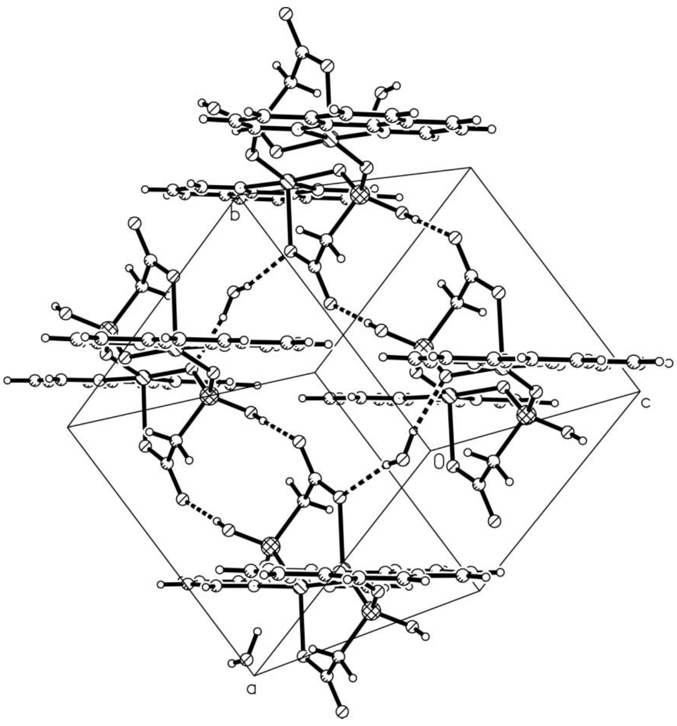

Figure 2
Packing diagram of (I), showing hydrogen bonds as dashed lines.

forming two six-membered chelate rings. The interdimer Cu1$\cdots$Cu1($1 - x, 1 - y, 2 - z$) distance is 5.068 (2) Å. The Cu^{II} atom has a distorted square-pyramidal coordination. Atoms O1, O5^i, N1 and N2 [symmetry code: (i) $1 - x, 1 - y, 2 - z$] form the basal plane and atom O2 is coordinated in the apical position. A typical 4+1 square-pyramidal environment around each Cu^{II} atom is formed. In addition, two uncoordinated water molecules complete the formula unit. In the phosphonate ligand, the O3—P1—O5 angle [115.35 (8)°] is larger than normal and the O5—P1—C13—C14 torsion angle is −175.06 (13)°, suggesting conformational rigidity around the P—C bond and that atom O5 favours being antiperiplanar to atom C14 (Bryndal *et al.*, 2003).

In the crystal structure, complex molecules are linked through one type of O—H$\cdots$O hydrogen bond, forming one-dimensional chains in the *b*-axis direction, while further O—H$\cdots$O hydrogen bonds involving the uncoordinated water molecules link molecules into a two-dimensional network (Table 2 and Fig. 2) which includes $R_6^6(22)$ rings (Etter *et al.*, 1990). Significant π–π stacking interactions [$Cg1\cdots Cg1$ = 3.5728 (14) and $Cg2\cdots Cg2$ = 3.5863 (13) Å; *Cg*1 and *Cg*2 are the centroids of atoms N2/C7—C10/C11 and C4—C12, respectively] also contribute to the stabilization of the crystal structure.

Experimental

The title compound was obtained as blue blocks by slow evaporation of a concentrated aqueous methanol solution (1:2) containing stoichiometric amounts of $Cu(Ac)_2 \cdot H_2O$, 1,10-phenanthroline and phosphonoacetic acid.

Crystal data

$[Cu_2(C_2H_3O_5P)_2(C_{12}H_{10}N_2)_2] \cdot 2H_2O$
M_r = 799.57
Triclinic, $P\bar{1}$
a = 8.1701 (16) Å
b = 8.6157 (17) Å
c = 11.698 (2) Å
α = 103.58 (3)°
β = 104.18 (3)°
γ = 105.03 (3)°
V = 730.9 (3) Å^3
Z = 1
D_x = 1.817 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5393 reflections
θ = 1.9–29.7°
μ = 1.64 mm^{-1}
T = 288 (2) K
Block, blue
0.25 × 0.20 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.679, T_{max} = 0.755
8861 measured reflections
3553 independent reflections
3272 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 29.7°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.078
S = 1.04
3553 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.2322P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O5^i	1.8340 (13)	P1—O3	1.4816 (13)
Cu1—N2	1.9578 (14)	P1—O5	1.5039 (14)
Cu1—O1	1.9842 (15)	P1—O1	1.6024 (15)
Cu1—N1	2.0757 (18)	P1—C13	1.8019 (19)
Cu1—O2	2.2774 (14)		
O5^i—Cu1—N2	155.95 (7)	O1—Cu1—N1	170.10 (5)
O5^i—Cu1—O1	94.68 (6)	O5^i—Cu1—O2	109.19 (6)
N2—Cu1—O1	93.67 (7)	N2—Cu1—O2	93.10 (6)
O5^i—Cu1—N1	90.08 (6)	O1—Cu1—O2	91.34 (6)
N2—Cu1—N1	78.66 (7)	N1—Cu1—O2	95.29 (6)
O4—C14—C13—P1	−112.56 (15)	O1—P1—C13—C14	−48.74 (15)
O2—C14—C13—P1	67.3 (2)	O3—P1—C13—C14	70.19 (14)
O5—P1—C13—C14	−175.06 (13)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*B*···O1	0.84 (3)	2.11 (3)	2.937 (2)	167 (3)
O6—H6···O2$^{\rm ii}$	0.82 (3)	2.22 (3)	3.026 (2)	168 (3)
O3—H3*A*···O4$^{\rm iii}$	0.82	1.80	2.599 (2)	167 (1)

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

H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.93 Å; $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) and C—H = 0.97 Å; $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for phenanthroline and methylene H atoms, respectively. H atoms bonded to O atoms were refined with O—H distances restrained to 0.82 (2)–0.85 (2) Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) or 1.2$U_{\rm eq}$(O$_{\rm water}$).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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