

**[Hydrogen *N*-(phosphonomethyl)imino-diacetato](1,10-phenanthroline)copper(II) trihydrate: a low-temperature redetermination**Filipe A. Almeida Paz,<sup>a\*</sup> Fa-Nian Shi,<sup>a</sup> Tito Trindade,<sup>a</sup> Jacek Klinowski<sup>b</sup> and João Rocha<sup>a</sup><sup>a</sup>Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal, and<sup>b</sup>Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

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**Key indicators**

Single-crystal X-ray study

T = 180 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.038

wR factor = 0.089

Data-to-parameter ratio = 14.8

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

The room-temperature crystal structure of the title compound,  $[\text{Cu}(\text{H}_2\text{pmida})(\text{phen})]\cdot 3\text{H}_2\text{O}$  [where  $\text{H}_2\text{pmida}^{2-}$  is hydrogen *N*-(phosphonomethyl)iminodiacetate,  $\text{C}_5\text{H}_{10}\text{NO}_7\text{P}^{2-}$ , and phen is 1,10-phenanthroline,  $\text{C}_{12}\text{H}_8\text{N}_2$ ], was recently determined by Pei Lu, Ke, Li, Qin, Zhou, Wu & Du [*Struct. Chem.* (2004), **15**, 207–210]. We report here a redetermination, at 180 (2) K, with greatly improved precision. Hydrogen bonds lead to the formation of one-dimensional tapes which run along the [100] direction of the unit cell. Adjacent tapes are interconnected *via*  $\pi$ - $\pi$  offset stacking (between the 1,10-phenanthroline ligands) and by hydrogen bonds involving the water molecules of crystallization.

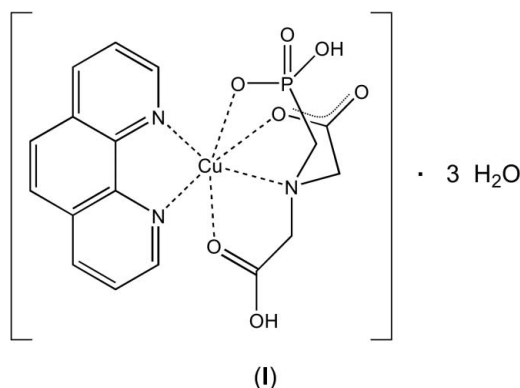
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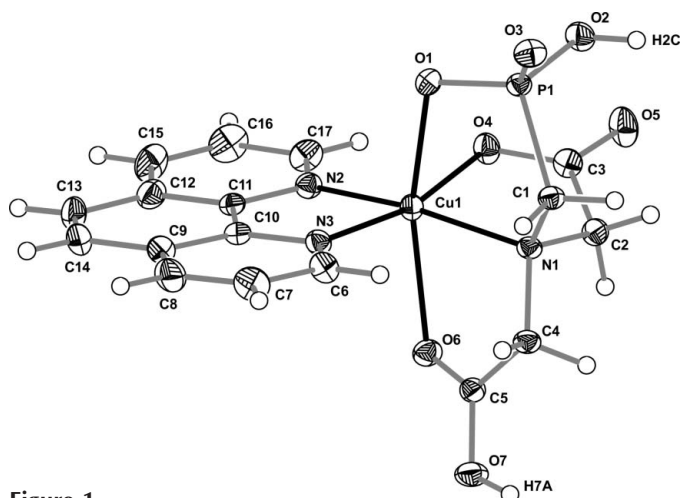
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**Comment**

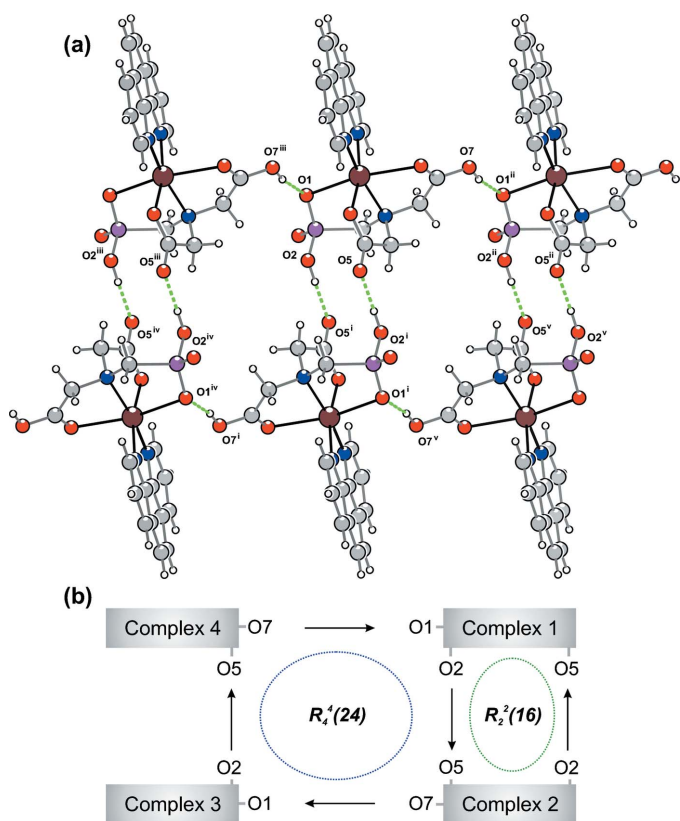
During the course of our research on novel crystalline organic–inorganic hybrid materials (Almeida Paz, Khimyak *et al.*, 2002; Almeida Paz *et al.*, 2005; Almeida Paz & Klinowski, 2004*a,b*), containing organic ligands with chelating and highly flexible ‘arms’, such as diethylenetriaminepentaacetic acid (Almeida Paz, Bond *et al.*, 2002), nitrilotriacetic acid (Almeida Paz & Klinowski, 2003) and *N*-(phosphonomethyl)iminodiacetic acid ( $\text{H}_4\text{pmida}$ ) (Mafra *et al.*, 2005; Shi *et al.*, 2005; Almeida Paz *et al.*, 2004), we recently isolated, in quantitative yield, large single crystals of the title compound, (I), which is composed of discrete complexes of  $\text{Cu}^{2+}$  with 1,10-phenanthroline (phen) and  $\text{H}_2\text{pmida}^{2-}$  ligands, co-crystallizing with three solvent molecules in space group  $P\bar{1}$ .



Although the crystal structure of this compound has recently been reported (Pei *et al.*, 2004), we redetermined it at 180 (2) K, with a final *R* value of 0.0376, to gain more precise data for our studies of the magnetic properties of such crystalline hybrid materials. The low-temperature redetermination allowed the direct location of all H atoms associated with the protonated carboxylic and phosphonic acid groups, and with the three water molecules of crystallization, thus giving a



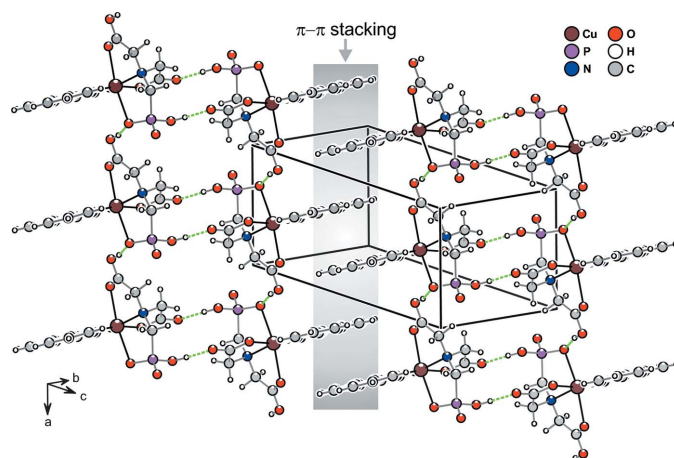
**Figure 1**  
A view of the  $[\text{Cu}(\text{H}_2\text{pmida})(\text{phen})]$  complex molecule present in the crystal structure of the title compound, showing the labelling scheme for all non-H atoms and for the two H atoms belonging to the carboxylic and phosphonic acid groups. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.



**Figure 2**  
Hydrogen bonding in (I) represented as green-filled dashed bonds giving a one-dimensional tape running along the  $[100]$  direction of the unit cell with a schematic diagram showing the two graph-set motifs, *viz.*  $R_2^2(16)$  and  $R_4^4(24)$ . [Symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $1+x, y, z$ ; (iii)  $-1+x, y, z$ ; (iv)  $-x, 1-y, -z$ ; (v)  $2-x, 1-y, -z$ .]

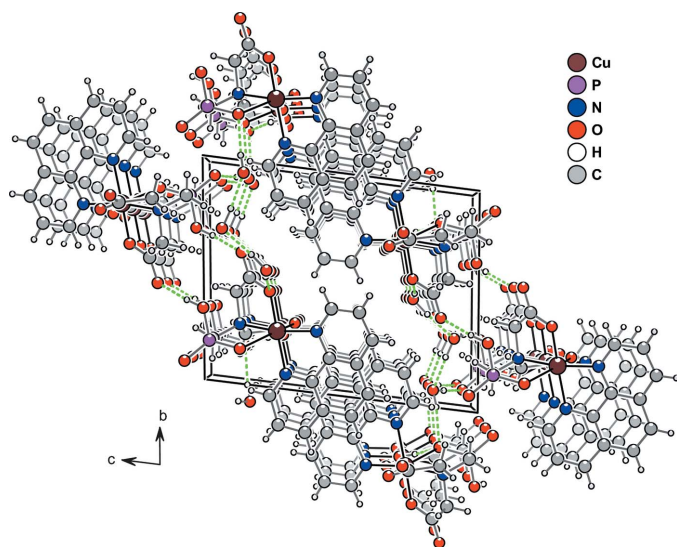
much better insight into the hydrogen-bond network present in the crystal structure of (I).

The unit-cell volume decreased by *ca*  $13 \text{ \AA}^3$ , consistent with determination at a lower temperature. The asymmetric unit



**Figure 3**  
 $\pi$ - $\pi$  offset interactions, running along the  $[100]$  direction of the unit cell between 1,10-phenanthroline residues belonging to adjacent one-dimensional hydrogen-bonded tapes (see Fig. 2). Hydrogen bonds are represented as green-filled dashed bonds.

composed of a complete  $[\text{Cu}(\text{H}_2\text{pmida})(\text{phen})]$  complex (Fig. 1) plus three water molecules of crystallization (O1W, O2W and O3W). The crystallographically unique  $\text{Cu}^{2+}$  atom is coordinated by one phen residue *via* the two N-donor atoms, leading to a bite angle of  $82.18(9)^\circ$ , which is in good agreement with that reported by Pei *et al.* [ $82.06(16)^\circ$ ], and also with those typically found in related compounds as revealed by a search in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002; Allen & Motherwell, 2002). The remaining four positions of the  $\text{Cu}^{2+}$  coordination are occupied by the N- and O-donor atoms from the  $\text{H}_2\text{pmida}^{2-}$  anionic ligand, leading to a typical Jahn–Teller distorted octahedral coordination geometry,  $\{\text{CuN}_3\text{O}_3\}$ . In general, the Cu–N and Cu–O bond lengths and angles (Table 1) are not significantly different from those obtained from the room-temperature determination (Pei *et al.*, 2004). Each  $[\text{Cu}(\text{H}_2\text{pmida})(\text{phen})]$  complex is connected to adjacent molecules *via* a series of hydrogen bonds between the protonated carboxylic and phosphonic acid groups (donors), and the coordinated carboxylate groups (acceptors) of a neighbouring complex (Fig. 2 and Table 2). Such a regular arrangement of hydrogen bonds between adjacent complexes leads to the formation of two graph-set motifs, *viz.*  $R_2^2(16)$  and  $R_4^4(24)$  (Fig. 2), which are recursively repeated along the  $[100]$  direction of the unit cell, creating a one-dimensional hydrogen-bonded tape. The intermetallic  $\text{Cu}1 \cdots \text{Cu}1^i$  distance across the  $\text{O}7 \cdots \text{O}1$  hydrogen-bond bridge is  $7.571(2) \text{ \AA}$ , while across the  $\text{O}2 \cdots \text{O}5$  bridge,  $\text{Cu}1 \cdots \text{Cu}1^{ii}$  is  $9.162(2) \text{ \AA}$  [symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $1-x, 1-y, -z$ ]. The one-dimensional tape is formed in such a way that the coordinated phen molecules are external to the hydrogen-bonded core (Fig. 2). Therefore, the aromatic residues are engaged in offset  $\pi$ - $\pi$  stacking along the  $[100]$  direction of the unit cell, thus linking neighbouring hydrogen-bonded tapes (Fig. 3). Further connections between tapes are made by hydrogen bonds involving the water molecules of crystallization (Fig. 4 and Table 2), thus leading, along with the above-mentioned  $\pi$ - $\pi$  interactions, to a three-



**Figure 4**  
Perspective view of the crystal packing of the title compound viewed along the [100] direction of the unit cell. Hydrogen bonds are represented as green-filled dashed bonds. For hydrogen-bonding geometry, see Table 2.

dimensional supramolecular arrangement of [Cu(H<sub>2</sub>pmida)(phen)] complexes.

## Experimental

Chemicals were readily available from commercial sources and were used as received without further purification, *i.e.* *N*-(phosphonomethyl)iminodiacetic acid hydrate (H<sub>4</sub>pmida, 97% Fluka), 1,10-phenanthroline monohydrate (phen, >99.0% Fluka) and copper(II) hydroxide [CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>, 55% in Cu, Panreac]. The title compound was synthesized from a mixture containing 0.19 g of CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>, 0.38 g of H<sub>4</sub>pmida and 0.23 g of phen in *ca.* 6.7 g of distilled water. The mixture was stirred at ambient temperature for 30 min, yielding a homogeneous suspension with a molar composition of *ca.* 1.0:1.9:1.4:433, which was transferred to PTFE-lined stainless steel reaction vessels (*ca.* 40 ml). Reactions took place over a period of 3 d, under autogeneous pressure and static conditions, in a preheated oven at 373 K. The vessels were left to cool to ambient temperature before opening. The mother liquor was filtered off and allowed to stand in the open air for approximately 2 d, yielding a large amount of a dark-green single-crystalline phase. Individual single crystals were washed with copious amounts of distilled water (3 × *ca.* 50 ml), and then air-dried at ambient temperature to give the title compound.

### Crystal data

[Cu(C<sub>5</sub>H<sub>10</sub>NO<sub>7</sub>P)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)]·3H<sub>2</sub>O  
*M<sub>r</sub>* = 522.89  
 Triclinic, *P* $\bar{1}$   
*a* = 7.5714 (15) Å  
*b* = 10.696 (2) Å  
*c* = 13.047 (3) Å  
 $\alpha$  = 81.98 (3)°  
 $\beta$  = 85.04 (3)°  
 $\gamma$  = 78.40 (3)°  
*V* = 1023.1 (4) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.697 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6202 reflections  
 $\theta$  = 1.0–27.5°  
 $\mu$  = 1.21 mm<sup>-1</sup>  
*T* = 180 (2) K  
 Block, green  
 0.10 × 0.10 × 0.07 mm

### Data collection

Nonius KappaCCD diffractometer  
 Thin-slice  $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
*T*<sub>min</sub> = 0.843, *T*<sub>max</sub> = 0.922  
 11202 measured reflections  
 4641 independent reflections

3999 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.038  
 $\theta$ <sub>max</sub> = 27.4°  
*h* = −9 → 9  
*k* = −13 → 13  
*l* = −14 → 16

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.089  
*S* = 1.06  
 4641 reflections  
 313 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.6723P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.81 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	2.474 (2)	Cu1—N3	2.032 (2)
Cu1—O4	1.9412 (18)	Cu1—N1	2.118 (2)
Cu1—N2	2.005 (2)	Cu1—O6	2.3489 (18)
O4—Cu1—N2	90.72 (8)	N3—Cu1—N1	104.59 (8)
O4—Cu1—N3	166.90 (8)	O4—Cu1—O6	102.28 (7)
N2—Cu1—N3	82.18 (9)	N2—Cu1—O6	94.96 (8)
O4—Cu1—N1	84.52 (8)	N3—Cu1—O6	89.34 (8)
N2—Cu1—N1	167.49 (8)	N1—Cu1—O6	74.86 (7)

**Table 2**

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>
O2—H2C···O5 <sup>i</sup>	0.90 (1)	1.67 (1)	2.564 (3)	175 (3)
O7—H7A···O1 <sup>ii</sup>	0.89 (3)	1.66 (3)	2.540 (3)	168 (3)
O1W—H1C···O3 <sup>iii</sup>	0.95 (1)	1.77 (1)	2.717 (3)	178 (3)
O1W—H1D···O1 <sup>iv</sup>	0.95 (1)	1.94 (2)	2.853 (3)	162 (3)
O2W—H2D···O1W	0.95 (1)	1.76 (1)	2.704 (4)	166 (3)
O2W—H2E···O2 <sup>iii</sup>	0.96 (3)	2.17 (2)	3.087 (3)	160 (3)
O3W—H3A···O2W <sup>v</sup>	0.97 (3)	1.85 (4)	2.805 (4)	166 (3)
O3W—H3B···O4	0.95 (3)	2.06 (3)	2.999 (3)	172 (3)

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

H atoms associated with the three water molecules of crystallization, and with the protonated carboxylic and phosphonic acid groups (H2C and H7A), were clearly visible in difference Fourier maps, and were included in subsequent least-squares refinements. For the water molecules, the O—H and H···H distances were restrained to 0.95 (1) and 1.55 (1) Å, respectively, to ensure a chemically reasonable geometry for these groups. For the hydroxyl groups, the O—H distances were restrained to 0.90 (1) Å. These H atoms were further refined with an isotropic displacement parameter fixed at 1.5*U*<sub>eq</sub> of the parent O atoms. H atoms bound to carbon were placed in idealized positions and allowed to ride on their parent atoms with relative isotropic displacement parameters (*U*<sub>iso</sub>) fixed at 1.2*U*<sub>eq</sub> of the parent C atom and C—H = 0.95 Å.

Data collection: COLLECT (Nonius 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL (Bruker 2001);

molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL* (Bruker 2001).

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