Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# [*N*-(2-Ammonioethyl)ethylenediamine-$\kappa^2N,N'$][hydrogen *N*-(phosphonatomethyl)-iminodiacetato]copper(II) sesquihydrate

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Received 12 December 2005
Accepted 10 January 2006

**Key indicators**

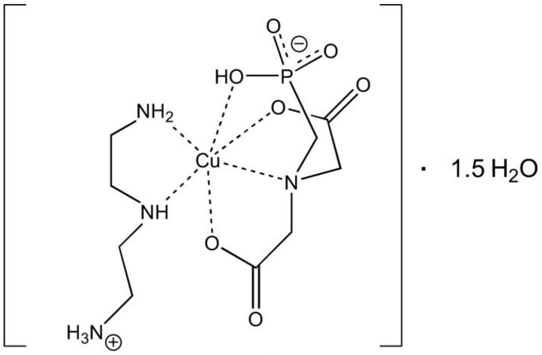
Single-crystal X-ray study
$T$ = 100 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.039
$wR$ factor = 0.095
Data-to-parameter ratio = 14.3

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

The title compound, $[Cu(C_5H_9NO_7P)(C_4H_{14}N_3)]\cdot1.5H_2O$, was isolated from the hydrothermal reaction (under mild conditions) between *N*-(phosphonomethyl)iminodiacetic acid ($H_4$pmida), diethylenetriamine (det) and copper(II) acetate. The structure contains discrete neutral [Cu(Hpmida)(Hdet)] complexes which are involved in a strong and extensive hydrogen-bonding network including the water molecules of crystallization. Interactions between adjacent complexes involve hydrogen bonds of two graph-set motifs, $R^1_2(6)$ and $R^2_2(8)$, which are also responsible for the highly asymmetrical Jahn–Teller distortion of the copper(II) environment.

## Comment

Crystalline organic–inorganic hybrid framework-based materials have recently been the subject of great research interest due to their unique topological architectures, peculiar properties and promising applications in areas as diverse as catalysis, gas storage, biochemistry, and magnetic materials (Rosi *et al.*, 2003; Vioux *et al.*, 2004; Xiang *et al.*, 2002). Crystal engineering approaches have produced a large number of novel hybrid compounds (commonly known as metal-organic frameworks, MOFs), largely based on coordination of carboxylate- or phosphonate-containing ligands to (mainly) *d*-block transition metal centres (Kong *et al.*, 2005; Song, Prosvirin *et al.*, 2004; Song, Zhao *et al.*, 2004; Yang *et al.*, 2003; Zhang, 2004). *N*-(Phosphonomethyl)iminodiacetic acid ($H_4$pmida) contains two types of the aforementioned functional groups, and can be envisaged as the precursor of a series of multidentate chelating ligands whose richness and versatility of coordination modes have been underexploited. For example, the single known material to date belonging to the $Cu^{II}$–$H_{4-x}$pmida$^{x-}$ family has only very recently been reported (Paz & Shi, 2005*a*; Pei *et al.*, 2004). Following our interest in MOFs (Paz & Klinowski, 2003*a*,*b*, 2004*a*,*b*,*c*; Paz *et al.*, 2002), we have lately focused our research on the use of



(I)

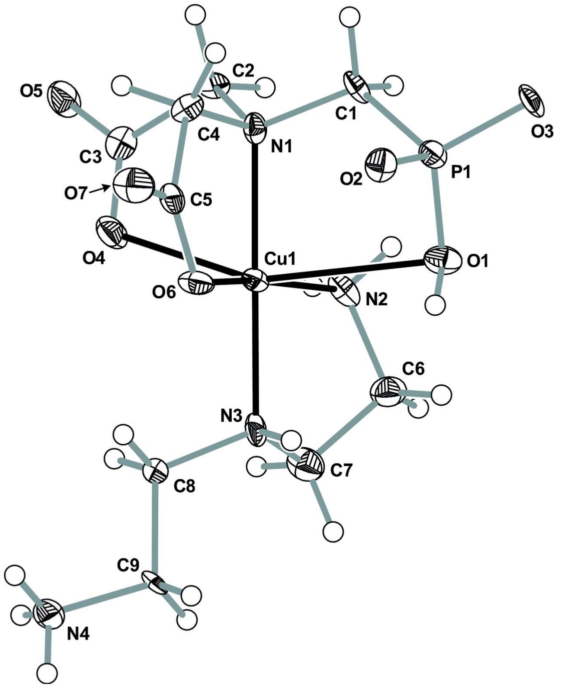


**Figure 1**
The neutral [Cu(Hpmida)(Hdet)] complex in (I). Displacement ellipsoids are drawn at the 80% probability level and H atoms are shown as small spheres.

this organic ligand. First, we employed the robust $[V_2O_2(pmida)_2]^{4-}$ anionic unit, originally reported by Crans *et al.* (1998) to construct multidimensional (one-, two- and three-dimensional) hybrid frameworks (Almeida Paz, Shi, Trindade *et al.*, 2005; Almeida Paz, Shi, Mafra *et al.*, 2005; Paz, Shi *et al.*, 2004; Shi *et al.*, 2005). More recently, a unit containing $Ge^{4+}$, $[Ge_2(pmida)_2(OH)_2]^{2-}$, was also isolated and extensively studied using solid-state NMR techniques (Mafra *et al.*, 2006). In this communication, we report the crystal structure of a discrete $Cu^{2+}$ complex, the second member belonging to the $Cu^{II}$–$H_{4-x}pmida^{x-}$ system, which also constitutes the first example in which a vacant coordination site of a typical metal–$H_{4-x}pmida^{x-}$ complex is occupied by an N-donor atom of diethylenetriamine (det).

The title compound, (I), crystallizes in the monoclinic space group $C2/c$, the asymmetric unit being composed of one whole [Cu(Hpmida)(Hdet)] complex [where $Hpmida^{3-}$ is hydrogen *N*-(phosphonatomethyl)iminodiacetate and $Hdet^{+}$ is *N*-(2-ammonioethyl)ethylenediamine] (Fig. 1), plus one and a half water molecules of crystallization. It is noteworthy that the coordination mode for the protonated diethylenetriamine residue ($Hdet^{+}$) is only observed in a handful of related structures (with $Pt^{4+}$, $Pt^{2+}$, $Cr^{3+}$ and $Ru^{3+}$), as revealed by a search in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002; Allen & Motherwell, 2002).

The structure contains a single $Cu^{2+}$ metal centre, which appears six-coordinated in a geometry resembling a highly distorted octahedron, $\{CuN_3O_3\}$: the Cu—(N,O) bond lengths are in the range 1.959 (2)–2.721 (3) Å, while the *cis* and *trans* angles of the octahedron are in the 75.92 (10)–106.21 (10) and 156.82 (8)–173.73 (11)° ranges, respectively (Table 1). Such a highly distorted geometry is attributed to the Jahn–Teller effect usually observed for this metallic centre. Indeed, the equatorial plane of the octahedron, which is formed by the N-coordinating atoms from the $Hdet^{+}$ residue plus an $—N—CH_2—CH_2—COO^{-}$ chelating segment from $Hpmida^{3-}$

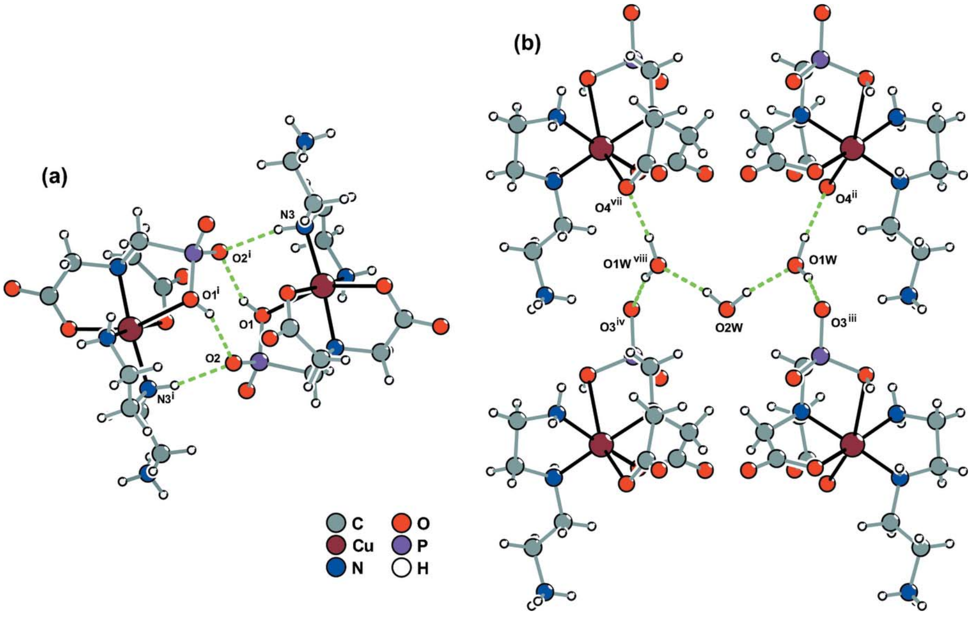


**Figure 2**
(*a*) Hydrogen bonds (green dashed lines) involving the protonated phosphonate and the coordinated –NH groups which interconnect, *via* $R_2^1(6)$ and $R_2^2(8)$ graph-set motifs, neighbouring [Cu(Hpmida)(Hdet)] complexes. (*b*) Schematic representation of the encapsulation of three water molecules between the four [Cu(Hpmida)(Hdet)] complexes, and their mutual interactions *via* O—H···$O^{-}$ hydrogen bonds (green dashed lines). [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$; (vii) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (viii) $-x, y, \frac{1}{2}-z$.]

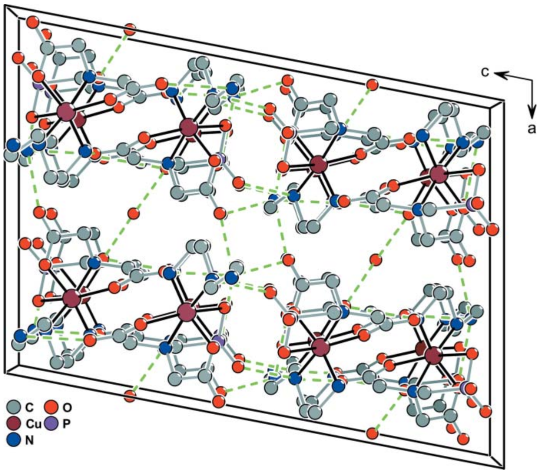


**Figure 3**
Perspective view of the crystal packing of the title compound, viewed along the [010] direction of the unit cell. Hydrogen bonds are represented as green dashed lines. H atoms have been omitted for clarity.

(Fig. 1), is very regular, with all the Cu—(N,O) bonds in the range 1.959 (2)–2.052 (3) Å and with an average (N,O)—Cu—(N,O) angle of 89.9°. Hence, the axial positions are mainly responsible for such a degree of distortion: while the coordination of the second carboxylate group of Hpmida$^{3-}$ leads to a Cu—O bond of 2.289 (2) Å, the contact with the protonated phosphonate group is indeed much longer [2.721 (3) Å] (Fig. 1).

Interestingly, in the [Cu($H_2$pmida)(phen)] complex (where phen is phenanthroline) (Almeida Paz, Shi, Trindade *et al.*, 2005; Pei *et al.*, 2004), the Jahn–Teller distortion was not so significant, with *trans* bond lengths of 2.349 (2) and 2.474 (2) Å. An explanation for such differences resides in the hydrogen bonds involving the [Cu(Hpmida)(Hdet)] complexes; the coordinating O atom from the phosphonate group, O1, is also protonated (Fig. 1) and engaged in a strong and highly directional O—H···O$^-$ interaction (Table 2) with a neighbouring complex (Fig. 2*a*), leading to the formation of an $R_2^2(8)$ graph-set motif, further surrounded by another two $R_2^1(6)$ motifs created by the coordinated —NH group from the Hdet$^+$ residue (Fig. 2*a*). Such a strong connection between adjacent complexes seems to be the driving force for the weakening of the Cu1—O1 interaction, and the consequent bond length increase. Moreover, when compared with the [Cu($H_2$pmida)(phen)] complex, the *trans* Cu1—O4 bond seems to increase in strength simply because, due to the weakening of the Cu1—O1 bond, the Cu$^{2+}$ centre is shifted from the equatorial plane towards O4 by *ca* 0.15 Å.

Water molecules appear in the crystal structure encapsulated in the spaces created by the close packing of individual [Cu(Hpmida)(Hdet)] complexes (Fig. 2*b*), and interacting with the carboxylate and phosphonate groups *via* strong O—H···O$^-$ hydrogen bonds (Table 2). Further hydrogen-bonding interactions involving the —$NH_2$ and —$NH_3$ groups of the Hdet$^+$ residue (Table 2) interconnect the complexes into a three-dimensional supramolecular arrangement (Fig. 3).

## Experimental

Chemicals were readily available from commercial sources and were used as received without further purification: *N*-(Phosphonomethyl)iminodiacetic acid hydrate ($H_4$pmida, 97% Fluka), copper(II) acetate monohydrate (98% Sigma-Aldrich) and diethylenetriamine (det, 97% Fluka). Syntheses were typically carried out in PTFE-lined stainless steel reaction vessels (*ca* 40 ml) under autogeneous pressure and static conditions in a preheated oven at 413 K. Reactions took place over a period of 6 d, after which the vessels were removed from the oven and left to cool to ambient temperature before opening. The title compound proved to be air- and light-stable.

The title compound was synthesized from a mixture containing 0.40 g of copper(II) acetate monohydrate, 0.36 g of $H_4$pmida, 0.20 g of det and *ca* 18 g of distilled water. The mixture was stirred through vigorously at ambient temperature for 30 min, yielding a suspension with a molar composition of 1.0:1.3:1.2:632, respectively, which was transferred to the reaction vessel. After reacting, an amount of metallic copper (confirmed by powder X-ray diffraction) was isolated directly from the autoclave contents by vacuum filtering. The mother liquor was allowed to stand in the open air at ambient temperature, over a period of one month, leading to the isolation of prismatic blue single crystals (*ca* 0.5 g) of the title compound which were harvested manually as a pure phase, washed with distilled water and dried.

Analysis calculated for for $C_{18}H_{48}Cu_2N_8O_{17}P_2$ (in %): C 25.81, H 5.78, N 13.43; found (in %): C 25.07, H 5.39, N 13.18. Selected IR (KBr pellet, cm$^{-1}$) data: 3472 (*s*), 3302 (*m*), 3240 (*s*), 3233 (*s*), 3175 (*m*), 3133 (*s*), 2963 (*m*), 2932 (*m*), 2904 (*m*), 2718 (*w*), 1644 (*s*), 1615 (*s*), 1603 (*s*), 1468 (*w*), 1419 (*w*), 1396 (*s*), 1377 (*m*), 1340 (*w*), 1303 (*w*), 1250 (*w*), 1192 (*w*), 1175 (*w*), 1111 (*m*), 1073 (*m*), 1024 (*m*), 976 (*w*), 970 (*w*), 899 (*m*), 773 (*w*), 710 (*w*), 615 (*w*), 531 (*m*), 478 (w).

### *Crystal data*

[Cu($C_5H_9NO_7P$)($C_4H_{14}N_3$)]·1.5$H_2O$
$M_r = 418.84$
Monoclinic, *C*2/*c*
$a = 15.554$ (3) Å
$b = 9.5377$ (19) Å
$c = 21.441$ (4) Å
$\beta = 100.86$ (3)°
$V = 3123.8$ (11) Å$^3$
$Z = 8$
$D_x = 1.781$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 846 reflections
$\theta = 3.0$–26.8°
$\mu = 1.55$ mm$^{-1}$
$T = 100$ (2) K
Prism, blue
0.13 × 0.09 × 0.09 mm

### *Data collection*

Bruker SMART CCD-1000 diffractometer
Thin–slice $\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.824$, $T_{max} = 0.873$
13186 measured reflections
3450 independent reflections
2507 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.2$°
$h = -19 \rightarrow 19$
$k = -12 \rightarrow 12$
$l = -27 \rightarrow 27$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.095$
$S = 1.02$
3450 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 9.0176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ e Å$^{-3}$
$\Delta\rho_{min} = -0.52$ e Å$^{-3}$

*Acta Cryst.* (2006). E**62**, m335–m338 Shi *et al.* • [Cu($C_5H_9NO_7P$)($C_4H_{14}N_3$)]·1.5$H_2O$ **m337**

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—O6 | 1.959 (2) | Cu1—N1 | 2.052 (3) |
| Cu1—N2 | 2.011 (3) | Cu1—O4 | 2.289 (2) |
| Cu1—N3 | 2.011 (3) | Cu1—O1 | 2.721 (3) |
| | | | |
| O6—Cu1—N2 | 166.47 (10) | N3—Cu1—O4 | 106.21 (10) |
| O6—Cu1—N3 | 89.68 (10) | N1—Cu1—O4 | 77.13 (9) |
| N2—Cu1—N3 | 85.51 (11) | O6—Cu1—O1 | 92.02 (8) |
| O6—Cu1—N1 | 84.68 (10) | N2—Cu1—O1 | 75.92 (10) |
| N2—Cu1—N1 | 99.38 (11) | N3—Cu1—O1 | 95.73 (9) |
| N3—Cu1—N1 | 173.73 (11) | N1—Cu1—O1 | 81.86 (9) |
| O6—Cu1—O4 | 95.43 (9) | O4—Cu1—O1 | 156.91 (8) |
| N2—Cu1—O4 | 98.05 (10) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$E$···O2$^{i}$ | 0.84 | 1.84 | 2.615 (3) | 153 |
| N2—H2$D$···O1$W$ | 0.86 (2) | 2.42 (2) | 3.183 (4) | 148 (3) |
| N2—H2$C$···O5$^{ii}$ | 0.86 (2) | 2.137 (14) | 2.980 (4) | 165 (3) |
| N3—H3$A$···O2$^{i}$ | 0.86 (2) | 2.132 (15) | 2.959 (3) | 162 (3) |
| N4—H4$C$···O5$^{iii}$ | 0.86 (2) | 2.248 (16) | 3.014 (4) | 148 (2) |
| N4—H4$C$···O7$^{iv}$ | 0.86 (2) | 2.35 (2) | 2.833 (4) | 116 (2) |
| N4—H4$D$···O3$^{v}$ | 0.86 (2) | 1.968 (11) | 2.819 (4) | 169 (2) |
| N4—H4$E$···O7$^{vi}$ | 0.86 (2) | 1.902 (11) | 2.750 (4) | 167 (3) |
| O1$W$—H1$C$···O3$^{iii}$ | 0.944 (10) | 1.942 (12) | 2.869 (3) | 166 (3) |
| O1$W$—H1$D$···O4$^{ii}$ | 0.938 (10) | 1.971 (15) | 2.874 (3) | 161 (3) |
| O2$W$—H2$E$···O1$W$ | 0.95 (2) | 1.89 (3) | 2.812 (3) | 166 (4) |

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

C-bound H-atoms were positioned geometrically and refined as riding with C—H = 0.99 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C). H atoms bound to nitrogen and those associated with the water molecules of crystallization were directly located in difference Fourier maps, and refined with N—H and O—H distances restrained to 0.86 (1) and 0.95 (1) Å, respectively, with $U_{\rm iso}$ fixed at $1.5U_{\rm eq}$(N,O). The H···H distances in the water molecules and the $NH_3^+$ terminal group were further restrained to 1.55 (1) and 1.40 (1) Å, respectively, to provide chemically reasonable chemical environments for these groups. The H atom associated with the protonated phosphonate group was also visible in a difference Fourier map and was included in the refinement as riding, with O—H set to 0.84 Å and $U_{\rm iso}$ fixed at $1.5U_{\rm eq}$(O).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to Fundação para a Ciência e Tecnologia (FCT, Portugal) for their gereric financial support under the POCTI programme (supported by FEDER), and the postdoctoral research Grant No. SFRH/BPD/9309/2002 (to FNS).

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