[Hydrogen N-(phosphonomethyl)iminodiacetato](1,10-phenanthroline)copper(II) trihydrate: a low-temperature redetermination

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The room-temperature crystal structure of the title compound, [Cu(H$_2$pmida)(phen)]·3H$_2$O [where H$_2$pmida^{2-} is hydrogen N-(phosphonomethyl)iminodiacetate, C$_5$H$_{10}$NO$_7$P^{2-}, and phen is 1,10-phenanthroline, C$_{12}$H$_8$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* π–π offset stacking (between the 1,10-phenanthroline ligands) and by hydrogen bonds involving the water molecules of crystallization.
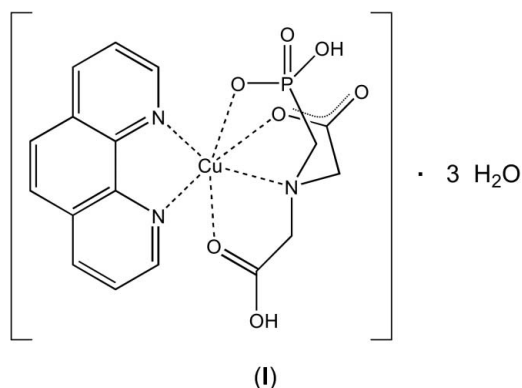
Comment

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 (H$_4$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 Cu^{2+} with 1,10-phenanthroline (phen) and H$_2$pmida^{2-} ligands, co-crystallizing with three solvent molecules in space group $P\bar{1}$.

(I)

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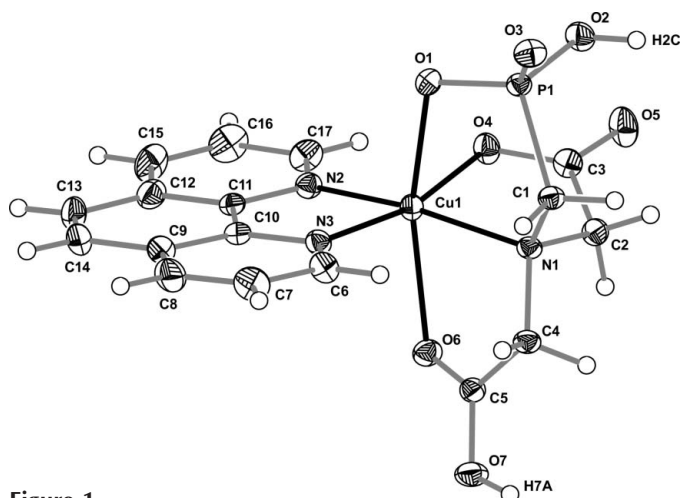
Figure 1
A view of the [Cu(H$_2$pmida)(phen)] complex molecule present in the crystal structure of the title compound, showing the labelling scheme for all non-H atoms and for the two H atoms belonging to the carboxylic and phosphonic acid groups. Displacement ellipsoids are drawn at the 50% probability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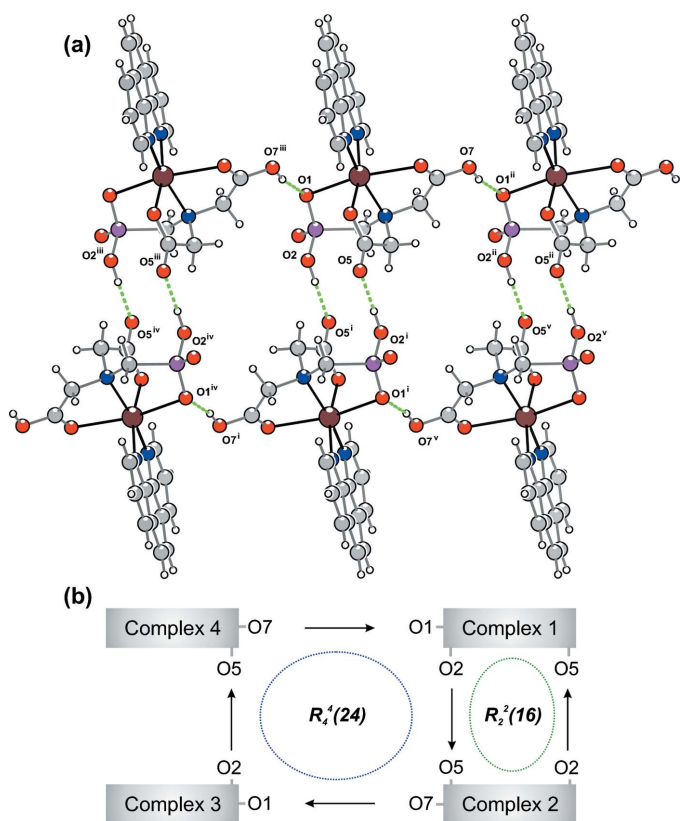

Figure 2
Hydrogen bonding in (I) represented as green-filled dashed bonds giving a one-dimensional tape running along the [100] direction of the unit cell with a schematic diagram showing the two graph-set motifs, viz. $R_2^2(16)$ and $R_4^4(24)$. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 + x, y, z$; (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 Å^3, consistent with determination at a lower temperature. The asymmetric unit
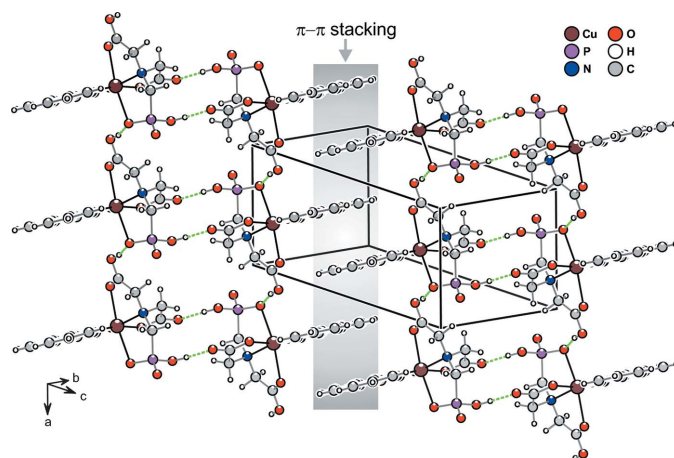

Figure 3
π-π offset interactions, running along the [100] direction of the unit cell between 1,10-phenanthroline residues belonging to adjacent one-dimensional hydrogen-bonded tapes (see Fig. 2). Hydrogen bonds are represented as green-filled dashed bonds.

composed of a complete [Cu(H$_2$pmida)(phen)] complex (Fig. 1) plus three water molecules of crystallization (O1W, O2W and O3W). The crystallographically unique Cu^{2+} atom is coordinated by one phen residue via the two N-donor atoms, leading to a bite angle of 82.18 (9)°, which is in good agreement with that reported by Pei et al. [82.06 (16)°], 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 Cu^{2+} coordination are occupied by the N- and O-donor atoms from the H$_2$pmida^{2-} anionic ligand, leading to a typical Jahn–Teller distorted octahedral coordination geometry, {CuN$_3$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 [Cu(H$_2$pmida)(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 Cu1$\cdots$Cu1^i distance across the O7$\cdots$O1 hydrogen-bond bridge is 7.571 (2) Å, while across the O2$\cdots$O5 bridge, Cu1$\cdots$Cu1^{ii} is 9.162 (2) Å [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 π–π 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 π–π interactions, to a three-
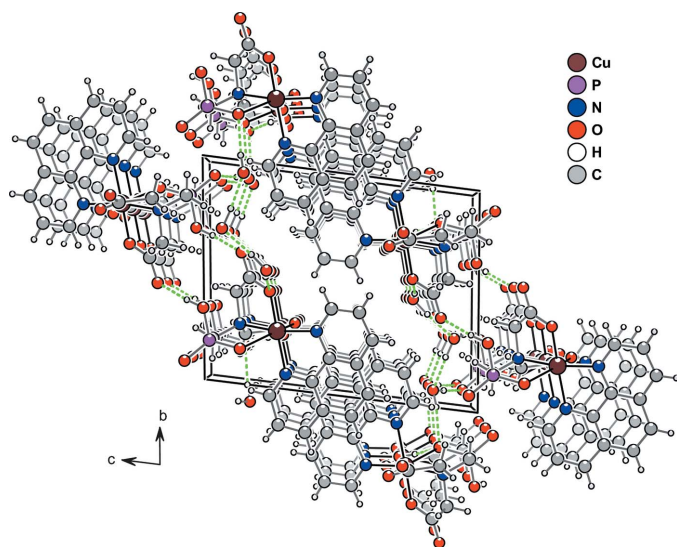
Figure 4
Perspective view of the crystal packing of the title compound viewed along the [100] direction of the unit cell. Hydrogen bonds are represented as green-filled dashed bonds. For hydrogen-bonding geometry, see Table 2.

dimensional supramolecular arrangement of [Cu(H$_2$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$_4$pmida, 97% Fluka), 1,10-phenanthroline monohydrate (phen, >99.0% Fluka) and copper(II) hydroxide [CuCO$_3$·Cu(OH)$_2$, 55% in Cu, Panreac]. The title compound was synthesized from a mixture containing 0.19 g of CuCO$_3$·Cu(OH)$_2$, 0.38 g of H$_4$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$_5$H$_{10}$NO$_7$P)(C$_{12}$H$_8$N$_2$)]·3H$_2$O
M_r = 522.89
Triclinic, $P\bar{1}$
a = 7.5714 (15) Å
b = 10.696 (2) Å
c = 13.047 (3) Å
α = 81.98 (3)°
β = 85.04 (3)°
γ = 78.40 (3)°
V = 1023.1 (4) Å^3

Z = 2
D_x = 1.697 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6202 reflections
θ = 1.0–27.5°
μ = 1.21 mm^{-1}
T = 180 (2) K
Block, green
0.10 × 0.10 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.843, T_{max} = 0.922
11202 measured reflections
4641 independent reflections

3999 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.4°
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 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 e Å^{-3}
$\Delta\rho_{min}$ = -0.51 e 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, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2C$\cdots$O5^i	0.90 (1)	1.67 (1)	2.564 (3)	175 (3)
O7—H7A$\cdots$O1^{ii}	0.89 (3)	1.66 (3)	2.540 (3)	168 (3)
O1W—H1C$\cdots$O3^{iii}	0.95 (1)	1.77 (1)	2.717 (3)	178 (3)
O1W—H1D$\cdots$O1^{iv}	0.95 (1)	1.94 (2)	2.853 (3)	162 (3)
O2W—H2D$\cdots$O1W	0.95 (1)	1.76 (1)	2.704 (4)	166 (3)
O2W—H2E$\cdots$O2^{iii}	0.96 (3)	2.17 (2)	3.087 (3)	160 (3)
O3W—H3A$\cdots$O2W^v	0.97 (3)	1.85 (4)	2.805 (4)	166 (3)
O3W—H3B$\cdots$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$\cdots$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 1.5U_{eq} 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_{iso}) fixed at 1.2U_{eq} 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);

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

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H. & Motherwell, W. D. S. (2002). *Acta Cryst.* B**58**, 407–422.
Almeida Paz, F. A., Bond, A. D., Khimyak, Y. Z. & Klinowski, J. (2002). *Acta Cryst.* C**58**, m608–m610.
Almeida Paz, F. A., Khimyak, Y. Z., Bond, A. D., Rocha, J. & Klinowski, J. (2002). *Eur. J. Inorg. Chem.* pp. 2823–2828.
Almeida Paz, F. A. & Klinowski, J. (2003). *J. Phys. Org. Chem.* **16**, 772–782.
Almeida Paz, F. A. & Klinowski, J. (2004*a*). *Inorg. Chem.* **43**, 3882–3893.
Almeida Paz, F. A. & Klinowski, J. (2004*b*). *Inorg. Chem.* **43**, 3948–3954.
Almeida Paz, F. A., Rocha, J., Klinowski, J., Trindade, T., Shi, F.-N. & Mafra, L. (2005). *Prog. Solid State Chem.* Submitted.
Almeida Paz, F. A., Shi, F.-N., Klinowski, J., Rocha, J. & Trindade, T. (2004). *Eur. J. Inorg. Chem.* pp. 2759–2768.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–58.
Brandenburg, K. (2001). *DIAMOND*. Version 2.1a. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc. Madison, Wisconsin, USA.
Mafra, L., Almeida Paz, F. A., Shi, F.-N., Rocha, J., Trindade, T., Fernandez, C., Makal, A., Wozniak, K. & Klinowski, J. (2005). *Chem. Eur. J.* In the press.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Pei, H., Lu, S., Ke, Y., Li, J., Qin, S., Zhou, S., Wu, X. & Du. W. (2004). *Struct. Chem.* **15**, 207–210.
Shi, F.-N., Almeida Paz, F. A., Girginova, P. I., Mafra, L., Amaral, V. S., Rocha, J., Wozniak, K., Klinowski, J. & Trindade, T. (2005). *J. Mol. Struct.* In the press.

supporting information

[Hydrogen *N*-(phosphonomethyl)iminodiacetato](1,10-phenanthroline)copper(II) trihydrate: a low-temperature redetermination

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[hydrogen *N*-(phosphonomethyl)iminodiacetato](1,10-phenanthroline)copper(II) trihydrate

Crystal data

$[Cu(C_5H_{10}NO_7P)(C_{12}H_8N_2)]\cdot 3H_2O$	$F(000) = 538$
$M_r = 522.89$	$D_x = 1.697$ Mg m^{-3}
Triclinic, $P\bar{1}$	D_m = no Mg m^{-3}
Hall symbol: -P 1	D_m measured by not measured
$a = 7.5714$ (15) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.696$ (2) Å	Cell parameters from 6202 reflections
$c = 13.047$ (3) Å	$\theta = 1.0$–27.5°
$\alpha = 81.98$ (3)°	$\mu = 1.21$ mm^{-1}
$\beta = 85.04$ (3)°	$T = 180$ K
$\gamma = 78.40$ (3)°	Block, green
$V = 1023.1$ (4) Å^3	$0.10 \times 0.10 \times 0.07$ mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	4641 independent reflections
Radiation source: fine-focus sealed tube	3999 reflections with $I > 2\sigma(I)$
Thin–slice ω and φ scans	$R_{int} = 0.038$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{max} = 27.4°$, $\theta_{min} = 3.6°$
$T_{min} = 0.843$, $T_{max} = 0.922$	$h = -9 \rightarrow 9$
11202 measured reflections	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: mixed
$wR(F^2) = 0.089$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	
4641 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.6723P]$ where $P = (F_o^2 + 2F_c^2)/3$
313 parameters	
11 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.81$ e Å^{-3}
	$\Delta\rho_{min} = -0.51$ e Å^{-3}

Special details

Experimental. (Please see the Experimental Section in the main paper)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cu1	0.46760 (4)	0.73527 (3)	0.27104 (2)	0.01480 (9)
P1	0.32199 (8)	0.80933 (6)	0.03658 (5)	0.01451 (14)
N1	0.6456 (3)	0.72640 (18)	0.13668 (16)	0.0141 (4)
O1	0.2374 (2)	0.82883 (17)	0.14408 (14)	0.0192 (4)
O2	0.2983 (2)	0.67179 (17)	0.01640 (15)	0.0213 (4)
H2C	0.356 (4)	0.647 (3)	−0.0425 (15)	0.032*
O3	0.2619 (2)	0.91124 (17)	−0.05012 (14)	0.0209 (4)
O4	0.4395 (2)	0.56551 (16)	0.24691 (14)	0.0206 (4)
O5	0.5322 (3)	0.41073 (17)	0.14714 (15)	0.0279 (4)
O6	0.7588 (2)	0.69422 (17)	0.33266 (14)	0.0196 (4)
O7	1.0177 (2)	0.75556 (19)	0.28737 (14)	0.0236 (4)
H7A	1.086 (4)	0.778 (3)	0.2311 (17)	0.035*
C1	0.5623 (3)	0.8038 (2)	0.04237 (19)	0.0156 (5)
H1A	0.6259	0.7679	−0.0197	0.019*
H1B	0.5825	0.8930	0.0390	0.019*
C2	0.6869 (3)	0.5863 (2)	0.1248 (2)	0.0184 (5)
H2A	0.8023	0.5464	0.1565	0.022*
H2B	0.7028	0.5765	0.0501	0.022*
C3	0.5413 (3)	0.5159 (2)	0.1743 (2)	0.0189 (5)
C4	0.8155 (3)	0.7684 (2)	0.15323 (19)	0.0166 (5)
H4A	0.8006	0.8627	0.1344	0.020*
H4B	0.9151	0.7267	0.1078	0.020*
C5	0.8630 (3)	0.7334 (2)	0.26503 (19)	0.0165 (5)
N2	0.3410 (3)	0.71320 (19)	0.41193 (16)	0.0168 (4)
N3	0.4347 (3)	0.91999 (19)	0.30146 (16)	0.0163 (4)
C6	0.4759 (3)	1.0235 (2)	0.2436 (2)	0.0204 (5)
H6	0.5387	1.0135	0.1781	0.024*
C7	0.4316 (4)	1.1467 (3)	0.2743 (2)	0.0264 (6)
H7	0.4618	1.2185	0.2297	0.032*
C8	0.3441 (4)	1.1628 (3)	0.3694 (2)	0.0270 (6)
H8	0.3136	1.2458	0.3915	0.032*
C9	0.2998 (3)	1.0555 (3)	0.4337 (2)	0.0213 (5)
C10	0.3469 (3)	0.9361 (2)	0.39543 (19)	0.0162 (5)
C11	0.2990 (3)	0.8240 (2)	0.45614 (19)	0.0166 (5)

C12	0.2099 (3)	0.8325 (3)	0.5542 (2)	0.0226 (5)
C13	0.1672 (4)	0.9556 (3)	0.5930 (2)	0.0268 (6)
H13	0.1089	0.9622	0.6600	0.032*
C14	0.2093 (4)	1.0615 (3)	0.5348 (2)	0.0262 (6)
H14	0.1784	1.1418	0.5615	0.031*
C15	0.1632 (4)	0.7192 (3)	0.6078 (2)	0.0296 (6)
H15	0.1035	0.7198	0.6749	0.035*
C16	0.2042 (4)	0.6079 (3)	0.5627 (2)	0.0306 (6)
H16	0.1724	0.5309	0.5979	0.037*
C17	0.2934 (3)	0.6086 (3)	0.4641 (2)	0.0235 (6)
H17	0.3208	0.5309	0.4335	0.028*
O1W	0.9747 (3)	0.9223 (2)	0.83545 (17)	0.0360 (5)
H1C	1.073 (3)	0.920 (3)	0.876 (2)	0.054*
H1D	0.885 (3)	0.995 (2)	0.846 (3)	0.054*
O2W	0.9472 (3)	0.6777 (2)	0.9103 (2)	0.0462 (6)
H2D	0.939 (5)	0.7657 (16)	0.880 (3)	0.069*
H2E	1.053 (4)	0.654 (3)	0.949 (3)	0.069*
O3W	0.0897 (3)	0.4767 (2)	0.2406 (2)	0.0468 (6)
H3A	0.098 (5)	0.418 (3)	0.189 (3)	0.070*
H3B	0.203 (3)	0.503 (4)	0.236 (3)	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01678 (16)	0.01334 (15)	0.01508 (16)	−0.00573 (11)	0.00260 (11)	−0.00256 (11)
P1	0.0135 (3)	0.0157 (3)	0.0150 (3)	−0.0049 (2)	−0.0002 (2)	−0.0017 (2)
N1	0.0136 (9)	0.0130 (10)	0.0170 (10)	−0.0049 (7)	−0.0011 (8)	−0.0023 (8)
O1	0.0160 (8)	0.0241 (9)	0.0182 (9)	−0.0056 (7)	0.0027 (7)	−0.0049 (7)
O2	0.0235 (9)	0.0192 (9)	0.0240 (10)	−0.0101 (7)	0.0012 (7)	−0.0049 (7)
O3	0.0201 (9)	0.0219 (9)	0.0196 (9)	−0.0044 (7)	−0.0037 (7)	0.0030 (7)
O4	0.0250 (9)	0.0176 (9)	0.0211 (9)	−0.0090 (7)	0.0041 (7)	−0.0053 (7)
O5	0.0405 (11)	0.0160 (9)	0.0301 (11)	−0.0130 (8)	0.0083 (9)	−0.0080 (8)
O6	0.0175 (9)	0.0227 (9)	0.0187 (9)	−0.0065 (7)	0.0004 (7)	−0.0009 (7)
O7	0.0176 (9)	0.0367 (11)	0.0188 (10)	−0.0121 (8)	−0.0014 (7)	−0.0012 (8)
C1	0.0141 (11)	0.0184 (12)	0.0148 (12)	−0.0048 (9)	−0.0012 (9)	−0.0007 (9)
C2	0.0179 (12)	0.0135 (11)	0.0247 (14)	−0.0036 (9)	0.0003 (10)	−0.0056 (10)
C3	0.0212 (12)	0.0150 (12)	0.0207 (13)	−0.0050 (9)	−0.0007 (10)	−0.0006 (10)
C4	0.0151 (11)	0.0187 (12)	0.0177 (12)	−0.0074 (9)	−0.0004 (9)	−0.0019 (9)
C5	0.0150 (11)	0.0148 (11)	0.0205 (13)	−0.0034 (9)	−0.0011 (9)	−0.0045 (10)
N2	0.0164 (10)	0.0177 (10)	0.0164 (10)	−0.0042 (8)	−0.0005 (8)	−0.0014 (8)
N3	0.0172 (10)	0.0173 (10)	0.0157 (10)	−0.0062 (8)	−0.0001 (8)	−0.0027 (8)
C6	0.0259 (13)	0.0182 (12)	0.0177 (13)	−0.0072 (10)	−0.0008 (10)	−0.0006 (10)
C7	0.0316 (15)	0.0183 (13)	0.0306 (16)	−0.0109 (11)	−0.0014 (12)	0.0008 (11)
C8	0.0301 (15)	0.0184 (13)	0.0343 (16)	−0.0042 (11)	−0.0033 (12)	−0.0096 (12)
C9	0.0202 (12)	0.0222 (13)	0.0225 (14)	−0.0033 (10)	−0.0026 (10)	−0.0064 (10)
C10	0.0131 (11)	0.0184 (12)	0.0174 (12)	−0.0030 (9)	−0.0024 (9)	−0.0026 (9)
C11	0.0121 (11)	0.0226 (13)	0.0156 (12)	−0.0032 (9)	−0.0016 (9)	−0.0034 (10)
C12	0.0189 (13)	0.0284 (14)	0.0191 (13)	−0.0026 (10)	0.0001 (10)	−0.0020 (11)

C13	0.0251 (14)	0.0369 (16)	0.0179 (13)	−0.0018 (12)	0.0026 (10)	−0.0101 (12)
C14	0.0251 (14)	0.0310 (15)	0.0239 (15)	−0.0013 (11)	−0.0018 (11)	−0.0138 (12)
C15	0.0290 (15)	0.0381 (17)	0.0179 (14)	−0.0056 (12)	0.0064 (11)	0.0032 (12)
C16	0.0328 (15)	0.0284 (15)	0.0276 (16)	−0.0090 (12)	0.0024 (12)	0.0091 (12)
C17	0.0230 (13)	0.0204 (13)	0.0260 (14)	−0.0054 (10)	0.0013 (11)	0.0014 (11)
O1W	0.0303 (11)	0.0443 (13)	0.0325 (12)	0.0029 (9)	−0.0091 (9)	−0.0116 (10)
O2W	0.0379 (13)	0.0457 (14)	0.0583 (17)	−0.0115 (11)	0.0007 (11)	−0.0157 (12)
O3W	0.0364 (13)	0.0486 (15)	0.0603 (17)	−0.0151 (11)	0.0086 (11)	−0.0214 (13)

Geometric parameters (Å, º)

Cu1—O1	2.474 (2)	N3—C6	1.326 (3)
Cu1—O4	1.9412 (18)	N3—C10	1.359 (3)
Cu1—N2	2.005 (2)	C6—C7	1.399 (4)
Cu1—N3	2.032 (2)	C6—H6	0.9500
Cu1—N1	2.118 (2)	C7—C8	1.371 (4)
Cu1—O6	2.3489 (18)	C7—H7	0.9500
P1—O3	1.4902 (19)	C8—C9	1.404 (4)
P1—O1	1.5145 (18)	C8—H8	0.9500
P1—O2	1.5775 (19)	C9—C10	1.405 (3)
P1—C1	1.816 (2)	C9—C14	1.436 (4)
N1—C4	1.486 (3)	C10—C11	1.435 (3)
N1—C2	1.495 (3)	C11—C12	1.399 (3)
N1—C1	1.496 (3)	C12—C15	1.406 (4)
O2—H2C	0.897 (10)	C12—C13	1.443 (4)
O4—C3	1.274 (3)	C13—C14	1.351 (4)
O5—C3	1.242 (3)	C13—H13	0.9500
O6—C5	1.219 (3)	C14—H14	0.9500
O7—C5	1.306 (3)	C15—C16	1.370 (4)
O7—H7A	0.89 (3)	C15—H15	0.9500
C1—H1A	0.9900	C16—C17	1.399 (4)
C1—H1B	0.9900	C16—H16	0.9500
C2—C3	1.508 (3)	C17—H17	0.9500
C2—H2A	0.9900	O1W—H1C	0.947 (10)
C2—H2B	0.9900	O1W—H1D	0.946 (10)
C4—C5	1.510 (3)	O2W—H2D	0.961 (10)
C4—H4A	0.9900	O2W—H2E	0.96 (3)
C4—H4B	0.9900	O3W—H3A	0.97 (3)
N2—C17	1.324 (3)	O3W—H3B	0.95 (3)
N2—C11	1.358 (3)		
O4—Cu1—N2	90.72 (8)	O6—C5—C4	122.4 (2)
O4—Cu1—N3	166.90 (8)	O7—C5—C4	116.4 (2)
N2—Cu1—N3	82.18 (9)	C17—N2—C11	118.1 (2)
O4—Cu1—N1	84.52 (8)	C17—N2—Cu1	129.03 (18)
N2—Cu1—N1	167.49 (8)	C11—N2—Cu1	112.88 (16)
N3—Cu1—N1	104.59 (8)	C6—N3—C10	117.5 (2)
O4—Cu1—O6	102.28 (7)	C6—N3—Cu1	130.76 (17)

N2—Cu1—O6	94.96 (8)	C10—N3—Cu1	111.66 (16)
N3—Cu1—O6	89.34 (8)	N3—C6—C7	123.2 (2)
N1—Cu1—O6	74.86 (7)	N3—C6—H6	118.4
O3—P1—O1	117.43 (11)	C7—C6—H6	118.4
O3—P1—O2	112.75 (11)	C8—C7—C6	119.3 (3)
O1—P1—O2	106.59 (10)	C8—C7—H7	120.4
O3—P1—C1	105.72 (11)	C6—C7—H7	120.4
O1—P1—C1	106.49 (11)	C7—C8—C9	119.5 (2)
O2—P1—C1	107.30 (11)	C7—C8—H8	120.3
C4—N1—C2	109.19 (18)	C9—C8—H8	120.3
C4—N1—C1	109.67 (18)	C8—C9—C10	117.2 (2)
C2—N1—C1	110.71 (19)	C8—C9—C14	124.0 (2)
C4—N1—Cu1	110.98 (15)	C10—C9—C14	118.9 (2)
C2—N1—Cu1	103.24 (14)	N3—C10—C9	123.4 (2)
C1—N1—Cu1	112.86 (14)	N3—C10—C11	116.9 (2)
P1—O2—H2C	113 (2)	C9—C10—C11	119.6 (2)
C3—O4—Cu1	116.37 (16)	N2—C11—C12	123.3 (2)
C5—O6—Cu1	109.37 (16)	N2—C11—C10	116.3 (2)
C5—O7—H7A	113 (2)	C12—C11—C10	120.3 (2)
N1—C1—P1	115.22 (16)	C11—C12—C15	117.0 (2)
N1—C1—H1A	108.5	C11—C12—C13	119.0 (2)
P1—C1—H1A	108.5	C15—C12—C13	124.0 (2)
N1—C1—H1B	108.5	C14—C13—C12	120.6 (2)
P1—C1—H1B	108.5	C14—C13—H13	119.7
H1A—C1—H1B	107.5	C12—C13—H13	119.7
N1—C2—C3	113.06 (19)	C13—C14—C9	121.6 (2)
N1—C2—H2A	109.0	C13—C14—H14	119.2
C3—C2—H2A	109.0	C9—C14—H14	119.2
N1—C2—H2B	109.0	C16—C15—C12	119.5 (3)
C3—C2—H2B	109.0	C16—C15—H15	120.2
H2A—C2—H2B	107.8	C12—C15—H15	120.2
O5—C3—O4	123.3 (2)	C15—C16—C17	119.4 (3)
O5—C3—C2	119.5 (2)	C15—C16—H16	120.3
O4—C3—C2	117.1 (2)	C17—C16—H16	120.3
N1—C4—C5	110.69 (19)	N2—C17—C16	122.6 (3)
N1—C4—H4A	109.5	N2—C17—H17	118.7
C5—C4—H4A	109.5	C16—C17—H17	118.7
N1—C4—H4B	109.5	H1C—O1W—H1D	109.3 (15)
C5—C4—H4B	109.5	H2D—O2W—H2E	107.8 (15)
H4A—C4—H4B	108.1	H3A—O3W—H3B	106 (3)
O6—C5—O7	121.1 (2)		
O4—Cu1—N1—C4	−133.86 (16)	O6—Cu1—N2—C11	88.28 (17)
N2—Cu1—N1—C4	−65.9 (4)	O4—Cu1—N3—C6	−119.3 (4)
N3—Cu1—N1—C4	55.73 (16)	N2—Cu1—N3—C6	−176.9 (2)
O6—Cu1—N1—C4	−29.53 (14)	N1—Cu1—N3—C6	13.8 (2)
O4—Cu1—N1—C2	−16.99 (14)	O6—Cu1—N3—C6	88.0 (2)
N2—Cu1—N1—C2	51.0 (4)	O4—Cu1—N3—C10	57.0 (4)

N3—Cu1—N1—C2	172.59 (14)	N2—Cu1—N3—C10	−0.72 (16)
O6—Cu1—N1—C2	87.33 (14)	N1—Cu1—N3—C10	−169.99 (16)
O4—Cu1—N1—C1	102.58 (16)	O6—Cu1—N3—C10	−95.82 (16)
N2—Cu1—N1—C1	170.6 (3)	C10—N3—C6—C7	−0.8 (4)
N3—Cu1—N1—C1	−67.84 (16)	Cu1—N3—C6—C7	175.2 (2)
O6—Cu1—N1—C1	−153.10 (16)	N3—C6—C7—C8	1.2 (4)
N2—Cu1—O4—C3	−162.28 (19)	C6—C7—C8—C9	−0.4 (4)
N3—Cu1—O4—C3	140.9 (3)	C7—C8—C9—C10	−0.8 (4)
N1—Cu1—O4—C3	6.14 (18)	C7—C8—C9—C14	179.6 (3)
O6—Cu1—O4—C3	−67.04 (19)	C6—N3—C10—C9	−0.4 (4)
O4—Cu1—O6—C5	105.68 (17)	Cu1—N3—C10—C9	−177.19 (19)
N2—Cu1—O6—C5	−162.50 (16)	C6—N3—C10—C11	178.5 (2)
N3—Cu1—O6—C5	−80.40 (17)	Cu1—N3—C10—C11	1.7 (3)
N1—Cu1—O6—C5	24.90 (16)	C8—C9—C10—N3	1.2 (4)
C4—N1—C1—P1	−158.30 (16)	C14—C9—C10—N3	−179.1 (2)
C2—N1—C1—P1	81.2 (2)	C8—C9—C10—C11	−177.6 (2)
Cu1—N1—C1—P1	−34.0 (2)	C14—C9—C10—C11	2.0 (4)
O3—P1—C1—N1	168.57 (16)	C17—N2—C11—C12	0.7 (4)
O1—P1—C1—N1	42.95 (19)	Cu1—N2—C11—C12	179.84 (19)
O2—P1—C1—N1	−70.88 (19)	C17—N2—C11—C10	−177.8 (2)
C4—N1—C2—C3	142.9 (2)	Cu1—N2—C11—C10	1.4 (3)
C1—N1—C2—C3	−96.3 (2)	N3—C10—C11—N2	−2.1 (3)
Cu1—N1—C2—C3	24.8 (2)	C9—C10—C11—N2	176.8 (2)
Cu1—O4—C3—O5	−176.5 (2)	N3—C10—C11—C12	179.4 (2)
Cu1—O4—C3—C2	7.5 (3)	C9—C10—C11—C12	−1.7 (4)
N1—C2—C3—O5	160.4 (2)	N2—C11—C12—C15	0.0 (4)
N1—C2—C3—O4	−23.5 (3)	C10—C11—C12—C15	178.4 (2)
C2—N1—C4—C5	−80.9 (2)	N2—C11—C12—C13	−178.3 (2)
C1—N1—C4—C5	157.64 (19)	C10—C11—C12—C13	0.1 (4)
Cu1—N1—C4—C5	32.3 (2)	C11—C12—C13—C14	1.2 (4)
Cu1—O6—C5—O7	160.49 (19)	C15—C12—C13—C14	−177.0 (3)
Cu1—O6—C5—C4	−14.7 (3)	C12—C13—C14—C9	−0.9 (4)
N1—C4—C5—O6	−10.2 (3)	C8—C9—C14—C13	178.9 (3)
N1—C4—C5—O7	174.4 (2)	C10—C9—C14—C13	−0.7 (4)
O4—Cu1—N2—C17	9.7 (2)	C11—C12—C15—C16	−0.6 (4)
N3—Cu1—N2—C17	178.7 (2)	C13—C12—C15—C16	177.6 (3)
N1—Cu1—N2—C17	−57.7 (5)	C12—C15—C16—C17	0.5 (4)
O6—Cu1—N2—C17	−92.7 (2)	C11—N2—C17—C16	−0.8 (4)
O4—Cu1—N2—C11	−169.33 (17)	Cu1—N2—C17—C16	−179.8 (2)
N3—Cu1—N2—C11	−0.38 (16)	C15—C16—C17—N2	0.2 (4)
N1—Cu1—N2—C11	123.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*C*···O5[i]	0.90 (1)	1.67 (1)	2.564 (3)	175 (3)
O7—H7*A*···O1[ii]	0.89 (3)	1.66 (3)	2.540 (3)	168 (3)
O1*W*—H1*C*···O3[iii]	0.95 (1)	1.77 (1)	2.717 (3)	178 (3)

O1W—H1D⋯O1^{iv}	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^{iii}	0.96 (3)	2.17 (2)	3.087 (3)	160 (3)
O3W—H3A⋯O2W^{v}	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) $-x+1, -y+1, -z+1$.