Crystal structure of magnesium copper(II) bis[orthophosphate(V)] monohydrate

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Single crystals of magnesium copper(II) bis[orthophosphate(V)] monohydrate, $Mg_{1.65}Cu_{1.35}(PO_4)_2 \cdot H_2O$, were grown under hydrothermal conditions. The crystal structure is formed by three types of cationic sites and by two unique $(PO_4)^{3-}$ anions. One site is occupied by Cu^{2+}, the second site by Mg^{2+} and the third site by a mixture of the two cations with an $Mg^{2+}:Cu^{2+}$ occupancy ratio of 0.657 (3):0.343 (3). The structure is built up from more or less distorted $[MgO_6]$ and $[(Mg/Cu)O_5(H_2O)]$ octahedra, $[CuO_5]$ square-pyramids and regular PO_4 tetrahedra, leading to a framework structure. Within this framework, two types of layers parallel to ($\overline{1}01$) can be distinguished. The first layer is formed by $[Cu_2O_8]$ dimers linked to PO_4 tetrahedra via common edges. The second, more corrugated layer results from the linkage between $[(Cu/Mg)_2O_8(H_2O)_2]$ dimers and $[MgO_6]$ octahedra by common edges. The PO_4 units link the two types of layers, leaving space for channels parallel [101], into which the H atoms of the water molecules protrude. The latter are involved in O—H···O hydrogen-bonding interactions (one bifurcated) with framework O atoms across the channels.

1. Chemical context

Transition metal phosphates are an important class of materials characterized by a great structural diversity originating from the presence of different coordination polyhedra MO_n (with n = 4, 5 and 6) or the possibility of phosphate groups to condense. The alternation of PO_4 tetrahedra and MO_n polyhedra can give rise to different anionic frameworks $[M^{II}PO_4]^-$ with pores or channels offering suitable environments to accommodate different other cations (Gao & Gao, 2005; Viter & Nagornyi, 2009). In previous studies, our focus of research was dedicated to the examination of mixed divalent orthophosphates with general formula $(M,M')_3(PO_4)_2 \cdot nH_2O$. For instance, we have succeeded in the preparation and structure determination of some new phosphates such as $Ni_2Sr(PO_4)_2 \cdot 2H_2O$ (Assani et al., 2010a).

In the context of our main research, we report here the hydrothermal synthesis and structural characterization of the mixed-metal orthophosphate $Mg_{1.65}Cu_{1.35}(PO_4)_2 \cdot H_2O$, isolated during investigation of the quinternary system $Ag_2O/MgO/CuO/P_2O_5/H_2O$. The title compound crystallizes in the $Fe_3(PO_4)_2 \cdot H_2O$ structure type (Moore & Araki, 1975) and is isotypic with other phases of the type $(M,M')_3(PO_4)_2 \cdot H_2O$ (Liao et al., 1995), viz. $Co_{2.59}Zn_{0.41}(PO_4)_2 \cdot H_2O$ (Sørensen et al., 2005), $Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$ (Assani et al., 2010b), $(Cu_{1-x}Co_x)_3(PO_4)_2 \cdot H_2O$ (0 < x < 0.20 and 0.55 < x < 0.65), and $(Cu_{1-x}Zn_x)_3(PO_4)_2 \cdot H_2O$ (0 < x < 0.19) (Viter & Nagornyi, 2006).
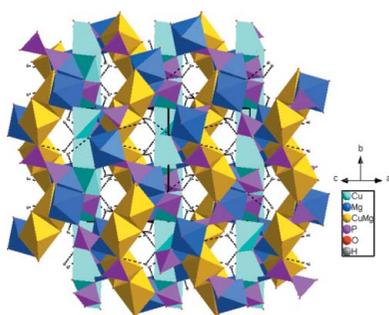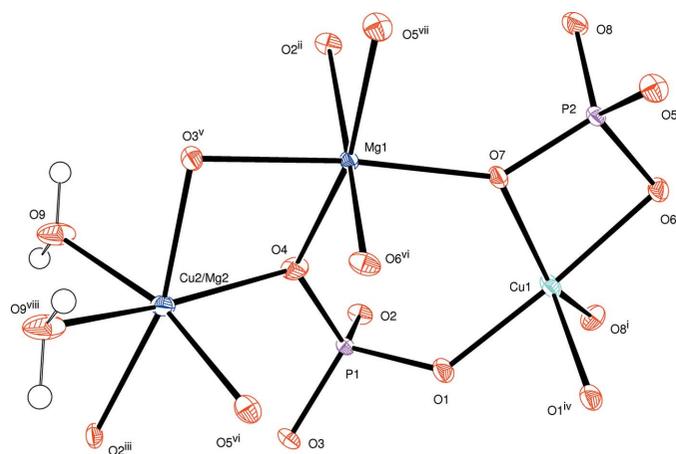
Figure 1
The principal building units in the crystal structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + 2, -y + 1, -z + 2$; (vii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (viii) $-x + 2, -y + 2, -z + 1$.]

2. Structural commentary

The principal building units of the crystal structure of the title compound are represented in Fig. 1. The metal cations are located in three crystallographically independent sites, one octahedrally surrounded site entirely occupied by Mg^{2+}, one site with a square-pyramidal coordination completely occupied by Cu^{2+} and one mixed-occupied (Mg^{2+}/Cu^{2+}) site with an octahedral coordination. The $[Cu1O_5]$ square pyramid is distorted, with Cu—O bond lengths ranging from 1.9073 (17) to 2.2782 (16) Å. Two $[Cu1O_5]$ polyhedra are linked together by edge-sharing to build up a $[Cu_2O_8]$ dimer. By sharing
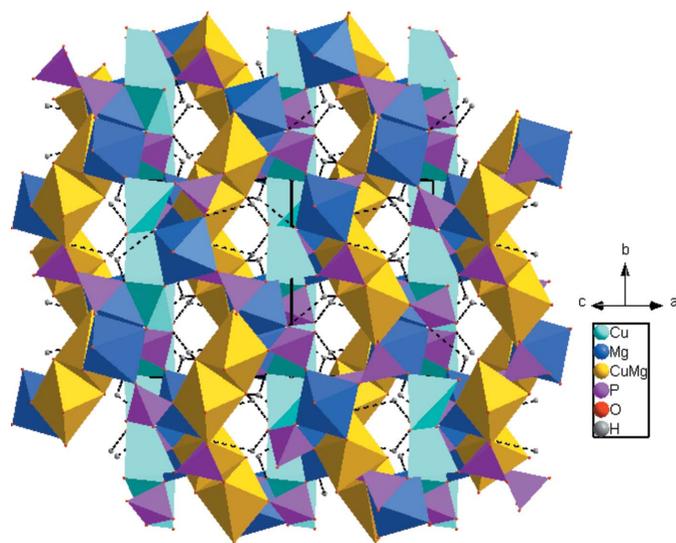

Figure 2
A polyhedral view of the title compound, showing the three-dimensional framework structure and O—H···O hydrogen bonding (dashed lines) in the channels.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9A···O1[i]	0.86	2.22	2.867 (2)	132
O9—H9A···O6[ii]	0.86	2.38	2.934 (2)	123
O9—H9B···O8[iii]	0.86	1.93	2.778 (2)	170

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

corners with PO_4 tetrahedra, a layered arrangement parallel to ($\bar{1}01$) is formed (Fig. 2). The mixed-occupied $[(Mg/Cu)O_5(H_2O)]$ octahedron is likewise distorted, with (Mg/Cu)—O distances varying between 2.0038 (18) and 2.384 (2) Å. Two $[(Mg/Cu)O_5(H_2O)]$ octahedra share a common edge to built up another dimer $[(Mg/Cu)_2O_8(H_2O)_2]$ that links $[MgO_6]$ octahedra and PO_4 tetrahedra via common vertices to build the second type of layer lying parallel to the first (Fig. 2). Adjacent layers are connected into a three-dimensional framework by common edges and vertices, and delimit channels parallel to [101], into which the hydrogen atoms of the water molecules protrude. O—H···O hydrogen-bonding interactions between the water molecules and framework O atoms are present (Table 1, Fig. 2).

3. Synthesis and crystallization

The title compound, $Mg_{1.65}Cu_{1.35}(PO_4)_2 \cdot H_2O$, was synthesized hydrothermally form a reaction mixture of $AgNO_3$, MgO,

Table 2
Experimental details.

Crystal data	
Chemical formula	$Mg_{1.65}Cu_{1.35}(PO_4)_2 \cdot H_2O$
M_r	333.65
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	8.0701 (1), 9.8661 (2), 8.9944 (2)
β (°)	115.242 (1)
V (Å³)	647.76 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	5.16
Crystal size (mm)	0.31 × 0.27 × 0.18
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (SADABS; Bruker, 2009)
T_{min}, T_{max}	0.574, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9233, 1673, 1617
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.058, 1.24
No. of reflections	1673
No. of parameters	129
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.55, −0.34

Computer programs: APEX2 and SAINT (Bruker, 2009), SHELXS97 and SHELXL97 (Sheldrick, 2008), ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006) and publCIF (Westrip, 2010).

metallic copper, and 85wt% phosphoric acid in the molar ratio Ag: Mg: Cu: P = 1: 4: 4.5: 6 in 12.5 ml of water. The hydrothermal reaction was conducted in a 23 ml Teflon-lined autoclave under autogenous pressure at 493 K for three days. The resulting product was filtered off, washed with deionized water and dried in air. The obtained blue crystals correspond to the title compound.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The $M2$ site features mixed occupation by Mg^{2+} and Cu^{2+} whereas the other two cationic sites do not show any significant disorder. Refinement of the occupancy of $M2$ resulted in a ratio of Mg^{2+}:Cu^{2+} = 0.657 (3):0.343 (3). The O-bound H atoms were initially located in a difference map and refined with O—H distance restraints of 0.83 (5). In the last refinement cycle, the distances were fixed at 0.86 Å and the H atoms refined in the riding-model approximation with U_{iso}(H) set to $1.5U_{eq}$(O). The highest remaining positive and negative electron densities observed in the final Fourier map are at 0.81 Å and 0.43 Å, respectively, from Cu1.

References

Assani, A., Saadi, M. & El Ammari, L. (2010*a*). *Acta Cryst.* E**66**, i44.
Assani, A., Saadi, M., Zriouil, M. & El Ammari, L. (2010*b*). *Acta Cryst.* E**66**, i86–i87.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Gao, D. & Gao, Q. (2005). *Micropor. Mesopor. Mater.* **85**, 365–373.
Liao, J. H., Leroux, F., Guyomard, D., Piffard, Y. & Tournoux, M. (1995). *Eur. J. Solid State Inorg. Chem.* **32**, 403–414.
Moore, P. B. & Araki, T. (1975). *Am. Mineral.* **60**, 454–459.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sørensen, M. B., Hazell, R. G., Bentien, A., Bond, A. D. & Jensen, T. R. (2005). *Dalton Trans.* pp. 598–606.
Viter, V. N. & Nagornyi, P. G. (2006). *Inorg. Mater.* **42**, 406–409.
Viter, V. N. & Nagornyi, P. G. (2009). *Russ. J. Appl. Chem.* **82**, 935–939.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Crystal structure of magnesium copper(II) bis[orthophosphate(V)] monohydrate

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Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Magnesium copper(II) bis[orthophosphate(V)] monohydrate

Crystal data

$Mg_{1.65}Cu_{1.35}(PO_4)_2 \cdot H_2O$	$F(000) = 651$
$M_r = 333.65$	$D_x = 3.421$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -p 2yn	Cell parameters from 1673 reflections
$a = 8.0701$ (1) Å	$\theta = 2.9–28.7°$
$b = 9.8661$ (2) Å	$\mu = 5.16$ mm^{-1}
$c = 8.9944$ (2) Å	$T = 296$ K
$\beta = 115.242$ (1)°	Prism, blue
$V = 647.76$ (2) Å^3	$0.31 \times 0.27 \times 0.18$ mm
$Z = 4$	

Data collection

Bruker X8 APEX diffractometer	9233 measured reflections
Radiation source: fine-focus sealed tube	1673 independent reflections
Graphite monochromator	1617 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$\theta_{max} = 28.7°$, $\theta_{min} = 2.9°$
	$h = -10 \rightarrow 10$
	$k = -11 \rightarrow 13$
$T_{min} = 0.574$, $T_{max} = 0.748$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.020$	H-atom parameters constrained
$wR(F^2) = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 1.2623P]$
$S = 1.24$	where $P = (F_o^2 + 2F_c^2)/3$
1673 reflections	$(\Delta/\sigma)_{max} = 0.001$
129 parameters	$\Delta\rho_{max} = 0.55$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0022 (6)

Special details

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 $F^2 > 2\sigma(F^2)$ 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*	$U_{iso}*/U_{eq}$	Occ. (<1)
Cu1	0.64417 (4)	0.37312 (3)	0.56030 (3)	0.00781 (10)	
Mg1	0.98357 (10)	0.62883 (7)	0.72316 (9)	0.00506 (16)	
Cu2	0.88601 (7)	0.86606 (5)	0.46685 (6)	0.00771 (19)	0.343 (3)
Mg2	0.88601 (7)	0.86606 (5)	0.46685 (6)	0.00771 (19)	0.657 (3)
P1	0.70807 (7)	0.57775 (6)	0.32947 (7)	0.00456 (13)	
P2	0.88138 (7)	0.33721 (6)	0.86197 (7)	0.00517 (13)	
O1	0.5825 (2)	0.51553 (17)	0.4023 (2)	0.0088 (3)	
O4	0.8713 (2)	0.64903 (17)	0.4655 (2)	0.0092 (3)	
O3	0.5882 (2)	0.68080 (16)	0.19945 (19)	0.0068 (3)	
O2	0.7722 (2)	0.46440 (16)	0.2486 (2)	0.0071 (3)	
O5	0.8579 (2)	0.36647 (17)	1.0187 (2)	0.0088 (3)	
O6	0.7227 (2)	0.24356 (17)	0.7487 (2)	0.0081 (3)	
O7	0.8521 (2)	0.46259 (17)	0.75021 (19)	0.0078 (3)	
O8	1.0684 (2)	0.27408 (17)	0.9037 (2)	0.0094 (3)	
O9	1.1046 (2)	0.9118 (2)	0.4255 (2)	0.0139 (4)	
H9A	1.0944	0.9060	0.3265	0.021*	
H9B	1.2106	0.8782	0.4857	0.021*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01066 (15)	0.00588 (15)	0.00473 (15)	−0.00143 (9)	0.00122 (11)	0.00069 (9)
Mg1	0.0054 (3)	0.0042 (3)	0.0049 (3)	−0.0001 (2)	0.0016 (3)	0.0003 (3)
Cu2	0.0060 (3)	0.0097 (3)	0.0068 (3)	0.00074 (16)	0.00216 (19)	0.00187 (17)
Mg2	0.0060 (3)	0.0097 (3)	0.0068 (3)	0.00074 (16)	0.00216 (19)	0.00187 (17)
P1	0.0056 (2)	0.0043 (3)	0.0034 (2)	0.00024 (18)	0.00156 (19)	−0.00019 (18)
P2	0.0064 (2)	0.0046 (2)	0.0041 (2)	−0.00022 (19)	0.00177 (19)	0.00026 (19)
O1	0.0092 (7)	0.0097 (8)	0.0091 (7)	0.0016 (6)	0.0054 (6)	0.0036 (6)
O4	0.0084 (7)	0.0097 (8)	0.0062 (7)	−0.0017 (6)	−0.0001 (6)	−0.0025 (6)
O3	0.0088 (7)	0.0052 (7)	0.0050 (7)	0.0016 (6)	0.0017 (6)	0.0011 (6)
O2	0.0084 (7)	0.0061 (7)	0.0064 (7)	0.0022 (6)	0.0027 (6)	−0.0014 (6)
O5	0.0111 (8)	0.0102 (8)	0.0053 (7)	−0.0004 (6)	0.0036 (6)	−0.0014 (6)
O6	0.0091 (7)	0.0078 (7)	0.0060 (7)	−0.0027 (6)	0.0019 (6)	0.0005 (6)
O7	0.0083 (7)	0.0056 (7)	0.0071 (7)	−0.0014 (6)	0.0011 (6)	0.0021 (6)
O8	0.0086 (7)	0.0099 (8)	0.0094 (8)	0.0025 (6)	0.0035 (6)	0.0030 (6)
O9	0.0085 (7)	0.0256 (10)	0.0073 (8)	0.0035 (7)	0.0032 (6)	0.0045 (7)

Geometric parameters (Å, º)

Cu1—O1	1.9073 (17)	Cu2—O3^{iv}	2.0837 (16)
Cu1—O8^{i}	1.9322 (17)	Cu2—O4	2.1442 (18)
Cu1—O6	1.9980 (16)	Cu2—O9^{viii}	2.384 (2)
Cu1—O7	2.0169 (16)	P1—O4	1.5340 (17)
Cu1—O1^{ii}	2.2782 (16)	P1—O2	1.5392 (16)
Mg1—O7	2.0236 (18)	P1—O3	1.5401 (16)
Mg1—O2^{iii}	2.0898 (17)	P1—O1	1.5491 (17)
Mg1—O4	2.1070 (18)	P2—O8	1.5241 (17)
Mg1—O3^{iv}	2.1071 (17)	P2—O5	1.5279 (17)
Mg1—O6^{v}	2.1156 (17)	P2—O7	1.5473 (17)
Mg1—O5^{vi}	2.1205 (18)	P2—O6	1.5550 (17)
Cu2—O9	2.0038 (18)	O9—H9A	0.8600
Cu2—O5^{v}	2.0268 (17)	O9—H9B	0.8600
Cu2—O2^{vii}	2.0535 (17)		
O1—Cu1—O8^{i}	96.29 (7)	O5^{v}—Cu2—O2^{vii}	80.18 (7)
O1—Cu1—O6	172.25 (7)	O9—Cu2—O3^{iv}	82.06 (7)
O8^{i}—Cu1—O6	91.43 (7)	O5^{v}—Cu2—O3^{iv}	107.59 (7)
O1—Cu1—O7	99.62 (7)	O2^{vii}—Cu2—O3^{iv}	163.32 (7)
O8^{i}—Cu1—O7	146.81 (7)	O9—Cu2—O4	105.96 (8)
O6—Cu1—O7	73.33 (7)	O5^{v}—Cu2—O4	87.11 (7)
O1—Cu1—O1^{ii}	77.52 (7)	O2^{vii}—Cu2—O4	117.13 (7)
O8^{i}—Cu1—O1^{ii}	116.46 (6)	O3^{iv}—Cu2—O4	78.56 (6)
O6—Cu1—O1^{ii}	99.65 (6)	O9—Cu2—O9^{viii}	89.45 (7)
O7—Cu1—O1^{ii}	95.41 (6)	O5^{v}—Cu2—O9^{viii}	80.53 (6)
O7—Mg1—O2^{iii}	98.29 (7)	O2^{vii}—Cu2—O9^{viii}	81.28 (6)
O7—Mg1—O4	101.96 (7)	O3^{iv}—Cu2—O9^{viii}	85.44 (6)
O2^{iii}—Mg1—O4	96.67 (7)	O4—Cu2—O9^{viii}	155.82 (7)
O7—Mg1—O3^{iv}	171.09 (8)	O4—P1—O2	111.26 (9)
O2^{iii}—Mg1—O3^{iv}	90.39 (7)	O4—P1—O3	110.54 (9)
O4—Mg1—O3^{iv}	78.89 (7)	O2—P1—O3	110.47 (9)
O7—Mg1—O6^{v}	86.54 (7)	O4—P1—O1	109.79 (9)
O2^{iii}—Mg1—O6^{v}	166.01 (7)	O2—P1—O1	108.93 (9)
O4—Mg1—O6^{v}	95.14 (7)	O3—P1—O1	105.69 (9)
O3^{iv}—Mg1—O6^{v}	84.55 (7)	O8—P2—O5	110.47 (9)
O7—Mg1—O5^{vi}	89.35 (7)	O8—P2—O7	110.33 (9)
O2^{iii}—Mg1—O5^{vi}	77.24 (7)	O5—P2—O7	113.81 (9)
O4—Mg1—O5^{vi}	167.90 (8)	O8—P2—O6	111.75 (10)
O3^{iv}—Mg1—O5^{vi}	90.60 (7)	O5—P2—O6	108.96 (9)
O6^{v}—Mg1—O5^{vi}	89.76 (7)	O7—P2—O6	101.22 (9)
O9—Cu2—O5^{v}	165.32 (8)	H9A—O9—H9B	104.9
O9—Cu2—O2^{vii}	87.74 (7)		

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*−1/2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) *x*+1/2, −*y*+3/2, *z*+1/2; (v) −*x*+3/2, *y*+1/2, −*z*+3/2; (vi) −*x*+2, −*y*+1, −*z*+2; (vii) −*x*+3/2, *y*+1/2, −*z*+1/2; (viii) −*x*+2, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9*A*···O1[vii]	0.86	2.22	2.867 (2)	132
O9—H9*A*···O6[iii]	0.86	2.38	2.934 (2)	123
O9—H9*B*···O8[ix]	0.86	1.93	2.778 (2)	170

Symmetry codes: (iii) −*x*+2, −*y*+1, −*z*+1; (vii) −*x*+3/2, *y*+1/2, −*z*+1/2; (ix) −*x*+5/2, *y*+1/2, −*z*+3/2.