inorganic compounds

Dicobalt copper bis[orthophosphate(V)] monohydrate, $Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$

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In an attempt to hydrothermally synthesize a phase with composition $Co_2Cu(PO_4)_2 \cdot H_2O$, we obtained the title compound, $Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$ instead. Chemical analysis confirmed the presence of copper in the crystal. The crystal structure of the title compound can be described as a three-dimensional network constructed from the stacking of two types of layers extending parallel to (010). These layers are made up from more or less deformed polyhedra: CoO_6 octahedra, $(Cu/Co)O_5$ square pyramids and PO_4 tetrahedra. The first layer is formed by pairs of edge-sharing $(Cu/Co)O_5$ square pyramids linked *via* a common edge of each end of the $(Cu/Co)_2O_8$ dimer to PO_4 tetrahedra. The second layer is undulating and is built up from edge-sharing CoO_6 octahedra. The linkage between the two layers is accomplished by PO_4 tetrahedra. The presence of water molecules in the $CoO_4(H_2O)_2$ octahedron also contributes to the cohesion of the layers through $O—H \cdots O$ hydrogen bonding.

Related literature

For the properties of and background to metal phosphates, see: Clearfield (1988); Gao & Gao (2005); Viter & Nagornyi (2009); Harrison *et al.* (1995). For compounds with the same structure, see: Anderson *et al.* (1976); Liao *et al.* (1995); Sørensen *et al.* (2004); Moore & Araki (1975).

Experimental

Crystal data

$Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$
$M_r = 387.57$
Monoclinic, $P2_1/n$
$a = 8.086$ (2) Å
$b = 9.826$ (3) Å
$c = 9.042$ (3) Å
$\beta = 114.621$ (1)°
$V = 653.1$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 8.49$ mm^{-1}
$T = 296$ K
$0.24 \times 0.12 \times 0.06$ mm

Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.306$, $T_{max} = 0.601$
13678 measured reflections
3531 independent reflections
3278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.051$
$S = 1.10$
3531 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

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

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$O9—H9A \cdots O1$	0.83	1.97	2.768 (2)	159
$O9—H9B \cdots O5^{i}$	0.92	2.27	2.942 (2)	130
$O9—H9B \cdots O4^{ii}$	0.92	2.30	2.905 (2)	123

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; 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, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Dicobalt copper bis[orthophosphate(V)] monohydrate, $Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$

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S1. Comment

Metal-phosphates have received great attention owing to their applications such as catalysts (Viter & Nagornyi, 2009; Gao & Gao, 2005) and as ion-exchangers (Clearfield, 1988)). Mainly, the flexibility of the metal coordination and the possibility to generate anionic frameworks $M^{II}PO_4^-$, analogous to $AlSiO_4^-$ in the well known aluminosilicate zeolites, offer a rich structural diversity of this family of compounds.

Our interest is particularly focused on the hydrothermally synthesized orthophosphates with formula $MM'_2(PO_4)_2.H_2O$ (M and M'= bivalent cations). In this work, a new dicobalt copper bis[orthophosphate] monohydrate, $Co_{2.39}Cu_{0.61}(PO_4)_2.H_2O$ was synthesized and structurally characterized.

A three-dimensional view of the crystal structure of the title compound is given in Fig. 1. It shows that the metal cations are located in three crystallographically different sites, two octahedra entirely occupied by cobalt and one square-pyramid statistically filled with Co/Cu. Refinement of the occupancy of this metal site has led to the following composition, $Co_{2.39}Cu_{0.61}(PO_4)_2.H_2O$. The cationic distributions indicate that Cu prefers the site with a lower coordination number, whereas Co prefers coordination number of 6. This may be attributed to a gain in crystal field stabilisation energy for Co^{2+} in the octahedral sites and to the small difference between the sizes of the two cations Co^{2+} and Cu^{2+}.

The network is built up from three different types of polyhedra more or less distorted: CoO_6 octahedra , $(Cu/Co)O_5$ square-pyramids and PO_4 tetrahedra. One octahedron (Co1), slightly distorted, has a coordination sphere composed of O atoms from PO_4 groups, while that of the other (Co2) is made up of four O atoms from PO_4 groups and by two water molecules (O9). This fact explains its more pronounced distortion, with Co—O bond lengths in the range 2.0407 (11)-2.3310 (13) Å.

All CoO_6 octahedra are linked together by edge-sharing and sharing three corners of PO_4 tetrahedra, in the way to built a layer parallel to (010) as shown in Fig. 2. Therefore, the presence of the water molecule involved in the formation of the $CoO_4(H_2O)_2$ octahedron causes a corrugation in this layer through O—H···O hydrogen bonds. Furthermore, Fig. 3 shows that each pair of distorted square-pyramids share an edge and built up a dimer linked to two regular PO_4 tetrahedra via a common edge. The sequence of $(Cu/Co)O_5$ and PO_4 polyhedra leads to the formation of another layer (Fig. 3). As a matter of fact, the network of this structure can be described by stacking these two types of layers as represented in Fig. 4.

Compounds isotypic with the title phase are relatively rare, however, there are four known compounds which adopt this structure, viz. $Co_3(PO_4)_2.H_2O$ (Anderson *et al.*, 1976), $CuMn_2(PO_4)_2.H_2O$ (Liao *et al.*, 1995), $Co_{2.59}Zn_{0.41}(PO_4)_2.H_2O$ (Sørensen *et al.*, 2004) and $Fe_3(PO_4)_2.H_2O$ (Moore & Araki, 1975).

S2. Experimental

The crystals of the title compound were hydrothermally synthesized starting from a mixture of metallic copper (0.0381 g), basic cobalt(II) carbonate (0.0318 g), 85 %$_{wt}$ phosphoric acid (0.10 ml) and 10 ml distilled water. The hydrothermal

synthesis was carried out in 23 ml Teflon-lined autoclave under autogeneous pressure at 468 K during 24 h. The product was filtered off, washed with deionized water and air dried. The reaction product consists of two types of crystals. The first one, dark violet crystals, corresponds to the title compound with the refined composition $Co_{2.39}Cu_{0.61}(PO_4)_2.H_2O$. An elemental chemical analysis (EDS) confirms the presence of copper in the crystal. The second type of crystals is identified to be the known cobalt hydroxy phosphate $Co_2(OH)PO_4$ (Harrison *et al.*, 1995).

S3. Refinement

All H atoms were initially located in a difference map and refined with a O—H distance restraint of 0.84 (1) Å. Later they were refined in the riding model approximation with $U_{iso}(H)$ set to 1.5 $U_{eq}(O)$. Refinements of the site ocupancy factors of the metal sites revealed the octahedrally coordinated sites solely occupied by Co, whereas the 5-coordinated site shows a mixed occupancy of Co:Cu = 0.387 (11):0.613 (11).
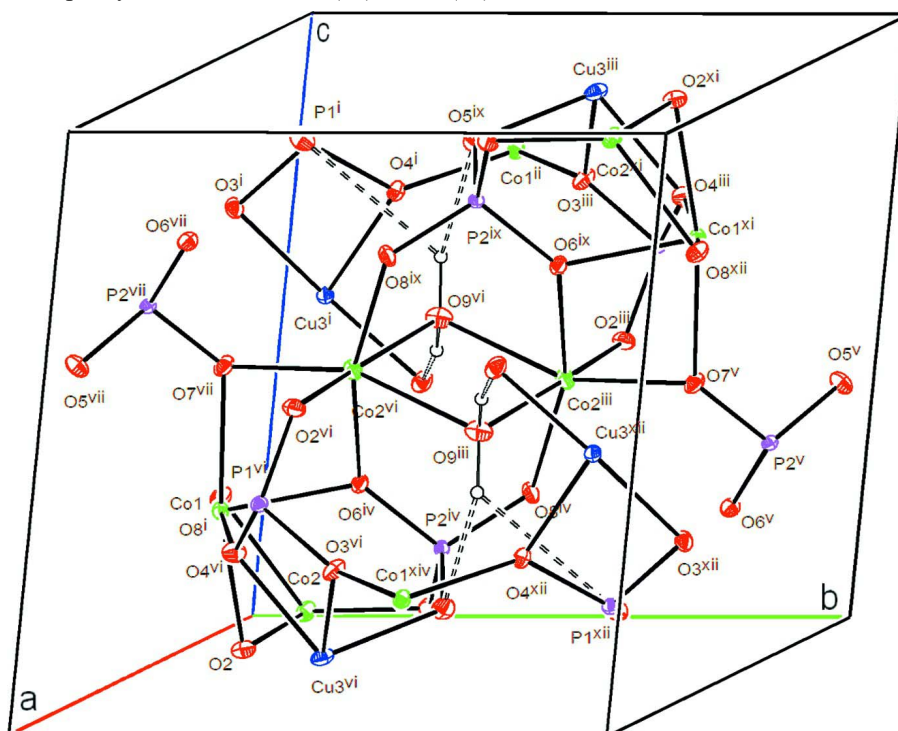
Figure 1

A three-dimensional view of the crystal structure of the $Co_{2.39}Cu_{0.61}(PO_4)_2.H_2O$ compound drawn with displacement parameters at the 60% probability level. H atoms are given as small spheres of arbitrary radius. For symmetry operators, see geometric parameters Table.
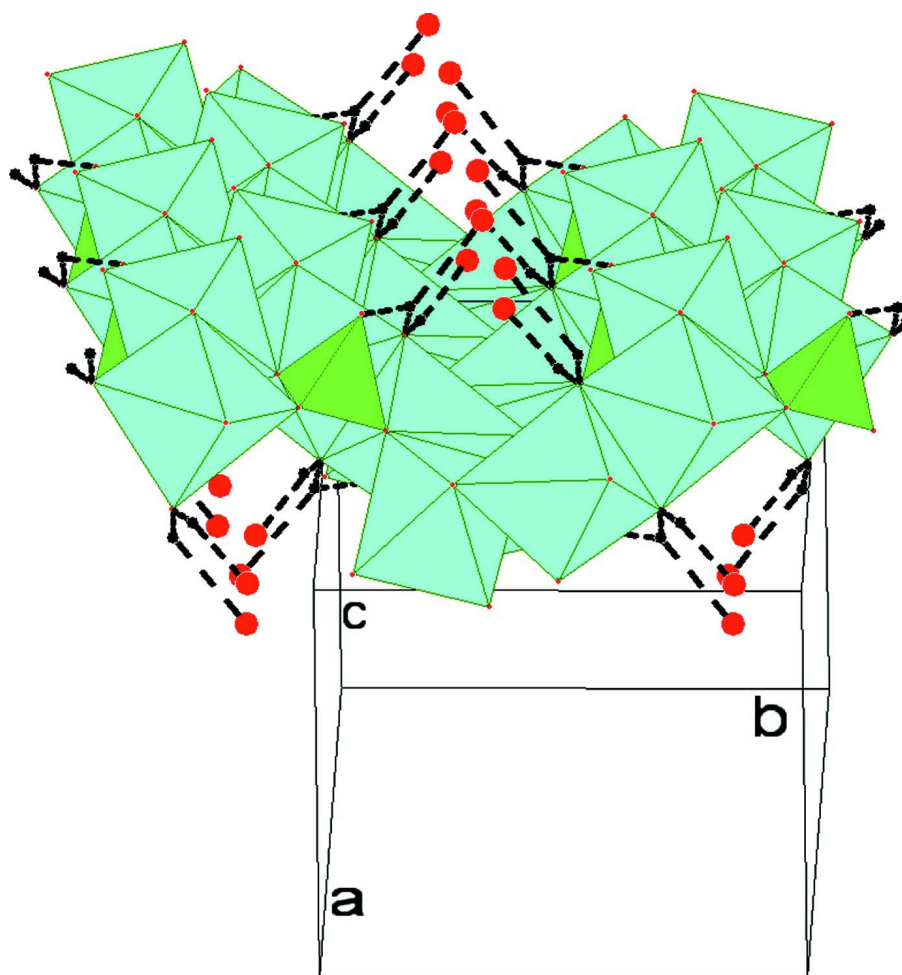
Figure 2

The undulated layer built up from edge sharing CoO_6 octahedra and water molecules.

Figure 3

A copper phosphate layer formed by $(Cu/Co)_2P_2O_{12}$ linked to PO_4 tetrahedra.
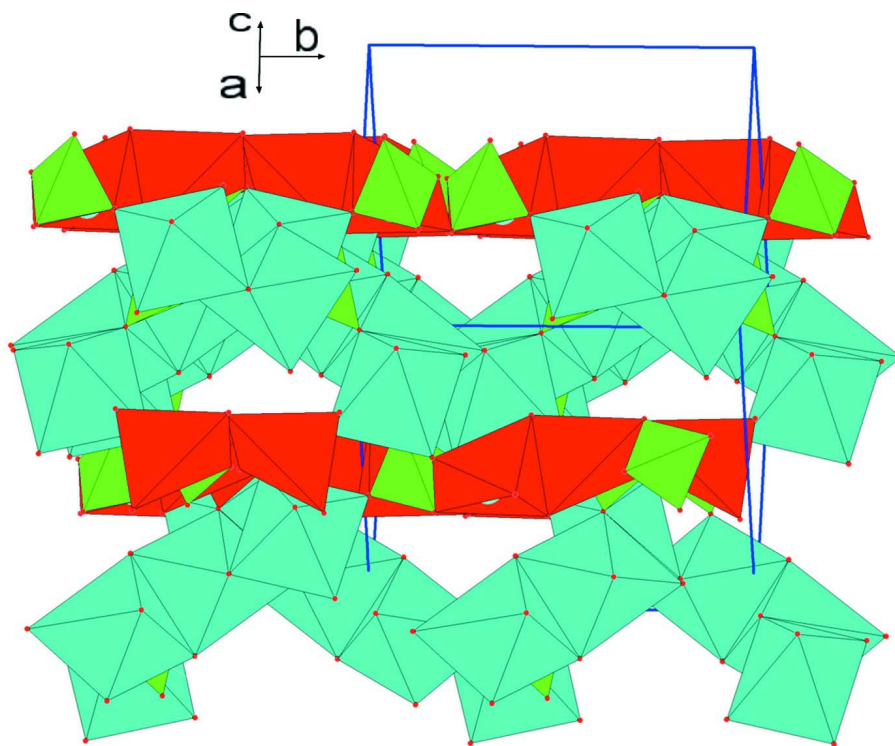
Figure 4

Stacking of the two types of layers projected approximately along [101].

Dicobalt copper bis[orthophosphate(V)] monohydrate

Crystal data

$Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$
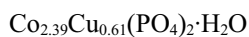
$M_r = 387.57$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 8.086 (2)$ Å

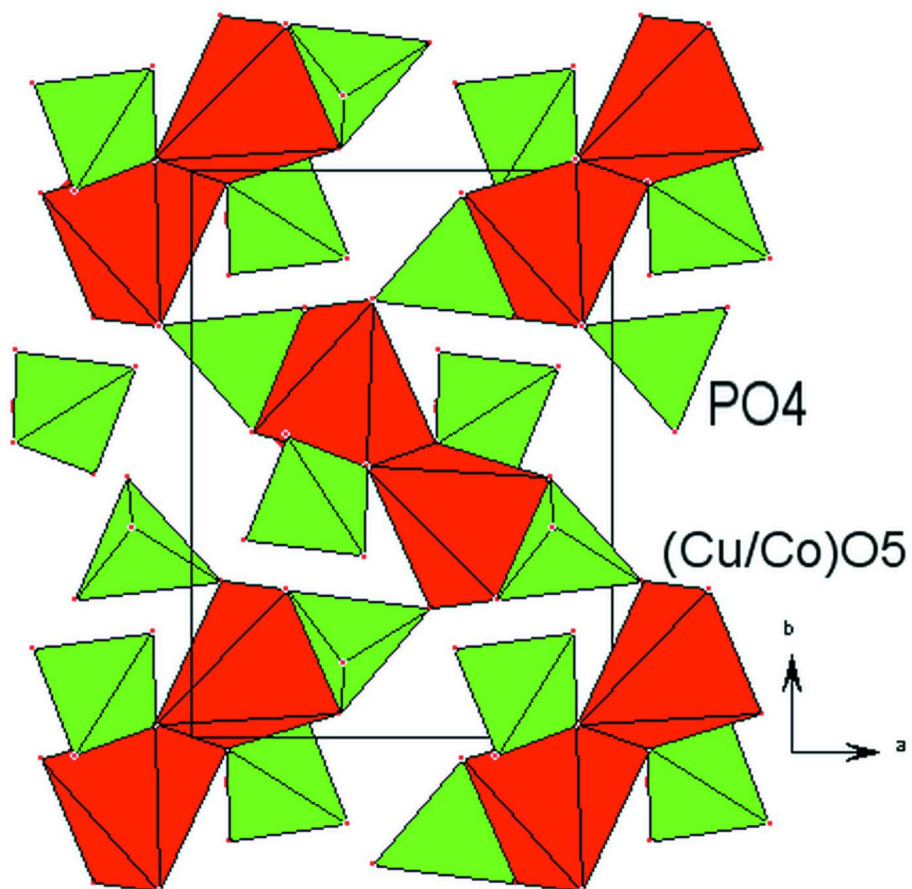$b = 9.826 (3)$ Å

$c = 9.042 (3)$ Å

$\beta = 114.621 (1)°$

$V = 653.1 (3)$ Å^3

$Z = 4$

$F(000) = 745$

$D_x = 3.942$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13678 reflections

$\theta = 2.9–38.0°$

$\mu = 8.49$ mm^{-1}

$T = 296$ K

Block, dark violet

$0.24 \times 0.12 \times 0.06$ mm

Data collection

Bruker X8 APEX diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2005)

$T_{min} = 0.306$, $T_{max} = 0.601$

13678 measured reflections

3531 independent reflections

3278 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$

$\theta_{max} = 38.0°$, $\theta_{min} = 2.9°$

$h = -11 \rightarrow 14$

$k = -16 \rightarrow 16$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from
Least-squares matrix: full	neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H-atom parameters constrained
$wR(F^2) = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2 + 0.5902P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
3531 reflections	$(\Delta/\sigma)_{max} = 0.001$
129 parameters	$\Delta\rho_{max} = 1.01$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.79$ e Å^{-3}
Primary atom site location: structure-invariant	Extinction correction: *SHELXL97* (Sheldrick,
direct methods	2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier	Extinction coefficient: 0.0034 (3)
map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu3	0.14535 (2)	0.125674 (19)	−0.43994 (2)	0.00920 (5)	0.613 (11)
Co3	0.14535 (2)	0.125674 (19)	−0.43994 (2)	0.00920 (5)	0.387 (11)
Co1	0.51531 (2)	0.129584 (19)	0.27594 (2)	0.00646 (4)	
Co2	0.11526 (2)	0.133641 (19)	0.03006 (2)	0.00808 (4)	
P1	0.38414 (4)	0.16385 (4)	−0.13938 (4)	0.00589 (6)	
P2	0.20915 (4)	−0.08141 (3)	−0.67010 (4)	0.00519 (6)	
O1	0.57091 (13)	0.22680 (11)	−0.09698 (12)	0.01030 (17)	
O2	0.36035 (14)	0.13059 (11)	0.01540 (12)	0.00958 (16)	
O3	0.35326 (13)	0.03970 (11)	−0.25406 (12)	0.00944 (16)	
O4	0.22753 (13)	0.25872 (11)	−0.25036 (12)	0.00952 (16)	
O5	0.08457 (14)	−0.02059 (11)	−0.59509 (12)	0.01044 (17)	
O6	0.08992 (13)	−0.18315 (10)	−0.80105 (11)	0.00813 (15)	
O7	0.37173 (13)	−0.15475 (11)	−0.53900 (12)	0.00950 (16)	
O8	0.27312 (13)	0.03376 (10)	−0.74946 (12)	0.00871 (16)	
O9	−0.10961 (14)	0.08498 (12)	0.07202 (12)	0.01199 (18)	
H9A	−0.2021	0.1199	−0.0001	0.018*	
H9B	−0.1031	0.0899	0.1749	0.018*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu3	0.01172 (8)	0.00784 (8)	0.00548 (7)	0.00309 (5)	0.00105 (6)	−0.00054 (5)
Co3	0.01172 (8)	0.00784 (8)	0.00548 (7)	0.00309 (5)	0.00105 (6)	−0.00054 (5)

Co1	0.00605 (7)	0.00578 (8)	0.00694 (7)	0.00026 (5)	0.00208 (5)	−0.00043 (5)
Co2	0.00620 (7)	0.00832 (8)	0.00848 (7)	−0.00025 (5)	0.00182 (6)	0.00165 (6)
P1	0.00590 (11)	0.00584 (13)	0.00529 (12)	0.00016 (10)	0.00170 (9)	−0.00011 (10)
P2	0.00508 (11)	0.00526 (13)	0.00475 (11)	−0.00017 (9)	0.00156 (9)	0.00037 (9)
O1	0.0077 (4)	0.0124 (5)	0.0107 (4)	−0.0029 (3)	0.0037 (3)	−0.0035 (3)
O2	0.0093 (4)	0.0125 (4)	0.0068 (4)	−0.0004 (3)	0.0033 (3)	0.0012 (3)
O3	0.0091 (4)	0.0081 (4)	0.0081 (4)	0.0015 (3)	0.0006 (3)	−0.0024 (3)
O4	0.0093 (4)	0.0095 (4)	0.0086 (4)	0.0038 (3)	0.0026 (3)	0.0017 (3)
O5	0.0102 (4)	0.0120 (4)	0.0115 (4)	−0.0003 (3)	0.0069 (3)	−0.0029 (3)
O6	0.0088 (4)	0.0067 (4)	0.0067 (3)	−0.0016 (3)	0.0011 (3)	−0.0004 (3)
O7	0.0087 (4)	0.0090 (4)	0.0076 (4)	0.0012 (3)	0.0002 (3)	0.0017 (3)
O8	0.0082 (3)	0.0081 (4)	0.0092 (4)	−0.0017 (3)	0.0029 (3)	0.0024 (3)
O9	0.0104 (4)	0.0165 (5)	0.0094 (4)	0.0019 (3)	0.0045 (3)	0.0015 (3)

Geometric parameters (Å, º)

Cu3—O5	1.9236 (11)	P1—O4	1.5558 (11)
Cu3—O1[i]	1.9411 (11)	P2—O7	1.5343 (11)
Cu3—O3	2.0026 (11)	P2—O8	1.5402 (11)
Cu3—O4	2.0347 (12)	P2—O6	1.5427 (11)
Cu3—O5[ii]	2.2614 (11)	P2—O5	1.5496 (10)
Co1—O3[iii]	2.0274 (11)	O1—Co3[vi]	1.9411 (11)
Co1—O6[iv]	2.0791 (11)	O1—Cu3[vi]	1.9411 (11)
Co1—O8[v]	2.0976 (11)	O3—Co1[iii]	2.0274 (11)
Co1—O4[vi]	2.1321 (11)	O4—Co1[i]	2.1320 (11)
Co1—O2	2.1588 (12)	O5—Co3[ii]	2.2613 (11)
Co1—O7[iii]	2.1779 (12)	O5—Cu3[ii]	2.2613 (11)
Co2—O2	2.0407 (11)	O6—Co1[viii]	2.0790 (11)
Co2—O9	2.0625 (11)	O6—Co2[ii]	2.1010 (11)
Co2—O7[iv]	2.0818 (13)	O7—Co2[viii]	2.0818 (12)
Co2—O6[ii]	2.1010 (11)	O7—Co1[iii]	2.1779 (12)
Co2—O8[v]	2.1088 (11)	O8—Co1[ix]	2.0976 (10)
Co2—O9[vii]	2.3310 (13)	O8—Co2[ix]	2.1087 (11)
P1—O2	1.5254 (11)	O9—Co2[vii]	2.3310 (13)
P1—O1	1.5257 (11)	O9—H9A	0.8342
P1—O3	1.5525 (11)	O9—H9B	0.9111
O5—Cu3—O1[i]	96.74 (5)	O9—Co2—O7[iv]	104.98 (4)
O5—Cu3—O3	99.61 (5)	O2—Co2—O6[ii]	109.20 (4)
O1[i]—Cu3—O3	145.59 (4)	O9—Co2—O6[ii]	80.81 (4)
O5—Cu3—O4	171.47 (4)	O7[iv]—Co2—O6[ii]	79.25 (4)
O1[i]—Cu3—O4	91.68 (5)	O2—Co2—O8[v]	80.38 (4)
O3—Cu3—O4	72.46 (4)	O9—Co2—O8[v]	87.19 (4)
O5—Cu3—O5[ii]	77.63 (4)	O7[iv]—Co2—O8[v]	115.29 (4)
O1[i]—Cu3—O5[ii]	114.90 (4)	O6[ii]—Co2—O8[v]	163.32 (4)
O3—Cu3—O5[ii]	98.14 (5)	O2—Co2—O9[vii]	79.64 (4)
O4—Cu3—O5[ii]	100.04 (4)	O9—Co2—O9[vii]	89.19 (4)
O3[iii]—Co1—O6[iv]	172.66 (4)	O7[iv]—Co2—O9[vii]	158.15 (4)

O3^{iii}—Co1—O8^{v}	97.15 (5)	O6^{ii}—Co2—O9^{vii}	86.90 (4)
O6^{iv}—Co1—O8^{v}	90.19 (4)	O8^{v}—Co2—O9^{vii}	81.36 (4)
O3^{iii}—Co1—O4^{vi}	86.13 (5)	O2—P1—O1	110.26 (6)
O6^{iv}—Co1—O4^{vi}	86.65 (4)	O2—P1—O3	113.44 (6)
O8^{v}—Co1—O4^{vi}	167.68 (4)	O1—P1—O3	110.69 (6)
O3^{iii}—Co1—O2	89.25 (4)	O2—P1—O4	109.89 (6)
O6^{iv}—Co1—O2	92.14 (4)	O1—P1—O4	111.95 (6)
O8^{v}—Co1—O2	77.97 (4)	O3—P1—O4	100.30 (6)
O4^{vi}—Co1—O2	90.24 (4)	O7—P2—O8	111.04 (6)
O3^{iii}—Co1—O7^{iii}	101.61 (4)	O7—P2—O6	110.42 (6)
O6^{iv}—Co1—O7^{iii}	77.57 (4)	O8—P2—O6	110.02 (6)
O8^{v}—Co1—O7^{iii}	96.78 (4)	O7—P2—O5	110.30 (6)
O4^{vi}—Co1—O7^{iii}	94.16 (4)	O8—P2—O5	109.04 (6)
O2—Co1—O7^{iii}	168.52 (4)	O6—P2—O5	105.87 (6)
O2—Co2—O9	164.36 (4)	H9A—O9—H9B	115.3
O2—Co2—O7^{iv}	89.00 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O9—H9*A*⋯O1	0.83	1.97	2.768 (2)	159
O9—H9*B*⋯O5^{v}	0.92	2.27	2.942 (2)	130
O9—H9*B*⋯O4^{x}	0.92	2.30	2.905 (2)	123

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