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A second polymorph with composition $Co_3(PO_4)_2{\cdot}H_2O$

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Key indicators: single-crystal X-ray study; T = 150 K; mean σ(P–O) = 0.003 Å; R factor = 0.033; wR factor = 0.095; data-to-parameter ratio = 12.8.

Single crystals of $Co_3(PO_4)_2{\cdot}H_2O$, tricobalt(II) bis[orthophosphate(V)] monohydrate, were obtained under hydrothermal conditions. The compound is the second polymorph of this composition and is isotypic with its zinc analogue, $Zn_3(PO_4)_2{\cdot}H_2O$. Three independent Co^{2+} cations are bridged by two independent orthophosphate anions. Two of the metal cations exhibit a distorted tetrahedral coordination while the third exhibits a considerably distorted [5 + 1] octahedral coordination environment with one very long Co—O distance of 2.416 (3) Å. The former cations are bonded to four different phosphate anions, and the latter cation is bonded to four anions (one of which is bidentate) and one water molecule, leading to a framework structure. Additional hydrogen bonds of the type O—H···O stabilize this arrangement.

Related literature

Besides crystals of the title compound, crystals of the related phase $Co_3(PO_4)_2{\cdot}4H_2O$ (Lee *et al.*, 2008) were also obtained under hydrothermal conditions. For a review of metal complexes of organophosphate esters and open-framework metal phosphates, see: Murugavel *et al.* (2008). For different cobalt(II) phosphates, see: Mellor (1935). The first polymorph of composition $Co_3(PO_4)_2{\cdot}H_2O$ was reported by Anderson *et al.* (1976), and the crystal structure of the isotypic Zn analogue $Zn_3(PO_4)_2{\cdot}H_2O$ was described by Riou *et al.* (1986).

Experimental

Crystal data

$Co_3(PO_4)_2{\cdot}H_2O$
M_r = 384.75
Monoclinic, $P2_1/c$
a = 8.7038 (15) Å
b = 4.8667 (9) Å
c = 16.705 (3) Å
β = 95.670 (3)°
V = 704.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 7.47 mm^{-1}
T = 150 (2) K
0.46 × 0.14 × 0.08 mm

Data collection

Siemens SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999) T_{min} = 0.247, T_{max} = 0.554
6569 measured reflections
1697 independent reflections
1603 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
S = 1.07
1697 reflections
133 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −1.39 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O3	1.897 (3)	Co3—O8^{ii}	2.075 (3)
Co1—O4	1.941 (3)	Co3—O5^{iii}	2.108 (3)
Co1—O2	1.992 (3)	Co3—O3^{iv}	2.416 (3)
Co1—O1	2.002 (3)	P1—O6	1.513 (3)
Co2—O9	1.887 (3)	P1—O4^{i}	1.534 (3)
Co2—O5	1.949 (3)	P1—O2^{v}	1.560 (3)
Co2—O1	1.986 (3)	P1—O1	1.561 (3)
Co2—O2^{i}	2.054 (3)	P2—O9	1.511 (3)
Co3—O6	2.019 (3)	P2—O8^{vi}	1.544 (3)
Co3—O7	2.061 (3)	P2—O3^{vii}	1.549 (3)
Co3—O8	2.065 (3)	P2—O5^{vi}	1.565 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H2···O6^{iii}	0.90 (3)	1.86 (4)	2.753 (4)	170 (5)
O7—H1···O4^{viii}	0.903 (10)	1.864 (15)	2.758 (4)	171 (5)

Symmetry codes: (iii) $x, y+1, z$; (viii) $x+1, y+1, z$.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997), *WebLab ViewerPro* (Molecular Simulations, 2000) and *POV-RAY* (Cason, 2002).; software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2194).

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supporting information

Acta Cryst. (2008). E**64**, i69–i70 [doi:10.1107/S1600536808028365]

A second polymorph with composition $Co_3(PO_4)_2{\cdot}H_2O$

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S1. Comment

Synthesis and structural investigations of transition-metal phosphates under various conditions, including high temperature and high pressure, have been investigated for many years (Murugavel *et al.*, 2008). This is not only because of the multifarious structural chemistry, but also due to many potential applications. For a listing of reviews on these materials, see Lee *et al.* (2008). We are currently investigating the synthesis of a variety of similar functional materials through templation effects under hydrothermal conditions. The title compound, $Co_3(PO_4)_2.H_2O$, (I), and the related compound $Co_3(PO_4)_2.4H_2O$ (Lee *et al.*, 2008) were synthesized as a part of these studies.

In the past, many different cobalt(II) orthophosphates have been described, ranging from the anhydrous form $Co_3(PO_4)_2$ to its corresponding octahydrate (Mellor, 1935). In 1976 Anderson *et al.* reported a first polymorph of $Co_3(PO_4)_2.H_2O$ formed under high pressure conditions. The second polymorph of $Co_3(PO_4)_2.H_2O$ presented here has a different unit cell and a considerably different cell volume (638.3 (Anderson *et al.*, 1976) versus 704.1 Å^3 (this study)) and exhibits also a different assembly of the structural building units. The second polymorph (I) is isotypic with its Zn analogue $Zn_3(PO_4)_2.H_2O$ (Riou *et al.*, 1986).

The structure of (I) contains three different Co^{2+} centres bridged by orthophosphate anions (Fig 1). The coordination spheres of Co1 and Co2 are distorted tetrahedral while that of Co3 is distorted octahedral, with one considerably longer Co—O bond of 2.416 (3) Å (Table 1). Co1 and Co2 are bonded to the O atoms of four phosphate ligands, whereas Co3 is bonded to five O atoms of four phosphate ligands (one bidentate) and the sixth coordination site is occupied by a water molecule. This assembly leads to the formation of a three-dimensional framework (Fig. 2), which is stabilized by additional O—H···O hydrogen bonds (Table 2).

S2. Experimental

Conditions of the hydrothermal single crystal growth of the hydrous cobalt(II) orthophosphates $Co_3(PO_4)_2.H_2O$ and $Co_3(PO_4)_2.4\ H_2O$ were described in detail in a preceding communication (Lee *et al.*, 2008).

S3. Refinement

Water H atoms were located in difference Fourier maps and were refined with U_{iso}(H) values fixed at 1.5U_{eq} of the parent O atoms. O—H bond length restraints of 0.89 (1) Å were also employed. The highest peak and the deepest hole in the final Fourier map are located 1.74 Å from O1 and 0.20 Å from P1, respectively.

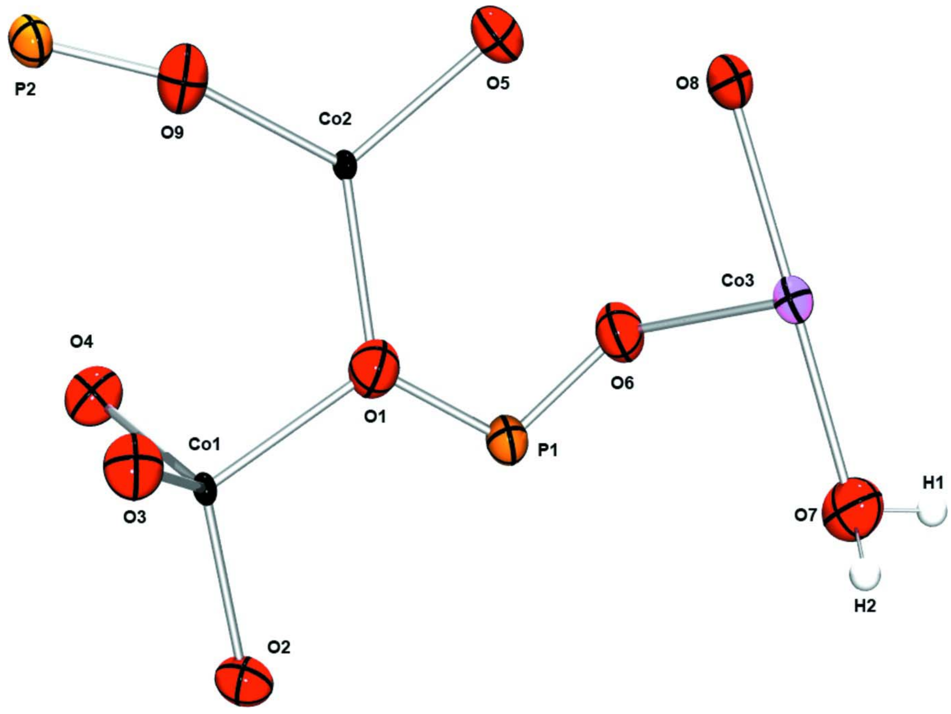

Figure 1

The asymmetric unit of compound (I), drawn with displacement parameters at the 50% probability level. H atoms are given as spheres of arbitrary radius.

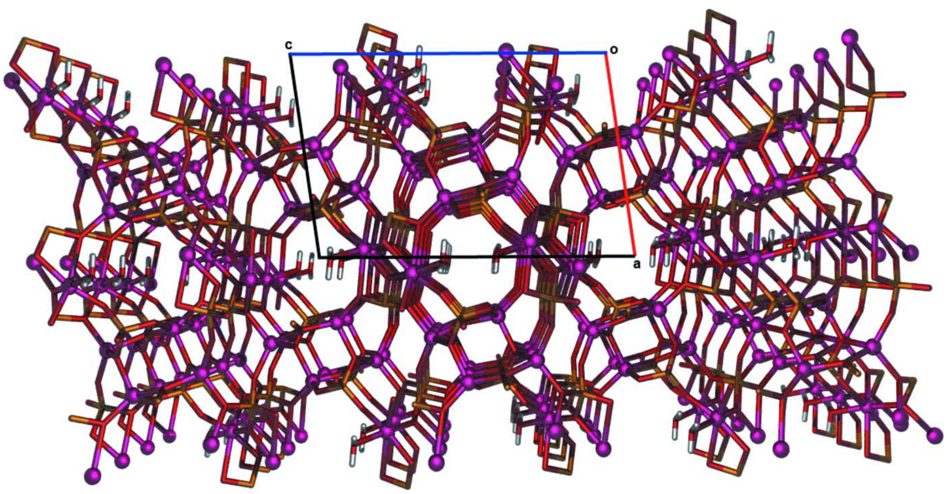

Figure 2

A schematic representation of a section of the three-dimensional network of (I) in a projection along [010]. Hydrogen atoms are omitted for clarity.

tricobalt(II) bis[orthophosphate(V)] monohydrate

Crystal data

$Co_3(PO_4)_2 \cdot H_2O$
M_r = 384.75
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.7038 (15) Å
b = 4.8667 (9) Å

c = 16.705 (3) Å
β = 95.670 (3)°
V = 704.1 (2) Å^3
Z = 4
F(000) = 740
D_x = 3.629 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4684 reflections
θ = 2.5–28.4°
μ = 7.47 mm^{-1}
T = 150 K
Plate, purple
0.46 × 0.14 × 0.08 mm

Data collection

Siemens SMART 1000 CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
T_{min} = 0.247, T_{max} = 0.554
6569 measured reflections
1697 independent reflections
1603 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 28.4°, θ_{min} = 2.4°
h = −11→11
k = −6→6
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
S = 1.07
1697 reflections
133 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 3.2629P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −1.39 e Å^{-3}

Special details

Experimental. The crystal was coated in Exxon Paratone N hydrocarbon oil and mounted on a thin mohair fibre attached to a copper pin. Upon mounting on the diffractometer, the crystal was quenched to 150(K) under a cold nitrogen gas stream supplied by an Oxford Cryosystems Cryostream.

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}
Co1	0.32855 (5)	0.20270 (9)	0.94291 (3)	0.00253 (14)
Co2	0.56640 (5)	−0.20252 (9)	0.84576 (3)	0.00303 (15)
Co3	0.92910 (6)	0.49852 (10)	0.82254 (3)	0.00814 (16)
P1	0.68190 (11)	0.29320 (19)	0.94510 (6)	0.0086 (2)
P2	0.23599 (11)	−0.51187 (19)	0.78087 (6)	0.0087 (2)
O1	0.5357 (3)	0.1481 (6)	0.90286 (17)	0.0114 (5)
O2	0.3621 (3)	0.3976 (6)	1.04804 (16)	0.0106 (5)

O3	0.1907 (3)	0.3427 (6)	0.85760 (17)	0.0119 (5)
O4	0.2836 (3)	−0.1747 (6)	0.96996 (17)	0.0121 (6)
O5	0.7445 (3)	−0.2368 (6)	0.78428 (17)	0.0116 (5)
O6	0.8153 (3)	0.2545 (6)	0.89463 (17)	0.0120 (5)
O7	0.9749 (4)	0.7679 (6)	0.91711 (18)	0.0137 (6)
O8	0.9060 (3)	0.1703 (6)	0.74391 (17)	0.0108 (5)
O9	0.3852 (3)	−0.3512 (6)	0.79103 (18)	0.0148 (6)
H1	1.0769 (18)	0.797 (12)	0.929 (3)	0.022*
H2	0.933 (6)	0.936 (5)	0.909 (3)	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0013 (2)	0.0038 (2)	0.0025 (2)	0.00007 (15)	−0.00013 (17)	0.00053 (15)
Co2	0.0006 (2)	0.0045 (3)	0.0040 (2)	−0.00041 (15)	0.00015 (17)	−0.00098 (15)
Co3	0.0077 (3)	0.0083 (3)	0.0088 (3)	−0.00123 (17)	0.00306 (19)	−0.00064 (17)
P1	0.0070 (5)	0.0090 (5)	0.0098 (5)	−0.0004 (3)	0.0014 (3)	−0.0002 (3)
P2	0.0067 (5)	0.0103 (4)	0.0091 (4)	0.0003 (3)	0.0008 (3)	0.0001 (3)
O1	0.0101 (13)	0.0112 (12)	0.0129 (13)	−0.0009 (10)	0.0004 (10)	−0.0005 (10)
O2	0.0114 (13)	0.0106 (13)	0.0099 (13)	0.0026 (10)	0.0011 (10)	−0.0003 (10)
O3	0.0121 (13)	0.0133 (13)	0.0102 (13)	−0.0003 (11)	0.0007 (11)	0.0014 (10)
O4	0.0135 (14)	0.0116 (13)	0.0110 (13)	−0.0005 (10)	−0.0004 (11)	0.0009 (10)
O5	0.0108 (14)	0.0131 (12)	0.0114 (13)	0.0007 (10)	0.0041 (10)	0.0008 (10)
O6	0.0106 (14)	0.0132 (12)	0.0127 (13)	−0.0009 (11)	0.0035 (11)	0.0007 (10)
O7	0.0110 (14)	0.0132 (13)	0.0164 (14)	0.0012 (11)	−0.0014 (11)	−0.0015 (11)
O8	0.0075 (13)	0.0122 (13)	0.0131 (13)	−0.0006 (10)	0.0026 (10)	−0.0022 (10)
O9	0.0109 (14)	0.0163 (13)	0.0171 (14)	−0.0033 (11)	0.0012 (11)	−0.0011 (11)

Geometric parameters (Å, º)

Co1—O3	1.897 (3)	Co3—O3^{iv}	2.416 (3)
Co1—O4	1.941 (3)	Co3—P2^{v}	2.8266 (12)
Co1—O2	1.992 (3)	P1—O6	1.513 (3)
Co1—O1	2.002 (3)	P1—O4^{i}	1.534 (3)
Co2—O9	1.887 (3)	P1—O2^{vi}	1.560 (3)
Co2—O5	1.949 (3)	P1—O1	1.561 (3)
Co2—O1	1.986 (3)	P2—O9	1.511 (3)
Co2—O2^{i}	2.054 (3)	P2—O8^{vii}	1.544 (3)
Co3—O6	2.019 (3)	P2—O3^{viii}	1.549 (3)
Co3—O7	2.061 (3)	P2—O5^{vii}	1.565 (3)
Co3—O8	2.065 (3)	P2—Co3^{ix}	2.8266 (12)
Co3—O8^{ii}	2.075 (3)	O7—H1	0.903 (10)
Co3—O5^{iii}	2.108 (3)	O7—H2	0.90 (3)
O3—Co1—O4	112.81 (13)	O4^{i}—P1—O2^{vi}	108.77 (15)
O3—Co1—O2	121.22 (12)	O6—P1—O1	109.15 (16)
O4—Co1—O2	105.11 (12)	O4^{i}—P1—O1	108.94 (16)
O3—Co1—O1	108.70 (12)	O2^{vi}—P1—O1	105.94 (16)

O4—Co1—O1	99.28 (12)
O2—Co1—O1	107.42 (12)
O9—Co2—O5	112.44 (13)
O9—Co2—O1	114.62 (13)
O5—Co2—O1	118.58 (12)
O9—Co2—O2^{i}	114.12 (12)
O5—Co2—O2^{i}	103.10 (12)
O1—Co2—O2^{i}	91.48 (11)
O6—Co3—O7	89.20 (12)
O6—Co3—O8	84.37 (11)
O7—Co3—O8	168.15 (12)
O6—Co3—O8^{ii}	164.15 (12)
O7—Co3—O8^{ii}	93.56 (12)
O8—Co3—O8^{ii}	90.02 (7)
O6—Co3—O5^{iii}	97.82 (11)
O7—Co3—O5^{iii}	85.85 (12)
O8—Co3—O5^{iii}	104.85 (11)
O8^{ii}—Co3—O5^{iii}	97.95 (11)
O6—Co3—O3^{iv}	100.18 (11)
O7—Co3—O3^{iv}	84.70 (11)
O8—Co3—O3^{iv}	86.65 (10)
O8^{ii}—Co3—O3^{iv}	64.61 (10)
O5^{iii}—Co3—O3^{iv}	159.51 (11)
O6—Co3—P2^{v}	131.88 (9)
O7—Co3—P2^{v}	94.83 (9)
O8—Co3—P2^{v}	82.21 (8)
O8^{ii}—Co3—P2^{v}	32.34 (8)
O5^{iii}—Co3—P2^{v}	130.28 (8)
O6—P1—O4^{i}	112.20 (17)
O6—P1—O2^{vi}	111.63 (16)
O9—P2—O8^{vii}	112.91 (17)
O9—P2—O3^{viii}	115.46 (17)
O8^{vii}—P2—O3^{viii}	102.81 (16)
O9—P2—O5^{vii}	106.80 (16)
O8^{vii}—P2—O5^{vii}	110.75 (16)
O3^{viii}—P2—O5^{vii}	108.04 (16)
O9—P2—Co3^{ix}	141.79 (13)
O8^{vii}—P2—Co3^{ix}	45.96 (10)
O3^{viii}—P2—Co3^{ix}	58.69 (11)
O5^{vii}—P2—Co3^{ix}	110.73 (12)
P1—O1—Co2	117.61 (16)
P1—O1—Co1	120.63 (16)
Co2—O1—Co1	116.29 (14)
P1^{vi}—O2—Co1	120.56 (16)
P1^{vi}—O2—Co2^{i}	115.98 (15)
Co1—O2—Co2^{i}	123.17 (15)
P2^{iii}—O3—Co1	126.29 (18)
P1^{i}—O4—Co1	123.07 (17)
P2^{x}—O5—Co2	116.94 (17)
P2^{x}—O5—Co3^{viii}	120.43 (16)
Co2—O5—Co3^{viii}	120.96 (14)
P1—O6—Co3	135.08 (18)
Co3—O7—H1	113 (4)
Co3—O7—H2	115 (4)
H1—O7—H2	105 (5)
P2^{x}—O8—Co3	129.77 (16)
P2^{x}—O8—Co3^{xi}	101.70 (14)
Co3—O8—Co3^{xi}	128.53 (14)
P2—O9—Co2	157.0 (2)

O6—P1—O1—Co2	36.4 (2)
O4^{i}—P1—O1—Co2	−86.41 (19)
O2^{vi}—P1—O1—Co2	156.73 (16)
O6—P1—O1—Co1	−170.63 (17)
O4^{i}—P1—O1—Co1	66.5 (2)
O2^{vi}—P1—O1—Co1	−50.3 (2)
O9—Co2—O1—P1	−176.28 (16)
O5—Co2—O1—P1	−39.6 (2)
O2^{i}—Co2—O1—P1	66.23 (18)
O9—Co2—O1—Co1	29.6 (2)
O5—Co2—O1—Co1	166.29 (13)
O2^{i}—Co2—O1—Co1	−87.91 (15)
O3—Co1—O1—P1	122.72 (19)
O4—Co1—O1—P1	−119.25 (19)
O2—Co1—O1—P1	−10.1 (2)
O3—Co1—O1—Co2	−83.97 (17)
O4—Co1—O1—Co2	34.06 (16)
O1—Co2—O5—P2^{x}	−54.5 (2)
O2^{i}—Co2—O5—P2^{x}	−153.51 (18)
O9—Co2—O5—Co3^{viii}	−111.58 (17)
O1—Co2—O5—Co3^{viii}	110.83 (17)
O2^{i}—Co2—O5—Co3^{viii}	11.79 (18)
O4^{i}—P1—O6—Co3	−132.6 (2)
O2^{vi}—P1—O6—Co3	−10.2 (3)
O1—P1—O6—Co3	106.6 (3)
O7—Co3—O6—P1	55.9 (3)
O8—Co3—O6—P1	−134.0 (3)
O8^{ii}—Co3—O6—P1	156.2 (3)
O5^{iii}—Co3—O6—P1	−29.8 (3)
P2^{v}—Co3—O6—P1	151.72 (19)
O6—Co3—O8—P2^{x}	44.9 (2)
O7—Co3—O8—P2^{x}	102.3 (6)
O8^{ii}—Co3—O8—P2^{x}	−150.0 (2)
O5^{iii}—Co3—O8—P2^{x}	−51.7 (2)

O2—Co1—O1—Co2	143.21 (14)	$P2^{v}$—Co3—O8—$P2^{x}$	178.6 (2)
O3—Co1—O2—$P1^{vi}$	−18.9 (2)	O6—Co3—O8—$Co3^{xi}$	−134.86 (19)
O4—Co1—O2—$P1^{vi}$	−148.23 (18)	O7—Co3—O8—$Co3^{xi}$	−77.4 (6)
O1—Co1—O2—$P1^{vi}$	106.71 (19)	$O8^{ii}$—Co3—O8—$Co3^{xi}$	30.29 (16)
O3—Co1—O2—$Co2^{i}$	154.62 (15)	$O5^{iii}$—Co3—O8—$Co3^{xi}$	128.52 (17)
O4—Co1—O2—$Co2^{i}$	25.34 (19)	$P2^{v}$—Co3—O8—$Co3^{xi}$	−1.19 (16)
O1—Co1—O2—$Co2^{i}$	−79.72 (18)	$O8^{vii}$—P2—O9—Co2	116.3 (5)
O4—Co1—O3—$P2^{iii}$	−129.2 (2)	$O3^{viii}$—P2—O9—Co2	−1.5 (6)
O2—Co1—O3—$P2^{iii}$	105.0 (2)	$O5^{vii}$—P2—O9—Co2	−121.7 (5)
O1—Co1—O3—$P2^{iii}$	−20.1 (2)	$Co3^{ix}$—P2—O9—Co2	69.4 (6)
O3—Co1—O4—$P1^{i}$	−150.21 (19)	O5—Co2—O9—P2	137.1 (5)
O2—Co1—O4—$P1^{i}$	−16.1 (2)	O1—Co2—O9—P2	−83.5 (6)
O1—Co1—O4—$P1^{i}$	94.9 (2)	$O2^{i}$—Co2—O9—P2	20.1 (6)
O9—Co2—O5—$P2^{x}$	83.1 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H2···$O6^{iii}$	0.90 (3)	1.86 (4)	2.753 (4)	170 (5)
O7—H1···$O4^{v}$	0.90 (1)	1.86 (2)	2.758 (4)	171 (5)

Symmetry codes: (iii) *x*, *y*+1, *z*; (v) *x*+1, *y*+1, *z*.