metal-organic compounds

Poly[diaqua-μ_4-oxalato-di-μ_6-phosphato-tetracobalt(II)]

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In the structure of the title compound, $[Co_4(C_2O_4)(PO_4)_2(H_2O)_2]_n$, there are layers composed of the phosphate anions and two independent Co^{II} cations. These layers are parallel to (001) and are bridged by the oxalate anions that are situated in special positions on centres of symmetry. One independent Co atom has an octahedral coordination, while the second independent Co atom is coordinated in a trigonal–bipyramidal coordination that includes the water molecule. The crystal packing is stabilized by O—H···O hydrogen bonds between the coordinated water molecules and oxalate O atoms.

Related literature

For general background, see Lethbridge *et al.* (2004). For the related structure $(C_4N_2H_{12})_{0.5}[Co_2(HPO_4)(C_2O_4)_{1.5}]$, which also contains the unusual CoO_5 trigonal–bipyramidal configuration, see Choudhury & Natarajan (2000). For the O—H···O hydrogen bonding, see Desiraju & Steiner (1999).
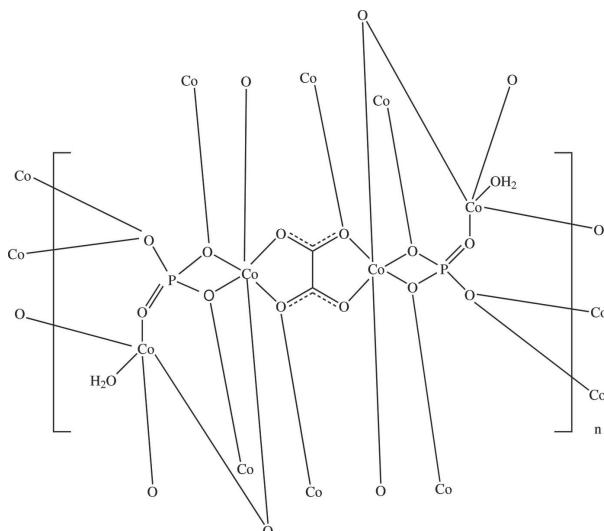
Experimental

Crystal data
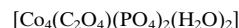
$[Co_4(C_2O_4)(PO_4)_2(H_2O)_2]$	V = 525.2 (2) Å^3
M_r = 549.72	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 7.8541 (17) Å	μ = 6.60 mm^{-1}
b = 4.7829 (10) Å	T = 293 (2) K
c = 14.057 (3) Å	$0.32 \times 0.20 \times 0.10$ mm
β = 95.937 (4)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2798 measured reflections
	1133 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	913 reflections with $I > 2\sigma(I)$
T_{min} = 0.22, T_{max} = 0.52	R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040	3 restraints
$wR(F^2)$ = 0.094	All H-atom parameters refined
S = 1.09	$\Delta\rho_{max}$ = 0.90 e Å^{-3}
1133 reflections	$\Delta\rho_{min}$ = −0.81 e Å^{-3}
107 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H2···O6^i	0.84 (2)	1.94 (3)	2.665 (5)	144 (5)
O7—H1···O6^{ii}	0.84 (2)	2.46 (4)	3.188 (5)	145 (5)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2000). *SADABS* (Version 2.03), *SAINT-Plus* (Version 6) and *SMART* (Version 5.0). Bruker AXS Inc., Madison, Wisconsin, USA.
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Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, p. 13. New York: Oxford University Press Inc.
Lethbridge, Z. A. D., Smith, M. J., Tiwary, S. K., Harrison, A. & Lightfoot, P. (2004). *Inorg. Chem.* **43**, 11–13.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Poly[diaqua-*μ*₄-oxalato-di-*μ*₆-phosphato-tetracobalt(II)]

Wen-Yuan Wu and Li-Xin Zhai

S1. Comment

A new class of metal phosphate-oxalates framework structures has been discovered in recent years. In this new class the anions $[PO_4]^{3-}$ (or $[HPO_4]^{2-}$) and $[C_2O_4]^{2-}$ act as bridging groups that link up with the metal atoms. Both main-group metals (Al, Ga, In, Sn) and transition metals (V, Mn, Fe, Co, Mo) are reported in these systems (Lethbridge *et al.*, 2004). Among these, to the best of our knowledge there is only one example containing Co^{II}: $[C_4N_2H_{12}]_{0.5}[Co_2(HPO_4)(C_2O_4)_{1.5}]$ (Choudhury & Natarajan, 2000). Here we report the synthesis and the crystal structure of a new oxalate phosphate framework structure containing Co^{II}, $[Co_4(C_2O_4)(PO_4)_2(H_2O)_2]$.

The asymmetric unit of the title structure contains two independent Co cations (Fig. 1). Co1 is octahedrally coordinated by six oxygen atoms and Co2 is coordinated by 5 O atoms in a trigonal-bipyramidal configuration. Each phosphate acts as a multiple bridging group, binding six Co atoms to compose the inorganic layer structure. The oxalate group is situated on an inversion centre and links up with two adjacent inorganic layers. The water molecule is coordinated to Co2 (Fig. 2).

S2. Experimental

A mixture of Co(ClO₄)₂.6H₂O (0.1830 g, 0.5 mmol), H₂C₂O₄.2H₂O (0.2521 g, 2 mmol), Na₄P₂O₇.10H₂O (0.8921 g, 2 mmol) and distilled water (10 ml) was placed into a 23 ml teflon-lined autoclave. The mixture was then heated for 72 h at 425 K. The insoluble purple crystals of the title structure were separated by filtration. The crystals were of rectangular plate-like shape with the average size of 0.4 × 0.3 × 0.1 mm.

S3. Refinement

The H atoms from the water molecule were located in the difference Fourier map and refined with the distance restraints O—H=0.84 (1), H—H=1.33 (2) Å, and with $U_{iso}(H)=1.5U_{eq}(O)$.
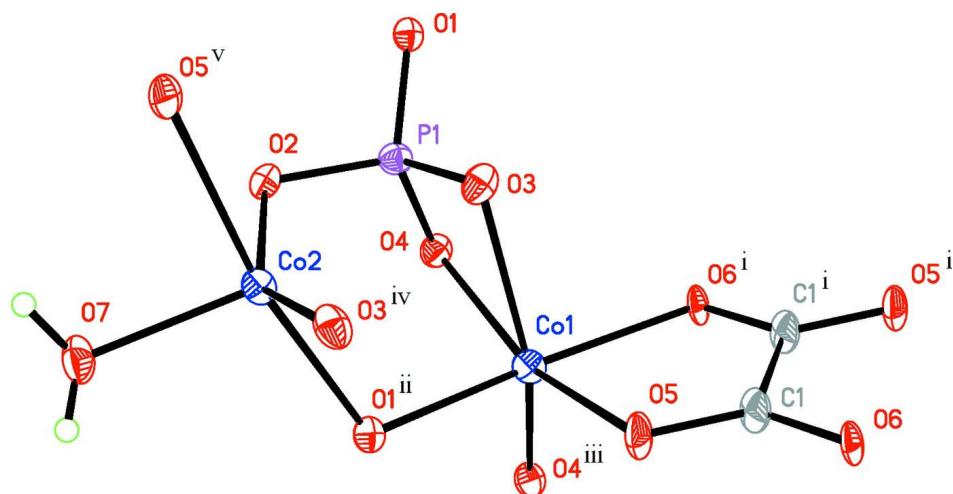
Figure 1

Coordination environment of Co and P atoms in the title structure. The displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $1 - x$, $1 - y$, $2 - z$; (ii) x, $1 + y$, z; (iii) $1/2 - x$, $1/2 + y$, $3/2 - z$; (iv) $3/2 - x$, $1/2 + y$, $3/2 - z$; (v) $3/2 - x$, $-1/2 + y$, $3/2 - z$.]
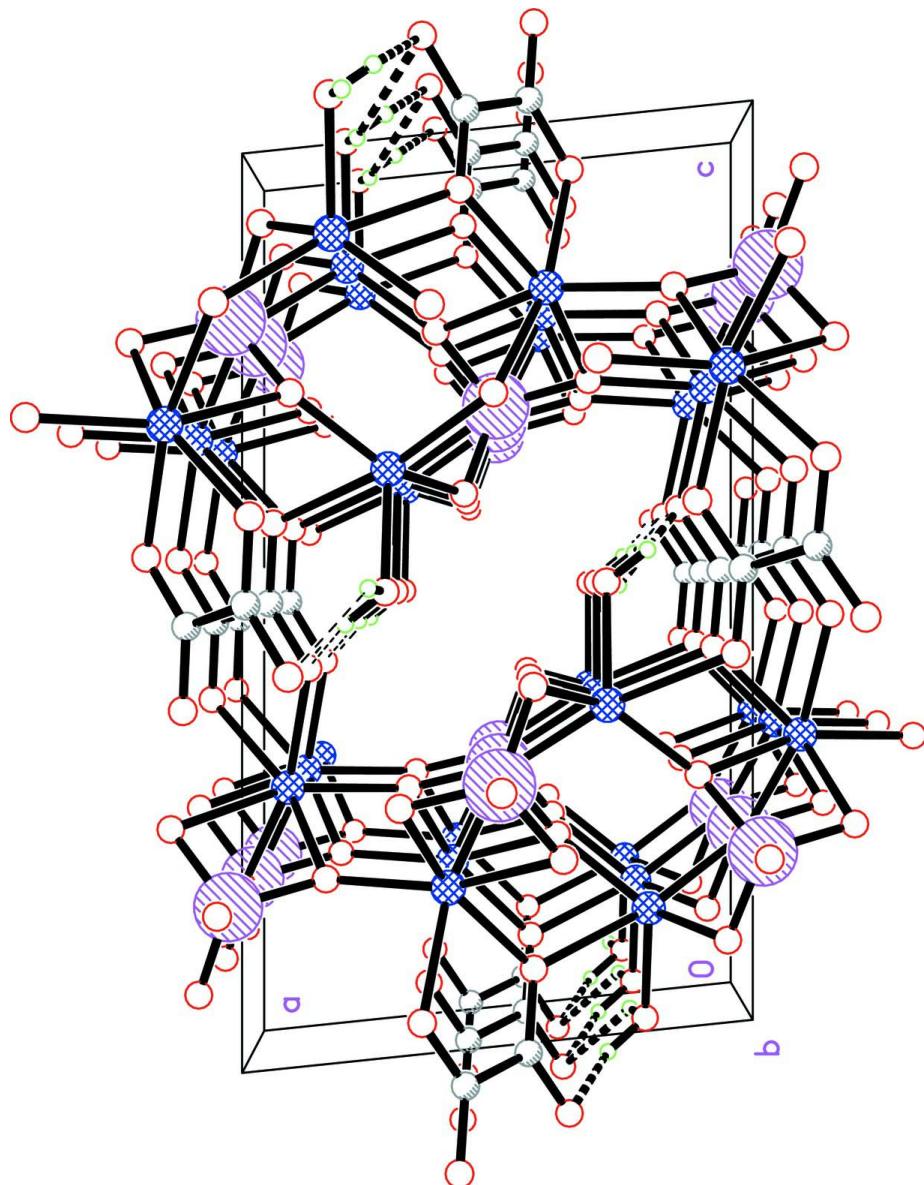
Figure 2

The packing of the title structure viewed down the *b* axis, showing the cobalt phosphate layers bridged by the oxalate ligands. The hydrogen bonds are shown as dashed lines.

Poly[diaqua-*μ*₄-oxalato-di-*μ*₆-phosphato-tetracobalt(II)]

Crystal data

$[Co_4(C_2O_4)(PO_4)_2(H_2O)_2]$	$V = 525.2\ (2)$ Å³
$M_r = 549.72$	$Z = 2$
Monoclinic, $P2_1/n$	$F(000) = 532$
Hall symbol: -P 2yn	$D_x = 3.476$ Mg m⁻³
$a = 7.8541\ (17)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 4.7829\ (10)$ Å	Cell parameters from 897 reflections
$c = 14.057\ (3)$ Å	$\theta = 2.9–27.0°$
$\beta = 95.937\ (4)°$	$\mu = 6.60$ mm⁻¹

T = 293 K

Plate, purple

$0.32 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2798 measured reflections
Radiation source: fine-focus sealed tube	1133 independent reflections
Graphite monochromator	913 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.034
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	θ_{max} = 27.0°, θ_{min} = 2.9°
	$h = -9 \rightarrow 10$
T_{min} = 0.22, T_{max} = 0.52	$k = -6 \rightarrow 6$
	$l = -10 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.040	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.094	All H-atom parameters refined
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$
1133 reflections	where $P = (F_o^2 + 2F_c^2)/3$
107 parameters	$(\Delta/\sigma)_{max} < 0.001$
3 restraints	$\Delta\rho_{max}$ = 0.90 e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min}$ = −0.81 e Å^{-3}
	Extinction correction: *SHELXTL* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.0094 (17)

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 $F^2 > \sigma(F^2)$ 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	0.40849 (8)	0.46997 (13)	0.80563 (5)	0.0130 (2)
Co2	0.70451 (8)	0.47453 (13)	0.63392 (5)	0.0122 (2)
P1	0.50343 (17)	0.0223 (3)	0.69630 (10)	0.0139 (3)
O1	0.5074 (4)	−0.2997 (7)	0.6975 (2)	0.0126 (7)
O2	0.5646 (4)	0.1346 (7)	0.6038 (2)	0.0155 (7)
O3	0.6187 (4)	0.1571 (8)	0.7802 (2)	0.0158 (7)
O4	0.3244 (4)	0.1379 (7)	0.7118 (2)	0.0148 (7)
C1	0.5588 (6)	0.6255 (11)	0.9925 (4)	0.0171 (10)
O5	0.5694 (4)	0.7013 (8)	0.9079 (2)	0.0183 (8)
O6	0.6373 (4)	0.7274 (7)	1.0660 (2)	0.0134 (7)
O7	0.7066 (4)	0.6605 (9)	0.5068 (2)	0.0197 (8)
H2	0.782 (4)	0.584 (4)	0.478 (3)	0.030*

H1	0.733 (4)	0.830 (4)	0.512 (3)	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0123 (4)	0.0124 (4)	0.0136 (4)	−0.0042 (2)	−0.0026 (3)	−0.0010 (2)
Co2	0.0129 (4)	0.0118 (4)	0.0109 (4)	−0.0044 (2)	−0.0034 (3)	−0.0011 (2)
P1	0.0132 (6)	0.0138 (6)	0.0146 (7)	0.0006 (4)	0.0005 (5)	−0.0003 (4)
O1	0.0105 (15)	0.0154 (17)	0.0116 (17)	−0.0009 (13)	−0.0003 (13)	0.0001 (13)
O2	0.0181 (17)	0.0162 (18)	0.0126 (18)	0.0010 (13)	0.0039 (13)	−0.0023 (13)
O3	0.0123 (16)	0.0203 (18)	0.0143 (18)	−0.0014 (13)	−0.0008 (14)	−0.0047 (14)
O4	0.0136 (16)	0.0171 (17)	0.0136 (16)	0.0010 (13)	0.0001 (12)	−0.0011 (14)
C1	0.019 (2)	0.022 (3)	0.012 (2)	−0.003 (2)	0.0089 (19)	0.0024 (19)
O5	0.0235 (19)	0.0231 (19)	0.0074 (17)	−0.0043 (14)	−0.0018 (14)	−0.0004 (14)
O6	0.0164 (17)	0.0176 (17)	0.0054 (16)	−0.0056 (13)	−0.0033 (12)	0.0010 (12)
O7	0.0190 (19)	0.028 (2)	0.0119 (19)	0.0034 (15)	0.0019 (14)	0.0053 (15)

Geometric parameters (Å, º)

Co1—O4[i]	1.989 (3)	P1—O4	1.547 (3)
Co1—O1[ii]	2.090 (3)	P1—O3	1.551 (3)
Co1—O6[iii]	2.101 (3)	O1—Co1[vi]	2.090 (3)
Co1—O5	2.124 (4)	O1—Co2[vi]	2.156 (3)
Co1—O4	2.126 (4)	O3—Co2[v]	1.950 (3)
Co1—O3	2.284 (3)	O4—Co1[vii]	1.989 (3)
Co2—O3[iv]	1.950 (3)	C1—O6	1.246 (6)
Co2—O2	1.983 (4)	C1—O5	1.254 (6)
Co2—O7	1.997 (4)	C1—C1[iii]	1.542 (10)
Co2—O1[ii]	2.156 (3)	O5—Co2[iv]	2.329 (4)
Co2—O5[v]	2.329 (4)	O6—Co1[iii]	2.101 (3)
P1—O2	1.530 (4)	O7—H2	0.84 (2)
P1—O1	1.541 (4)	O7—H1	0.84 (2)
O4[i]—Co1—O1[ii]	95.97 (14)	O2—P1—O4	111.3 (2)
O4[i]—Co1—O6[iii]	92.87 (14)	O1—P1—O4	111.9 (2)
O1[ii]—Co1—O6[iii]	166.14 (13)	O2—P1—O3	106.9 (2)
O4[i]—Co1—O5	110.36 (15)	O1—P1—O3	113.4 (2)
O1[ii]—Co1—O5	88.72 (13)	O4—P1—O3	102.26 (19)
O6[iii]—Co1—O5	78.19 (13)	P1—O1—Co1[vi]	121.8 (2)
O4[i]—Co1—O4	90.16 (9)	P1—O1—Co2[vi]	120.69 (19)
O1[ii]—Co1—O4	93.29 (13)	Co1[vi]—O1—Co2[vi]	111.99 (15)
O6[iii]—Co1—O4	97.35 (14)	P1—O2—Co2	108.8 (2)
O5—Co1—O4	159.08 (14)	P1—O3—Co2[v]	127.4 (2)
O4[i]—Co1—O3	156.31 (14)	P1—O3—Co1	90.96 (15)
O1[ii]—Co1—O3	84.41 (13)	Co2[v]—O3—Co1	132.59 (17)
O6[iii]—Co1—O3	91.76 (13)	P1—O4—Co1[vii]	132.5 (2)
O5—Co1—O3	93.33 (13)	P1—O4—Co1	97.21 (17)
O4—Co1—O3	66.20 (12)	Co1[vii]—O4—Co1	126.90 (16)

O3^{iv}—Co2—O2	147.43 (15)	O6—C1—O5	126.7 (4)
O3^{iv}—Co2—O7	106.46 (15)	O6—C1—C1^{iii}	116.3 (5)
O2—Co2—O7	103.26 (16)	O5—C1—C1^{iii}	117.0 (6)
O3^{iv}—Co2—O1^{ii}	90.85 (14)	C1—O5—Co1	113.4 (3)
O2—Co2—O1^{ii}	95.36 (13)	C1—O5—Co2^{iv}	121.9 (3)
O7—Co2—O1^{ii}	102.74 (14)	Co1—O5—Co2^{iv}	122.52 (15)
O3^{iv}—Co2—O5^{v}	83.95 (13)	C1—O6—Co1^{iii}	115.0 (3)
O2—Co2—O5^{v}	84.61 (13)	Co2—O7—H2	108 (2)
O7—Co2—O5^{v}	86.98 (14)	Co2—O7—H1	113 (5)
O1^{ii}—Co2—O5^{v}	169.97 (13)	H2—O7—H1	107 (3)
O2—P1—O1	110.7 (2)		
O2—P1—O1—Co1^{vi}	−173.41 (19)	O3—P1—O4—Co1^{vii}	−142.9 (3)
O4—P1—O1—Co1^{vi}	−48.6 (3)	O2—P1—O4—Co1	−97.2 (2)
O3—P1—O1—Co1^{vi}	66.5 (3)	O1—P1—O4—Co1	138.41 (17)
O2—P1—O1—Co2^{vi}	35.0 (3)	O3—P1—O4—Co1	16.7 (2)
O4—P1—O1—Co2^{vi}	159.81 (19)	O4^{i}—Co1—O4—P1	166.4 (2)
O3—P1—O1—Co2^{vi}	−85.1 (3)	O1^{ii}—Co1—O4—P1	70.39 (18)
O1—P1—O2—Co2	−141.52 (19)	O6^{iii}—Co1—O4—P1	−100.71 (18)
O4—P1—O2—Co2	93.3 (2)	O5—Co1—O4—P1	−24.6 (5)
O3—P1—O2—Co2	−17.6 (2)	O3—Co1—O4—P1	−12.03 (15)
O3^{iv}—Co2—O2—P1	42.8 (4)	O4^{i}—Co1—O4—Co1^{vii}	−32.3 (2)
O7—Co2—O2—P1	−161.77 (19)	O1^{ii}—Co1—O4—Co1^{vii}	−128.3 (2)
O1^{ii}—Co2—O2—P1	−57.3 (2)	O6^{iii}—Co1—O4—Co1^{vii}	60.6 (2)
O5^{v}—Co2—O2—P1	112.6 (2)	O5—Co1—O4—Co1^{vii}	136.7 (3)
O2—P1—O3—Co2^{v}	−108.5 (3)	O3—Co1—O4—Co1^{vii}	149.3 (3)
O1—P1—O3—Co2^{v}	13.8 (3)	O6—C1—O5—Co1	−179.2 (4)
O4—P1—O3—Co2^{v}	134.4 (2)	C1^{iii}—C1—O5—Co1	2.9 (7)
O2—P1—O3—Co1	101.70 (17)	O6—C1—O5—Co2^{iv}	17.1 (7)
O1—P1—O3—Co1	−136.07 (17)	C1^{iii}—C1—O5—Co2^{iv}	−160.8 (4)
O4—P1—O3—Co1	−15.39 (19)	O4^{i}—Co1—O5—C1	86.3 (4)
O4^{i}—Co1—O3—P1	7.9 (4)	O1^{ii}—Co1—O5—C1	−177.8 (4)
O1^{ii}—Co1—O3—P1	−84.19 (17)	O6^{iii}—Co1—O5—C1	−2.4 (3)
O6^{iii}—Co1—O3—P1	109.16 (17)	O4—Co1—O5—C1	−82.0 (5)
O5—Co1—O3—P1	−172.57 (17)	O3—Co1—O5—C1	−93.5 (4)
O4—Co1—O3—P1	11.90 (15)	O4^{i}—Co1—O5—Co2^{iv}	−110.0 (2)
O4^{i}—Co1—O3—Co2^{v}	−139.2 (3)	O1^{ii}—Co1—O5—Co2^{iv}	−14.1 (2)
O1^{ii}—Co1—O3—Co2^{v}	128.6 (2)	O6^{iii}—Co1—O5—Co2^{iv}	161.3 (2)
O6^{iii}—Co1—O3—Co2^{v}	−38.0 (2)	O4—Co1—O5—Co2^{iv}	81.7 (4)
O5—Co1—O3—Co2^{v}	40.3 (2)	O3—Co1—O5—Co2^{iv}	70.2 (2)
O4—Co1—O3—Co2^{v}	−135.3 (3)	O5—C1—O6—Co1^{iii}	−177.6 (4)
O2—P1—O4—Co1^{vii}	103.2 (3)	C1^{iii}—C1—O6—Co1^{iii}	0.3 (7)
O1—P1—O4—Co1^{vii}	−21.2 (4)		

Symmetry codes: (i) −x+1/2, y+1/2, −z+3/2; (ii) x, y+1, z; (iii) −x+1, −y+1, −z+2; (iv) −x+3/2, y+1/2, −z+3/2; (v) −x+3/2, y−1/2, −z+3/2; (vi) x, y−1, z; (vii) −x+1/2, 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···O6ᵛ	0.84 (2)	1.94 (3)	2.665 (5)	144 (5)
O7—H1···O6ⁱᵛ	0.84 (2)	2.46 (4)	3.188 (5)	145 (5)

Symmetry codes: (iv) −*x*+3/2, *y*+1/2, −*z*+3/2; (v) −*x*+3/2, *y*−1/2, −*z*+3/2.