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Pentacobalt(II) divanadium(III) tetrakis(diphosphate), $Co_5V_2(P_2O_7)_4$

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Key indicators: single-crystal X-ray study; T = 293 K; P = 0.0 kPa; mean σ(Co–O) = 0.005 Å; disorder in main residue; R factor = 0.046; wR factor = 0.110; data-to-parameter ratio = 18.9.

$Co_5V_2(P_2O_7)_4$ was crystallized by chemical vapour transport using HCl as transport agent. Its crystal structure is isotypic to that of $Fe^{II}_5Fe^{III}_2(P_2O_7)_4$ and can be regarded as a member of the thortveitite structure family with corrugated layers of metal–oxygen polyhedra extending parallel to (010). Significant occupational disorder between cobalt(II) and vanadium(III) is observed. Four of the five cation sites are occupied by both cobalt and vanadium. The fifth cation site (Co1) is occupied by cobalt only. Sites Co1, *M*3 and *M*4 are located on twofold axes. Sites Co1, *M*2, *M*3 and *M*4 show octahedral coordination by oxygen; *M*5 has a square-pyramidal environment.

Related literature

For related structures, see: Cruickshank *et al.* (1962); Gossner & Mussgnug (1929); Krishnamachari & Calvo (1972); Litterscheid (2009); Malaman *et al.* (1992); Palkina *et al.* (1985); Stefanidis & Nord (1984); Zachariasen (1930). For the preparation, see: Binnewies *et al.* (2012); Litterscheid (2009).

Experimental

Crystal data

$Co_5V_2(P_2O_7)_4$
M_r = 1092.29
Orthorhombic, $C222_1$
a = 8.3551 (4) Å
b = 9.7067 (5) Å
c = 23.8555 (11) Å
V = 1934.69 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.92 mm^{-1}
T = 293 K
0.08 × 0.08 × 0.08 mm

Data collection

Stoe IPDS 2T diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.495, T_{max} = 0.647
9445 measured reflections
3800 independent reflections
2832 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.110
S = 0.92
3800 reflections
201 parameters
1 restraint
$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$\Delta\rho_{min}$ = −1.17 e Å^{-3}
Absolute structure: Flack (1983), 2275 Friedel pairs
Flack parameter: −0.02 (2)

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

We thank Dr G. Schnakenburg (University of Bonn) for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2223).

References

Binnewies, M., Glaum, R., Schmidt, M. & Schmidt, P. (2012). In *Chemical Vapor Transport Reactions*. Berlin: W. de Gruyter.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brandenburg, K. (2008). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.
Cruickshank, D. W. J., Lynton, H. & Barclay, G. A. (1962). *Acta Cryst.* **15**, 491–498.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gossner, B. & Mussgnug, F. (1929). *Centr. Min. Abt.* No. I.
Krishnamachari, N. & Calvo, C. (1972). *Acta Cryst.* B**28**, 2883–2885.
Litterscheid, C. (2009). Dissertation, Universität Bonn, Germany. URL: http://hss.ulb.uni-bonn.de/2009/1928/1928.pdf.
Malaman, B., Ijjaali, M., Gerardin, R., Venturini, G. & Gleitzer, C. (1992). *Eur. J. Solid State Inorg. Chem.* **29**, 1269–1284.
Palkina, K. K., Maksimova, S. I., Chibiskova, N. T., Schlesinger, K. & Ladwig, G. (1985). *Z. Anorg. Allg. Chem.* **529**, 89–96.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stefanidis, T. & Nord, A. G. (1984). *Acta Cryst.* C**40**, 1995–1999.
Stoe & Cie (2002). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Zachariasen, W. H. (1930). *Z. Kristallogr.* **73**, 1–6.

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Pentacobalt(II) divanadium(III) tetrakis(diphosphate), $Co_5V_2(P_2O_7)_4$

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S1. Comment

Equilibrium investigations in the ternary system $CoO/V_2O_3/P_2O_5$ revealed three new phosphates: $Co^{II}_3V^{III}_4(PO_4)_6$, $Co^{II}_3V^{III}_2(P_2O_7)_3$, and $Co^{II}_5V^{III}_2(P_2O_7)_4$ (Litterscheid, 2009).

$Co^{II}_5V^{III}_2(P_2O_7)_4$ crystallizes in the orthorhombic space group $C222_1$. The crystal structure is isotopic to that of $Fe^{II}_5Fe^{III}_2(P_2O_7)_4$ (Malaman *et al.*, 1992). It consists of P_2O_7 groups and five independent polyhedra $[MO_n]$ (n = 5 or 6; Fig. 1). Four of the five cation sites are occupied by both cobalt and vanadium, two lying on a two-fold axis. The fifth cation site (Co1) is occupied by cobalt only. Sites Co1, M3 and M4 are located on two-fold axes. Sites Co1, M2, M3 and M4 show octahedral coordination by oxygen. M5 has a square-pyramidal enviroment. The metal oxygen polyhedra form corrugated layers (stacked along the *b*-axis). These layers are separated by P_2O_7 groups (Fig. 3).

The pyrophosphate groups display bridging angles (P1,O5,P3)=134.8 ° and (P2,O9,P4)=135.2 °. The displacement parameters for O5 and O9 do not exhibit any anomalies. The pyrophosphate group ($P1P3O_7$) shows a staggered conformation while ($P2P4O_7$) has an almost eclipsed one (Fig.2).

Allowing for disorder in the crystal structure of $Co_5V_2(P_2O_7)_4$ led to significantly improved residuals. This refinement revealed disorder for four metal sites whereas the fifth site Co1 is fully occupied by cobalt (see table). The mean inter-atomic distances *d*(M-O) for the sites with mixed metal occupancy range from 2.01 Å to 2.17 Å. The average distance *d*(M-O) = 2.15 Å is found for $[Co1O_6]$. All distances *d*(M-O) are in agreement with those already known from other cobalt(II) (Krishnamachari and Calvo, 1972) and vanadium(III) (Palkina *et al.*, 1985) phosphates.

The crystal structure of $Co^{II}_5V^{III}_2(P_2O_7)_4$ shows close similarity to the thortveitite structure family (Gossner & Mussgnug, 1929; Cruickshank *et al.*, 1962; Zachariasen *et al.*, 1930). This relation is visualized in Fig. 4 by comparison of the structures of $Co^{II}_5V^{III}_2(P_2O_7)_4$ and $Mn_2P_2O_7$ (Stefanidis *et al.*, 1984). With respect to the composition of the latter pyrophosphate 5/8 of the Mn^{2+} sites are occupied by Co^{2+}, 2/8 by V^{3+} and 1/8 remains empty for charge balance. In contrast to the honeycomb network of $[MnO_6]$ octahedra (Fig. 4) in $Mn_2P_2O_7$ the polyhedra $[MO_n]$ in $Co^{II}_5V^{III}_2(P_2O_7)_4$ show lower connectivity. This follows from the presence of octahedral voids and the reduced coordination number for polyhedron $[M5O_5]$.

S2. Experimental

For the synthesis of $Co^{II}_5V^{III}_2(P_2O_7)_4$ a pellet was prepared of thoroughly ground $V_4(P_2O_7)_3$ (82.97 mg) and $Co_2P_2O_7$ (166.99 mg). This pellet was transferred into a silica tube and sealed under vacuum. Heating at 1173 K for three days led to a single phase product. Pink single-crystals of $Co_5V_2(P_2O_7)_4$ were obtained by chemical vapour transport (Binnewies *et al.*, 2012) in a temperature gradient 1273 → 1173 K for seven days using HCl as transport agent. HCl was obtained by *in situ* reaction of NH_4Cl (2.7 mg) and $PtCl_2$ (19.9 mg). In agreement with chemical vapour transport of other phosphates by HCl(g) as transport agent, we suggest the following transport reaction:

$$Co_5V_2(P_2O_7)_4(s) + 16\ HCl(g) = 5\ CoCl_2(g) + VCl_2(g) + VCl_4(g) + 2\ P_4O_{10}(g) + 8\ H_2O(g)$$

S3. Refinement

Cobalt/vanadium disorder has been refined assuming full occupancy of metal sites *M*1 to *M*5. To maintain charge balance the refinement was constrained to a total of 20 Co^{2+} and 8 V^{3+} in the unit cell. The refinement indicated no disorder for site *M*1, for which in the final refinement cycles full occupancy by cobalt was assumed. Displacement parameters for sites with mixed occupancy Co/V were constrained to be identical for Co^{2+} and V^{3+}. No hint on racemic twinning was observed.

Even after several hundred refinement cycles the occupancy ratio Co:V for site M2 showed a rather large value of 0.01 for the ratio shift/esd. Since there are no other hints on hidden problems with the crystal structure we think that this indicator just reflects the problems generally encountered when refining occupancy factors for atoms of similar atomic number. Actually, it was quite unexpected that the refinement of the mixed occupancies Co/V proceeded without further problems.

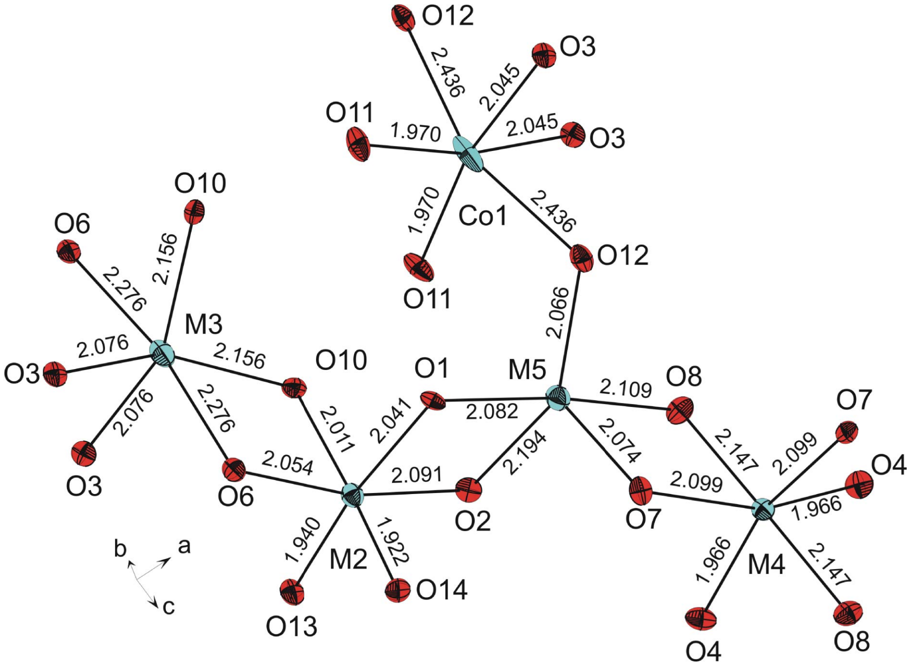

Figure 1

ORTEP style representation of metal-oxygen coordination polyhedra in $Co_5V_2(P_2O_7)_4$. *M*1: Co, *M*2: $Co_{0.45}V_{0.55}$, *M*3: $Co_{0.86}V_{0.14}$, *M*4: $Co_{0.69}V_{0.31}$, *M*5: $Co_{0.77}V_{0.23}$. Ellipsoids at 50% probability level.

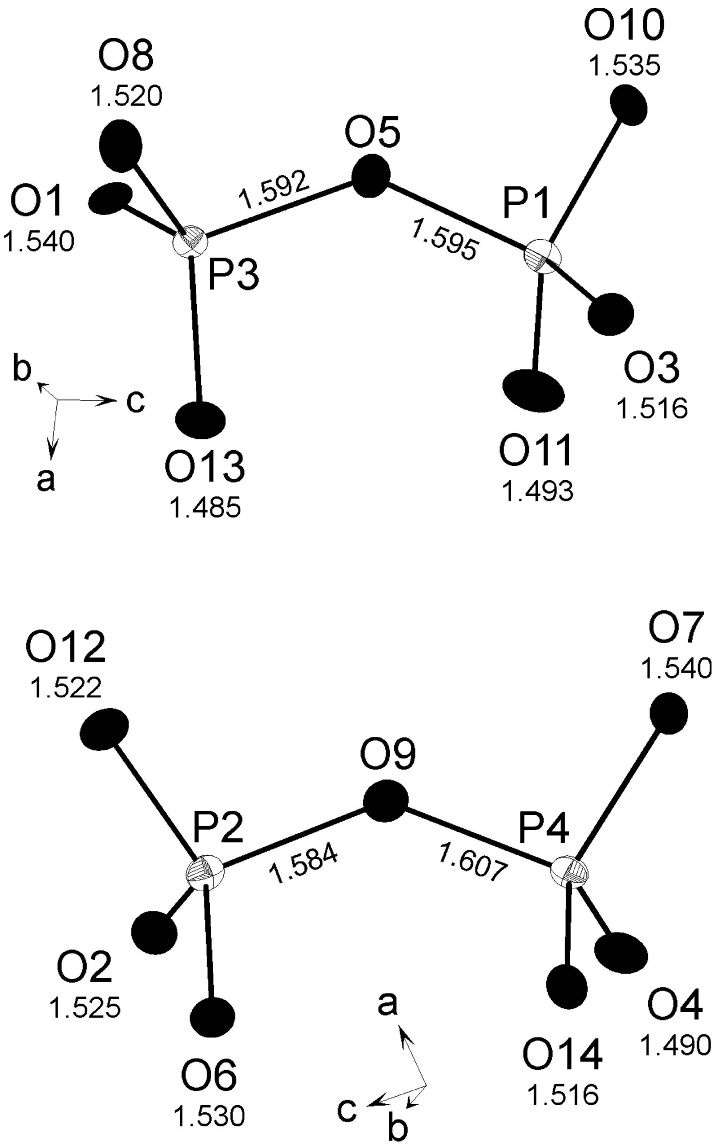

Figure 2

ORTEP style representation of the pyrophosphate groups. Ellipsoids at 50% probability level.

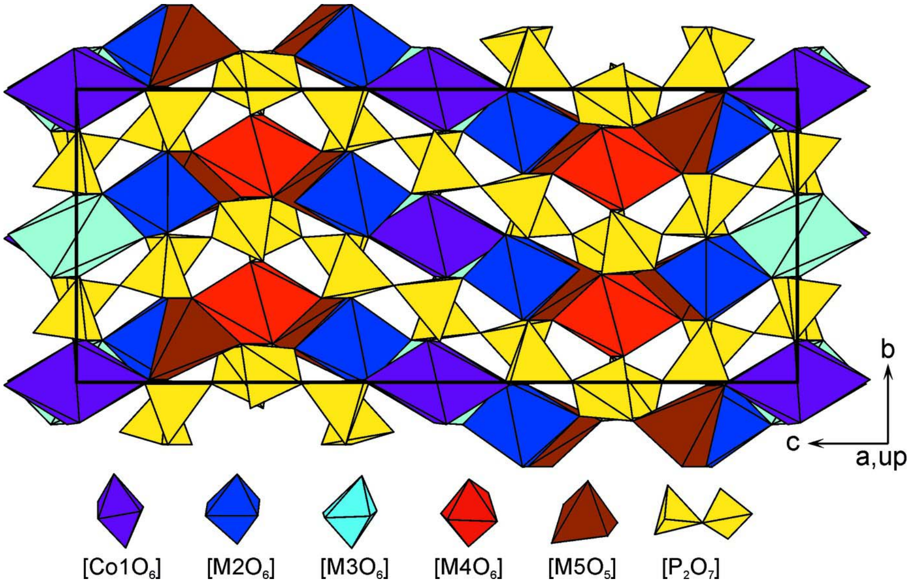

Figure 3

Projection along the a axis of the crystal structure of $Co_5V_2(P_2O_7)_4$ with schematic coordination polyhedra. $M1$: Co, $M2$: $Co_{0.45}V_{0.55}$, $M3$: $Co_{0.86}V_{0.14}$, $M4$: $Co_{0.69}V_{0.31}$, $M5$: $Co_{0.77}V_{0.23}$.

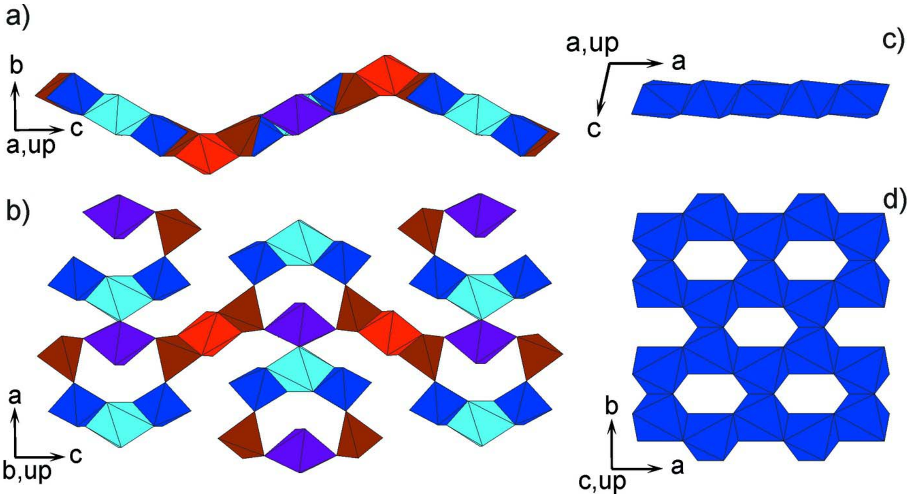

Figure 4

Comparison of the metal-oxygen co-ordination polyhedra and of their linkage in the crystal structures of $Co_5V_2(P_2O_7)_4$ and $Mn_2P_2O_7$. The same colour scheme as in Fig. 3 has been used.

Pentacobalt(II) divanadium(III) tetrakis(diphosphate)

Crystal data

$Co_5V_2(P_2O_7)_4$
$M_r = 1092.29$
Orthorhombic, $C222_1$
Hall symbol: C 2c 2
$a = 8.3551$ (4) Å
$b = 9.7067$ (5) Å
$c = 23.8555$ (11) Å
$V = 1934.69$ (16) Å^3
$Z = 4$
$F(000) = 2100$
$D_x = 3.75$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4330 reflections
$\theta = 1.0$–29.1°

$\mu = 5.92$ mm^{-1}
$T = 293$ K
Isometric, pink
0.08 × 0.08 × 0.08 mm

Data collection

Stoe IPDS 2T 2-circle goniometer diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Graphite monochromator
profile data from $\theta/2\theta$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.495$, $T_{\max} = 0.647$
9445 measured reflections
3800 independent reflections
2832 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.082$
$\theta_{\max} = 34.1°$, $\theta_{\min} = 3.6°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 15$
$l = -28 \rightarrow 35$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.110$
$S = 0.92$
3800 reflections
201 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.058$
$\Delta\rho_{\max} = 1.02$ e Å^{-3}
$\Delta\rho_{\min} = -1.17$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.00114 (15)
Absolute structure: Flack (1983), 2275 Friedel pairs
Absolute structure parameter: −0.02 (2)

Special details

Experimental. To reach the desired data resolution with the given experimental setup the image plate had been tilted by 15 degrees. This is also the explanation for the asymmetrie in the upper and lower limits of observed *hkl* values.

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}	Occ. (<1)
Co1	−0.08177 (13)	0	−0.5	0.0231 (3)	
Co2	−0.06997 (9)	−0.35558 (9)	−0.38065 (4)	0.01028 (16)	0.3452 (5)
V2	−0.06997 (9)	−0.35558 (9)	−0.38065 (4)	0.01028 (16)	0.6548 (5)
Co3	0.29241 (13)	0	−0.5	0.0162 (3)	0.934 (19)
V3	0.29241 (13)	0	−0.5	0.0162 (3)	0.066 (19)
Co4	0	−0.71981 (12)	−0.25	0.0106 (3)	0.72 (2)
V4	0	−0.71981 (12)	−0.25	0.0106 (3)	0.28 (2)
Co5	0.31161 (9)	−0.36011 (9)	−0.35848 (4)	0.0146 (2)	0.827 (12)
V5	0.31161 (9)	−0.36011 (9)	−0.35848 (4)	0.0146 (2)	0.173 (12)

P1	0.09658 (15)	−0.29386 (13)	−0.49912 (6)	0.0084 (2)
P2	0.11867 (16)	−0.05623 (14)	−0.37555 (6)	0.0088 (3)
P3	0.10814 (15)	−0.64697 (13)	−0.37996 (6)	0.0075 (2)
P4	0.23708 (16)	−0.46167 (13)	−0.23058 (6)	0.0088 (2)
O1	0.1176 (4)	−0.4895 (4)	−0.37362 (15)	0.0091 (7)
O2	0.1166 (5)	−0.2135 (4)	−0.37347 (17)	0.0128 (7)
O3	0.1028 (4)	−0.1378 (4)	−0.49593 (17)	0.0119 (7)
O4	0.1778 (5)	−0.5885 (4)	−0.25902 (18)	0.0148 (8)
O5	0.0296 (5)	−0.3310 (4)	−0.55996 (17)	0.0161 (8)
O6	−0.2299 (4)	−0.5048 (4)	−0.40502 (16)	0.0119 (7)
O7	−0.1713 (4)	−0.8684 (4)	−0.27171 (17)	0.0121 (7)
O8	−0.0110 (5)	−0.7125 (4)	−0.33991 (17)	0.0144 (8)
O9	0.1241 (4)	−0.0051 (4)	−0.31260 (17)	0.0138 (7)
O10	−0.0396 (4)	−0.3561 (4)	−0.46426 (16)	0.0116 (7)
O11	−0.2444 (5)	0.1430 (5)	−0.48668 (19)	0.0174 (8)
O12	0.4680 (4)	−0.4907 (5)	−0.39934 (16)	0.0132 (7)
O13	−0.2302 (5)	−0.2113 (4)	−0.38130 (18)	0.0131 (7)
O14	0.1101 (5)	−0.3849 (4)	−0.19772 (17)	0.0132 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0073 (4)	0.0060 (4)	0.0559 (9)	0	0	−0.0023 (5)
Co2	0.0092 (3)	0.0085 (3)	0.0131 (4)	0.0004 (3)	−0.0003 (3)	0.0004 (3)
V2	0.0092 (3)	0.0085 (3)	0.0131 (4)	0.0004 (3)	−0.0003 (3)	0.0004 (3)
Co3	0.0109 (5)	0.0116 (5)	0.0260 (7)	0	0	−0.0022 (5)
V3	0.0109 (5)	0.0116 (5)	0.0260 (7)	0	0	−0.0022 (5)
Co4	0.0102 (5)	0.0075 (5)	0.0140 (6)	0	0.0005 (4)	0
V4	0.0102 (5)	0.0075 (5)	0.0140 (6)	0	0.0005 (4)	0
Co5	0.0118 (3)	0.0124 (4)	0.0197 (4)	−0.0005 (3)	0.0000 (3)	−0.0020 (3)
V5	0.0118 (3)	0.0124 (4)	0.0197 (4)	−0.0005 (3)	0.0000 (3)	−0.0020 (3)
P1	0.0081 (5)	0.0056 (5)	0.0114 (6)	0.0001 (4)	0.0015 (5)	0.0001 (5)
P2	0.0078 (5)	0.0064 (5)	0.0123 (7)	−0.0010 (4)	−0.0001 (5)	−0.0002 (5)
P3	0.0081 (5)	0.0043 (5)	0.0100 (5)	0.0012 (5)	−0.0004 (5)	0.0004 (5)
P4	0.0086 (6)	0.0070 (5)	0.0107 (6)	−0.0016 (4)	0.0009 (5)	0.0008 (4)
O1	0.0080 (14)	0.0060 (15)	0.0132 (18)	0.0023 (14)	0.0035 (14)	0.0015 (14)
O2	0.0141 (16)	0.0110 (17)	0.0133 (19)	−0.0008 (15)	0.0011 (16)	0.0030 (15)
O3	0.0112 (16)	0.0081 (15)	0.0162 (18)	0.0030 (14)	−0.0014 (16)	0.0017 (16)
O4	0.0163 (18)	0.0109 (17)	0.017 (2)	−0.0048 (15)	0.0022 (16)	−0.0004 (15)
O5	0.0145 (18)	0.019 (2)	0.0147 (19)	−0.0017 (15)	0.0007 (16)	−0.0063 (16)
O6	0.0106 (15)	0.0094 (16)	0.0157 (18)	−0.0007 (15)	0.0007 (14)	−0.0009 (14)
O7	0.0112 (15)	0.0103 (17)	0.0148 (18)	−0.0009 (14)	−0.0018 (14)	0.0043 (15)
O8	0.0179 (19)	0.0112 (18)	0.0142 (18)	−0.0027 (15)	−0.0001 (16)	−0.0004 (15)
O9	0.0102 (15)	0.0141 (17)	0.0171 (19)	−0.0014 (15)	0.0002 (14)	−0.0024 (16)
O10	0.0116 (16)	0.0128 (17)	0.0104 (17)	0.0014 (15)	0.0032 (14)	0.0001 (15)
O11	0.0107 (16)	0.0112 (17)	0.030 (2)	0.0046 (15)	0.0018 (16)	0.0011 (17)
O12	0.0080 (15)	0.0157 (18)	0.0158 (19)	−0.0022 (14)	0.0008 (14)	0.0036 (16)
O13	0.0114 (16)	0.0065 (16)	0.021 (2)	0.0020 (13)	−0.0019 (16)	−0.0014 (15)

O14	0.0122 (16)	0.0170 (19)	0.0102 (17)	0.0015 (15)	0.0014 (15)	−0.0011 (14)

Geometric parameters (Å, º)

Co1—O11	1.968 (4)	Co5—O12	2.065 (4)
Co1—O11^{i}	1.968 (4)	Co5—O7^{iv}	2.076 (4)
Co1—O3^{i}	2.044 (4)	Co5—O1	2.082 (4)
Co1—O3	2.044 (4)	Co5—O8^{iv}	2.109 (4)
Co2—O14^{ii}	1.921 (4)	Co5—O2	2.192 (4)
Co2—O13	1.937 (4)	P1—O11^{v}	1.493 (4)
Co2—O10	2.010 (4)	P1—O3	1.518 (4)
Co2—O1	2.043 (3)	P1—O10	1.533 (4)
Co2—O6	2.055 (4)	P1—O5	1.597 (4)
Co2—O2	2.089 (4)	P2—O12^{vi}	1.520 (4)
Co3—O3^{i}	2.075 (4)	P2—O2	1.527 (4)
Co3—O3	2.075 (4)	P2—O6^{iv}	1.531 (4)
Co3—O10^{iii}	2.156 (4)	P2—O9	1.582 (4)
Co3—O10^{iv}	2.156 (4)	P3—O13^{v}	1.489 (4)
Co3—O6^{iii}	2.274 (4)	P3—O8	1.519 (4)
Co3—O6^{iv}	2.274 (4)	P3—O1	1.538 (4)
Co4—O4^{ii}	1.969 (4)	P3—O5^{vii}	1.591 (4)
Co4—O4	1.969 (4)	P4—O4	1.490 (4)
Co4—O7	2.097 (4)	P4—O14	1.515 (4)
Co4—O7^{ii}	2.097 (4)	P4—O7^{iv}	1.539 (4)
Co4—O8	2.148 (4)	P4—O9^{viii}	1.608 (4)
Co4—O8^{ii}	2.148 (4)		
O11—Co1—O11^{i}	92.7 (3)	O11^{v}—P1—O3	111.7 (2)
O11—Co1—O3^{i}	93.86 (16)	O11^{v}—P1—O10	113.0 (2)
O11^{i}—Co1—O3^{i}	167.12 (17)	O3—P1—O10	113.1 (2)
O11—Co1—O3	167.12 (17)	O11^{v}—P1—O5	113.6 (2)
O11^{i}—Co1—O3	93.86 (16)	O3—P1—O5	106.4 (2)
O3^{i}—Co1—O3	82.0 (2)	O10—P1—O5	98.3 (2)
O14^{ii}—Co2—O13	89.68 (18)	O12^{vi}—P2—O2	114.9 (3)
O14^{ii}—Co2—O10	170.85 (19)	O12^{vi}—P2—O6^{iv}	112.1 (2)
O13—Co2—O10	94.66 (17)	O2—P2—O6^{iv}	110.5 (2)
O14^{ii}—Co2—O1	87.68 (16)	O12^{vi}—P2—O9	104.3 (2)
O13—Co2—O1	172.15 (17)	O2—P2—O9	106.4 (2)
O10—Co2—O1	89.03 (15)	O6^{iv}—P2—O9	108.1 (2)
O14^{ii}—Co2—O6	93.29 (17)	O13^{v}—P3—O8	115.6 (2)
O13—Co2—O6	93.32 (16)	O13^{v}—P3—O1	111.9 (2)
O10—Co2—O6	78.44 (16)	O8—P3—O1	112.8 (2)
O1—Co2—O6	94.22 (15)	O13^{v}—P3—O5^{vii}	107.4 (2)
O14^{ii}—Co2—O2	98.53 (17)	O8—P3—O5^{vii}	103.9 (2)
O13—Co2—O2	92.24 (16)	O1—P3—O5^{vii}	104.1 (2)
O10—Co2—O2	89.36 (16)	O4—P4—O14	114.2 (2)
O1—Co2—O2	80.85 (15)	O4—P4—O7^{iv}	111.2 (2)
O6—Co2—O2	166.96 (16)	O14—P4—O7^{iv}	112.9 (2)

O3^{i}—Co3—O3	80.5 (2)	O4—P4—O9^{viii}	108.3 (2)
O3^{i}—Co3—O10^{iii}	153.63 (15)	O14—P4—O9^{viii}	107.6 (2)
O3—Co3—O10^{iii}	95.61 (15)	O7^{iv}—P4—O9^{viii}	101.8 (2)
O3^{i}—Co3—O10^{iv}	95.62 (15)	P3—O1—Co2	125.8 (2)
O3—Co3—O10^{iv}	153.62 (15)	P3—O1—Co5	131.1 (2)
O10^{iii}—Co3—O10^{iv}	98.8 (2)	Co2—O1—Co5	103.14 (16)
O3^{i}—Co3—O6^{iii}	82.97 (15)	P2—O2—Co2	131.7 (3)
O3—Co3—O6^{iii}	89.84 (15)	P2—O2—Co5	130.2 (2)
O10^{iii}—Co3—O6^{iii}	70.88 (14)	Co2—O2—Co5	98.01 (17)
O10^{iv}—Co3—O6^{iii}	115.74 (14)	P1—O3—Co1	128.7 (2)
O3^{i}—Co3—O6^{iv}	89.84 (15)	P1—O3—Co3	131.9 (2)
O3—Co3—O6^{iv}	82.97 (15)	Co1—O3—Co3	98.73 (16)
O10^{iii}—Co3—O6^{iv}	115.73 (14)	P4—O4—Co4	137.3 (3)
O10^{iv}—Co3—O6^{iv}	70.88 (14)	P3^{vii}—O5—P1	134.8 (3)
O6^{iii}—Co3—O6^{iv}	170.60 (19)	P2^{ix}—O6—Co2	129.6 (2)
O4^{ii}—Co4—O4	99.4 (3)	P2^{ix}—O6—Co3^{ix}	122.1 (2)
O4^{ii}—Co4—O7	87.52 (17)	Co2—O6—Co3^{ix}	102.37 (16)
O4—Co4—O7	158.93 (16)	P2^{ix}—O6—V3^{ix}	122.1 (2)
O4^{ii}—Co4—O7^{ii}	158.93 (16)	Co2—O6—V3^{ix}	102.37 (16)
O4—Co4—O7^{ii}	87.52 (17)	P4^{ix}—O7—V5^{ix}	128.6 (2)
O7—Co4—O7^{ii}	93.1 (2)	P4^{ix}—O7—Co5^{ix}	128.6 (2)
O4^{ii}—Co4—O8	93.18 (17)	P4^{ix}—O7—Co4	125.9 (2)
O4—Co4—O8	84.36 (17)	V5^{ix}—O7—Co4	105.46 (17)
O7—Co4—O8	75.35 (15)	Co5^{ix}—O7—Co4	105.46 (17)
O7^{ii}—Co4—O8	107.37 (16)	P3—O8—V5^{ix}	127.8 (2)
O4^{ii}—Co4—O8^{ii}	84.36 (17)	P3—O8—Co5^{ix}	127.8 (2)
O4—Co4—O8^{ii}	93.18 (17)	P3—O8—Co4	127.9 (2)
O7—Co4—O8^{ii}	107.37 (16)	V5^{ix}—O8—Co4	102.55 (18)
O7^{ii}—Co4—O8^{ii}	75.35 (15)	Co5^{ix}—O8—Co4	102.55 (18)
O8—Co4—O8^{ii}	176.2 (2)	P2—O9—P4^{x}	135.3 (3)
O12—Co5—O7^{iv}	113.79 (16)	P1—O10—Co2	129.1 (2)
O12—Co5—O1	92.30 (15)	P1—O10—V3^{ix}	121.6 (2)
O7^{iv}—Co5—O1	101.71 (15)	Co2—O10—V3^{ix}	108.17 (17)
O12—Co5—O8^{iv}	94.11 (16)	P1—O10—Co3^{ix}	121.6 (2)
O7^{iv}—Co5—O8^{iv}	76.62 (15)	Co2—O10—Co3^{ix}	108.17 (17)
O1—Co5—O8^{iv}	173.51 (15)	P1^{vi}—O11—Co1	150.7 (3)
O12—Co5—O2	142.34 (16)	P2^{v}—O12—Co5	127.2 (2)
O7^{iv}—Co5—O2	103.80 (15)	P3^{vi}—O13—Co2	158.5 (3)
O1—Co5—O2	77.59 (14)	P4—O14—V2^{ii}	134.3 (3)
O8^{iv}—Co5—O2	96.63 (16)	P4—O14—Co2^{ii}	134.3 (3)

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