inorganic compounds

Lithium cobalt(II) pyrophosphate, Li$_{1.86}$CoP$_2$O$_7$, from synchrotron X-ray powder data

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Structure refinement of high-resolution X-ray powder diffraction data of the title compound gave the composition Li$_{1.865}$CoP$_2$O$_7$, which is also verified by the ICP measurement. Two Co sites exist in the structure: one is a CoO$_5$ square pyramid and the other is a CoO$_6$ octahedron. They share edges and are further interconnected through P$_2$O$_7$ groups, forming a three-dimensional framework, which exhibits different kinds of intersecting tunnels containing Li cations and could be of great interest in Li ion battery chemistry. The structure also exhibits cation disorder with 13.5% Co residing at the lithium (Li1) site. Co seems to have an average oxidation state of 2.135, as obtained from the strutural stochiometry that closely supports the magnetic susceptibility findings.

Related literature

For related structures, see: Adam *et al.* (2008); Nishimura *et al.* (2010); Zhou *et al.* (2011). For related materials with Na$^+$ and K$^+$ cations, see: Erragh *et al.* (1991); Sanz *et al.* (1999); Beaury *et al.* (2004); Gopalakrishna *et al.* (2005); Bih *et al.* (2006); Guesmi *et al.* (2007). For related structural frameworks, see: Beaury *et al.* (2004); Fagginani & Calvo (1976); Sandström *et al.* (2003); Etheredge & Hwu (1995); El Maadi *et al.* (1995); Huang & Hwa (1998); Sanz *et al.* (1999); Erragh *et al.* (1998). Pseudovoigt profile coefficients as parameterized in Thompson *et al.* (1987) and Finger *et al.* (1994).

Experimental

Crystal data

CoLi$_{1.865}$O$_7$P$_2$	$c = 10.95952$ (4) Å
$M_r = 245.82$	$\beta = 101.7664$ (2)°
Monoclinic, $P2_1/a$	$V = 1015.83$ (1) Å^3
$a = 9.76453$ (4) Å	$Z = 8$
$b = 9.69622$ (4) Å	

Synchrotron radiation, $\lambda = 0.413988$ Å	$T = 297$ K
$\mu = 0.89$ mm^{-1}	irregular shape, 15×13 mm

Data collection

Advanced Photon Source diffractometer	Data collection mode: transmission
Specimen mounting: kapton capillary	Scan method: continuous

Refinement

$R_p = 0.057$	$\chi^2 = 2.624$
$R_{wp} = 0.080$	24500 data points
$R_{exp} = 0.049$	269 parameters
$R(F^2) = 0.04534$	

References

Adam, L., Guesdon, A. & Raveau, B. (2008). *J. Solid State Chem.* **181**, 3110–3115.
Beaury, L., Derouet, J., Binet, J., Sanz, F. & Ruiz-Valero, C. (2004). *J. Solid State Chem.* **177**, 1437–1443.
Bih, H., Saadoune, I. & Mansori, M. (2006). *Moroc. J. Condens. Matter*, **7**, 74–76.
Dragoe, N. (2001). *J. Appl. Cryst.* **34**, 535.
El Maadi, A., Boukhari, A. & Holt, E. M. (1995). *J. Chem. Crystallogr.* **25**, 531–536.
Erragh, F., Boukhari, A., Elouadi, B. & Holt, E. M. (1991). *J. Cryst. Spect. Res.* **21**, 321–326.
Erragh, F., Boukhari, A., Sadel, A. & Holt, E. M. (1998). *Acta Cryst.* C**54**, 1373–1376.
Etheredge, K. M. S. & Hwu, S. J. (1995). *Inorg. Chem.* **34**, 1495–1499.
Fagginani, R. & Calvo, C. (1976). *Can. J. Chem.*, **54**, 3319–3324.
Finger, L. W., Cox, D. E. & Jephcoat, A. P. (1994). *J. Appl. Cryst.* **27**, 892–900.
Gopalakrishna, G. S., Mahesh, M. J., Ashamanjari, K. G. & Shashidharaprasad, J. (2005). *J. Cryst. Growth*, **281**, 604–610.
Guesmi, A., Ouerfelli, N., Mazza, D. & Driss, A. (2007). *Acta Cryst.* A**63**, s277–s278.
Huang, Q. & Hwu, S. J. (1998). *Inorg. Chem.* **37**, 5869–5874.
Larson, A. C. & Von Dreele, R. B. (2000). *GSAS.* Report LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
Nishimura, S., Nakamura, M., Natsui, R. & Yamada, A. (2010). *J. Am. Chem. Soc.* **132**, 13596–13597.
Palmer, D. (2005). *CrystalMaker.* CrystalMaker Software Ltd, Yarnton, England.

Sandström, M., Fischer, A. & Boström, D. (2003). *Acta Cryst.* E**59**, i139–i141.

Sanz, F., Parada, C., Rojo, J. M., Reuiz-Valero, C. & Saez-Puche, R. (1999). *J. Solid State Chem.* **145**, 604–611.

Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhou, H., Upreti, S., Chernova, N., Hautier, G., Ceder, G. & Whittingham, M. S. (2011). *Chem. Mater.* **23**, 293–300.

supporting information

Lithium cobalt(II) pyrophosphate, Li$_{1.86}$CoP$_2$O$_7$, from synchrotron X-ray powder data

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S1. Comment

A$_2$MP$_2$O$_7$ is a large family, in which various frameworks are encountered consisting of MO$_6$ octahedra (Fagginani *et al.*, 1976; Sandström *et.al.*, 2003) and MO$_4$ polyhedra (Etheredge *et al.*, 1995; Erragh *et al.*, 1998; Sanz *et al.*, 1999) interconnected through P$_2$O$_7$ groups (Fig. 1). Dimeric M_2O$_{10}$ units, built up of two edge-sharing MO$_6$ octahedra, are only observed for some A$_2$MP$_2$O$_7$ pyrophosphates (El Maadi *et al.* 1995; Huang *et al.* 1998) and dimeric M_2O$_{11}$ units(corner-shared MO$_6$) seem to be much more rare, just observed for Na$_2$CoP$_2$O$_7$ (Erragh *et al.* 1991). Two forms of structures were found for Na$_2$CoP$_2$O$_7$ by Erragh *et al.* 1991: one is triclinic and another one is orthorhombic. The tetragonal structure of Na$_2$CoP$_2$O$_7$ was reported by Sanz *et al.* 1999 and they found that the tetragonal form could be a derivative of the orthorhombic form, with a higher point symmetry for the former. In addition, the tetragonal structured Na$_2$CoP$_2$O$_7$ was described by Guesmi *et al.* 2007. To our knowledge, the A$_2$CoP$_2$O$_7$ with Li as cation has never been reported.

  Here, we report a new Li containing solid with a three-dimensional framework (Fig. 2) crystallizing in the monoclinic space group $P2_1/a$. Its structure is similar to the recently reported Li$_2$MnP$_2$O$_7$ (Adam *et al.* 2008), a new member of the A$_2$MP$_2$O$_7$ family: original M_2O$_9$ units, built up of one MO$_5$ trigonal bipyramid sharing one edge with one MO$_6$ octahedron, sharing corners with P$_2$O$_7$ pyrophosphate groups to form undulating $(M_4$P$_8$O$_{32})_\infty$ layers. A 3-D framework results from the interconnection between metal oxide and pyrophosphate groups, and the lithium cations are located in the tunnels thus formed (Fig 2). The structure of the related Fe-compound has been studied by us (Zhou *et al.* 2011) and Nishimura *et al.* (2010), as well as the electrochemical properties, which showed that it is a good candidate for the cathode material of lithium-ion batteries. The title compound also has the potential to work as the cathode material for lithium-ion batteries. We present here its crystal structure, as determined and refined from synchrotron powder X-ray diffraction data (Fig. 3).

S2. Experimental

The powder sample was synthesized through a "wet" method based on mixing stoichiometric aqueous solutions of the precursors followed by thermal treatments. The general procedure involves the mixing of soluble precursors in distilled water followed by a slow evaporation through continuous stirring to dryness before annealing the resultant solids. The precursors for the synthesis were Li(CH$_3$COO),Co(CH$_3$COO)$_2$. 4H$_2$O,and NH$_4$H$_2$PO$_4$, which were dissolved in 100 ml distilled water in a molar ratio of 2:1:2 (1.32 g, 2.49 g and 2.3 g respectively) to give a 0.02 molar lithium solution. The self-adjusted pH of all the solutions were found to be around 4.5. The solution was stirred and evaporated on a hot-plate in the hood followed by vacuum oven drying overnight at 363 K. The resulting solid was preheated in a H2/He (8.5°/91.5° by volume) atmosphere at 673 K for 4h to decompose the precursors followed by reheating under the same atmosphere up to 873 K for 16h with intermittent grinding to obtain the pink colored powder as final product. The sample was also analyzed with a Perkin-Elmer ICP-OES Optima 7000 DV for the elemental content. The average result of 3

analyses showed that the ratio of Li: Co: P is 1.85: 0.996:2. In addition, the SQUID magnetic study on the sample using a Quantum Design MPMS XL SQUID magnetometer showed that the effective magnetic moment of it is 5.23$m_B$which is typical divalent Co.

S3. Refinement

During structural refinement, occupancy factor for Li1 and Co3 were refined using constrains for atomic coordinate, atomic displacement parameter, and keeping the sum of occupancy facter equals to unity, which later were fixed to their close refined values as 0.73 and 0.27 respectively. Occupancy for Co1 was also observed to be deficient and fixed to it's closely refined value of 0.739 to 0.73, in final refinement cycles.
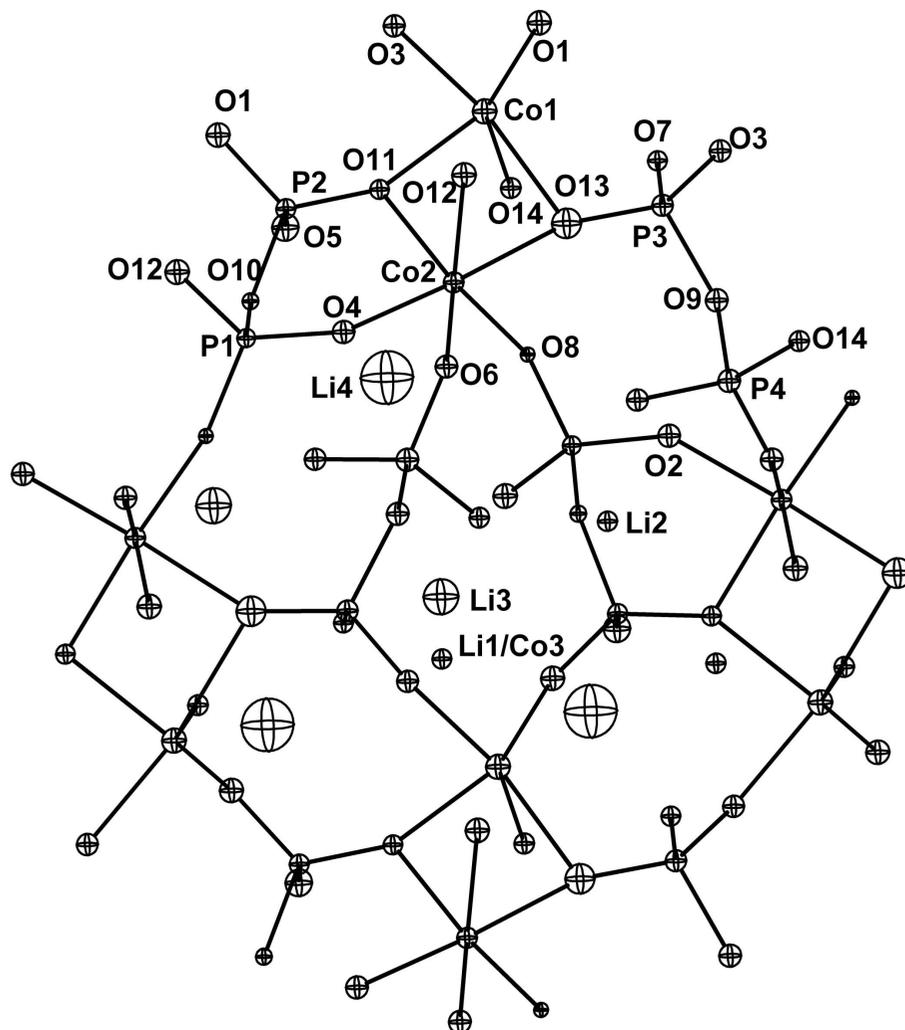

Figure 1

Thermal ellipsoid view of $Li_{1.86}CoP_2O_7$ framework, having edge shared CoO_5 and CoO_6 interconnected through P_2O_7 moities.
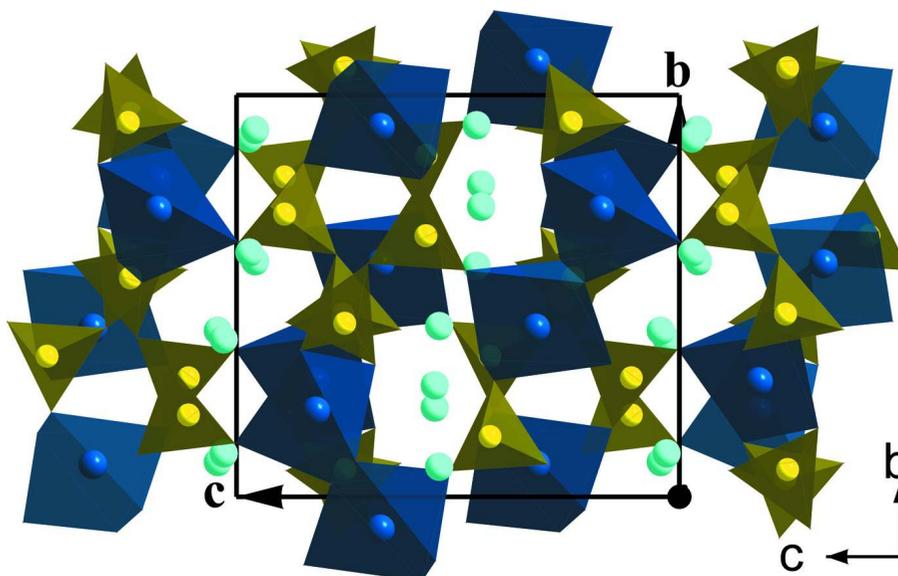
Figure 2

Polyhedral view of unit cell packing showing tunneled structures containing Li ions, viewed along [100].
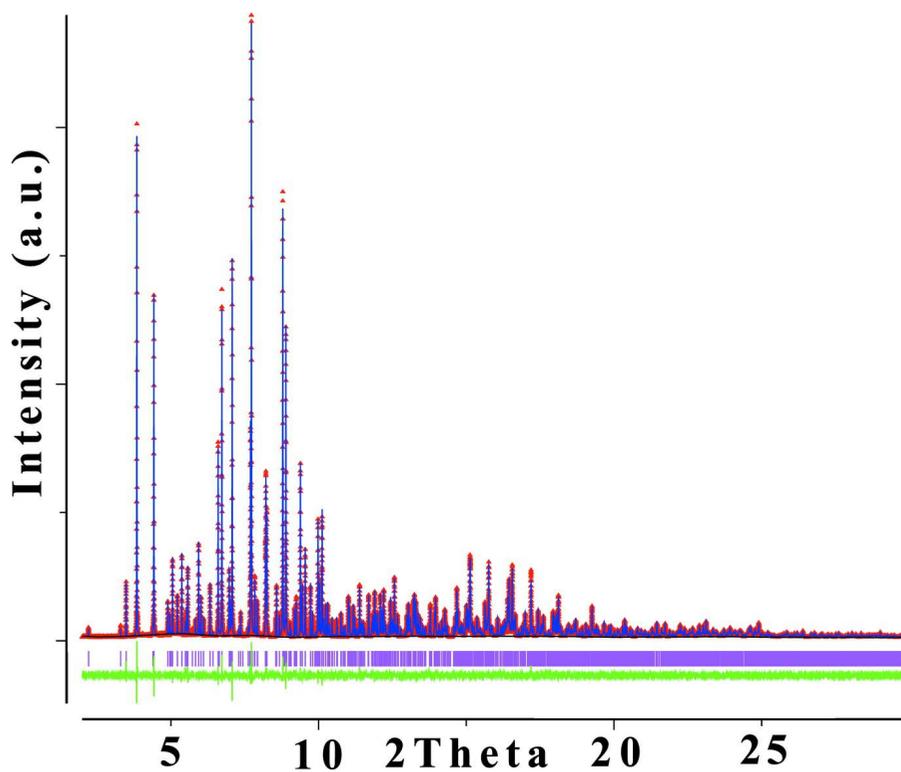
Figure 3

X-ray Rietveld refinement profiles for $Li_{1.86}CoP_2O_7$, data recorded at room temperature. Triangles mark the experimental points (red), solid line is the calculated profile (blue) and bottom trace shows the difference curve (green).

Lithium cobalt(II) pyrophosphate

Crystal data

$CoLi_{1.865}O_7P_2$
$M_r = 245.82$
Monoclinic, $P2_1/a$
Hall symbol: -P 2yab
$a = 9.76453$ (4) Å
$b = 9.69622$ (4) Å
$c = 10.95952$ (4) Å
$\beta = 101.7664$ (2)°
$V = 1015.83$ (1) Å^3
$Z = 8$
$F(000) = 948.7$

$D_x = 3.214$ Mg m^{-3}
Melting point: 1023 K
Synchrotron radiation, $\lambda = 0.413988$ Å
$\mu = 0.89$ mm^{-1}
$T = 297$ K
Particle morphology: block
pink
irregular, 15×13 mm
Specimen preparation: Prepared at 873 K and
101.325 kPa

Data collection

Advanced Photon Source
   diffractometer
Radiation source: Synchrotron
Si monochromator

Specimen mounting: kapton capillary
Data collection mode: transmission
Scan method: continuous

Refinement

Least-squares matrix: full
$R_p = 0.057$
$R_{wp} = 0.080$
$R_{exp} = 0.049$
$R(F^2) = 0.04534$
24500 data points
Excluded region(s): Reflections exceeding 2-
   theta 30 were omitted for the ease of
   refinement.

Profile function: CW Profile function number 3
   with 19 terms Pseudovoigt profile coefficients
   as parameterized in Thompson *et al.*, (1987) and
   Finger *et al.* (1994).
   #1(GU) = 6.454 #2(GV) = -0.998 #3(GW) =
   0.075 #4(GP) = 0.000 #5(LX) = 0.327 #6(LY) =
   0.000 #7(S/L) = 0.0011 #8(H/L) = 0.0014
   #9(trns) = 0.00 #10(shft)= 0.0000 #11(stec)=
   0.00 #12(ptec)= 0.00 #13(sfec)= 0.00 #14(L11)
   = 0.067 #15(L22) = 0.070 #16(L33) = 0.058
   #17(L12) = 0.010 #18(L13) = 0.010 #19(L23) =
   -0.004 Peak tails are ignored where the intensity
   is below 0.0010 times the peak Aniso.
   broadening axis 0.0 0.0 1.0
269 parameters
0 restraints
$(\Delta/\sigma)_{max} = 0.03$
Background function: GSAS Background
   function number 1 with 36 terms. Shifted
   Chebyshev function of 1st kind 1: 165.338 2:
   -31.4210 3: -8.19118 4: 6.28432 5: -10.8524 6:
   14.3842 7: -8.22810 8: -0.949190 9: 13.3092
   10: -14.8044 11: 4.75285 12: -1.09442 13:
   -0.739293 14: 5.47743 15: -2.87265 16:
   1.05489 17: -3.22764 18: 1.21714 19: 0.537209
   20: -3.25962 21: 2.18736 22: -1.12437 23:
   -2.15219 24: 3.41374 25: -3.88852 26: 1.14500
   27: 3.06741 28: -3.05038 29: 0.529274 30:
   0.298855 31: -4.06399 32: 1.50867 33: 1.15056
   34: -2.20673 35: 0.550944 36: 5.540140E-02

Special details

Experimental. Data was collected with powder sample packed in Kapton capillary

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.25281 (15)	0.71550 (15)	0.18010 (14)	0.0137 (4)*	0.73
Co2	0.30165 (11)	0.43043 (11)	0.32719 (10)	0.0095 (3)*	
P1	0.3790 (2)	0.6536 (2)	0.5771 (2)	0.0078 (5)*	
P2	0.0613 (2)	0.9265 (2)	0.24116 (18)	0.0089 (5)*	
P3	0.0210 (2)	0.4551 (2)	0.75861 (19)	0.0103 (5)*	
P4	0.6144 (2)	0.7956 (2)	−0.1113 (2)	0.0117 (6)*	
O1	0.1615 (5)	0.8210 (5)	0.3113 (5)	0.0130 (14)*	
O2	0.4709 (5)	0.7806 (5)	−0.0792 (4)	0.0106 (12)*	
O3	0.3911 (5)	0.8599 (4)	0.1472 (5)	0.0107 (13)*	
O4	0.0302 (5)	0.8437 (5)	0.5592 (4)	0.0116 (14)*	
O5	0.4330 (5)	0.4292 (5)	−0.1033 (4)	0.0168 (13)*	
O6	0.1790 (5)	0.8356 (5)	−0.1511 (4)	0.0115 (13)*	
O7	0.0189 (5)	0.4120 (4)	0.6224 (4)	0.0087 (13)*	
O8	0.1866 (5)	0.2976 (4)	0.4146 (4)	0.0047 (12)*	
O9	0.1013 (5)	0.6017 (4)	0.7747 (4)	0.0116 (13)*	
O10	0.3827 (5)	0.5734 (5)	0.7087 (4)	0.0061 (12)*	
O11	0.4152 (5)	0.5900 (4)	0.2661 (4)	0.0085 (13)*	
O12	0.2775 (5)	0.5646 (5)	0.4803 (4)	0.0134 (13)*	
O13	0.3713 (5)	1.0314 (5)	−0.2124 (5)	0.0205 (15)*	
O14	0.2204 (5)	0.6299 (5)	−0.0018 (4)	0.0094 (13)*	
Li1	1.3433 (3)	0.9255 (3)	−0.0397 (3)	0.0087 (7)*	0.73
Li2	0.0807 (17)	0.1083 (15)	0.0261 (15)	0.009 (4)*	
Li3	0.6728 (15)	0.0711 (14)	0.5465 (14)	0.029 (4)*	
Li4	0.400 (2)	0.246 (2)	0.5725 (17)	0.065 (7)*	
Co3	1.3433 (3)	0.9255 (3)	−0.0397 (3)	0.0087 (7)*	0.27

Geometric parameters (Å, º)

Co1—O1	2.105 (5)	P2—O5^v	1.524 (4)
Co1—O3	2.028 (4)	P2—O10^{iv}	1.584 (5)
Co1—O11	2.067 (4)	P2—O11^{vi}	1.516 (5)
Co1—O13^i	2.226 (5)	P3—O3^{ii}	1.514 (5)
Co1—O14	2.123 (5)	P3—O7	1.546 (5)
Co2—O4^{ii}	2.030 (5)	P3—O9	1.616 (4)
Co2—O6^i	2.180 (5)	P3—O13^{vii}	1.563 (5)
Co2—O8	2.068 (4)	P4—O2	1.519 (5)
Co2—O11	2.091 (4)	P4—O6^{iii}	1.524 (4)
Co2—O12	2.173 (4)	P4—O9^{viii}	1.582 (5)
Co2—O13^i	2.128 (5)	P4—O14^{iii}	1.589 (5)
P1—O4^{iii}	1.529 (5)	Co3—O2^{ix}	1.983 (5)
P1—O8^{iv}	1.547 (4)	Co3—O3^{ix}	2.104 (6)
P1—O10	1.633 (5)	Co3—O6^{ix}	2.006 (6)

P1—O12	1.556 (4)	Co3—O13ix	2.220 (5)
P2—O1	1.512 (5)	Co3—O14x	2.154 (5)
O1—Co1—O3	100.14 (19)	O8—Co2—O11	169.24 (17)
O1—Co1—O11	111.53 (19)	O8—Co2—O13i	96.85 (19)
O1—Co1—O14	145.9 (2)	O11—Co2—O13i	83.05 (18)
O3—Co1—O11	90.63 (18)	O8iv—P1—O10	108.2 (3)
O3—Co1—O14	94.6 (2)	O8iv—P1—O12	109.1 (3)
O11—Co1—O14	98.73 (18)	O10—P1—O12	103.6 (3)
O4ii—Co2—O8	84.60 (18)	O1—P2—O5v	111.4 (3)
O4ii—Co2—O11	95.03 (18)	O1—P2—O10iv	106.9 (3)
O4ii—Co2—O13i	177.0 (2)	O5v—P2—O10iv	104.4 (3)

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