Multiple Cobalt Phosphate Ring System from 1-Alkyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquids

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Abstract: Open-framework phosphate $Co_7(PO_4)_2(HPO_4)_4$ with a multiple ring system was ionothermally synthesized by using 1-alkyl-3-methylimidazolium tetrafluoroborates as solvent. The crystals of $Co_7(PO_4)_2(HPO_4)_4$ were large enough to do single crystal X-ray diffraction analysis, which crystallize in the space group *P*-1 (No.2), with cell parameters of a = 6.471(3) Å, b = 7.881(3) Å, c = 9.488(4) Å, α = 104.288(6)°, β = 109.062(5)° and γ = 101.345(5)°. The systematic increase in alkyl chain length from 2 to 4 carbon atoms in 1-alkyl-3-methylimidazolium tetrafluoroborates was investigated in this ionothermal synthesis system. The effect of different anions, such as Cl^-, Br^- and BF_4^-, on the synthesis result will also be presented in this paper.

1. Introduction

Ionothermal synthesis (ITS), the use of ionic liquids as both solvent and template (structure-directing agent) to synthesize inorganic microporous materials and inorganic-organic hybrids etc., as a new material-synthesis method has attracted more and more attention in recent years (1). It has many advantages comparing with hydrothermal and solvothermal methods. First of all, the reaction can take place at ambient pressure, eliminating some safety concerns (2, 3). Secondly, ionic liquids (ILs) play both solvent and structure-directing agent roles, removing the competition interaction between template-framework and solvent-framework, and leading potentially to new frameworks. At last but not least, ionic liquids as solvent changes the traditional synthetic system to a completely new ionic system, open a huge unknown research field.

Up to now, most studies of ITS concentrate on using ionic liquids with bromide anions. By using 1-ethyl-3-methylimidazolium bromide (EmimBr), two new aluminophosphates SIZ-1 (2) and SIZ-6 (4) with new "interrupt" structures and hanging P-O bonds, and one cobalt aluminophosphate SIZ-7 (5) with new SIV zeotype framework consisting of double-crankshaft chains were obtained. Besides, the research work by using ionic liquids with of PF_6^- and TF_2N^- instead of Br^- were also developed (6, 7). In this work, we use BF_4^- based 1-alkyl-3-methyl imidazolium (alkyl = Et, Pr and n-Bu) ionic liquids to synthesize inorganic heterocyclic compounds. A cobalt phosphate $Co_7(PO_4)_2(HPO_4)_4$ with multiple ring system was obtained. The effect of different anions, comparing with Cl^- and Br^- were also discussed.

2. Experiments

2.1. Synthesis

1-butyl-3-methylimidazolium chloride (BmimCl): 1-Methylimidazole was purified through distillation before use. 1-methylimidazole (123 g, 1.5 mol) and 1-chlorobutane (157 g, 1.7 mol) were placed in a round-bottomed flask and stirred under reflux at 70 °C for 96 hrs. A slight excess of the 1-chlorobutane was used to guarantee the total consumption of 1-methylimidazole. After that, the mixture was cooled down to room temperature, and crystals of BmimCl are formed. The product was recrystallized several times until it was colorless (8). ^{1}H NMR (DMSO): 9.62 (s, 1H), 7.94 (s, 1H), 7.86 (s, 1H), 4.23 (t, 2H), 3.91 (s, 3H), 1.79 (m, 2H), 1.25 (m, 2H), 0.90 (t, 3H).

1-butyl-3-methylimidazolium bromide (BmimBr): The similar apparatus and procedure were used as for BmimCl expect 1-butylbromide was used instead of 1-chlorobutane. The reaction time was shortened to 24 hrs. ^{1}H NMR (DMSO): 9.35 (s, 1H), 7.91 (s, 1H), 7.84 (s, 1H), 4.27 (t, 2H), 3.95 (s, 3H), 1.84 (m, 2H), 1.32 (m, 2H), 0.98 (t, 3H).

1-propyl-3-methylimidazolium bromide (PmimBr): The similar apparatus and procedure were used as for BmimBr expect 1-propylbromide was used instead of 1-butylbromide. ^{1}H NMR (DMSO): 9.35 (s, 1H), 7.88 (s, 1H), 7.81 (s, 1H), 4.17 (t, 2H), 3.90 (s, 3H), 1.82 (m, 2H), 0. 85 (t, 3H).

1-ethyl-3-methylimidazolium bromide (EmimBr): The similar apparatus and procedure were used as for BmimBr expect 1-ethylbromide was used instead of 1-butylbromide. ^{1}H NMR (DMSO): 9.35 (s, 1H), 7.88 (s, 1H), 7.81 (s, 1H), 4.18 (t, 2H), 3.95 (s, 3H), 1.82 (m, 2H), 0.98 (t, 3H).

1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$): Equal molar amounts of BmimBr or BmimCl and $NaBF_4$ were dissolved in acetone at room temperature. After stirring for 48 hours, the reactant mixture was filtered through filter paper, and then volatiles in filtrate were removed by rotary evaporator. This process was repeated until no solid were precipitate (8). ^{1}H NMR (DMSO): 9.01 (s, 1H), 7.71 (s, 1H), 7.64 (s, 1H), 4.16 (t, 3H), 3.85 (s, 2H), 1.77 (m, 2H), 1.25 (m, 2H), 0.89 (t, 3H).

1-propyl-3-methylimidazolium tetrafluoroborate ($PmimBF_4$): The similar apparatus and procedure were used as for $BmimBF_4$ except PmimBr was used instead of BmimBr. ^{1}H NMR (acetone-d_3): 8.99 (s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 4.29 (t, 3H), 4.02 (s, 2H), 1.94 (m, 2H), 0.93 (t, 3H).

1-ethyl-3-methylimidazolium tetrafluoroborate ($EmimBF_4$): the similar apparatus and procedure were used as for $BmimBF_4$ except EmimBr was used instead of BmimBr. ^{1}H NMR (DMSO): 9.38 (s, 1H), 7.89 (s, 1H), 7.78 (s, 1H), 4.22 (t, 3H), 3.87 (s, 2H), 1.39 (t, 3H).

$Co_7(PO_4)_2(HPO_4)_4$: A typical synthesis procedure was as follows: [Bmim]BF_4 (Bmim = 1-butyl-3-methylimidazolium), H_3PO_4 (85% in H_2O) and $Co(OAc)_2{\cdot}4H_2O$ with a molar ratio of 9 : 1 : 1 were charged into a 15 mL Teflon-lined stainless steel autoclave and heated under 180 °C for 5 days, and then the autoclave was cooled to room temperature. The final product containing large rhombic blue single crystals was washed with water and acetone, and then it was dried in air.

2.2 Crystal Structure Determination.

A suitable rhombic single crystal of $Co_7(PO_4)_2(HPO_4)_4$ was fixed on a glass fiber with two-component glue. The data were collected on a Bruker SMART Apex II CCD system with graphite-monochromated Mo *Ka* radiation (λ = 0.71073 Å) at 293 K. The structure was solved in the space group *P*-1 (No. 2) by direct methods [9] and refined by a full-matrix least-squares procedure using SHELXTL crystallographic software package [10]. All non-hydrogen atoms Co, P, and O could be unambiguously located from the difference Fourier map and refined with anisotropic thermal parameters. H(1) and H(2) atoms attached to O(7) and O(3), respectively, were located from the difference Fourier map. Structural details and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

3. Results and discussion

Compound $Co_7(PO_4)_2(HPO_4)_4$ was firstly hydrothermally synthesized by using $CoCl_2{\cdot}6H_2O$ and $NH_4H_2PO_4$ at 220 °C [11]. In this work the ionic liquid BmimBF_4 was used as reaction media, and H_3PO_4 and $Co(OAc)_2{\cdot}4H_2O$ as reactant, rhombic single crystals of $Co_7(PO_4)_2(HPO_4)_4$ were obtained at 180 °C for 5 days. The ^1H NMR spectrum of BmimBF_4 after the reaction was collected, and there was not any apparent change detected. The effect of the cation size was investigated by using PmimBF_4 and EmimBF_4 as solvents instead of BmimBF_4. It shows that when PmimBF_4 was used under the same reaction condition, a powder phase of $Co_7(PO_4)_2(HPO_4)_4$ can be obtained. However, when EmimBF_4 is employed, another cobalt phosphate $(CoHPO_4)_2{\cdot}3H_2O$ was formed. Figure 1 shows the simulated XRD pattern from the structure of $Co_7(PO_4)_2(HPO_4)_4$ and experimental ones from as-synthesized samples by different solvents. In order to study the influence of BF_4^- anions, BmimBr and BmimCl ionic liquids were used, however, no solid products could be obtained no matter which reaction conditions were applied. This effect may be due to the different complexation capacity of ions with Co^{2+}.

The crystal structure of $Co_7(PO_4)_2(HPO_4)_4$ was determined by the single crystal X-ray diffraction method. $Co_7(PO_4)_2(HPO_4)_4$ crystallizes in the space group *P*-1 (No.2), with cell parameters of a = 6.471(3) Å, b = 7.881(3) Å, c = 9.488(4) Å, α = 104.288(6)°, β = 109.062(5)° and γ = 101.345(5)°. The asymmetric unit of $Co_7(PO_4)_2(HPO_4)_4$, as shown in Figure 2, contains three crystallographically distinct tetrahedrally coordinated P atoms, and four unique Co sites. All Co atoms are six coordinated except an penta-folded Co(2). The structure features in many multiple ring systems. Octahedra $Co(1)O_6$, trigonal bipyramids $Co(2)O_5$ and octahedra Co(3) were connected alternatively by sharing edges forming Co-O 4-ring-chains extending along the *c* axis, as shown in Figure 3a. Six-coordinated Co(4) atoms locate on inversion center positions, which join the 4-ring-chains together by sharing common O atoms with Co(1) and Co(2) forming a three-dimensional frameworks. The Co-O bond distances change in the range of 2.021(4) to 2.222(4) Å. The joint of all Co atoms by sharing O atoms implies the possible existence of magnetic interactions. The study of magnetic property is undergoing. The three four-coordinated P atoms further link the Co-O 4-ring chains to form more complicated ring systems. Figure 3b presents that P(3) atom shares μ_3-O(1) and μ_3-O(5) atoms with Co(2) and Co(3) forming a 6-membered oxygen-heterocycle. Analogously, P(2) shares O atoms with Co(1) and Co(3), and P(1) shares O atoms with Co(3) and Co(4), resulting alternative cobalt-phosphor-oxygen 8-membered heterocycles, respectively. All the P-O bond distances are comparable with those of phosphates (11). The extension of P(1)-O(3) and P(2)-O(7) bonds to 1.574(4) and 1.577(5) Å confirms the location of the H atoms.

4. Conclusions

Cobalt phosphate $Co_7(PO_4)_2(HPO_4)_4$ with a complicated inorganic heterocycle structure was prepared by using a ionothermal method. Both $BmimBF_4$ and $PmimBF_4$ ionic liquids can be used as solvent to get this phase. However, when $EmimBF_4$ was used as solvent, another cobalt phosphate $(CoHPO_4)_2{\cdot}3H_2O$ was obtained as the final product. Using BmimBr or BmimCl as solvent leads only to blue gel. This work shows that the synthesis of inorganic heterocyclic compounds by using ITS method is possible after selection of the right ionic liquid as solvent.

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Captions

Figure 1 Simulated XRD patterns from the structure of $Co_7(PO_4)_2(HPO_4)_4$ and experimental XRD patterns of samples synthesized by different solvents.

Figure 2 Thermal ellipsoid plots (50% probability) and atomic labeling schemes of $Co_7(PO_4)_2(HPO_4)_4$.

Figure 3 (a) Ball and stick presentation of 4-ring cobalt-oxygen chain. (b) The open framework of $Co_7(PO_4)_2(HPO_4)_4$.

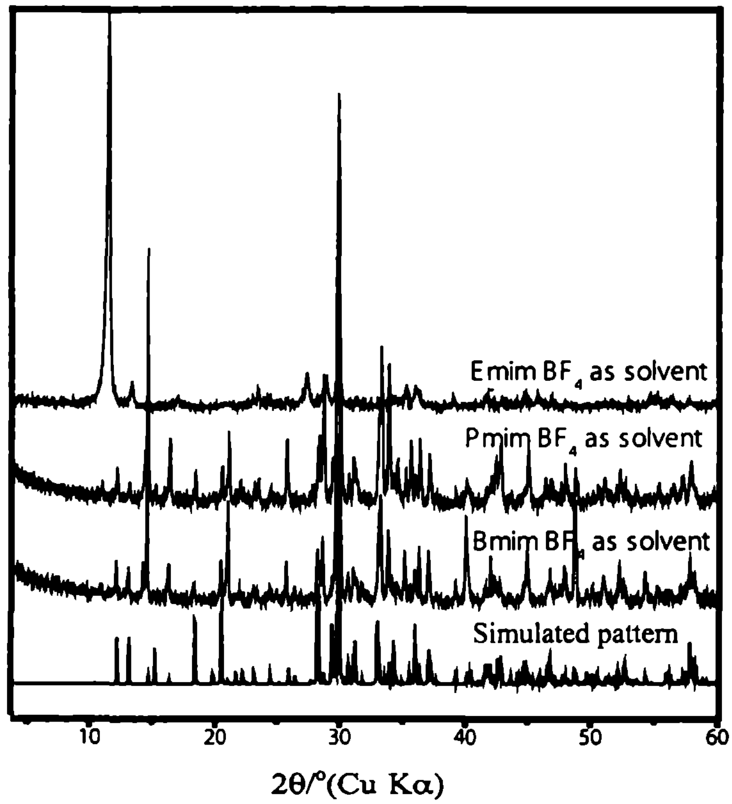

Fig. 1

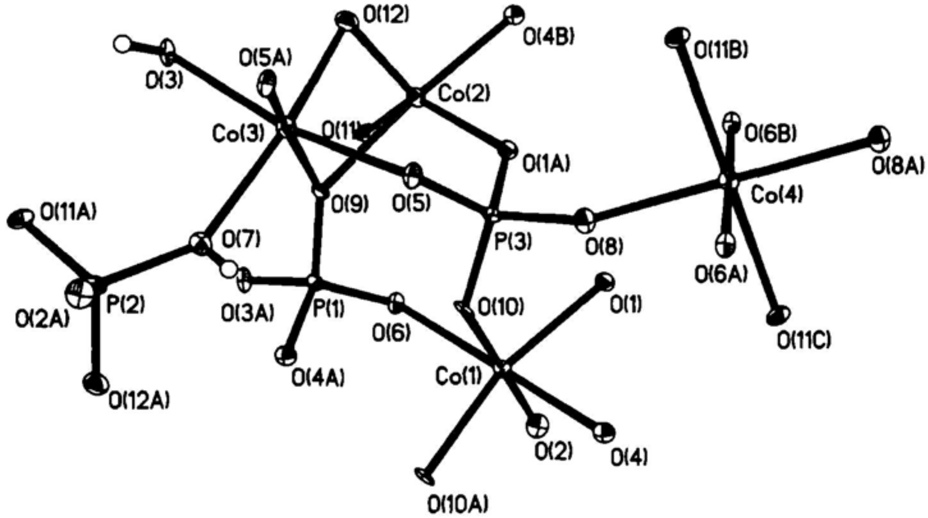
O(12)
O(4B)
O(11B)
O(3)
O(5A)
Co(2)
Co(3)
O(6B)
O(8A)
O(1A)
O(9)
O(5)
Co(4)
O(11A)
O(7)
P(3)
O(8)
O(6A)
O(2A)
P(2)
O(3A)
P(1)
O(10)
O(1)
O(6)
O(11C)
O(4A)
Co(1)
O(12A)
O(2)
O(4)
O(10A)

Fig. 2

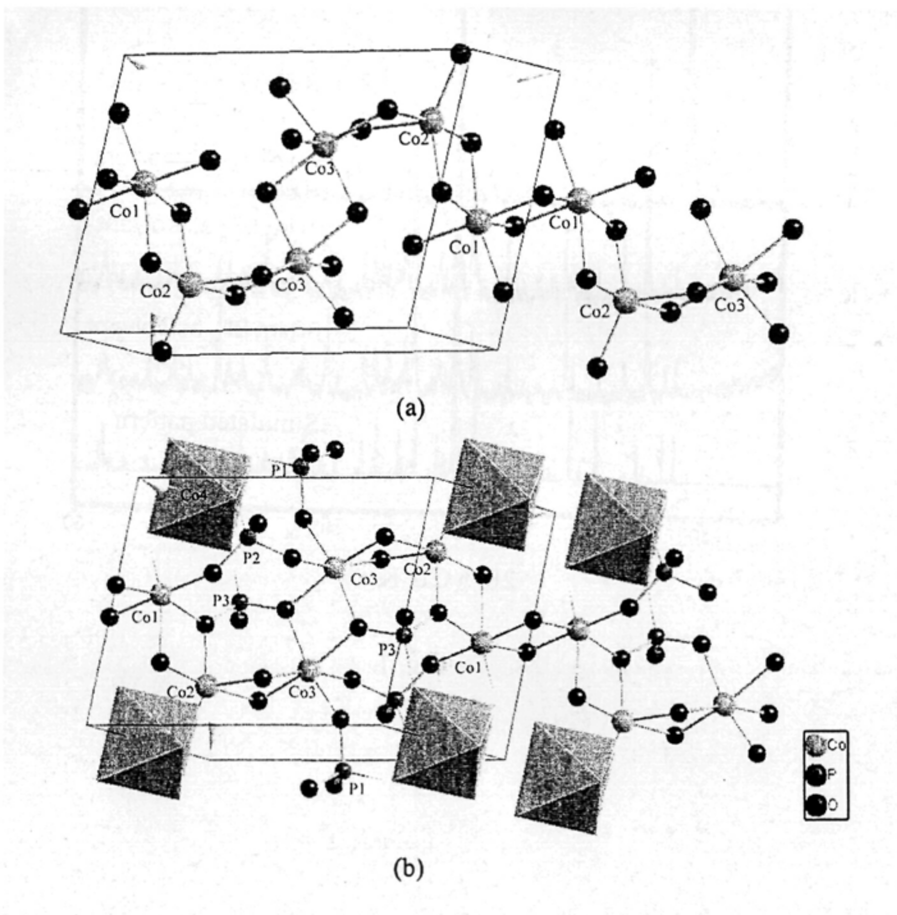
Co2
Co3
Co1
Co1
Co1
Co2
Co3
Co2
Co3
(a)
P1
Co4
P2
Co3
Co2
Co1
P3
P3
Co1
Co2
Co3
P1
Co
P
O
(b)

Fig. 3

Table 1 Crystal data and structure refinement for $Co_7(PO_4)_2(HPO_4)_4$[a]

Compound	
Empirical formula	$Co_7H_4(PO_4)_6$
Formula weight	701.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	a = 6.471(3) Å, α = 104.288(6)°
	b = 7.881(3) Å, β = 109.062(5)°
	c = 9.488(4) Å, γ = 101.345(5)°
Volume	422.3(3) $Å^3$
Z, Calculated density	6, 16.547 Mg/m^3
Absorption coefficient	42.182 mm^{-1}
F(000)	2004
Crystal size	0.23 × 0.12 × 0.08 mm^3
Theta range for data collection	2.41 to 28.90 °
Limiting indices	$-8 \le h \le 7$, $-10 \le k \le 10$, $-6 \le l \le 12$
Reflections collected / unique	2633 / 1947 [R(int) = 0.0185]
Completeness to theta =	25, 97.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1947 / 0 / 176
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R_1 = 0.0437, wR_2 = 0.1146
R indices (all data)	R_1 = 0.0569, wR_2 = 0.1235
Largest diff. peak and hole	1.459 and -1.146 e $Å^{-3}$

[a] $R_1=\Sigma(\Delta F/\Sigma(F_o))$; $wR_2=(\Sigma[w(F_o^2-F_c^2)])/\Sigma[w(F_o^2)^2]^{1/2}$, $w=1/\sigma^2(F_o^2)$

Table 2 Selected Bond Lengths [Å] and Angles [deg] for $Co_7(PO_4)_2(HPO_4)_4$[a]

Co(1)-O(10)	2.054(4)	Co(4)-O(8)	2.099(4)
Co(1)-O(2)	2.057(4)	Co(4)-O(8)#4	2.099(4)
Co(1)-O(10)#1	2.087(4)	Co(4)-O(6)#2	2.130(4)
Co(1)-O(1)	2.094(4)	Co(4)-O(6)#5	2.130(4)
Co(1)-O(6)	2.120(4)	Co(4)-O(11)#2	2.222(4)
Co(1)-O(4)	2.195(4)	P(1)-O(9)	1.531(4)
Co(2)-O(1)#2	2.021(4)	P(1)-O(4)#1	1.536(4)
Co(2)-O(11)	2.053(4)	P(1)-O(6)	1.550(4)
Co(2)-O(4)#2	2.062(4)	P(1)-O(3)#6	1.574(4)
Co(2)-O(12)	2.065(5)	P(2)-O(2)#7	1.525(4)
Co(2)-O(9)	2.181(4)	P(2)-O(11)#6	1.527(4)
Co(3)-O(5)	2.070(4)	P(2)-O(12)#8	1.535(4)
Co(3)-O(3)	2.071(4)	P(2)-O(7)	1.577(5)
Co(3)-O(9)	2.072(4)	P(3)-O(10)	1.526(4)
Co(3)-O(5)#3	2.109(4)	P(3)-O(5)	1.532(4)
Co(3)-O(7)	2.113(5)	P(3)-O(1)#2	1.542(4)
Co(3)-O(12)	2.115(5)	P(3)-O(8)	1.546(4)

Co(4)-O(11)#5	2.222(4)	O(5)-Co(3)-O(3)	162.98(17)
O(10)-Co(1)-O(2)	178.04(16)	O(5)-Co(3)-O(9)	89.82(17)
O(10)-Co(1)-O(10)#1	84.91(16)	O(3)-Co(3)-O(9)	105.94(17)
O(2)-Co(1)-O(10)#1	93.72(17)	O(5)-Co(3)-O(5)#3	78.35(18)
O(10)-Co(1)-O(1)	90.87(16)	O(3)-Co(3)-O(5)#3	86.76(17)
O(2)-Co(1)-O(1)	90.00(17)	O(9)-Co(3)-O(5)#3	166.01(17)
O(10)#1-Co(1)-O(1)	161.58(17)	O(5)-Co(3)-O(7)	96.34(19)
O(10)-Co(1)-O(6)	84.93(17)	O(3)-Co(3)-O(7)	89.62(18)
O(2)-Co(1)-O(6)	96.53(17)	O(9)-Co(3)-O(7)	92.07(18)
O(10)#1-Co(1)-O(6)	92.07(17)	O(5)#3-Co(3)-O(7)	81.97(18)
O(1)-Co(1)-O(6)	105.44(17)	O(5)-Co(3)-O(12)	95.22(17)
O(10)-Co(1)-O(4)	81.36(16)	O(3)-Co(3)-O(12)	81.85(18)
O(2)-Co(1)-O(4)	97.10(17)	O(9)-Co(3)-O(12)	78.97(16)
O(10)#1-Co(1)-O(4)	83.30(16)	O(5)#3-Co(3)-O(12)	109.25(17)
O(1)-Co(1)-O(4)	78.34(16)	O(7)-Co(3)-O(12)	165.34(19)
O(6)-Co(1)-O(4)	165.86(16)	O(8)-Co(4)-O(8)#4	179.999(1)
O(1)#2-Co(2)-O(11)	134.87(17)	O(8)-Co(4)-O(6)#2	89.19(16)
O(1)#2-Co(2)-O(4)#2	83.16(17)	O(8)#4-Co(4)-O(6)#2	90.81(16)
O(11)-Co(2)-O(4)#2	105.17(17)	O(8)-Co(4)-O(6)#5	90.81(16)
O(1)#2-Co(2)-O(12)	97.23(18)	O(8)#4-Co(4)-O(6)#5	89.19(16)
O(11)-Co(2)-O(12)	123.35(18)	O(6)#2-Co(4)-O(6)#5	180.00(19)
O(4)#2-Co(2)-O(12)	100.82(17)	O(8)-Co(4)-O(11)#2	90.47(16)
O(1)#2-Co(2)-O(9)	88.65(16)	O(8)#4-Co(4)-O(11)#2	89.53(16)
O(11)-Co(2)-O(9)	82.46(16)	O(6)#2-Co(4)-O(11)#2	86.66(16)
O(4)#2-Co(2)-O(9)	171.42(16)	O(6)#5-Co(4)-O(11)#2	93.34(16)
O(12)-Co(2)-O(9)	77.60(16)	O(8)-Co(4)-O(11)#5	89.53(16)
O(9)-P(1)-O(4)#1	111.6(2)	O(8)#4-Co(4)-O(11)#5	90.47(16)
O(9)-P(1)-O(6)	111.0(2)	O(6)#2-Co(4)-O(11)#5	93.34(16)
O(4)#1-P(1)-O(6)	114.7(2)	O(6)#5-Co(4)-O(11)#5	86.66(16)
O(9)-P(1)-O(3)#6	108.5(2)	O(11)#2-Co(4)-O(11)#5	179.999(1)
O(4)#1-P(1)-O(3)#6	106.4(2)	O(10)-P(3)-O(5)	108.8(2)
O(6)-P(1)-O(3)#6	104.0(2)	O(10)-P(3)-O(1)#2	111.0(2)
O(2)#7-P(2)-O(11)#6	111.9(3)	O(5)-P(3)-O(1)#2	110.0(2)
O(2)#7-P(2)-O(12)#8	111.5(3)	O(10)-P(3)-O(8)	110.1(2)
O(11)#6-P(2)-O(12)#8	111.2(2)	O(5)-P(3)-O(8)	108.5(2)
O(2)#7-P(2)-O(7)	107.5(3)	O(1)#2-P(3)-O(8)	108.5(2)
O(11)#6-P(2)-O(7)	109.7(3)	O(12)#8-P(2)-O(7)	104.7(3)

[a] Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2 #2 -x+1,-y+1,-z+2 #3 -x+1,-y+1,-z+3 #4 -x+1,-y,-z+2 #5 x,y-1,z
#6 -x+1,-y+2,-z+3 #7 x,y,z+1 #8 x-1,y,z