

KCo(H₂O)₂BP₂O₈·0.48H₂O and K_{0.17}Ca_{0.42}Co(H₂O)₂BP₂O₈·H₂O: two cobalt borophosphates with helical ribbons and disordered (K,Ca)/H₂O schemes

 Abderrahmen Guesmi^{a,b*} and Ahmed Driss^a

^aLaboratoire de Matériaux et Cristallographie, Faculté des Sciences, El Manar II, 2092 Tunis, Tunisia, and ^bInstitut Préparatoire aux Etudes d'Ingénieurs d'El Manar, BP 244, El Manar II, 2092 Tunis, Tunisia

Correspondence e-mail: abdrarhmen.guesmi@ipeim.rnu.tn

Received 14 June 2012

Accepted 3 July 2012

Online 25 July 2012

The two title compounds, potassium diaquacobalt(II) borodiphosphate 0.48-hydrate and potassium–calcium(0.172/0.418) diaquacobalt(II) borodiphosphate monohydrate, were synthesized hydrothermally. They are new members of the borophosphate family characterized by $\infty[\text{BP}_2\text{O}_8]^{3-}$ helices running along [001] and constructed of boron (Wyckoff position $6b$, twofold axis) and phosphorus tetrahedra. The $[\text{CoBP}_2\text{O}_8]^-$ anionic frameworks in the two materials are structurally similar and result from a connection in the ab plane between the $\text{CoO}_4(\text{H}_2\text{O})_2$ coordination octahedra ($6b$ position) and the helical ribbons. Nevertheless, the two structures differ in the disorder schemes of the K,Ca and H₂O species. The alkali cations in the structure of the pure potassium compound are disordered over three independent positions, one of them located on a $6b$ site. Its framework is characterized by double occupation of the tunnels by water molecules located on twofold rotation axes ($6b$) and a fraction of alkali cations; its cell parameters, compared with those for the mixed K,Ca compound, show abnormal changes, presumably due to the disorder. For the K,Ca compound, the K and Ca cations are on twofold axes ($6b$) and the channels are occupied only by disordered solvent water molecules. This shows that it is possible, due to the flexibility of the helices, to replace the alkali and alkaline earth cations while retaining the crystal framework.

Comment

Borophosphates (BPOs), intermediate phases of $A-M-B-P-O$ systems (where A is an alkali cation, H_3O^+ , NH_4^+ or alkaline earth, and M is a transition metal cation), have attracted the attention of many scientists due to their particularly rich structural chemistry which is the source of many promising properties. For instance, the combination of phosphate and

borate groups may provide exciting structural architectures and properties, and several BPOs have applications in the optical and petroleum industries, in catalysis, as ion-conductive solids, as corrosion protectors *etc.*

The main structural features of borophosphates are the diversity of connection modes between the PO_4 tetrahedra and the trigonal–planar or tetrahedrally coordinated B atoms, and the spectrum of BPO structures ranges from densely packed to microporous and organo-templated frameworks. Most varieties of BPOs belong to the family with the general formula $A_x\text{MBP}_2\text{O}_8 \cdot y\text{H}_2\text{O}$ ($x = 0-1$ and $y = 0.5-1$), reported first by Kniep *et al.* (1997), who among other researchers proposed the classification, terminology and nomenclature of BPO structural chemistry (Kniep *et al.*, 2004; Ewald *et al.*, 2007). The anionic partial structure of these materials is composed of one-dimensional $\infty[\text{BP}_2\text{O}_8]^{3-}$ helices wound around the sixfold screw axes, and the octahedral–tetrahedral framework is related to the zeolite CZP topology (Harrison *et al.*, 1996). The possibility of realising de/rehydration processes in this class of compounds has also been reported (Boy, Stowasser *et al.*, 2001). To date, the only potassium- and calcium-containing members are $\text{KFe}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot 0.5\text{H}_2\text{O}$ (Boy, Schäfer & Kniep, 2001) and $\text{Ca}_{0.5}\text{M}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot \text{H}_2\text{O}$ ($M = \text{Fe}, \text{Co}, \text{Ni}$; Menezes *et al.*, 2007, 2008*a,b*; Menezes, 2009). As for cobalt BPOs, we have already reported the structure of $\text{NaCoH}_2\text{BP}_2\text{O}_9$ obtained hydrothermally (Guesmi & Driss, 2004). The lithium- and sodium–cobalt members of the helical BPO family were reported previously (Shi, Shan, Dai *et al.*, 2003; Menezes *et al.*, 2008*b*). In addition, Zouhri *et al.* (2012)

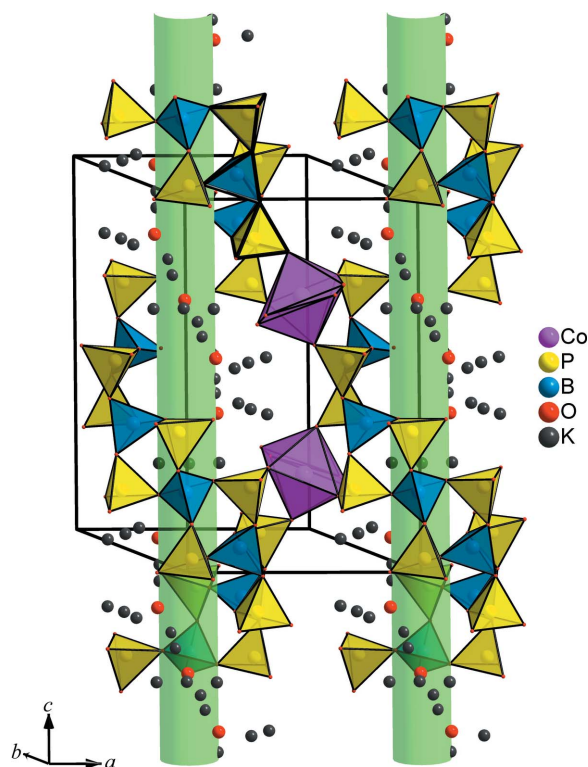
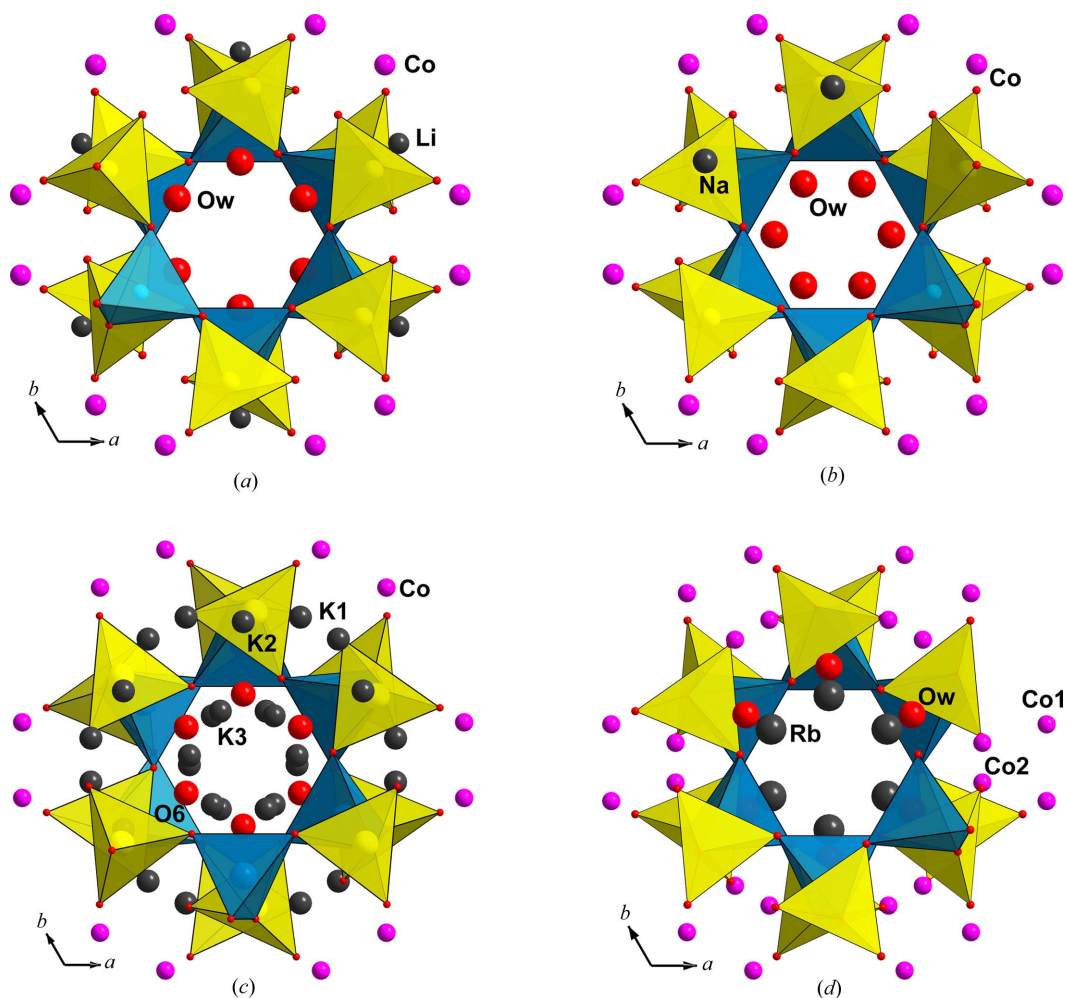


Figure 1
The linkage of the helices and location of the K/H₂O entities in (I). The anionic framework is represented by coordination polyhedra.


Figure 2

The helical arrangements, viewed along [001], in the structures of (a) lithium (Menezes *et al.*, 2008b), (b) sodium (Shi, Shan, Dai *et al.*, 2003), (c) potassium, (I), and (d) rubidium (Engelhardt, 2000) cobalt borophosphates. Atom labels refer to one of the symmetry-equivalent positions of the respective atoms.

have recently reported the structure of $(\text{Ag}_{0.79}\text{Co}_{0.11})\text{Co}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot 0.67\text{H}_2\text{O}$, where Co and Ag share the same site. We report here the structures of the potassium and potassium–calcium cobalt borophosphates, $\text{KCo}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot y\text{H}_2\text{O}$ ($y \simeq 0.5$), (I), and $\text{K}_{0.17}\text{Ca}_{0.42}\text{Co}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot \text{H}_2\text{O}$, (II), grown hydrothermally and characterized by qualitative energy-dispersive X-ray (EDX) spectroscopic analysis and single-crystal X-ray diffraction.

The two compounds emerged in the same batch and have similar shapes but different colours, *viz.* purple and pink. The purple crystals, (I), are the major phase and the EDX analysis reveals the existence of the elements K, Co, P and O. The pink crystals of (II), as a minor phase, contain calcium in addition, according to the same technique. The X-ray crystal structure determinations reveal that the anionic frameworks in the two compounds are composed of two unique tetrahedral P and B sites, one octahedral Co site and six O sites, two of which are coordinated, and solvent water molecules. The Co1–O1 distances (Table 1) are significantly different in (I) and (II).

Both structures are characterized by corner-sharing PO_4 and BO_4 tetrahedra, leading to the fundamental building unit

(FBU) $[\text{BP}_2\text{O}_8]^{3-}$. The BO_4 tetrahedron shares two of its vertices with two PO_4 tetrahedra from the same FBU, and the other two with two phosphorus tetrahedra from two adjacent units. An infinite one-dimensional anionic ribbon then results, giving rise to a helical arrangement around the 6_5 screw axis. The phosphate groups occupy the borders of the ribbons, with two terminal O atoms acting as ligands to complete the coordination of the Co^{II} ions. The helices are interconnected *via* cobalt coordination octahedra along the *a* and *b* axes to form a tubular three-dimensional mixed framework, where each octahedron shares four O atoms with four phosphorus tetrahedra from two ribbons.

Although the $[\text{Co}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8]^-$ frameworks are structurally similar, their occupation by the alkali and alkaline earth cations and the solvent water molecules are different. This affects the lattice parameters, revealing significant differences between the two compounds. The first assignment of the structure of (I) seems to fit the BPO reported by Kniep *et al.* (1997), with parameters determined by powder X-ray diffraction ($a = 9.48$ and $c = 15.83$ Å). Although the volume is almost the same, the cell parameters differ slightly, with a

compression and an expansion of the c and a parameters, respectively, compared with those already reported (Kniep *et al.*, 1997). The contraction along the c axis observed in $(\text{H}_3\text{O})\text{ZnBP}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$ (Shi, Shan, He *et al.*, 2003) is attributed to the existence of oxonium groups and hydrogen bonds; the same abnormal structure changes caused by hydrogen-bond interactions are also reported in the structure of $(\text{NH}_4)\text{CdBP}_2\text{O}_8 \cdot 2.72\text{H}_2\text{O}$ (Ge *et al.*, 2005). The structural model corresponding to the existence of H atoms in the form of oxonium groups in the structure of (I) is thus to be verified.

With regard to the solvent water content in the single potassium BPO in this family, $\text{KFe}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot 0.5\text{H}_2\text{O}$ (Boy, Schäfer & Kniep, 2001), the tunnels are half-occupied by solvent water molecules. The refinement of the structure of (I) was thus devoted to determining the solvent water content and verifying the existence of a fraction of oxonium groups, a possibility which requires the existence of less than six alkali cations per unit cell. When all atoms of the anionic framework were located, four significant peaks with different heights appeared in the difference Fourier map. The highest electron density (in general position 12c) and the next highest were assigned as partially occupied K^+ cations; charge neutrality was not achieved yet. The last two positions, 6a and 6b, both incompletely occupied, were attributed to the water molecules and alkali cations, respectively. However, the isotropic displacement parameter of the K^+ ions in the 6b position was abnormally high and again the charge was not balanced. If the last two attributions are inverted, the result corresponds to almost six alkali cations per unit cell, with one of the three alkali positions in the tunnels (K3). The result was improved significantly when the K3 cations were displaced from the special 6a position to a general 12a position, with exactly one alkali cation per unit formula; the problem of charge neutrality was resolved and the hypothesis of the existence of a fraction of oxonium was therefore dismissed. The 6b position attributed to solvent water was refined freely to an occupancy of 0.48 (4) and no significant peaks were observed in the difference electron-density map. The result matches the formula $\text{KCo}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot 0.48\text{H}_2\text{O}$ (Fig. 1).

It has been reported in several cases (Engelhardt, 2000; Schäfer *et al.*, 2002; Birsöz *et al.*, 2007) that if the size of the monovalent cations (NH_4^+ , Rb^+ or Cs^+) is large enough, these entities shift to the tunnels and their total occupancies will be lower than one per unit formula. Thus, to achieve charge balance, the transition metal cation occupies a second position on the border of the ribbons. The solvent water positions within the helical channels in all these structures are partially occupied. Compound (I) does not correspond to this case, as the metal cation is only octacoordinated. Another model frequently observed is double disorder of alkali or alkaline earth cations and solvent water at both the periphery and inside the ribbons, respectively. Although in (I) these two entities are disordered, to the best of our knowledge this is the only case where there is just one cobalt octahedron with a fraction of the alkali metal cations shifted to the tunnels at short distances from the water molecules, whose 'territory' is now shared with a fraction of these cations (Fig. 2). It is worth

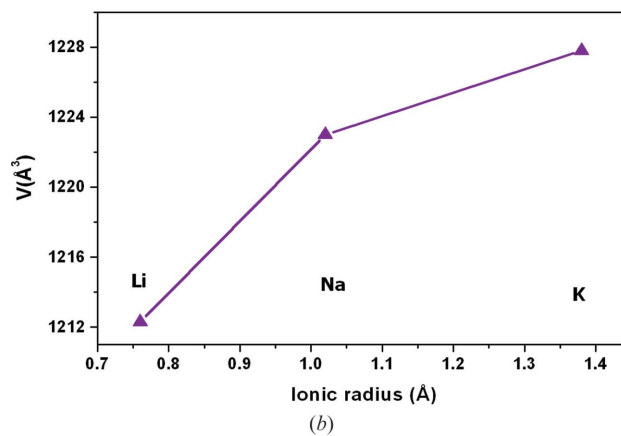
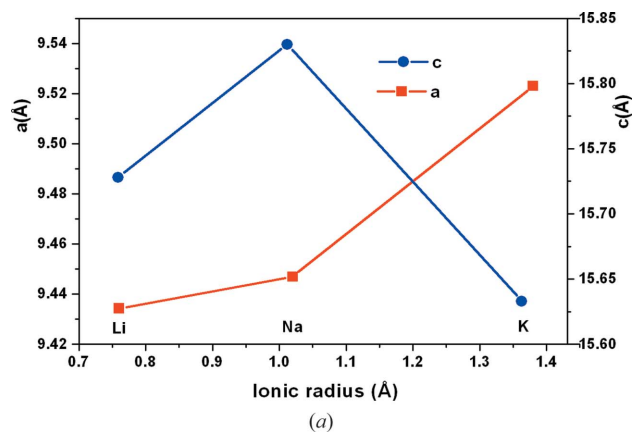


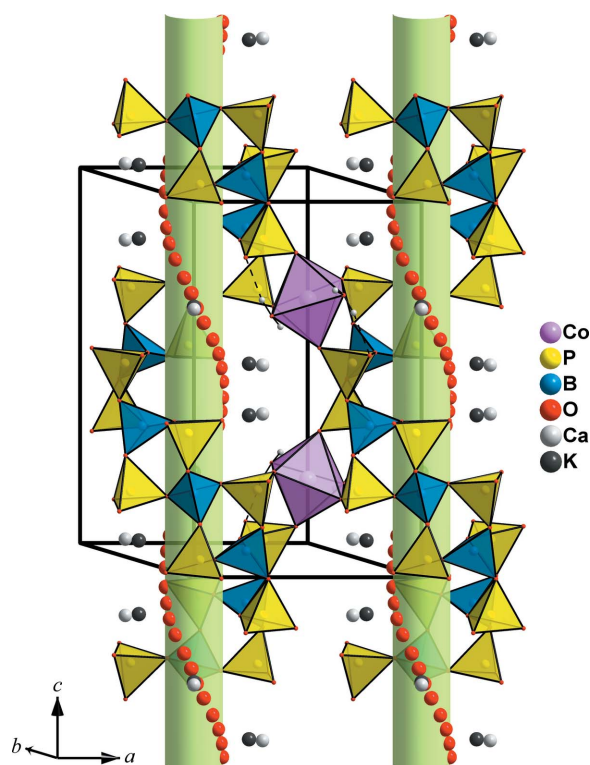
Figure 3

The dependence of a , c and V on A^+ ($A = \text{Li-K}$) alkali metal radius in hexagonal cobalt borophosphates.

noting that the structures of this family are characterized mainly by the flexibility of their BPO groups, which can then accommodate several species, charged or neutral, and with different patterns of disorder.

If we plot the lattice parameters of cobalt compounds as a function of the radius of the alkali cations (Shannon, 1976) in the different materials (Fig. 3), we note that, in the Li and Na cases, these parameters change with the radius of these species with a c/a ratio of about 1.666. An exception is observed for (I): the c parameter is shorter and the a parameter longer, and this alters the c/a ratio to 1.642. The volume is not affected by these changes and, as in the other cases, it increases with the radius of the alkali cation. We can conclude that the occupancy of the cobalt anionic framework is dependent on the size of the monovalent cation. It is fully occupied by water molecules in the case of the small Li^+ and Na^+ cations. In the case of the intermediate-sized K^+ ion, the tunnels are almost half-occupied by water molecules with a full occupancy for K^+ ions. Finally, for the larger alkaline metal Rb^+ and Cs^+ ions, the two occupancies are less than unity (Engelhardt, 2000).

The contraction along the c axis in $(\text{H}_3\text{O})\text{ZnBP}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$ (Shi, Shan, He *et al.*, 2003) is attributed to the existence of oxonium. In the case of (I), it seems that the distribution of K^+ cations with closest positions accompanied by oxygen attraction, with short K-O distances, 'elongates' the unit cell in the


Figure 4

A perspective view of part of the structure of (II). The anionic framework is represented by coordination polyhedra. The helices of disordered solvent water molecules are shown. Hydrogen bonds are shown as dashed lines.

ab plane and then the *c* axis decreases. The influence of other structure characteristics (hydrogen-bond network, cobalt environment *etc.*) cannot be excluded.

Refinement of (II) (Fig. 4) was quite straightforward. When correctly attributed, the two site occupancies of the K1 and Ca1 cations refine freely to values ensuring charge neutrality. The two cations occupy the free loops of the borophosphate helices and their two positions are 0.65 Å apart. Alkali cations populate the inner walls of the helices with shorter K1–O(water) distances. The coordinated solvent water molecules are involved as donors in O–H···O hydrogen bonds (Table 2 and Fig. 4). The channels are filled with disordered solvent water molecules having two partially occupied positions.

A systematic investigation of the structures of alkaline earth and cobalt borophosphates has been presented elsewhere (Menezes *et al.*, 2007, 2008*a,b*; Menezes, 2009). Compound (II) is the only mixed alkali–alkaline earth member. Compared with the pure calcium compound $\text{Ca}_{0.5}\text{CoBP}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$ (Menezes, 2009), its structure reveals some differences: the cell parameters of (II) are slightly longer, mainly along the *c* direction, with a *c/a* ratio of 1.676, slightly higher than the ratio of 1.661 in the pure calcium compound. These changes are due to the partial substitution of calcium by a cation with a larger radius. The solvent water molecules are not disordered in $\text{Ca}_{0.5}\text{CoBP}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$, but they are disordered in (II), and the consequent hydrogen-bond network can also influence the crystal structure.

Experimental

The title compounds were synthesized hydrothermally and the reactions were carried out in thick-walled Pyrex tubes. A mixture of KNO_3 (1.49 g), cobalt acetate tetrahydrate (1.84 g), H_3BO_3 (0.91 g) and H_3PO_4 (2 ml) was dissolved in deionized water ($V_{\text{solution}} = 25$ ml). The mixture was then heated at 453 K for four weeks and the degrees of filling (30–50%) were modified to vary the autogenous pressure. Hexagonal pyramidal and bipyramidal purple crystals of (I) as the major phase, accompanied by some pink crystals of (II), were obtained in the most filled tube. A qualitative energy-dispersive X-ray (EDX) analysis revealed the presence of K, Co, P and O, with the calcium in the pink-coloured phase diffusing from the reaction container.

Compound (I)

Crystal data

$\text{KCo}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot 0.48\text{H}_2\text{O}$
 $M_r = 343.46$
 Hexagonal, $P6_522$
 $a = 9.5231$ (14) Å
 $c = 15.633$ (2) Å
 $V = 1227.8$ (3) Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 3.05$ mm⁻¹
 $T = 293$ K
 $0.26 \times 0.26 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.505$, $T_{\text{max}} = 0.581$
 5187 measured reflections

895 independent reflections
 891 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 2 standard reflections every 120 reflections
 intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.03$
 895 reflections
 81 parameters

$\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³
 Absolute structure: Flack (1983), with 309 Friedel pairs
 Flack parameter: 0.05 (5)

Compound (II)

Crystal data

$\text{K}_{0.17}\text{Ca}_{0.42}\text{Co}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8 \cdot \text{H}_2\text{O}$
 $M_r = 336.94$
 Hexagonal, $P6_522$
 $a = 9.4720$ (15) Å
 $c = 15.872$ (6) Å
 $V = 1233.2$ (5) Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 2.88$ mm⁻¹
 $T = 293$ K
 $0.17 \times 0.17 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.641$, $T_{\text{max}} = 0.706$
 3480 measured reflections

902 independent reflections
 854 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.094$
 2 standard reflections every 120 reflections
 intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.071$
 $S = 0.98$
 902 reflections
 92 parameters
 3 restraints

Only H-atom coordinates refined
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³
 Absolute structure: Flack (1983), with 311 Friedel pairs
 Flack parameter: 0.01 (3)

Table 1

Selected bond lengths (Å) of the coordination polyhedra in (I) and (II).

Bond	(I)	(II)
Co1—O1†	2.043 (3)	2.087 (2)
Co1—O2†	2.083 (4)	2.090 (2)
Co1—O5†	2.182 (11)/2.439 (17)‡	2.190 (2)
P1—O2 ⁱⁱ	1.512 (4)	1.513 (2)
P1—O1	1.513 (4)	1.511 (2)
P1—O3	1.553 (4)	1.562 (2)
P1—O4 ⁱⁱⁱ	1.554 (3)	1.571 (2)
B1—O3 ^{iv}	1.462 (5)	1.460 (3)
B1—O3	1.462 (5)	1.460 (3)
B1—O4	1.483 (5)	1.484 (3)
B1—O4 ^{iv}	1.483 (5)	1.484 (3)

† The distances are the same for O atoms generated by symmetry code (i). ‡ The shorter Co1—O5 distances in (I) correspond to the O51 and the longer to the partially occupied O52 positions. Symmetry codes: (i) $-y + 1, -x + 1, -z + \frac{1}{6}$; (ii) $x - y, -y + 1, -z$; (iii) $x - y, x, z - \frac{1}{6}$; (iv) $x, x - y, -z - \frac{1}{6}$.

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H52 \cdots O4 ⁱ	0.83 (3)	1.95 (3)	2.762 (3)	168 (4)
O5—H51 \cdots O2 ⁱⁱ	0.84 (3)	1.92 (3)	2.746 (3)	164 (5)

Symmetry codes: (i) $x - y, -y + 1, -z$; (ii) $y, -x + y + 1, z + \frac{1}{6}$.

In (I), disorder of the coordinated water O atom was found and atoms O51/O52 were refined isotropically with complementary occupancy factors. The alkali cations are also disordered over three independent K1, K2 and K3 positions which, as well as solvent water atom O6, were treated isotropically. The H atoms were not located.

For (II), the H atoms associated with atom O5 of the coordinated water molecule were located in a difference Fourier map and refined with an O—H restraint of 0.85 (3) Å and with displacement parameters fixed at $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O5})$. The two O6 sites belonging to the disordered solvent water molecules were constrained to the same displacement parameters and the sum of their occupancies was restrained to 0.5, because the refined value was close to 0.50; their H atoms were not located. The K and Ca atoms were refined isotropically without any restraints.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *pubCIF* (Westrip, 2010).

The authors are grateful to Dr Stefan Hoffmann (Max-Planck-Institut für Chemische Physik) and to Dr Olga V. Yakubovich (Department of Geology, Moscow State Lomonosov University) for bibliographic data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3086). Services for accessing these data are described at the back of the journal.

References

- Birsöz, B., Baykal, A., Toprak, M. & Köseoglu, Y. (2007). *Cent. Eur. J. Chem.* **5**, 536–545.
- Boy, I., Schäfer, G. & Kniep, R. (2001). *Z. Kristallogr.* **216**, 13–14.
- Boy, I., Stowasser, F., Schäfer, G. & Kniep, R. (2001). *Chem. Eur. J.* **7**, 834–839.
- Brandenburg, K. (2001). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Engelhardt, H. (2000). Dissertation, Darmstadt University of Technology, Germany.
- Enraf-Nonius (1995). *CAD-4 EXPRESS*. Enraf-Nonius, Delft, The Netherlands.
- Ewald, B., Huang, Y. X. & Kniep, R. (2007). *Z. Anorg. Allg. Chem.* **633**, 1517–1540.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Ge, M.-H., Liu, W., Chen, H.-H., Li, M.-R., Yang, X.-X. & Zhao, J.-T. (2005). *Z. Anorg. Allg. Chem.* **631**, 1213–1217.
- Guesmi, A. & Driss, A. (2004). *Adv. Eng. Mater.* **6**, 840–842.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Harrison, W. T. A., Gier, T. E., Stucky, G. D., Broach, R. W. & Bedard, R. A. (1996). *Chem. Mater.* **8**, 145–151.
- Kniep, R., Durif, A., Parthe, E., Sevov, S. & Zhao, J. T. (2004). IUPAC Project Number 2003-034-1-200.
- Kniep, R., Horst, G., Will, H. G., Boy, I. & Röhr, C. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 1013–1014.
- Menezes, P. W. (2009). Dissertation, University of Dresden, Germany.
- Menezes, P. W., Hoffmann, S., Prots, Y. & Kniep, R. (2007). *Z. Kristallogr.* **222**, 1–2.
- Menezes, P. W., Hoffmann, S., Prots, Y. & Kniep, R. (2008a). *Z. Kristallogr.* **223**, 9–10.
- Menezes, P. W., Hoffmann, S., Prots, Y. & Kniep, R. (2008b). *Z. Kristallogr.* **223**, 333–334.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Schäfer, G., Carrillo-Cabrera, W., Schnelle, W., Borrmann, H. & Kniep, R. (2002). *Z. Anorg. Allg. Chem.* **628**, 289–294.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Shi, H.-Z., Shan, Y.-K., Dai, L.-Y., Liu, Y.-Y. & Weng, L.-H. (2003). *Chin. J. Struct. Chem.* **7**, 391–394.
- Shi, H.-Z., Shan, Y.-K., He, M.-Y., Liu, Y.-Y. & Weng, L.-H. (2003). *Chin. J. Chem.* **21**, 1170–1173.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zouhri, H., Saadi, M., Jaber, B. & El Ammari, L. (2012). *Acta Cryst.* **E68**, i3–i4.

supplementary materials

Acta Cryst. (2012). C68, i55–i59 [doi:10.1107/S0108270112030284]

KCo(H₂O)₂BP₂O₈·0.48H₂O and K_{0.17}Ca_{0.42}Co(H₂O)₂BP₂O₈·H₂O: two cobalt borophosphates with helical ribbons and disordered (K,Ca)/H₂O schemes

Abderrahmen Guesmi and Ahmed Driss

(I) Potassium diaquacobalt(II) *catena*-borodiphosphate 0.48-hydrate

Crystal data

KCo(H₂O)₂BP₂O₈·0.48H₂O

$M_r = 343.46$

Hexagonal, $P6_322$

Hall symbol: P 65 2 (0 0 1)

$a = 9.5231$ (14) Å

$c = 15.633$ (2) Å

$V = 1227.8$ (3) Å³

$Z = 6$

$F(000) = 1019$

$D_x = 2.787$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 11.4$ – 15.0°

$\mu = 3.05$ mm⁻¹

$T = 293$ K

Prism, purple

$0.26 \times 0.26 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: ψ scan

(North *et al.*, 1968)

$T_{\min} = 0.505$, $T_{\max} = 0.581$

5187 measured reflections

895 independent reflections

891 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -12 \rightarrow 4$

$k = -1 \rightarrow 12$

$l = -19 \rightarrow 19$

2 standard reflections every 120 reflections

intensity decay: 4%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.095$

$S = 1.03$

895 reflections

81 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 9.9801P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.62$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ e Å⁻³

Absolute structure: Flack (1983), with 309

Friedel pairs

Flack parameter: 0.05 (5)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.45063 (6)	0.54937 (6)	0.0833	0.0175 (2)	
P1	0.21823 (15)	0.38551 (15)	-0.08005 (8)	0.0141 (3)	
B1	0.3023 (8)	0.1511 (4)	-0.0833	0.0119 (14)	
O1	0.3768 (5)	0.5133 (5)	-0.0414 (2)	0.0230 (9)	
O2	0.6855 (5)	0.6164 (5)	0.0453 (2)	0.0232 (8)	
O3	0.1927 (4)	0.2131 (4)	-0.0648 (2)	0.0164 (7)	
O4	0.4152 (4)	0.1794 (4)	-0.0116 (2)	0.0167 (7)	
O51	0.4996 (17)	0.7950 (14)	0.0577 (10)	0.021 (4)*	0.47 (5)
O52	0.541 (2)	0.8241 (19)	0.0330 (13)	0.042 (4)*	0.53 (5)
K1	0.6838 (6)	0.0570 (6)	0.0830 (3)	0.0224 (16)*	0.239 (6)
K2	0.8189 (8)	0.1811 (8)	0.0833	0.070 (5)*	0.241 (11)
K3	0.884 (2)	0.012 (2)	0.0205 (10)	0.064 (6)*	0.140 (7)
O6	0.9141 (16)	0.0859 (16)	0.0833	0.098 (12)*	0.48 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0191 (4)	0.0191 (4)	0.0166 (4)	0.0112 (4)	-0.0081 (3)	-0.0081 (3)
P1	0.0148 (6)	0.0116 (5)	0.0153 (5)	0.0061 (4)	-0.0078 (5)	-0.0021 (5)
B1	0.008 (3)	0.013 (3)	0.013 (3)	0.0039 (15)	0.000	0.010 (3)
O1	0.0239 (19)	0.0134 (18)	0.0218 (18)	0.0019 (16)	-0.0141 (16)	-0.0012 (15)
O2	0.0160 (19)	0.031 (2)	0.0226 (17)	0.0118 (17)	-0.0004 (15)	-0.0053 (17)
O3	0.0138 (17)	0.0127 (17)	0.0213 (18)	0.0057 (14)	0.0006 (13)	0.0025 (14)
O4	0.0118 (17)	0.0202 (18)	0.0148 (16)	0.0056 (14)	-0.0018 (13)	0.0052 (13)

Geometric parameters (\AA , $^\circ$)

Co1—O1	2.043 (3)	K1—K3 ^{viii}	2.726 (16)
Co1—O1 ⁱ	2.043 (3)	K2—K1 ⁱ	1.238 (5)
Co1—O2	2.083 (4)	K2—O6	1.57 (3)
Co1—O2 ⁱ	2.083 (4)	K2—O52 ^v	2.05 (2)
Co1—O51	2.182 (11)	K2—O52 ^{vii}	2.05 (2)
Co1—O51 ⁱ	2.182 (11)	K2—K3	2.22 (2)
Co1—O52	2.439 (17)	K2—K3 ⁱ	2.22 (2)
Co1—O52 ⁱ	2.439 (17)	K2—O51 ^v	2.519 (19)
P1—O2 ⁱⁱ	1.512 (4)	K2—O51 ^{viii}	2.519 (19)
P1—O1	1.513 (4)	K2—K3 ^{viii}	2.683 (19)

P1—O3	1.553 (4)	K2—K3 ^{ix}	2.683 (19)
P1—O4 ⁱⁱⁱ	1.554 (3)	K2—O1 ^v	2.800 (11)
B1—O3	1.462 (5)	K3—K3 ^{viii}	0.67 (3)
B1—O3 ^{iv}	1.462 (5)	K3—O6	1.158 (16)
B1—O4	1.483 (5)	K3—O6 ^{viii}	1.814 (17)
B1—O4 ^{iv}	1.483 (5)	K3—K3 ⁱ	2.20 (3)
K1—K2	1.238 (5)	K3—K2 ^{viii}	2.683 (19)
K1—O6	2.07 (2)	K3—K1 ^{viii}	2.726 (16)
K1—O52 ^v	2.08 (2)	K3—O3 ^x	2.803 (18)
K1—O52 ^{vi}	2.088 (13)	K3—O52 ^{vi}	2.84 (3)
K1—O1 ^{vii}	2.208 (6)	K3—K1 ⁱ	2.838 (19)
K1—O51 ^{vi}	2.254 (12)	K3—O52 ^v	2.85 (3)
K1—O2 ^{vii}	2.269 (6)	O6—K3 ⁱ	1.158 (16)
K1—K3	2.363 (15)	O6—K3 ^{viii}	1.814 (17)
K1—K1 ⁱ	2.469 (10)	O6—K3 ^{ix}	1.814 (17)
K1—O51 ^v	2.566 (19)	O6—K1 ⁱ	2.07 (2)
K1—O52 ^{vii}	2.620 (18)		
O1—Co1—O1 ⁱ	162.4 (2)	O51—Co1—O51 ⁱ	83.9 (8)
O1—Co1—O2	90.31 (15)	O2 ⁱⁱ —P1—O1	114.8 (2)
O1 ⁱ —Co1—O2	101.39 (15)	O2 ⁱⁱ —P1—O3	106.4 (2)
O1—Co1—O2 ⁱ	101.39 (15)	O1—P1—O3	110.8 (2)
O1 ⁱ —Co1—O2 ⁱ	90.31 (15)	O2 ⁱⁱ —P1—O4 ⁱⁱⁱ	111.9 (2)
O2—Co1—O2 ⁱ	96.7 (2)	O1—P1—O4 ⁱⁱⁱ	105.9 (2)
O1—Co1—O51	82.9 (3)	O3—P1—O4 ⁱⁱⁱ	106.84 (19)
O1 ⁱ —Co1—O51	84.1 (4)	O3—B1—O3 ^{iv}	103.6 (5)
O2—Co1—O51	89.9 (4)	O3—B1—O4	112.10 (19)
O2 ⁱ —Co1—O51	172.1 (5)	O3 ^{iv} —B1—O4	113.62 (18)
O1—Co1—O51 ⁱ	84.1 (4)	O3—B1—O4 ^{iv}	113.62 (18)
O1 ⁱ —Co1—O51 ⁱ	82.9 (3)	O3 ^{iv} —B1—O4 ^{iv}	112.10 (19)
O2—Co1—O51 ⁱ	172.1 (5)	O4—B1—O4 ^{iv}	102.1 (5)
O2 ⁱ —Co1—O51 ⁱ	89.9 (4)		

Symmetry codes: (i) $-y+1, -x+1, -z+1/6$; (ii) $x-y, -y+1, -z$; (iii) $x-y, x, z-1/6$; (iv) $x, x-y, -z-1/6$; (v) $x-y+1, -y+1, -z$; (vi) $x, y-1, z$; (vii) $y, -x+y, z+1/6$; (viii) $x-y, -y, -z$; (ix) $y+1, -x+y+1, z+1/6$; (x) $x-y+1, -y, -z$.

(II) Potassium calcium diaquacobalt(II) catena-borodiphosphate monohydrate

Crystal data

$K_{0.17}Ca_{0.42}Co(H_2O)_2BP_2O_8 \cdot H_2O$

$M_r = 336.94$

Hexagonal, $P6_522$

Hall symbol: P 65 2 (0 0 1)

$a = 9.4720$ (15) Å

$c = 15.872$ (6) Å

$V = 1233.2$ (5) Å³

$Z = 6$

$F(000) = 1005$

$D_x = 2.722$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 11.2$ – 14.5°

$\mu = 2.88$ mm⁻¹

$T = 293$ K

Prism, pink

$0.17 \times 0.17 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	902 independent reflections 854 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.094$
Graphite monochromator	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.5^\circ$
$\omega/2\theta$ scans	$h = -12 \rightarrow 10$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$k = -1 \rightarrow 12$
$T_{\text{min}} = 0.641$, $T_{\text{max}} = 0.706$	$l = -1 \rightarrow 20$
3480 measured reflections	2 standard reflections every 120 reflections intensity decay: 3%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	Only H-atom coordinates refined
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 1.9694P]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} < 0.001$
902 reflections	$\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
92 parameters	$\Delta\rho_{\text{min}} = -0.60 \text{ e } \text{\AA}^{-3}$
3 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0046 (5)
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), with 311 Friedel pairs Flack parameter: 0.01 (3)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co	0.44756 (3)	0.55244 (3)	0.0833	0.00868 (17)	
P	0.21986 (9)	0.38868 (9)	-0.08133 (5)	0.00638 (19)	
B	0.3045 (5)	0.1522 (3)	-0.0833	0.0069 (8)	
O1	0.3790 (3)	0.5172 (3)	-0.04331 (13)	0.0116 (5)	
O2	0.6836 (3)	0.6142 (3)	0.04701 (13)	0.0116 (4)	
O3	0.1938 (3)	0.2142 (3)	-0.06638 (14)	0.0097 (5)	
O4	0.4184 (3)	0.1826 (2)	-0.01242 (12)	0.0093 (4)	
O5	0.5114 (3)	0.8039 (3)	0.05529 (15)	0.0172 (5)	
H51	0.544 (6)	0.859 (5)	0.100 (2)	0.026*	
H52	0.433 (4)	0.809 (6)	0.035 (3)	0.026*	
Ca	0.7990 (3)	0.2010 (3)	0.0833	0.0419 (15)*	0.418 (10)
K	0.8386 (7)	0.1614 (7)	0.0833	0.031 (3)*	0.172 (10)
O61	0.975 (3)	0.110 (3)	0.143 (2)	0.045 (16)	0.214 (9)

O62 0.915 (2) 0.062 (3) 0.0635 (9) 0.045 (16) 0.286 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0087 (2)	0.0087 (2)	0.0088 (3)	0.0045 (2)	-0.00176 (19)	-0.00176 (19)
P	0.0074 (3)	0.0069 (3)	0.0055 (3)	0.0041 (3)	-0.0012 (3)	-0.0010 (3)
B	0.0086 (19)	0.0070 (15)	0.006 (2)	0.0043 (10)	0.000	-0.0003 (15)
O1	0.0116 (10)	0.0115 (11)	0.0086 (9)	0.0033 (9)	-0.0037 (9)	-0.0014 (9)
O2	0.0097 (11)	0.0153 (11)	0.0101 (9)	0.0065 (9)	-0.0013 (9)	-0.0015 (9)
O3	0.0095 (10)	0.0092 (11)	0.0122 (10)	0.0060 (8)	0.0033 (8)	0.0025 (8)
O4	0.0083 (10)	0.0132 (10)	0.0063 (9)	0.0054 (8)	-0.0011 (8)	0.0009 (8)
O5	0.0203 (12)	0.0173 (13)	0.0177 (11)	0.0122 (10)	-0.0075 (10)	-0.0030 (10)
O61	0.039 (11)	0.064 (13)	0.04 (5)	0.031 (10)	0.005 (15)	0.002 (14)
O62	0.039 (11)	0.064 (13)	0.04 (5)	0.031 (10)	0.005 (15)	0.002 (14)

Geometric parameters (\AA , $^\circ$)

Co—O1	2.087 (2)	Ca—O1 ^v	2.509 (4)
Co—O1 ⁱ	2.087 (2)	Ca—O1 ^{vi}	2.509 (4)
Co—O2	2.090 (2)	Ca—O61 ^{vii}	3.04 (3)
Co—O2 ⁱ	2.090 (2)	Ca—O61 ^{viii}	3.04 (3)
Co—O5	2.190 (3)	Ca—O2 ^v	3.070 (3)
Co—O5 ⁱ	2.190 (3)	K—O62	1.481 (19)
P—O1	1.511 (2)	K—O62 ⁱ	1.481 (19)
P—O2 ⁱⁱ	1.513 (2)	K—O61 ⁱ	1.85 (2)
P—O3	1.562 (2)	K—O61	1.85 (2)
P—O4 ⁱⁱⁱ	1.571 (2)	K—O61 ^{vii}	2.55 (3)
B—O3	1.460 (3)	K—O61 ^{viii}	2.55 (3)
B—O3 ^{iv}	1.460 (3)	K—O5 ^v	2.626 (7)
B—O4	1.484 (3)	K—O5 ^{vi}	2.626 (7)
B—O4 ^{iv}	1.484 (3)	K—O2 ^v	2.989 (2)
Ca—K	0.649 (9)	K—O2 ^{vi}	2.989 (2)
Ca—O62	2.119 (16)	K—O1 ^v	3.009 (10)
Ca—O62 ⁱ	2.119 (16)	O61—O62 ⁱ	0.70 (2)
Ca—O5 ^v	2.357 (3)	O61—O61 ^{viii}	0.86 (6)
Ca—O5 ^{vi}	2.357 (3)	O61—O62	1.36 (5)
Ca—O61 ⁱ	2.42 (2)	O61—O62 ^{ix}	1.56 (5)
Ca—O61	2.42 (2)		
O1—Co—O1 ⁱ	164.95 (13)	O5—Co—O5 ⁱ	90.72 (14)
O1—Co—O2	89.02 (8)	O1—P—O2 ⁱⁱ	114.95 (13)
O1 ⁱ —Co—O2	101.32 (9)	O1—P—O3	110.96 (13)
O1—Co—O2 ⁱ	101.32 (9)	O2 ⁱⁱ —P—O3	106.10 (13)
O1 ⁱ —Co—O2 ⁱ	89.02 (8)	O1—P—O4 ⁱⁱⁱ	106.40 (12)
O2—Co—O2 ⁱ	93.63 (13)	O2 ⁱⁱ —P—O4 ⁱⁱⁱ	111.36 (12)
O1—Co—O5	82.70 (9)	O3—P—O4 ⁱⁱⁱ	106.85 (12)
O1 ⁱ —Co—O5	86.74 (9)	O3—B—O3 ^{iv}	103.1 (3)
O2—Co—O5	87.97 (10)	O3—B—O4	112.39 (12)

O2 ⁱ —Co—O5	175.69 (9)	O3 ^{iv} —B—O4	113.70 (12)
O1—Co—O5 ⁱ	86.74 (9)	O3—B—O4 ^{iv}	113.70 (12)
O1 ⁱ —Co—O5 ⁱ	82.70 (9)	O3 ^{iv} —B—O4 ^{iv}	112.39 (12)
O2—Co—O5 ⁱ	175.69 (9)	O4—B—O4 ^{iv}	102.0 (3)
O2 ⁱ —Co—O5 ⁱ	87.97 (10)		

Symmetry codes: (i) $-y+1, -x+1, -z+1/6$; (ii) $x-y, -y+1, -z$; (iii) $x-y, x, z-1/6$; (iv) $x, x-y, -z-1/6$; (v) $x-y+1, -y+1, -z$; (vi) $y, -x+y, z+1/6$; (vii) $x-y, x-1, z-1/6$; (viii) $-x+2, -x+y+1, -z+1/3$; (ix) $y+1, -x+y+1, z+1/6$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O5—H52 \cdots O4 ⁱⁱ	0.83 (3)	1.95 (3)	2.762 (3)	168 (4)
O5—H51 \cdots O2 ^x	0.84 (3)	1.92 (3)	2.746 (3)	164 (5)

Symmetry codes: (ii) $x-y, -y+1, -z$; (x) $y, -x+y+1, z+1/6$.

Selected bond lengths (Å) of the coordination polyhedra in (I) and (II)

D	(I)	(II)
Co1—O1 ^a	2.043 (3)	2.087 (2)
Co1—O2 ^a	2.083 (4)	2.090 (2)
Co1—O5 ^a	2.182 (11)/2.439 (17) ^b	2.190 (2)
P1—O2 ⁱⁱ	1.512 (4)	1.513 (2)
P1—O1	1.513 (4)	1.511 (2)
P1—O3	1.553 (4)	1.562 (2)
P1—O4 ⁱⁱⁱ	1.554 (3)	1.571 (2)
B1—O3 ^{iv}	1.462 (5)	1.460 (3)
B1—O3	1.462 (5)	1.460 (3)
B1—O4	1.483 (5)	1.484 (3)
B1—O4 ^{iv}	1.483 (5)	1.484 (3)

(a) The distances are the same for (i) symmetry-related O atoms. (b) The shorter Co1—O5 distances in (I) correspond to O51 and the longer to O52 partially-occupied positions. Symmetry codes: (i) $-y+1, -x+1, -z+1/6$; (ii) $x-y, -y+1, -z$; (iii) $x-y, x, z-1/6$; (iv) $x, x-y, -z-1/6$.