Crystal growth, structure elucidation and CHARDI/BVS investigations of $\beta$-KCoFe(PO$_4$)$_2$

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Single crystals of $\beta$-KCoFe(PO$_4$)$_2$, potassium cobalt(II) iron(III) bis(orthophosphate), were grown from the melt under atmospheric conditions. This phosphate crystallizes isotypically with KZnFe(PO$_4$)$_2$ in space group C2/c, adopting a zeolite-ABW type of structure. The structure of the present phosphate is distinguished by an occupational disorder of the two transition-metal sites with ratios Fe:Co of 0.5725:0.4275 for the first and 0.4275:0.5725 for the second site. In the crystal structure, PO$_4$ and (Co,Fe)O$_4$ tetrahedra are linked through vertices to form elliptical rings with the sequence DDDDUUDD of up (U) and down (D) pointing vertices. Each eight-membered ring is surrounded by four other rings of the same type, delimiting interstices with rectangular shape. This arrangement leads to the formation of \([(\text{Co/Fe})(\text{PO}_4)]^{\infty}\) sheets parallel to (001). Stacking of the sheets into a three-dimensional framework results in the formation of two types of channels. The first one is occupied by potassium cations, whereas the second one remains vacant. Calculations of bond-valence sums and charge distribution were used to confirm the structure model.

1. Chemical context

Transition-metal (TM) phosphates have been widely studied as potential candidates for various applications such as catalysis (Bautista et al., 2007), ion exchange (Szirtes et al., 2007), electrochemistry (Trad et al., 2010) or as magnetic materials (Ofer et al., 2012). In this context, zinc phosphates are of interest because the Zn$^{2+}$ cation with its d$^{10}$ electronic configuration is susceptible to strong polarization and thus can be used to design new non-linear optical (NLO) materials (Shen et al., 2016). In the family of transition-metal phosphate compounds, the anionic network is formed from PO$_4$ tetrahedra bonded to different types of coordination polyhedra of the form \([\text{TM}O_n] (n = 4, 5 \text{ and } 6)\), leading to a wide variety of crystal structure types such as NaZnAl(PO$_4$)$_2$ (Yakubovich et al., 2019). The structural diversity is mainly associated with the ability of TM cations to adopt different oxidation states with various types of coordination polyhedra (Moore & Ito, 1979; Hatert et al., 2004).

It is in this context that our research team was involved with investigations of new phosphates with $A^I$, $M^{II}$ and $M^{III}$ cations where $A$ is an alkali metal, and $M^{II}$ and $M^{III}$ are bivalent and trivalent cations, respectively. For example, Na$_2$Co$_2$Fe(PO$_4$)$_3$ (Bouraima et al., 2015) and NaCuIn(PO$_4$)$_2$ (Benhsina et al., 2020) are among the recently studied compounds. The present
work is devoted to synthesis and crystal structure analysis of β-KCoFe(PO₄)₂, a new compound in the family of transition-metal phosphates.

2. Structural commentary

The title compound crystallizes isotypically with KZnFe(PO₄)₂ (Badri et al., 2015). The principal building units of β-KCoFe(PO₄)₂ are shown in Fig. 1, revealing that three types of more or less distorted tetrahedra build up the framework structure. The two TM sites are characterized by partial disorder (see Refinement) with (Fe/Co)₁—O distances varying between 1.877 (2) and 1.900 (2) Å and (Co/Fe)₂—O distances between 1.881 (2) and 1.927 (2) Å. The two PO₄ tetrahedra are more regular with the P—O bonds lengths between 1.5172 (19) and 1.5306 (19) Å for P₁O₄ and 1.509 (2) and 1.533 (2) Å for P₂O₄.

The three different types of tetrahedra are linked through vertices to form ellipse-shaped rings with the sequence DDDDUUUU of up (U) and down (D) pointing vertices, as shown in Fig. 2. Each eight-membered ring is surrounded by four other rings of the same type, delimiting two interstices with rectangular shape constituted by two PO₄ and two (Fe/Co)₁O₄ tetrahedra or two PO₄ and two (Co/Fe)₂O₄ tetrahedra. This assembly leads to the formation of [(Co/Fe)(PO₄)]₀ sheets extending parallel to (001) at z = 0, ½. Stacking of these sheets along [001] leads to the formation of a three-dimensional framework structure with two types of channels. The first one is occupied by potassium cations, whereas the second one remains vacant, as shown in Fig. 3. The K⁺ cation is surrounded by nine oxygen atoms with bond lengths between 2.694 (2) and 3.172 (2) Å.

Bond-valence sum (BVS) calculations (Brown, 1977,1978; Brown & Altermatt, 1985) and charge distribution (CHARDI) (Hoppe et al., 1989) were used to confirm the structure model of β-KCoFe(PO₄)₂. BVS and CHARDI computations were carried out with EXPO2014 (Altomare et al., 2013) and CHARDI2015 (Nespolo & Guillot, 2016), respectively. Table 1 compiles the valences Vᵢ of cations

| Cation     | qᵢ × sofᵢ | CNᵢ  | ECoNᵢ | Vᵢ  | Qᵢ  | qᵢ/Qᵢ |
|------------|------------|------|-------|-----|-----|-------|
| (Fe/Co)₁   | 2.57       | 4    | 4.00  | 2.48| 2.57| 1.00  |
| (Fe/Co)₂   | 2.43       | 4    | 3.99  | 2.27| 2.43| 1.00  |
| K₁         | 1.00       | 9    | 8.71  | 0.94| 0.99| 1.00  |
| P₁         | 5.00       | 4    | 4.00  | 5.14| 5.00| 1.00  |
| P₂         | 5.00       | 4    | 3.99  | 5.15| 5.01| 1.01  |

Table 1
CHARDI and BVS analysis for the cations in the title compound.

qᵢ = formal oxidation number; sofᵢ = site occupation factor; CNᵢ = classical coordination number; Qᵢ = calculated charge; Vᵢ = calculated valence; ECoNᵢ = effective coordination number.
determined with the BVS approach, as well as their corresponding charges $Q_{i}$ calculated with the CHARDI concept. The data reveal that the values $Q_{i}$ and $V_{i}$ are all very close to the corresponding charges $q_{i}\times\text{sof}_{i}$ (formal oxidation numbers $q_{i}$ weighted by site occupation factors $\text{sof}_{i}$). For all cations, the internal criterion $q_{i}/Q_{i}$ is very close to 1, and the mean absolute percentage deviation (MAPD) that evaluates the agreement between the $q_{i}$ and $Q_{i}$ charges is 0.3%, confirming the validity of the structural model (Eon & Nespolo, 2015). The global instability index ($GII$) was also used to check the plausibility of the crystal-structure model (Salinas-Sanchez et al., 1992). The $GII$ index evaluates the deviation of BVS parameters from the theoretical valence $V_{i}$ averaged across all the constitutive atoms of the asymmetric unit. In an unstrained structure, $GII$ is less than 0.1 and reaches 0.2 for those with lattice-induced deformations (Adams et al., 2004). For the current crystal structure $GII$ amounts to 0.1, indicating its stability.

3. Database survey

The phosphate KCoFe(PO$_4$)$_2$ crystallizes in two polymorphs in the same crystal system but with different unit-cell parameters and space groups. The $\alpha$-form of KCoFe(PO$_4$)$_2$ reported by Badri et al. (2019) crystallizes in space group $P2_1/c$ with unit-cell parameters $a = 5.148$ (1), $b = 14.403$ (2), $c = 9.256$ (1) Å, $\beta = 104.87$ (2). The title compound crystallizes in space group $C2/c$. Whereas the environments around the two TM sites are tetrahedral in the title compound, an octahedral coordination is found for one site (Co) in the $\alpha$-form. The crystal structure of $\beta$-KCoFe(PO$_4$)$_2$ is isotypic with that of KZnFe(PO$_4$)$_2$ (Badri et al., 2014), while that of $\alpha$-KCoFe(PO$_4$)$_2$ is isotypic with those of KNiFe(PO$_4$)$_2$ and KMgFe(PO$_4$)$_2$ (Badri et al., 2015).

4. Synthesis and crystallization

The phosphate $\beta$-KCoFe(PO$_4$)$_2$ was synthesized by mixing cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O), iron nitrate [Fe(NO$_3$)$_3$·9H$_2$O] orthophosphoric acid (H$_3$PO$_4$) and potassium nitrate (KNO$_3$) in molar ratios of 1:1:1:2. The mixture was placed in a small beaker containing distilled water and homogenized for 24 h. After evaporation to dryness, the reaction mixture underwent heat treatments at 573 and 773 K before being brought to fusion for crystal growth at 1223 K, followed by slow cooling. Crystals of purple color and of sufficient size for the analysis by X-ray diffraction were obtained from the final product.

A Quattro ESEM scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS), operating under 20 kV accelerating voltage, was used for chemical analysis and photographs of the obtained crystals (Fig. 4). Determined mass percentage (+/-3%), calculated mass percentage: K (10.7, 11.4) Fe (12.4, 16.2), Co (13.4, 17.1), P (20.2, 18.0), O (43.3, 37.3)

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. During the refinement, several models were tested, with the best result for a model with occupational disorder of the two TM sites. Since the Co:Fe ratio determined from EDS measurements is almost 1:1, this ratio was constrained for the refinement of the individual site occupation, also taking into account full occupancy of both TM sites. For the TM1 site a ratio of Fe:Co = 0.5725:0.4275 was obtained, for the TM2 site a ratio of Co:Fe = 0.5725/0.4275. The maximum and minimum remaining electron density are located at 0.69 Å and 0.31 Å, respectively, from O8.

Acknowledgements

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Table 2

| Crystal data   | KCoFe(PO$_4$)$_2$          |
|----------------|---------------------------|
| Chemical formula | KCoFe(PO$_4$)$_2$          |
| $M_r$          | 343.82                    |
| Crystal system, space group | Monoclinic, $C2/c$        |
| Temperature (K) | 296                      |
| $a$, $b$, $c$ (Å) | 13.5860 (6), 13.2320 (6), 8.7316 (4) |
| $\beta$ (°)    | 90.335 (2)                |
| $V$ (Å$^3$)    | 1544.21 (12)              |
| $Z$            | 8                        |
| Radiation type | Mo $K\alpha$              |
| $\mu$ (mm$^{-1}$) | 4.99                     |
| Crystal size (mm) | 0.36 × 0.27 × 0.15        |

Data collection

| Diffractometer              | Bruker D8 VENTURE Super DUO |
|-----------------------------|-----------------------------|
| Absorption correction       | Multi-scan (SADABS: Krause et al., 2015) |
| $T_{min}$, $T_{max}$        | 0.391, 0.747                |
| No. of measured, independent and observed $| 30042, 3574, 2633 |
| $R_{e}$, $wR_{e}$, $S$     | 0.036, 0.088, 1.04          |
| No. of reflections          | 3574                       |
| No. of parameters           | 118                        |
| $\Delta p_{max}$, $\Delta p_{min}$ (e Å$^{-3}$) | 0.98, −0.91 |

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXT2014/7 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006) and pubICP (Westrip, 2010).

Figure 4

(a) EDS spectrum and (b) SEM micrographs of the title compound.
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Crystal growth, structure elucidation and CHARDI/BVS investigations of $\beta$-KCoFe(PO$_4$)$_2$

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT2014/7 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

Potassium cobalt(II) iron(III) bis(orthophosphate)

Crystal data

KCoFe(PO$_4$)$_2$ $F(000) = 1328$
$M_r = 343.82$ $D_x = 2.958$ Mg m$^{-3}$

Monoclinic, $C2/c$ Mo Kα radiation, $λ = 0.71073$ Å

$a = 13.5860$ (6) Å

$\theta = 2.2$–$35.6^\circ$

$b = 13.2320$ (6) Å

$\mu = 4.99$ mm$^{-1}$

$c = 8.7316$ (4) Å

$T = 296$ K

$\beta = 100.335$ (2)$^\circ$

Parallelpiped, purple

$V = 1544.21$ (12) Å$^3$

$0.36 \times 0.27 \times 0.15$ mm

Data collection

Bruker D8 VENTURE Super DUO diffractometer $T_{\text{min}} = 0.391$, $T_{\text{max}} = 0.747$

Radiation source: INCOATEC $\text{I}_\mu$S micro-focus source 30042 measured reflections

HELIOS mirror optics monochromator $R_{\text{int}} = 0.068$

Detector resolution: 10.4167 pixels mm$^{-1}$ $\theta_{\text{max}} = 35.6^\circ$, $\theta_{\text{min}} = 2.2^\circ$

$φ$ and $ω$ scans $h = -13$→$22$

Absorption correction: multi-scan $k = -21$→$21$

(SADABS; Krause et al., 2015) $l = -14$→$14$

Refinement

Refinement on $F^2$ 0 restraints

Least-squares matrix: full Primary atom site location: structure-invariant direct methods

$R[F^2 > 2\sigma(F^2)] = 0.036$ Secondary atom site location: difference Fourier map

$wR(F^2) = 0.088$ $w = 1/[σ^2(F^2) + (0.0363P)^2 + 2.2954P]$

$S = 1.04$ where $P = (F^2 + 2F_c^2)/3$

3574 reflections 118 parameters

$\sum w(a_i^2) = 1.00$

$\sum w(a_i^2) = 1.00$
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.98 \text{ e Å}^{-3}

Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|    | x          | y          | z          | U_{iso}*/U_{eq} | Occ. (<1) |
|----|------------|------------|------------|----------------|-----------|
| Fe1| 0.37263 (3)| 0.06558 (3)| 0.61452 (4)| 0.01728 (8)   | 0.5725    |
| Co1| 0.37263 (3)| 0.06558 (3)| 0.61452 (4)| 0.01728 (8)   | 0.4275    |
| Co2| 0.07555 (3)| 0.11785 (3)| 0.04344 (4)| 0.01854 (8)   | 0.5725    |
| Fe2| 0.07555 (3)| 0.11785 (3)| 0.04344 (4)| 0.01854 (8)   | 0.4275    |
| P1 | 0.42702 (5)| 0.14198 (5)| −0.01872 (7)| 0.01656 (12)  |           |
| P2 | 0.14880 (5)| 0.06783 (5)| 0.41434 (7) | 0.01769 (12)  |           |
| K1 | 0.31255 (6)| 0.25345 (6)| 0.27514 (8) | 0.03896 (17)  |           |
| O1 | 0.39529 (17)| 0.07417 (15)| 0.1059 (2) | 0.0288 (4)    |           |
| O2 | 0.54020 (16)| 0.13970 (16)| −0.0087 (2)| 0.0313 (4)    |           |
| O3 | 0.39339 (19)| 0.24769 (14)| 0.0152 (3) | 0.0338 (5)    |           |
| O4 | 0.37488 (19)| 0.1089 (2) | −0.1801 (2) | 0.0411 (6)    |           |
| O5 | 0.14870 (17)| −0.04718 (15)| 0.4068 (2) | 0.0312 (4)    |           |
| O6 | 0.1372 (2) | 0.11411 (18)| 0.2542 (2) | 0.0431 (6)    |           |
| O7 | 0.24615 (14)| 0.11037 (15)| 0.5076 (2) | 0.0262 (4)    |           |
| O8 | 0.06510 (17)| 0.1025 (2) | 0.4989 (3) | 0.0475 (7)    |           |

**Atomic displacement parameters (Å²)**

|       | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|-------|-------|-------|-------|-------|-------|-------|
| Fe1   | 0.01435 (16) | 0.02100 (16) | 0.01659 (14) | 0.00191 (12) | 0.00307 (11) | −0.00249 (11) |
| Co1   | 0.01435 (16) | 0.02100 (16) | 0.01659 (14) | 0.00191 (12) | 0.00307 (11) | −0.00249 (11) |
| Co2   | 0.01525 (16) | 0.02218 (16) | 0.01902 (15) | 0.00088 (12) | 0.00533 (11) | 0.00266 (11) |
| Fe2   | 0.01525 (16) | 0.02218 (16) | 0.01902 (15) | 0.00088 (12) | 0.00533 (11) | 0.00266 (11) |
| P1    | 0.0185 (3)   | 0.0157 (2)  | 0.0169 (2)  | 0.0005 (2)   | 0.0071 (2)   | −0.00144 (19) |
| P2    | 0.0128 (3)   | 0.0229 (3)  | 0.0171 (2)  | −0.0018 (2)  | 0.0021 (2)   | 0.0034 (2)    |
| K1    | 0.0399 (4)   | 0.0476 (4)  | 0.0342 (3)  | −0.0028 (3)  | 0.0197 (3)   | −0.0083 (3)   |
| O1    | 0.0370 (12)  | 0.0246 (9)  | 0.0273 (9)  | −0.0062 (8)  | 0.0130 (8)   | 0.0033 (7)    |
| O2    | 0.0196 (10)  | 0.0354 (11) | 0.0416 (11) | 0.0015 (8)   | 0.0129 (8)   | −0.0039 (9)   |
| O3    | 0.0478 (14)  | 0.0212 (9)  | 0.0388 (11) | 0.0109 (8)   | 0.0254 (10)  | 0.0033 (8)    |
| O4    | 0.0407 (14)  | 0.0625 (16) | 0.0201 (9)  | −0.0067 (11) | 0.0057 (9)   | −0.0133 (9)   |
| O5    | 0.0352 (12)  | 0.0231 (9)  | 0.0373 (11) | −0.0083 (8)  | 0.0116 (9)   | 0.0011 (8)    |
| O6    | 0.0560 (16)  | 0.0449 (13) | 0.0247 (10) | −0.0090 (11) | −0.0027 (10) | 0.0135 (9)    |
| O7    | 0.0160 (9)   | 0.0289 (10) | 0.0314 (10) | −0.0003 (7)  | −0.0019 (7)  | −0.0038 (7)   |
| O8    | 0.0173 (11)  | 0.0795 (19) | 0.0482 (14) | 0.0017 (11)  | 0.0124 (10)  | −0.0163 (13)  |
### Geometric parameters (Å, °)

| Bond/Angle                  | Distance (Å) | Angle (°) | Note |
|-----------------------------|--------------|-----------|------|
| Fe1/Co1—O4i                 | 1.877 (2)    |           |      |
| Fe1/Co1—O1ii                | 1.8783 (19)  |           |      |
| Fe1/Co1—O7                  | 1.8972 (19)  |           |      |
| Fe1/Co1—O7i                 | 1.900 (2)    |           |      |
| Co2/Fe2—O6                  | 1.881 (2)    |           |      |
| Co2/Fe2—O8iv                | 1.891 (2)    |           |      |
| Co2/Fe2—O3v                 | 1.9191 (19)  |           |      |
| Co2/Fe2—O5vi                | 1.927 (2)    |           |      |
| P1—O3                       | 1.5172 (19)  |           |      |
| P1—O4                       | 1.524 (2)    |           |      |
| P1—O2                       | 1.525 (2)    |           |      |
| P1—O1                       | 1.5306 (19)  |           |      |
| P2—O6                       | 1.509 (2)    |           |      |
| O4i—Fe1/Co1—O1ii            | 111.34 (10)  |           |      |
| O4i—Fe1/Co1—O7              | 103.45 (10)  |           |      |
| O1ii—Fe1/Co1—O7             | 115.36 (9)   |           |      |
| O4i—Fe1/Co1—O2iii           | 113.73 (10)  |           |      |
| O1ii—Fe1/Co1—O2iii          | 111.57 (9)   |           |      |
| O7—Fe1/Co1—O2ii             | 100.83 (9)   |           |      |
| O6—Co2/Fe2—O8iv             | 116.47 (11)  |           |      |
| O6—Co2/Fe2—O3v              | 101.81 (11)  |           |      |
| O8iv—Co2/Fe2—O3v            | 108.09 (12)  |           |      |
| O6—Co2/Fe2—O5vi             | 113.85 (11)  |           |      |
| O8iv—Co2/Fe2—O5vi           | 116.25 (11)  |           |      |
| O3v—Co2/Fe2—O5vi            | 97.02 (9)    |           |      |
| O3—P1—O4                    | 109.84 (14)  |           |      |
| O3—P1—O2                    | 110.05 (13)  |           |      |
| O3—P1—O1                    | 110.14 (13)  |           |      |
| O3—P1—O1                    | 105.59 (12)  |           |      |
| O4—P1—O1                    | 110.20 (13)  |           |      |
| O2—P1—O1                    | 110.93 (12)  |           |      |
| O6—P2—O5                    | 111.47 (13)  |           |      |
| O6—P2—O7                    | 106.28 (13)  |           |      |
| O5—P2—O7                    | 112.60 (12)  |           |      |
| O6—P2—O8                    | 111.23 (16)  |           |      |
| O5—P2—O8                    | 108.96 (14)  |           |      |
| O7—P2—O8                    | 106.18 (13)  |           |      |
| O3—K1—O7ii                  | 142.04 (6)   |           |      |
| O3—K1—O6                    | 111.80 (7)   |           |      |
| O7ii—K1—O6                  | 96.69 (7)    |           |      |
| O3—K1—O2ii                  | 103.65 (7)   |           |      |
| O7ii—K1—O2ii                | 95.61 (6)    |           |      |
| O6—K1—O2ii                  | 99.16 (6)    |           |      |
| O3—K1—O8ii                  | 107.98 (8)   |           |      |
| O7ii—K1—O8ii                | 49.37 (6)    |           |      |

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| Bond                  | Bond Angle (°) (E) | Bond Angle (°) (F) |
|----------------------|--------------------|--------------------|
| O6—K1—O8vii         | 140.19 (7)         | O4v—K1—O3v        | 44.42 (5) |
| O2iii—K1—O8vii      | 69.51 (7)          | O5viii—K1—O3v     | 79.62 (6) |
| O3—K1—O7            | 139.67 (6)         |                    |          |

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