Acta Cryst. (1997). C**53**, 1754–1756

Potassium Cobalt Aluminium Mixed Phosphate, $K(Co^{II},Al)_2(PO_4)_2$

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(*Received 4 October 1996; accepted 19 May 1997*)

Abstract

The framework of $K(Co^{II},Al)_2(PO_4)_2$ consists of corner-sharing $(Co/Al)O_4$ and PO_4 tetrahedra, which form large intersecting tunnels running along the three crystallographic axes, with the K atoms situated in the tunnels. Co^{II} and Al atoms are distributed over two tetrahedral sites with almost equal probability. The average Co(1)/Al(1)—O distance of 1.826 (19) Å and average Co(2)/Al(2)—O distance of 1.829 (13) Å reflect mixing of Co and Al at the metal-atom sites.

Comment

Crystal structures of the orthophosphates $M_3^{II}(PO_4)_2$, where *M* is an alkaline earth or bivalent transition metal, have been extensively investigated. For example, single-crystal data may be found in the literature for α-$Ca_3(PO_4)_2$ (Mathew, Schroeder, Dickens & Brown, 1977), α-$Sr_3(PO_4)_2$ and α-$Ba_3(PO_4)_2$ (Zachariasen, 1948), $Co_3(PO_4)_2$ (Anderson, Kostiner, Miller & Rea, 1975), $Ni_3(PO_4)_2$ (Calvo & Fagiani, 1975), $Cu_3(PO_4)_2$ (Shoemaker, Anderson & Kostiner, 1977) and α-$Zn_3(PO_4)_2$ (Calvo, 1965). Mixed phosphates with the generic formula $M_x^{II}A_{3-x}^{II}(PO_4)_2$ (*A* = alkaline earth metal, *M* = divalent transition metal) have also been reported: $BaNi_2(PO_4)_2$ (Cabric, Zizic & Napijalo, 1982), α-$SrZn_2(PO_4)_2$ (Hemon & Courbion, 1990) and $Sr_2Ni(PO_4)_2$ (Elbali, Boukhari, Holt & Aride, 1993). While attempting to prepare the compound $K_2CoP_2O_7$, we obtained a new mixed orthophosphate with the formula $K(Co^{II},Al)_2(PO_4)_2$. In this paper we describe its synthesis and crystal structure.

Projections of the structure of this new phase along the directions of the three principal axes *a*, *b* and *c* show that it is characterized by the existence of intersecting tunnels running parallel to the principal axes. As an example, the projection along the *c* axis is illustrated in Fig. 1. In this projection, the three-dimensional framework is made up of corner-sharing $(Co/Al)O_4$ and PO_4 tetrahedra, with the K atoms situated in the tunnels within the framework. There are three kinds of tunnels running parallel to the *c* axis. The larger octagonal-shaped tunnels are created from the edges of four $(Co/Al)O_4$ and four PO_4 corner-linked tetrahedra and are occupied by two K atoms. These two K atoms are related by the symmetry transformation $(-x + \frac{1}{2}, -y + \frac{1}{2}, -z)$; two diagonal tunnels along the *c* axis are related by an inversion centre. The other eight-sided and four-sided channels are too small to accommodate K atoms. In this structure, each PO_4 tetrahedron shares all four O atoms with different $(Co/Al)O_4$ tetrahedra, and likewise each $(Co/Al)O_4$ tetrahedron is linked to four different PO_4 tetrahedra. The two independent PO_4 tetrahedra are not linked to each other.

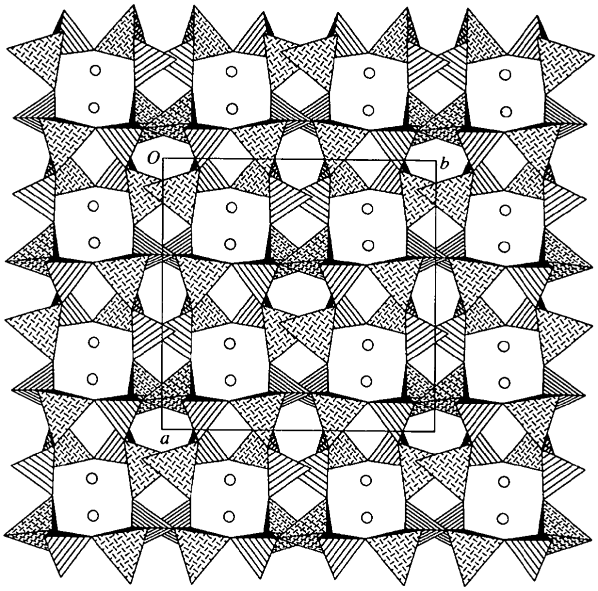

Fig. 1. Polyhedral representation of $K(Co^{II},Al)_2(PO_4)_2$ projected along the *c* axis. The corners of the tetrahedra are O atoms. The mixed Co/Al and P atoms are at the centre of each tetrahedron with herringbone and parallel-line patterns, respectively.

It can be seen from Table 1 that all distances are in good agreement with published values (Anderson *et al.*, 1975; Hamady, Jouini & Driss, 1995). The average P(1)—O bond distance is 1.519 (8) Å and the average P(2)—O bond distance is 1.522 (4) Å. Each PO_4 tetrahedron is slightly distorted, with values of the O—P—O angles being near the tetrahedral value. Bond-valence sum calculations (Brown & Altermatt, 1985) give valences of 5.22 for P(1) and 5.17 for P(2).

The K atoms are coordinated to ten O atoms with K—O distances exhibiting a wide range [2.746 (3)–3.382 (4) Å]. The average value of 3.04 (18) Å is comparable with the sum (2.95 Å) of the Shannon (1976) crystal radii of ten-coordinate K^+ (1.73 Å) and three-coordinate O^{2-} (1.22 Å) ions. A similar coordination environment has been observed for K^+ in KYP_4O_{12} (Hamady *et al.*, 1995), where the ten-coordinate K atom has O-atom neighbours with an almost equal range of bond lengths, 2.735 (3)–3.370 (3) Å [average 3.1 (3) Å]. Bond-valence analysis gives a value of 0.95 for the K atom.

The mixed site *M*(1), occupied statistically by Co and Al, is surrounded by four O-atom neighbours [O(1), O(2), O(3) and O(8)] forming a distorted tetrahedron. The *M*(1)—O distances vary between 1.806 (3) and 1.849 (2) Å with a mean value of 1.826 (19) Å. A second independent site, *M*(2), showing the same mixed Co and Al composition, is surrounded by atoms O(4), O(5), O(6) and O(7). The *M*(2)—O distances are between 1.810 (3) and 1.837 (3) Å with a mean value of 1.829 (13) Å. Both of the average *M*—O distances are longer than normal Al—O bond lengths, such as the average of 1.728 (9) Å for AlO_4 coordination found in $Cs_9Mo_9Al_3P_{11}O_{59}$ (Guesdon, Borel, Leclaire, Grandin & Raveau, 1995), supporting mixing of Co and Al at these atomic sites. The presence of Co^{II} and Al on the same crystallographic site is rather uncommon and is unexpected owing to the significant size difference between these two cations. Nevertheless, it has been observed previously for $Co_{0.12}Al_{5.88}P_6O_{24}(OH)_2.C_2H_{10}N_2.2H_2O$ (Cheetham, Harding, Rizkallah, Laučič & Rajić, 1991), in which the replacement of tetrahedral Al^{3+} ions by Co^{2+} ions was observed and the average Al/Co—O distance was found to be only 1.748 (19) Å due to its low Co content.

Experimental

Single crystals of the title compound were extracted from an experiment attempting to prepare $K_2CoP_2O_7$. First, an appropriate stoichiometric mixture of K_2CO_3, $CoCl_2.6H_2O$ and $(NH_4)_2HPO_4$ was successively preheated at 573 and 773 K in air for 50 h with intermediate grinding. The resulting product (composition $K_2CoP_2O_7$) was placed in an alumina crucible, which was sealed in a silica tube under argon. The sample was heated gradually to 1173 K, where it was kept for 2 d, then cooled at a rate of 5 K h^{-1} to 873 K, and finally quenched at room temperature. Several violet prisms were isolated mechanically from the sample. Microprobe analysis detected the presence of four kinds of heavier elements, K, Co, Al and P, in the crystal, with the aluminium constituent coming from the reaction container. Microcrystalline $K(Co^{II},Al)_2(PO_4)_2$ was obtained by heating pellets of stoichiometric mixtures of $K_2CoP_2O_7$ and powder Al_2O_3 in an alumina crucible at 1123 K for 2 d. The powder X-ray diffraction pattern was in agreement with the single-crystal structure.

Crystal data

$K(Co,Al)_2(PO_4)_2$
$M_r = 314.95$
Monoclinic
$C2/c$
$a = 13.3179 (15)$ Å
$b = 13.1523 (13)$ Å
$c = 8.6827 (12)$ Å
$\beta = 100.19 (1)^\circ$
$V = 1496.9 (3)$ Å^3
$Z = 8$
$D_x = 2.795$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 10.0$–17.5°
$\mu = 3.404$ mm^{-1}
$T = 293$ K
Prism
0.6 × 0.3 × 0.2 mm
Violet

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991*b*)
$T_{min} = 0.310$, $T_{max} = 0.510$
2634 measured reflections
2180 independent reflections

1842 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0299$
$\theta_{max} = 30^\circ$
$h = -1 \rightarrow 18$
$k = -1 \rightarrow 18$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.104$
$S = 1.198$
1842 reflections
119 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 3.5722P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.601$ e Å^{-3}
$\Delta\rho_{min} = -0.521$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0024 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

K—O(4^{i})	2.746 (3)	Co(1)—O(1^{vii})	1.849 (2)
K—O(2^{ii})	2.855 (3)	Co(2)—O(7^{iii})	1.810 (3)
K—O(1)	2.973 (3)	Co(2)—O(6^{viii})	1.830 (3)
K—O(6^{ii})	2.976 (3)	Co(2)—O(5)	1.837 (3)
K—O(7^{iii})	2.982 (3)	Co(2)—O(4^{iv})	1.837 (3)
K—O(2^{iii})	3.044 (3)	P(1)—O(7)	1.509 (3)
K—O(3^{i})	3.082 (3)	P(1)—O(5)	1.516 (3)
K—O(8^{iv})	3.127 (3)	P(1)—O(2)	1.524 (2)
K—O(5^{v})	3.211 (3)	P(1)—O(6)	1.526 (3)
K—O(4^{iv})	3.382 (4)	P(2)—O(4)	1.517 (2)
Co(1)—O(8^{iv})	1.806 (3)	P(2)—O(8)	1.520 (3)
Co(1)—O(3^{vi})	1.816 (3)	P(2)—O(1)	1.524 (2)
Co(1)—O(2^{ii})	1.831 (2)	P(2)—O(3)	1.527 (3)

Symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vi) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (viii) $1-x, -y, 1-z$.

In the unit cell, two independent tetrahedral sites were found for both Co and Al. Co and Al were placed at both sites with the constraint that their positional and displacement parameters were equal and that the total occupation for that site was 1.0. The refinement of population parameters led to Co/Al ratios of 0.441 (4)/0.559 (4) and 0.481 (4)/0.519 (4) for the two tetrahedral sites, which are very close to the ideal value. Therefore, in the final refinement, Co and Al were assumed to be completely statistically distributed over these two tetrahedral sites with an equal probability of 50%.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *XP* (Siemens, 1991*a*). Software used to prepare material for publication: *SHELXL*93.

Financial support by the Director Foundation, Institute of Chemistry, Academia Sinica, is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1136). Services for accessing these data are described at the back of the journal.

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