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Synthesis and crystal structure of $K_2CuP_2O_7$

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Abstract

$K_2CuP_2O_7$ crystallizes in the orthorhombic space group *Pbnm*, $a = 9.509(4)$, $b = 14.389(6)$, $c = 5.276(2)$ Å, $D_{calc} = 2.904$ g cm^{-3}, $Z = 4$, $R/R_w = 4.6/5.9\%$ for 1172 observed reflections. The solid state structure shows square pyramidal coordination for Cu^{2+} (Cu^{2+}–O, average 2.043(5) Å) and sevenfold or ninefold coordination for the two potassium atoms (K–O, average 2.748(3) and 2.966(5) Å respectively). Comparisons may be drawn with the crystal structures of α-$Sr_2P_2O_7$, α-$Ca_2P_2O_7$ and the low temperature form of $Na_2CuP_2O_7$.

Keywords: Synthesis; Phosphates; Crystal structure

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1. Introduction

Despite the abundant literature references to the chemistry and structure of phosphates, and their potential importance in industrial applications, little is known about mixed monovalent alkaline ion–bivalent ion phosphates of formula $A^{I}_2B^{II}P_2O_7$. It has been reported that $Na_2MP_2O_7$ (M ≡ Zn, Co) and $K_2MP_2O_7$ (M ≡ Zn, Co, Cu) are isotypical and crystallize in a tetragonal unit cell [1]. However, the single-crystal structure of $Na_2CoP_2O_7$ [2] has shown the existence of two allotropic forms: triclinic (rose color) and orthorhombic (blue) which display tetrahedral and octahedral coordination of Co^{II} respectively. $Na_2CuP_2O_7$ [3] similarly exists in two allotropic forms (both monoclinic) which differ in coordination geometry of copper (tetrahedral in the high temperature form and square pyramidal in the low temperature form).

The single-crystal structures of $K_2NiP_2O_7$ [4], $Na_{7.39}Ni_{4.24}(P_2O_7)_4$ [3], $Na_{7.13}Mg_{4.36}(P_2O_7)_4$ [3] and $Na_7Mg_{4.5}(P_2O_7)_4$ [5] are also known.

The unit cell dimensions of $K_2MnP_2O_7$ [6], $K_2CdP_2O_7$ [7], $Na_2CuP_2O_7$ (low temperature) [3] and $K_2SrP_2O_7$ [8] appear at first consideration to resemble those of α-$Ca_2P_2O_7$ [9]; however, while all four crystallize in monoclinic cells, the space groups of these compounds are respectively *P*2$_1$/*n*, *C*2/*c*, *P*2$_1$/*n* and *P*2$_1$/*c*. Further consideration shows that neither space group nor cell dimensions permit identification of an isotypical relationship.

α-$Ca_2P_2O_7$ has two metal sites, 1 in the fold of the $P_2O_7^{4-}$ group and 2 located at the ends of these groups [9]. In some compounds of type $A^{II}B^{II}P_2O_7$ (radius of A greater than radius of B; A, B ≡ Ba,Pb; Pb,Co; Pb,Mn; Pb,Cu; Ca,Cu; Sr,Cu; Sr,Cd; Sr,Co) the A atom is seen in site 1 whereas the B atom is seen in site 2 (Fig. 1(a)). The similarity between α-$Ca_2P_2O_7$ (*P*2$_1$/*n*) and α-$Sr_2P_2O_7$ (*Pbnm*) has been noted [10,11]. The latter shows Sr and $P_2O_7^{4-}$ groups lying on mirror planes at $z = 0.25$ and 0.75. The presence of the mirror enforces an O–P..P–O dihedral angle of 0° (Fig. 1(b)). The absence of this mirror in α-$Ca_2P_2O_7$ is seen in small displacements of atoms from the $z = 0.25$ and 0.75 planes and in the O–P...P–O angle of 18°.

The structure of $Na_2CuP_2O_7$ (low temperature) shows a relationship with the structure of α-$Ca_2P_2O_7$. One Na atom and the Cu atom are seen in site 1. The second Na atom is seen in site 2 (Fig. 1(c)).

$K_2MnP_2O_7$ [6] and $K_2CdP_2O_7$ [7] show the reverse placement. A single K atom is seen in the fold of the $P_2O_7^{4-}$ group and the second K atom with the Mn or Cd is seen at the ends of the anion. However, a rearrangement of $P_2O_7^{4-}$ groups is in evidence as well (Fig. 1(d)). A further change is the observation of O–P...P–O angles of 56.36° and 55.74° respectively in

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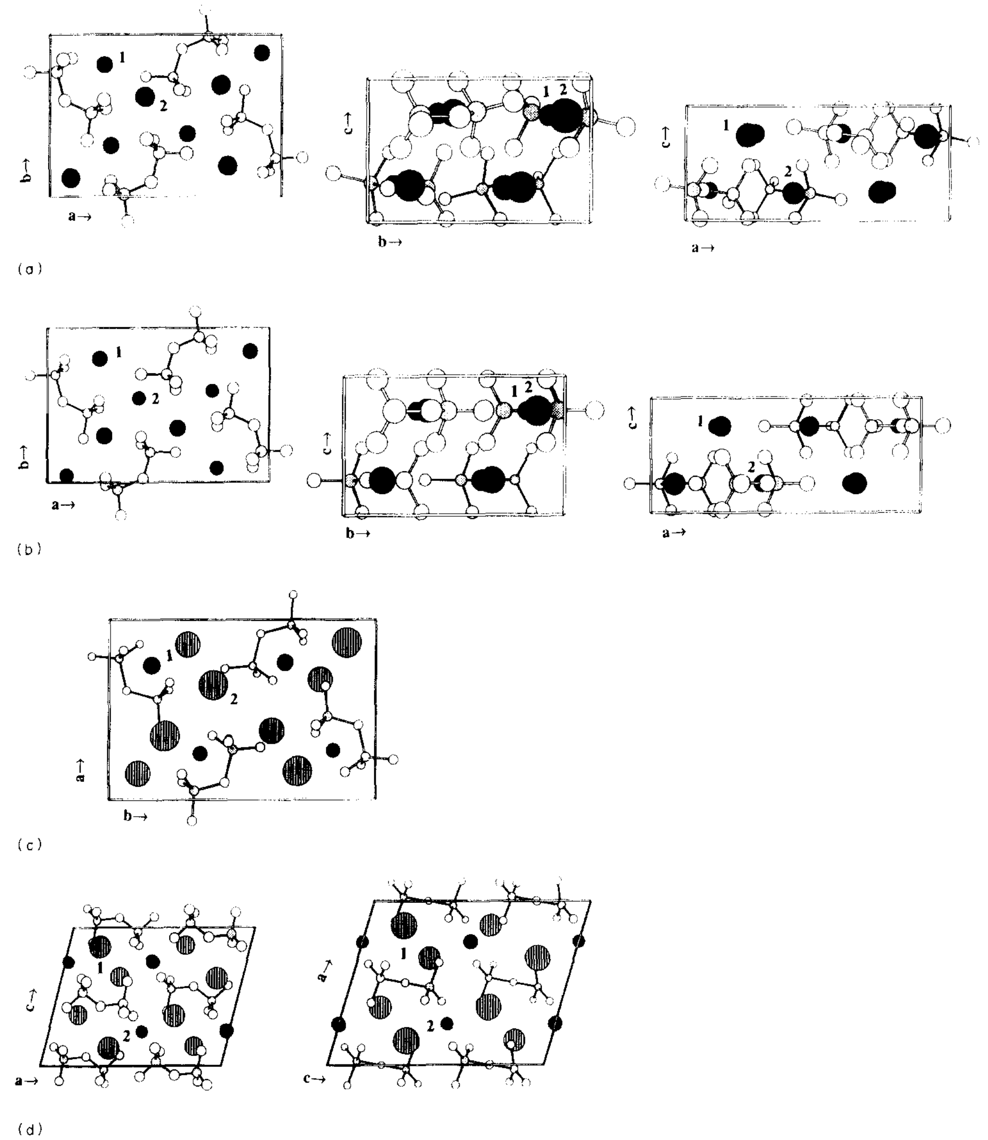


Fig. 1. (a) Projection views of α-$Ca_2P_2O_7$, $a = 12.66(1)$ Å, $b = 8.542(8)$ Å, $c = 5.315(5)$ Å, $\beta = 90.3(1)°$, $P2_1/n$, Ref. [9]. (b) Projection views of α-$Sr_2P_2O_7$, $a = 13.1054(4)$ Å, $b = 8.9104(6)$ Å, $c = 5.4035(4)$ Å, *Pbnm*, Ref. [10]. (c) Projection view of $Na_2CuP_2O_7$ (low temperature), Ref. [3]. (d) Projection views of $K_2MnP_2O_7$, Ref. [6], and $K_2CdP_2O_7$, Ref. [7].

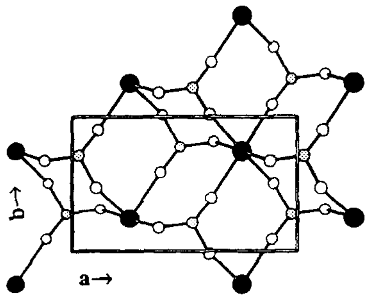


Fig. 2. View of metal planes in $K_2CdP_2O_7$.

the two compounds. $K_2SrP_2O_7$ is similar in structure to these two [8].

The four compounds $K_2MnP_2O_7$ [6], $K_2CdP_2O_7$ [7], $Na_2CuP_2O_7$ (low temperature) [3] and $K_2SrP_2O_7$ [8] show a similar disposition of the B atom on planes of centered hexagons with each of the near pairs of neighboring B atoms separated by more than 4 Å and bridged by two O–P–O bridges (Fig. 2).

$K_2NiP_2O_7$ [4] shows no obvious similarity tô α-$Sr_2P_2O_7$ or α-$Ca_2P_2O_7$ either in space group ($P2_1$) or cell dimensions.

We report here the synthesis and single crystal study of $K_2CuP_2O_7$.

2. Experimental

Crystals of $K_2CuP_2O_7$ were prepared by direct fusion of a stoichiometric mixture of $(NH_4)_2HPO_4$, K_2CO_3 and CuO (purity of starting materials greater than 99%).

These materials were ground together and heated progressively to fusion (1073 K) for 24 h followed by slow cooling to 473 K (5 K h^{-1}) where heating was discontinued. Blue crystals of $K_2CuP_2O_7$ were obtained.

3. Single-crystal X-ray diffraction

A single crystal of $K_2CuP_2O_7$ ($0.1 \times 0.1 \times 0.1$ mm^3) was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 1) were determined by least squares refinement of the best angular positions for 15 independent reflections ($2\theta > 20°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (1172 independent points after removal of redundant and space group forbidden data) were collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. The intensities of these reflections showed less than 5% variation. Data were corrected for Lorentz, polarization, centering and background effects [12]. Observed reflections (800 points ($I > 3.0\sigma(I)$)) were used for solution of heavy atom positions by direct methods using MULTAN80 [13]. K, P and O atoms were located from a difference Fourier synthesis. Refinement [14] of scale factor, positional and anisotropic thermal parameters for these atoms was carried out to convergence. Final refinement (function minimized $\Sigma(|F_0| - |F_c|)^2$) led to a final agreement factor $R = 4.6\%$ ($R = (\Sigma||F_0| - |F_c||/\Sigma|F_0|) \times 100$). Scattering factors were taken from Cromer and Mann [15]. In the final stages of refinement a weight of $1/\sigma(F)^2$ was used, $R_w = 5.9\%$. Corrections for anomalous scattering were made for K and Cu atoms [16].

Table 1
Crystal data for $K_2CuP_2O_7$

Formula	$K_2CuP_2O_7$
MWT	315.68
a (Å)	9.509(4)
b (Å)	14.389(6)
c (Å)	5.276(2)
α (deg)	90.0
β (deg)	90.0
γ (deg)	90.0
V (Å)	721.8(5)
F(000)	612
μMo Kα (cm^{-1})	46.17
λMo Kα (Å)	0.71069
D_{calc} (g cm^{-3})	2.904
Z	4
Space group	*Pbnm*
Observed reflections	1172
Octants measured	h, k, l
R/R_w(%)	4.6/5.9

4. Description of the structure

Fig. 3 shows a projection view of the structure of $K_2CuP_2O_7$ on the (001) plane based on the positional parameters of Table 2. The cell dimensions and space group (*Pbnm*) suggest a structural relationship with α-$Sr_2P_2O_7$. Both show metal atoms and $P_2O_7^{4-}$ groups sharing mirror planes at $z = 0.25$ and 0.75. Both show O–P..P–O angles constrained to 0° by the mirror.

As in the structure of $Na_2CuP_2O_7$ (low temperature), the copper atom and one alkali cation of $K_2CuP_2O_7$ are found in the fold of the $P_2O_7^{4-}$ group and the second alkali ion is located at the ends of these groups. The conformation of a $P_2O_7^{4-}$ group may be quantitated as a dihedral angle, O–P...P–O, if a bond between the two phosphorus atoms is envisioned. $Na_2CuP_2O_7$ (low temperature) shows an O–P..P–O angle of 30.69° which indicates a conformation between the eclipsed conformation of a dichromate structure and the staggered arrangement seen in thortveitite structures while retaining the pairing of $P_2O_7^{4-}$ structures about a center of symmetry which is typical of dichromates.

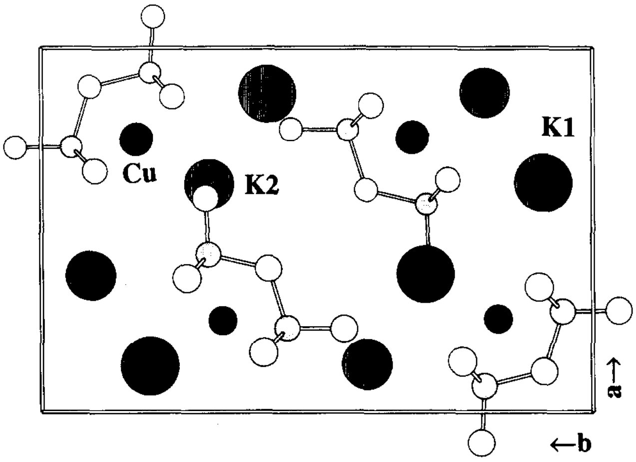


Fig. 3. Projection view of $K_2CuP_2O_7$ on the (001) plane.

Table 2
Positional parameters for $K_2CuP_2O_7$

Atom	$X(\sigma(X))$	$Y(\sigma(Y))$	$Z(\sigma(Z))$
Cu1	0.7476(1)	0.8277(1)	0.7500
K1	0.6283(2)	0.0898(1)	0.7500
K2	0.6244(2)	0.6960(1)	0.2500
P1	0.4303(2)	0.6973(1)	0.7500
P2	0.2269(2)	0.5552(1)	0.7500
O12	0.3638(4)	0.7368(2)	0.9920(8)
O13	0.5864(6)	0.7027(5)	0.7500
O14	0.3909(6)	0.5883(4)	0.7500
O22	0.1604(4)	0.5974(3)	0.5125(9)
O23	0.2253(8)	0.4524(4)	0.7500

Cu^{2+} ions show square pyramidal geometry with apical distance, Cu–O, 2.363(6) Å. K^+ ions are found in two different crystallographic sites. K1 shows ninefold coordination, average K1–O 2.966(5) Å, whereas K2 is surrounded by seven oxygen atoms, average K2–O 2.748(3) Å.

$P_2O_7^{4-}$ groups show a P–O–P angle of 120.4(4)°. The average P–O distance is 1.541(5) Å. These values are close to those observed in other diphosphate structures (see Table 3).

Comparison of cell dimensions and space groups as well as projection views of the pairs of structures ($K_2CuP_2O_7$ and α-$Sr_2P_2O_7$; $Na_2CuP_2O_7$ (low temperature) and α-$Ca_2P_2O_7$) shows that there has been a shrinkage of one cell dimension and the growth of another in both cases in passage from a $B^{II}{}_2P_2O_7$ to an $A^{I}{}_2B^{II}P_2O_7$ structure. The 13.1054(4) Å cell edge of α-$Sr_2P_2O_7$ has diminished to 9.509(4) Å, and the 8.9104(6) Å edge has grown to 14.389(6) Å on passage from α-$Sr_2P_2O_7$ (Fig. 1(b)) to $K_2CuP_2O_7$ (Fig. 4(a)). The *c* cell edge remains relatively unchanged.

Table 3
Bond angles (deg) and distances (Å) for $K_2CuP_2O_7$

Cu1–O13	2.363(6)	O13–Cu1–O22^{i}	98.4(2)
Cu1–O22^{i}	1.941(5)	O13–Cu1–O12^{ii}	90.3(2)
Cu1–O12^{ii}	1.984(4)	O13–Cu1–O12^{iii}	90.3(2)
Cu1–O12^{iii}	1.984(4)	O13–Cu1–O22^{iv}	98.4(2)
Cu1–O22^{iv}	1.941(5)	O22^{i}–Cu1–O12^{ii}	170.9(2)
		O22^{i}–Cu1–O12^{iii}	90.5(2)
K1–O12^{vi}	2.843(4)	O22^{i}–Cu1–O22^{iv}	91.0(2)
K1–O12^{vii}	2.843(4)	O12^{ii}–Cu1–O12^{iii}	86.6(2)
K1–O13^{viii}	3.162(7)	O12^{ii}–Cu1–O22^{iv}	90.5(2)
K1–O22^{ix}	3.019(5)	O12^{iii}–Cu1–O22^{iv}	170.9(2)
K1–O22^{x}	3.044(5)		
K1–O22^{xi}	3.044(5)	O14–P1–O13	106.4(3)
K1–O22^{xii}	3.019(5)	O14–P1–O12	105.3(2)
K1–O23^{xiii}	2.860(3)	O14–P1–O12^{v}	105.3(2)
K1–O23^{xi}	2.860(3)	O13–P1–O12	113.1(2)
		O13–P1–O12^{v}	113.1(2)
K2–O12^{xiv}	2.888(4)	O12–P1–O12^{v}	112.8(2)
K2–O12^{iv}	2.783(4)		
K2–O12^{ii}	2.783(4)	O22–P2–O23	113.1(2)
K2–O12^{v}	2.888(4)	O22–P2–O14	106.2(2)
K2–O13	2.664(1)	O22–P2–O22^{v}	110.0(3)
K2–O13^{xv}	2.664(1)	O23–P2–O14	107.6(4)
K2–O23^{xvi}	2.570(7)	O23–P2–O22^{v}	113.1(2)
		O14–P2–O22^{v}	106.2(2)
P1–O14	1.613(6)		
P1–O13	1.486(6)	P1–O14–P2	120.4(4)
P1–O12	1.534(4)		
P1–O12^{v}	1.534(4)		
P2–O22	1.529(5)		
P2–O23	1.480(6)		
P2–O14	1.631(6)		
P2–O22^{v}	1.529(5)		

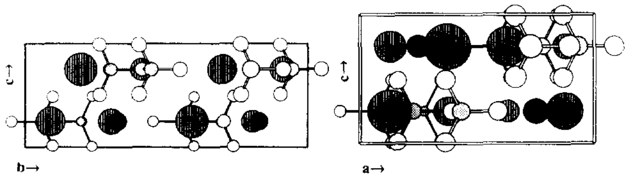
i = 0.5 + x, 1.5 − y, 0.5 + z.
ii = 0.5 + x, 1.5 − y, −0.5 + z.
iii = 0.5 + x, 1.5 − y, 2 − z.
iv = 0.5 + x, 1.5 − y, −z.
v = x, y, 1.5 − z.
vi = −x, −y, −0.5 + z.
vii = −x, −y, 2 − z.
viii = 1.5 − x, −0.5 + y, z.
ix = 0.5 − x, −0.5 + y, 1.5 − z.
x = 0.5 + x, 0.5 − y, −z.
xi = 0.5 + x, 0.5 − y, 0.5 + z.
xii = 0.5 − x, −0.5 + y, z.
xiii = 0.5 + x, 0.5 − y, −0.5 + z.
xiv = x, y, −1 + z.
xv = x, y, 0.5 − z.
xvi = −x, −y, −z.

A similar change in cell edges is seen by comparison of Fig. 4(b) (low temperature $Na_2CuP_2O_7$) with the α-$Ca_2P_2O_7$ projections of Fig. 1(a).

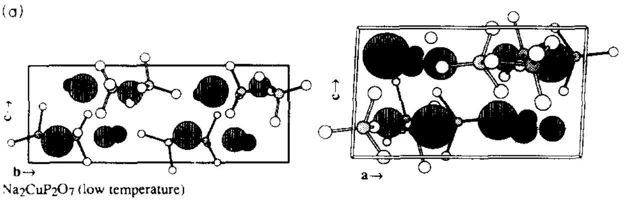
The changes in cell dimensions may be seen to arise from two factors, differences in K, Na, Cu, Ca and Sr distances to oxygen atoms and the relative ionic radii of K, Na, Cu, Ca and Sr. Passage from α-$Sr_2P_2O_7$ to $K_2CuP_2O_7$ involves replacement of Sr (ionic radii 1.31 Å; nine coordination) with Cu (ionic radii 0.65 Å, five coordination) and K2 (1.46 Å, seven coordination); passage from α-$Ca_2P_2O_7$ to $Na_2CuP_2O_7$ (low temperature) involves replacement of Ca (ionic radius 1.12 Å, eight coordination) with Na (1.18 Å, eight coordination) and Cu (ionic radii 0.65 Å, five coordination). These substitutions result in the growth of one cell dimension. Comparison of the *bc* projection for α-$Sr_2P_2O_7$ with the *bc* projection for $K_2CuP_2O_7$ shows the placement of K1 and Cu to have resulted in the separation of $P_2O_7^{4-}$ groups along the *b* axis. A similar effect is observed by comparison of the *bc* projections for $Na_2CuP_2O_7$ (low temperature) and α-$Ca_2P_2O_7$.

At the same time, Sr–O bonds, average 2.65 Å at the ends of the P_2O_7 groups are being replaced with Cu–O bonds (average 2.043(5) Å) in one case, and Ca1–O bonds (average 2.545(8) Å) are being replaced by Cu–O bonds (average 1.968(2) Å) in the other case. This results in a drawing in of the other cell dimension. Comparison of the *ac* projections for α-$Sr_2P_2O_7$ and $K_2CuP_2O_7$ shows this shrinkage of the *a* cell dimension.

The single-crystal analysis of $K_2CuP_2O_7$ thus shows it to resemble the structure of α-$Sr_2P_2O_7$ with important changes in the lengths of the *a* and *b* axes due to the substitution of two K and one Cu atoms for two Sr atoms in the solid lattice.



$K_2CuP_2O_7$
(a)



$Na_2CuP_2O_7$ (low temperature)
(b)

Fig. 4. (a) Projection views of $K_2CuP_2O_7$. (b) Projection views of low temperature $Na_2CuP_2O_7$.

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