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$CaK_2P_2O_7$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.001 Å
R factor = 0.025
wR factor = 0.067
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Crystals of the title compound, calcium dipotassium diphosphate, have been synthesized from a melt and structurally characterized using single-crystal X-ray diffraction. The $CaK_2P_2O_7$ structure can be described as a layer structure, with alternating $[K_2P_2O_7^{2-}]_\infty$ and $[Ca^{2+}]_\infty$ layers parallel to the *ab* plane. Ca^{2+} is coordinated by six O atoms in a distorted octahedron. K^+ is coordinated by nine O atoms in two different polyhedra.

Comment

Significant amounts of phosphorus are contained in many biomass fuels and sludges. However, available identification tools such as structural characteristics for ash species containing phosphates, formed during combustion and gasification of biomass fuels, are insufficient. To remedy this situation, structural studies of a number of phases in the system CaO–K_2O–P_2O_5 have been initiated by single-crystal as well as powder X-ray diffraction investigations.

The structure of the title compound can be described as a layer structure with alternating $[K_2P_2O_7^{2-}]_\infty$ and $[Ca^{2+}]_\infty$ layers parallel to the *ab* plane. Fig. 1 depicts a projection along the *b* axis. All atoms are located in general positions. The Ca^{2+}

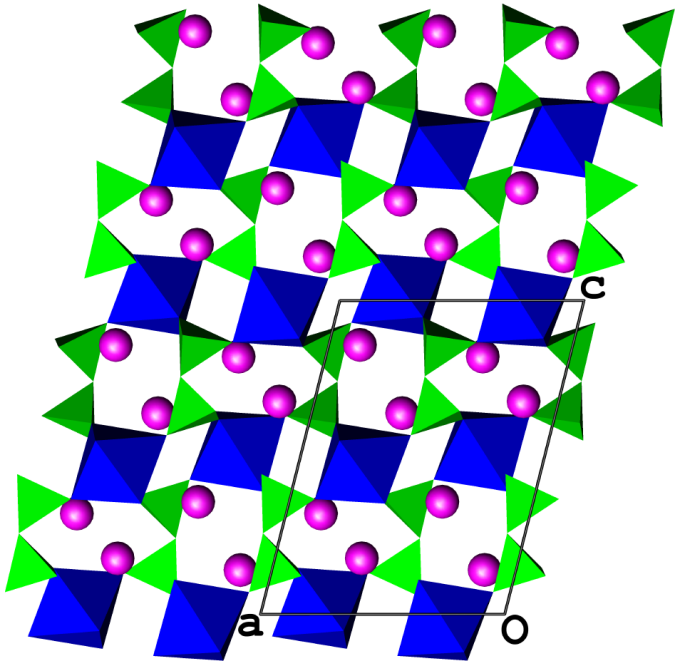

Figure 1
Projection of the crystal structure of $CaK_2P_2O_7$ along the *b* axis. Layers of $[K_2P_2O_7^{2-}]$ (potassium ions as pink spheres and phosphate groups as green tetrahedra) parallel to the *ab* plane alternate with layers of Ca^{2+} depicted here as blue distorted octahedra. The unit cell is outlined.

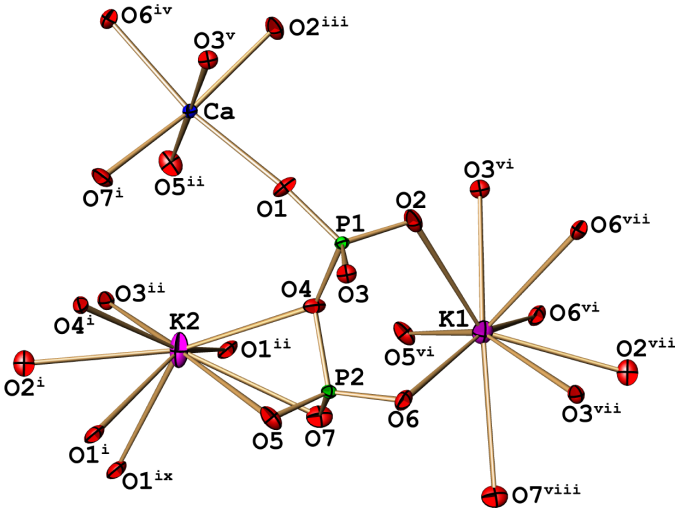

Figure 2
View of the extended asymmetric unit of $CaK_2P_2O_7$, shown with anisotropic displacement ellipsoids at the 50% probability level. Symmetry codes refer to those given in Table 1.

ions are coordinated by six O atoms in a distorted octahedron; the six Ca—O contacts range between 2.3018 (11) and 2.3869 (10) Å, with an average of 2.330 (3) Å. The O—Ca—O angles range between 84.23 (4) and 97.15 (4)°. The asymmetric unit contains two crystallographically independent potassium ions that are both coordinated by nine O atoms, eight from the same and one from an adjacent $[K_2P_2O_7^{2-}]_\infty$ layer. The nine K—O distances range between 2.7785 (11) and 3.099 (12) Å, with an average of 2.946 (5) Å. The asymmetric unit also has two crystallographically independent P atoms. Both are tetrahedrally bound to four O atoms and share a common vertex to form the diphosphate group (Fig. 2). The P—O distances for the terminal O atoms range between 1.5056 (11) and 1.5171 (10) Å, with an average of 1.511 (3) Å, and those to the bridging O atom are 1.6314 (11) and 1.6359 (11) Å. The bridging angle P1—O4—P2 is 127.72 (7)°.

$CaK_2P_2O_7$ shows common structural features with the compound $SrK_2P_2O_7$ (Trunov *et al.*, 1991). Both structures have alternating $[K_2P_2O_7^{2-}]_\infty$ and cation layers. However, the stacking of the diphosphate group within the layer differs between the two structures.

Experimental

Polycrystalline $CaK_2P_2O_7$ was prepared by mixing K_2CO_3 (Merck, p.a.) and $Ca(PO_3)_2$ [calcinated $Ca(H_2PO_4)_2$, Sigma 98%] at 1273 K in a 1:1 ratio. According to the pseudo-binary phase diagram $CaK_2P_2O_7$–KPO_3 by Znameriowska (1978), a melt with this composition will encounter the liquidus curve of $CaK_2P_2O_7$ at approximately 1373 K and allow for precipitation of the title compound during the chosen temperature interval. Crystals of the title compound were grown by heating a mixture consisting of 59 wt% $CaK_2P_2O_7$ and 41 wt% KH_2PO_4 (Merck, p.a.) in a platinum crucible at 1323 K for about 12 h, followed by cooling at a rate of 6 K h^{-1} to 1023 K and finally quenching to room temperature. The solidified liquid was crushed and the resulting colourless crystals were picked out.

Crystal data

$CaK_2(P_2O_7)$	D_x = 2.763 Mg m^{-3}
M_r = 292.23	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4000 reflections
a = 9.8180 (3) Å	θ = 3.0–30.0°
b = 5.6760 (3) Å	μ = 2.53 mm^{-1}
c = 13.0060 (7) Å	T = 293 (2) K
β = 104.220 (3)°	Fragment, colourless
V = 702.58 (6) $Å^3$	0.24 × 0.22 × 0.06 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	1948 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.072
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	θ_{max} = 30.0°
T_{min} = 0.784, T_{max} = 0.862	$h = -13 \rightarrow 13$
31100 measured reflections	$k = -7 \rightarrow 7$
2038 independent reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 0.5877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.025	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.067	$\Delta\rho_{max}$ = 0.82 e $Å^{-3}$
S = 1.09	$\Delta\rho_{min}$ = −1.05 e $Å^{-3}$
2038 reflections	Extinction correction: *SHELXL*
110 parameters	Extinction coefficient: 0.0499 (17)

Table 1
Selected geometric parameters (Å, °).

Ca—O7^{i}	2.3018 (11)	K2—O7	2.9124 (12)
Ca—O5^{ii}	2.3090 (11)	K2—O4	2.9149 (11)
Ca—O1	2.3214 (12)	K2—O2^{i}	2.9332 (11)
Ca—O2^{iii}	2.3309 (11)	K2—O1^{ix}	2.9597 (13)
Ca—O6^{iv}	2.3312 (11)	K2—O1^{ii}	2.9849 (12)
Ca—O3^{v}	2.3869 (10)	K2—O1^{i}	3.0050 (12)
K1—O5^{vi}	2.7881 (12)	K2—O4^{i}	3.0372 (11)
K1—O2^{vii}	2.8373 (11)	K2—O5	3.0999 (12)
K1—O6	2.8684 (11)	P1—O2	1.5109 (11)
K1—O3^{vi}	2.8729 (11)	P1—O1	1.5112 (12)
K1—O3^{vii}	2.8796 (11)	P1—O3	1.5171 (10)
K1—O6^{vi}	2.9434 (11)	P1—O4	1.6314 (11)
K1—O6^{vii}	3.0363 (12)	P2—O7	1.5056 (11)
K1—O2	3.0772 (12)	P2—O6	1.5115 (11)
K1—O7^{viii}	3.0939 (12)	P2—O5	1.5145 (11)
K2—O3^{ii}	2.7785 (11)	P2—O4	1.6359 (11)
O2—P1—O1	113.48 (6)	O7—P2—O5	113.08 (6)
O2—P1—O3	113.94 (6)	O6—P2—O5	113.70 (6)
O1—P1—O3	113.40 (6)	O7—P2—O4	102.39 (6)
O2—P1—O4	104.44 (6)	O6—P2—O4	106.74 (6)
O1—P1—O4	102.44 (6)	O5—P2—O4	104.29 (6)
O3—P1—O4	107.85 (6)	P1—O4—P2	127.72 (7)
O7—P2—O6	115.10 (6)		

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

The highest peak and deepest hole ar located at distances of 0.76 and 0.72 Å, respectively, from atom K2.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97 and local procedures.

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