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Calcium potassium *cyclo*-triphosphate

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Crystals of calcium potassium *cyclo*-triphosphate, $CaKP_3O_9$, have been synthesized from a melt and structurally characterized using single-crystal X-ray diffraction. The compound is isostructural with the mineral benitoite ($BaTiSi_3O_9$).

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.001 Å
R factor = 0.024
wR factor = 0.056
Data-to-parameter ratio = 22.8

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

Comment

In the course of extended studies recently undertaken concerning thermodynamic and structural characterization of ternary phases in the system $CaO–K_2O–P_2O_5$ (Sandström *et al.*, 2003), we report here the crystal structure of a hexagonal high-temperature modification of calcium potassium *cyclo*-triphosphate. A rhombohedral modification (Andrieu *et al.*, 1966) and an orthorhombic modification (Masse *et al.*, 1975) have also been found for $CaKP_3O_9$. The present structure is isostructural with benitoite, $BaTiSi_3O_9$ (Zachariasen, 1930; Fischer, 1969). In this family, one also finds some germanates, fluoroberyllates, phosphates and other silicates. Andrieu *et al.* (1966) and Masse *et al.* (1967) suggested, from comparison of X-ray powder diffraction patterns, that *cyclo*-triphosphates with the general formula $M^{II}M^{I}P_3O_9$ (M^{II} = Ca, Cd, Co, Mn, Mg and Zn; M^{I} = K or NH_4) should be isotypic with benitoite. Previously, Andrieu *et al.* (1966) reported the cell parameters for $CaKP_3O_9$ as a = 6.795 (1) Å and c = 10.336 (1) Å, which are close to those reported here. Pouchot *et al.* (1966) also suggested that $CdAgP_3O_9$, $CdRbP_3O_9$ and $CdTlP_3O_9$ are isotypic with benitoite. Prisset (1982) presented a refined crystal structure of $CaNH_4P_3O_9$.

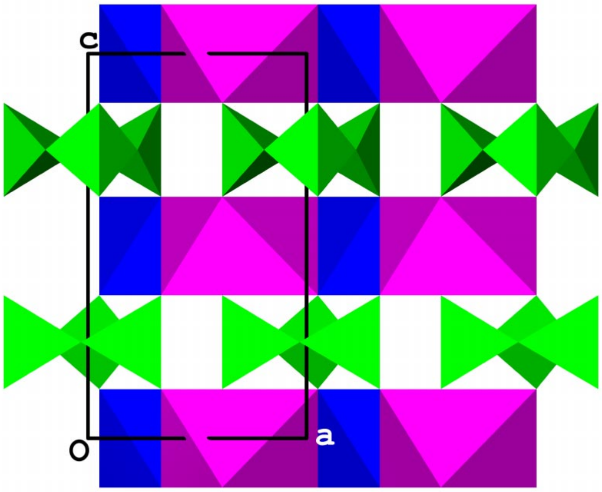

Figure 1
Packing scheme of the $CaKP_3O_9$ structure, viewed along the *b* axis. The tetrahedra represent the phosphate groups, while the blue and pink octahedra represent the coordination spheres around calcium and potassium, respectively. The unit cell is outlined.

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Fig. 1 depicts a projection of the structure along the *b* axis, showing the layer character of the structure. The structure consists of planar tricyclic phosphate rings ($P_3O_9^{3-}$) perpendicular to the *c*-axis. A $\overline{6}$ axis runs through these groups. The calcium and potassium ions are situated between the phosphate layers and are each coordinated by six terminal phosphate O atoms (O2). The calcium ion has a slightly distorted octahedron and the potassium ion has a flattened trigonal octahedron as coordination figure. All atoms except O2 are situated at special sites. The Ca^{2+} ion (point symmetry 32) has Ca—O distances of 2.3309 (12) Å and the K^+ ion (point symmetry 32) has K—O distances of 2.7955 (14) Å. Atoms P and O1 are both situated at the same crystallographic site (6*k*), having point symmetry *m*. The bridging P—O1 distances are 1.592 (2) and 1.595 (2) Å, and the terminal P—O2 distances are 1.4785 (12) Å. The bridging angle P—O1—P is 136.40 (14)°.

Experimental

Polycrystalline $CaKP_3O_9$ was prepared by mixing KPO_3 (obtained from dehydrated $KHPO_4$, Merck, p.a., at 873 K) and $Ca(PO_3)_2$ (obtained from dehydrated $Ca(H_2PO_4)_2$, Sigma 98%, at 873 K) at 1073 K in a 1:1 ratio. Crystals were grown by heating a mixture consisting of 91 wt% $CaKP_3O_9$ and 9 wt% KPO_3 in a platinum crucible at 1173 K for about 12 h, followed by cooling at a rate of 6 K h^{-1} to 997 K, and finally quenching to room temperature. According to the binary phase diagram $Ca(PO_3)_2$–KPO_3 by Andrieu & Diament (1964), a melt with this composition will encounter the liquidus curve of $CaKP_3O_9$ at approximately 1084 K and allow for precipitation of the title compound during the chosen temperature interval. The solidified liquid was crushed and the colourless crystals which had grown were picked out.

Crystal data

$CaK(P_3O_9)$
$M_r = 316.10$
Hexagonal, $P\overline{6}c2$
$a = 6.8090$ (3) Å
$c = 10.3760$ (9) Å
$V = 416.61$ (4) Å^3
$Z = 2$
$D_x = 2.520$ Mg m$^{-3$}
Mo *Kα* radiation
Cell parameters from 455 reflections
$\theta = 2.9$–$33.1°$
$\mu = 1.85$ mm^{-1}
$T = 293$ (2) K
Fragment, colourless
0.19 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.794$, $T_{max} = 0.914$
25323 measured reflections
639 independent reflections
628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.077$
$\theta_{max} = 34.9°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.056$
$S = 1.18$
639 reflections
28 parameters
$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 0.3146P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.130 (6)
Absolute structure: Flack (1983), 282 Friedel pairs
Flack parameter = −0.02 (7)

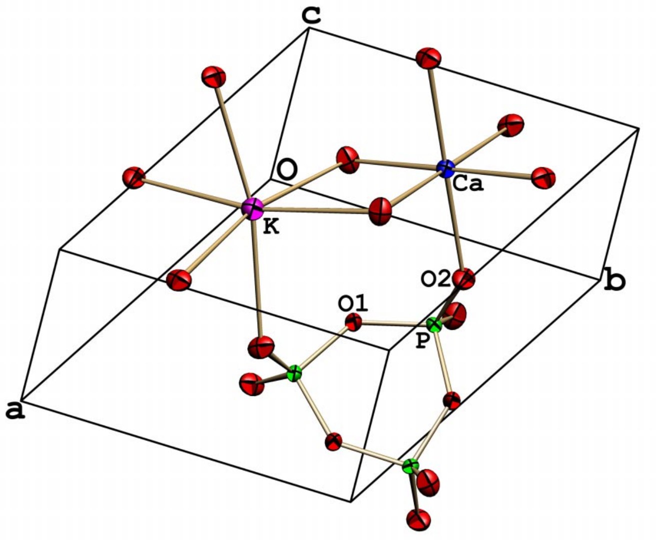

Figure 2
Extended view of the asymmetric unit of $CaKP_3O_9$, showing the cation–oxygen coordination. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

Ca—O2	2.3309 (13)	P—O1^{ii}	1.5950 (18)
K—O2^{i}	2.7955 (14)	P—O2	1.4785 (12)
P—O1	1.592 (2)		
O2^{iii}—Ca—O2^{iv}	179.66 (8)	O2^{v}—K—O2^{i}	167.27 (6)
O2^{iii}—Ca—O2	88.99 (7)	O1—P—O1^{ii}	103.60 (13)
O2^{iv}—Ca—O2	90.77 (5)	O2—P—O1	109.31 (7)
O2—Ca—O2^{v}	89.47 (8)	O2—P—O1^{ii}	107.89 (7)
O2^{iv}—K—O2^{v}	71.52 (5)	O2—P—O2^{vii}	117.87 (13)
O2^{iv}—K—O2^{vi}	91.04 (7)	P—O1—P^{viii}	136.40 (13)
O2^{v}—K—O2^{vi}	99.31 (3)		

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

Attempts to solve the structure in any corresponding centrosymmetric space group failed. The refined Flack (1983) parameter is indicative of a correct absolute configuration of the structure. The highest electron-density peak is located 0.36 Å from O1, while the deepest hole is 0.57 Å from P.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO and SCALEPACK* (Otwinowski & Minor, 1997); 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 (Sheldrick, 1997) and local procedures.

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