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Caesium calcium *cyclo*-triphosphate, $CsCaP_3O_9$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.002 Å
R factor = 0.020
wR factor = 0.041
Data-to-parameter ratio = 20.3

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

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Crystals of the title compound, $CsCd(P_3O_9)$, were grown from a melt. The structure is isotypic with $CsCdP_3O_9$. The three-dimensional framework is built up from $[CaO_6]$ octahedra linked together *via* corner-sharing to cyclic $[P_3O_9]^{3-}$ anions. The Cs cations are situated in large cavities in the $[CaP_3O_9]^-_\infty$ anion framework. Except for one P and three O atoms, all other atoms (one Cs, one Ca, one P and three O atoms) are located on mirror planes.

Comment

The condensation of tetrahedral phosphate anions *via* two common vertices leads to the formation of polyphosphate anions. The two groups of polyphosphates are *cyclo*-polyphosphates, with the general anion formula $[P_nO_{3n}]^{n-}$, and *catena*-polyphosphates, $[P_nO_{3n+1}]^{(n+2)-}$. The *cyclo*-phosphate anion with the smallest ring size is the *cyclo*-triphosphate anion, *viz*. $P_3O_9^{3-}$. It has been found in, for example, $K_3P_3O_9$ (Bagieu-Beucher *et al.*, 1976), $Na_3P_3O_9$ (Ondik, 1965), $CsCdP_3O_9$ (Averbuch-Pouchot & Durif, 1977), $CdK_4(P_3O_9)_2{\cdot}2H_2O$ (Averbuch-Pouchot, 1978), $BaKP_3O_9{\cdot}H_2O$ (Seethanen & Durif, 1978) and $NH_4CaP_3O_9$ (Masse *et al.*, 1975). We report here the synthesis and structural characterization of the condensed phosphate $CsCaP_3O_9$, (I), which is isotypic with $CsCdP_3O_9$ (Averbuch-Pouchot & Durif, 1977).

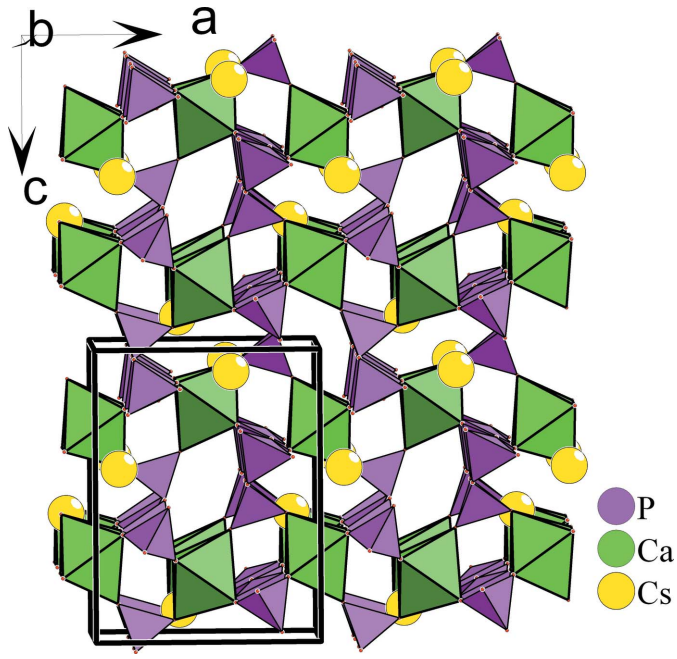

Figure 1
The crystal structure of (I), in a projection approximately along [010]. The hexagonally shaped tunnels running parallel to [010] are visible.

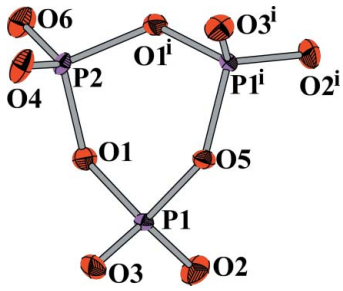

Figure 2
The *cyclo*-triphosphate anion in (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $x, \frac{3}{2} - y, z$.]

The structure of (I) contains $[CaO_6]$ octahedra and $[P_3O_9]^{3-}$ *cyclo*-polyphosphate anions linked together *via* vertices to form a three-dimensional framework structure. In this arrangement, hexagonally shaped tunnels are also present (Fig. 1). The O atoms around Ca form a slightly distorted octahedron. The equatorial Ca—O bond lengths are 2.3148 (16) and 2.3443 (15) Å, whereas the axial bond lengths range from 2.284 (2) to 2.355 (2) Å (Table 1).

The $[P_3O_9]^{3-}$ *cyclo*-polyphosphate anion is made up of three $[PO_4]$ tetrahedra (Fig. 2). The lengths of the bridging P—O bonds are in the range 1.6072 (9)–1.6196 (16) Å, and the terminal P—O bond lengths are in the range 1.466 (2)–1.480 (2) Å, in good agreement with other *cyclo*-$[P_3O_9]^{3-}$ anions.

The Cs ions occupy sites in the large cavities of the $[CaP_3O_9]^-_\infty$ framework. They show a coordination number of 13, with Cs—O distances ranging from 3.1918 (15) to 3.8029 (2) Å (Table 1, Fig. 3).

Experimental

The title polyphosphate, (I), was prepared by the flux technique in the Cs_2O–P_2O_5–CaO melt system. A mixture of $(NH_4)_2HPO_4$ (2.11 g), $CsPO_3$ (5.0 g) and $CaHPO_4$ (0.952 g) was ground in an agate mortar, placed in a porcelain crucible and heated to 973 K for 3 h. The resulting melt was kept at this temperature for 30 min and finally cooled to room temperature. Colourless crystals of (I) were separated from the rest of the glassy matrix by washing with hot deionized water. The purity of (I) was confirmed by the powder XRD (Siemens D500 Ni-filtered Cu $K\alpha$ radiation). Elemental analysis indicated the presence of Cs, Ca and P in the atomic ratio 1:1:3.

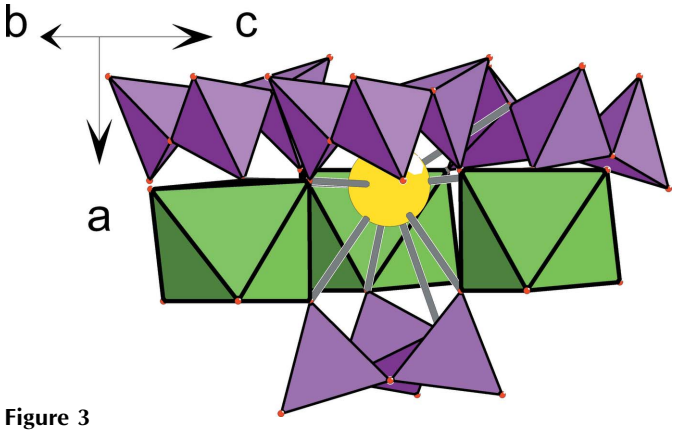

Figure 3
A view of the cage where the Cs ion is located.

Crystal data

$CsCa(P_3O_9)$	$Z = 4$
$M_r = 409.9$	$D_x = 2.863$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation
$a = 9.8287$ (2) Å	$\mu = 4.96$ mm^{-1}
$b = 7.5642$ (1) Å	$T = 293$ (2) K
$c = 12.7905$ (2) Å	Prism, colourless
$V = 950.93$ (3) Å^3	0.05 × 0.04 × 0.03 mm

Data collection

Oxford Diffraction Xcalibur-3 CCD area-detector diffractometer	13085 measured reflections
	1482 independent reflections
φ and ω scans	1278 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{int} = 0.030$
	$\theta_{max} = 30°$
$T_{min} = 0.790$, $T_{max} = 0.865$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 0.1458P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.020$	
$wR(F^2) = 0.041$	
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.001$
1482 reflections	$\Delta\rho_{max} = 0.70$ e Å^{-3}
73 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cs—O3	3.1918 (15)	Ca—O3^{iv}	2.3443 (15)
Cs—O4^{i}	3.201 (2)	Ca—O4	2.355 (2)
Cs—O2^{ii}	3.2168 (17)	P1—O2	1.4729 (15)
Cs—O3^{i}	3.2628 (16)	P1—O3	1.4791 (15)
Cs—O5^{i}	3.409 (2)	P1—O5	1.6072 (9)
Cs—O5^{ii}	3.448 (2)	P1—O1	1.6108 (15)
Cs—O1	3.6166 (15)	P2—O6	1.466 (2)
Cs—O4	3.8029 (2)	P2—O4	1.480 (2)
Ca—O6^{iii}	2.284 (2)	P2—O1	1.6196 (16)
Ca—O2^{ii}	2.3148 (16)	P2—O1^{v}	1.6196 (16)
O5—P1—O1	102.61 (9)	P1—O1—P2	125.47 (10)
O1—P2—O1^{v}	100.81 (11)	P1^{v}—O5—P1	135.84 (13)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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