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A new polymorph of $CsPr(PO_3)_4$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(P–O) = 0.003 Å
R factor = 0.025
wR factor = 0.062
Data-to-parameter ratio = 14.3

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

A new polymorph of caesium praseodymium polyphosphate, $CsPr(PO_3)_4$, features PrO_8 polyhedra sharing O atoms with PO_4 groups, yielding a three-dimensional framework. The latter delimits intersecting channels in which the Cs ions are located.

Comment

Rare earth phosphate materials have been extensively investigated due to their efficient luminescent and scintillation properties (Dornauf & Heber, 1979; Mazurak *et al.*, 1984; Wolinski *et al.*, 1990; Horchani *et al.*, 2002, 2003; Horchani-Naifer *et al.*, 2006; Makhov *et al.*, 2002). Many rare earth polyphosphates have been reported in the literature (Amami *et al.*, 2005; Durif, 1995). These phosphates are obtained by the flux method after study of the phase-equilibrium diagrams of the $M^{I}PO_3$–$Ln(PO_3)_3$ systems (M^{I} = alkali metal; Ln = rare earth element) (Férid *et al.*, 1998). This work was carried out within the framework of a systematic investigation of the crystal structures and luminescent properties of double polyphosphates of the type $M^{I}Ln(PO_3)_4$ (Férid, 2006). This paper deals with the structure of a new polymorph of $CsPr(PO_3)_4$ [previous polymorph: Palkina *et al.* (1978)].

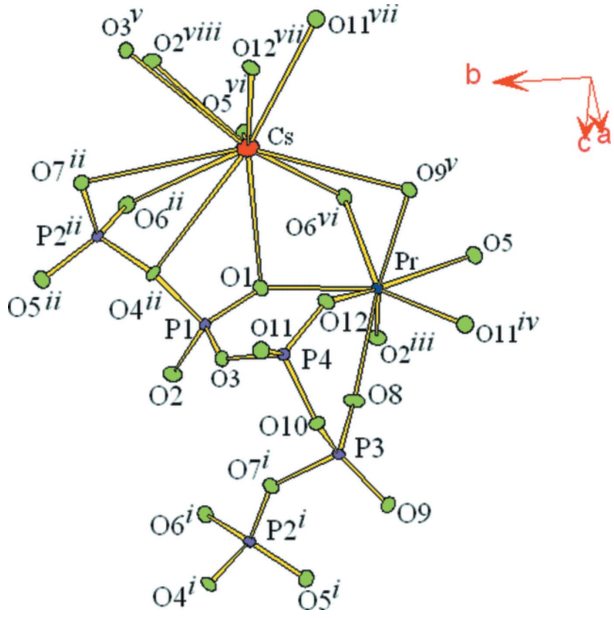

Figure 1
A segment of the polyphosphate chain with PO_4 tetrahedra; anisotropic displacement parameters are drawn at the 50% probability level. [Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x, y+1, z$; (iii) $-x, -y+2, -z+1$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $-x, -y+2, -z$; (viii) $x-\frac{1}{2}, -y+\frac{5}{2}, z-\frac{1}{2}$.]

$CsPr(PO_3)_4$ is isostructural with $TlNd(PO_3)_4$ (Palkina *et al.*, 1977). The central feature is a Pr^{3+} ion, which is coordinated by PO_4 groups, yielding a PrO_8 dodecahedron with Pr—O distances ranging from 2.394 (3) to 2.526 (3) Å. The PrO_8 dodecahedron shares all its O atoms with the corners of neighbouring PO_4 tetrahedra, whereas 11 O atoms constitute the coordination of the Cs atom, forming CsO_{11} polyhedra with Cs—O distances ranging from 3.092 (3) to 3.568 (3) Å. The P—O distances of the PO_4 tetrahedra may be divided into linking or bridging P—O_i distances [1.589 (3)–1.612 (3) Å] and terminal P—O_j distances [1.480 (3)–1.492 (3) Å] (Fig. 1). The O—P—O angles are in the range 98.33 (15)–121.18 (18)°, which is in good agreement with those usually observed in polyphosphate anions (Durif, 1995).

Experimental

All reagents were used as purchased (Fluka, 99.9%). Single crystals of $CsPr(PO_3)_4$ were prepared by the flux method. At room temperature, Cs_2CO_3 (5 g) and Pr_6O_{11} (0.4 g) were added slowly to phosphoric acid, H_3PO_4 (85%; 12 ml). The mixture was then heated slowly to 573 K and kept at this temperature for 7 d. Green crystals of (I) were separated from the excess phosphoric acid by washing the product in boiling water.

Crystal data

$CsPr(PO_3)_4$
M_r = 589.70
Monoclinic, $P2_1/n$
a = 10.4938 (3) Å
b = 9.0744 (2) Å
c = 11.2525 (5) Å
β = 106.414 (2)°
V = 1027.85 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.92 mm^{-1}
T = 298 (2) K
0.14 × 0.13 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.314, T_{max} = 0.320
3875 measured reflections
2339 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
2 standard reflections
every 150 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.062
S = 1.16
2339 reflections
164 parameters
$\Delta\rho_{max}$ = 1.39 e Å^{-3}
$\Delta\rho_{min}$ = −2.29 e Å^{-3}

The highest peak and the deepest hole in the residual electron density are located 0.01 Å and 0.78 Å, respectively, from Pr.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

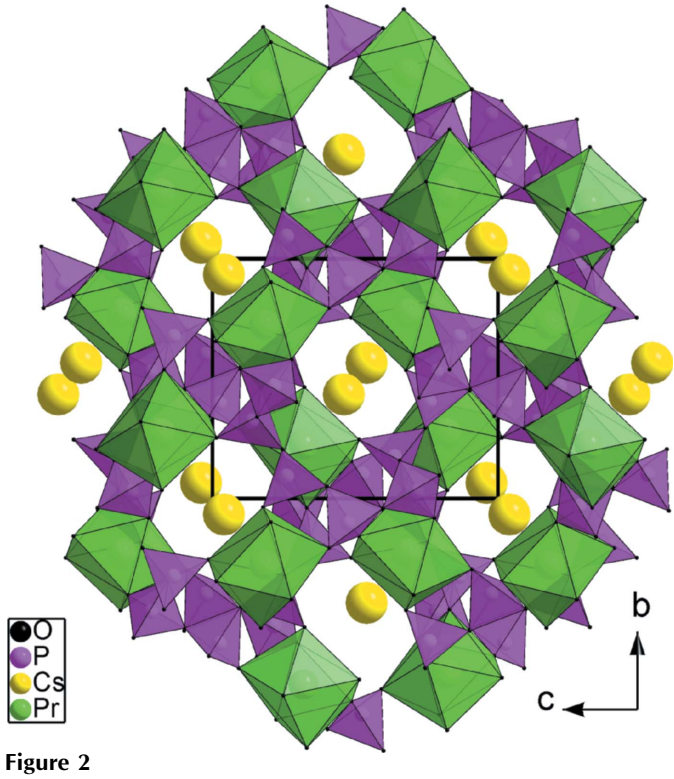

Figure 2
A projection of $CsPr(PO_3)_4$ along the *a* axis, showing the arrangement of the PrO_8 polyhedra and PO_4 tetrahedra.

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