

CsTiP₂O₇

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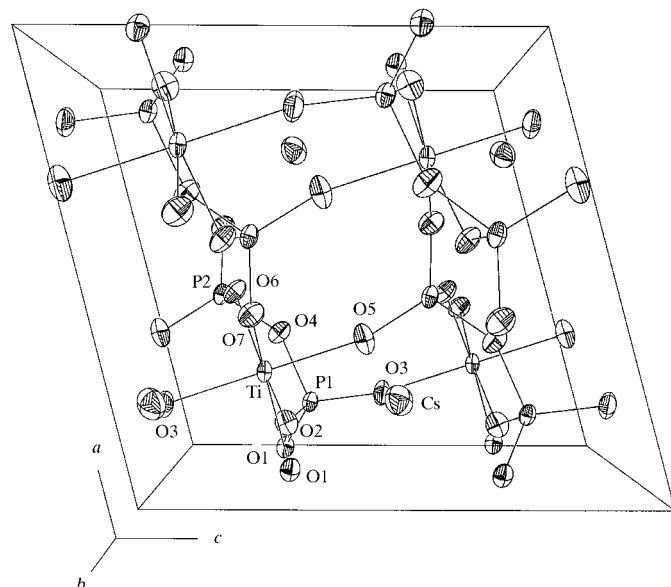
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From single-crystal X-ray data, cesium titanium pyrophosphate, CsTiP₂O₇, is found to crystallize in the KAIP₂O₇ structure type. It possesses a three-dimensional tunnel structure built by the corner-sharing of distorted TiO₆ octahedra and P₂O₇ pyrophosphate groups. The Cs⁺ cations are in the tunnels.

Comment

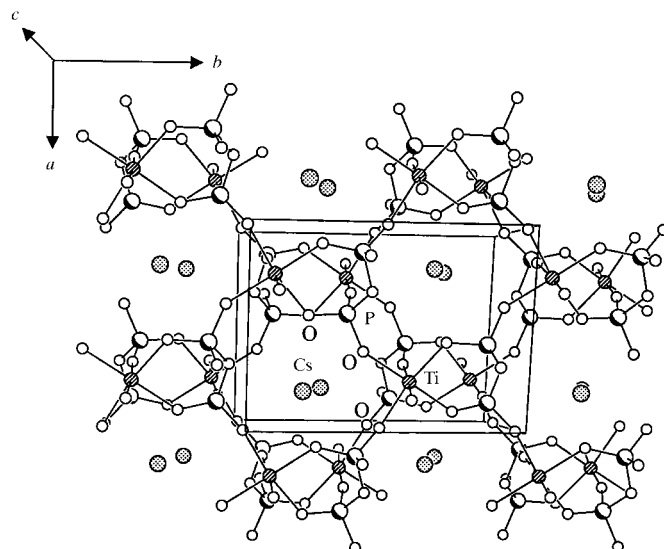
The chemistry of alkali-metal titanium phosphate compounds, especially those possessing layered or tunnel structures, is of interest owing to the remarkable ionic conductivity and the potential value as solid electrolytes (Daidouh *et al.*, 1997; Maximov *et al.*, 1994) that some possess, and to the considerable success of KTiOPO₄ as an excellent optical medium (Fan *et al.*, 1987; Zumsteg *et al.*, 1976). In general, the AMP₂O₇ (*A* = alkali metal, *M* = trivalent metal) structures crystallize in two large families, *i.e.* the NaAlP₂O₇ (Gamondés *et al.*, 1971) and KAIP₂O₇ (Ng & Calvo, 1973) structure types. The compounds AMP₂O₇ with *A* = Na and *M* = V, Mo (Wang *et al.*, 1989; Leclaire, Borel *et al.*, 1988) are isostructural to NaAlP₂O₇, and those of AMP₂O₇ with *A* = K, Rb, Cs, and *M* = V, Mo (Benhamada *et al.*, 1991; Leclaire *et al.*, 1989; Riou *et al.*, 1989; Lii & Haushalter, 1987; Chen *et al.*, 1989; Wang & Lii, 1989) are isostructural to KAIP₂O₇. In the ATiP₂O₇ system, α-NaTiP₂O₇ (Leclaire, Benmoussa *et al.*, 1988) is isostructural to NaAlP₂O₇, but β-NaTiP₂O₇ (Leclaire, Benmoussa *et al.*, 1988) and ATiP₂O₇ (*A* = K, Rb, Cs; Wang & Hwu, 1991) are isostructural to KAIP₂O₇, where in the latter series, only the structure of RbTiP₂O₇ has been determined from single-crystal X-ray data. The structure of CsTiP₂O₇, reported here, is isostructural to KAIP₂O₇.

The structure of CsTiP₂O₇ consists of a three-dimensional framework of [TiP₂O₇]⁻, as shown in Figs. 1 and 2. The rigid framework is built by corner-sharing distorted TiO₆ octahedra and P₂O₇ pyrophosphate groups which form the tunnels running along the *c* axis (Fig. 2). There is only one crystallographically unique Cs atom with four equivalent ones in the unit cell. The Cs⁺ cations in a tunnel run in a zigzag chain parallel to the *c* axis; the distance between two Cs⁺ cations is 4.2986 (3) Å. Each Cs⁺ cation is surrounded by an irregular polyhedron of ten O²⁻ anions, as is Rb⁺ in the isostructural

**Figure 1**

The unit cell of CsTiP₂O₇ viewed down [010] with 90% probability displacement ellipsoids.

RbTiP₂O₇. However, Na⁺ is coordinated to nine O²⁻ anions in α-NaTiP₂O₇ and eight in β-NaTiP₂O₇. The Cs—O distances ranging from 2.9840 (18) to 3.452 (2) Å are comparable to those in CsVP₂O₇ which range from 2.978 (5) to 3.301 (5) Å (Wang & Lii, 1989). Each TiO₆ octahedron shares its six corners with five P₂O₇ groups, whereas the TiO₆ octahedron in α-TiP₂O₇ is linked to six P₂O₇ groups. This difference results in two different structures for ATiP₂O₇. In CsTiP₂O₇, the Ti—O distances in the distorted TiO₆ octahedron range from 1.974 (2) to 2.091 (2) Å (Table 1), the Ti—O3 and Ti—O5 distances being shorter than the other four, and this distortion is typical for Ti³⁺. Each P₂O₇ group is built from one P1 and

**Figure 2**

The unit cell of CsTiP₂O₇ viewed down [001] with 80% probability displacement ellipsoids.

one P2 tetrahedron, and shares its six corners with five TiO₆ octahedra. The PO₄ tetrahedra are distorted, the P—O distances range from 1.511 (2) to 1.615 (2) Å (Table 1), and the P—O4 distances are about 0.1 Å longer than the others. The Ti—O and P—O distances in this structure are comparable to those in RbTiP₂O₇ [1.970 (8)–2.0769 (8) and 1.493 (8)–1.611 (8) Å, respectively; Wang & Hwu, 1991].

Experimental

Crystals of CsTiP₂O₇ were obtained from an initial mixture of Ti (0.67 mmol, Alfa, 99.9%), Se (4.0 mmol, Aldrich, 99.5+%), P (0.5 mmol, Aldrich, 99.99+%), and Cs₂Se₃ (0.5 mmol), synthesized from a reaction of stoichiometric amounts of elemental Cs (Aldrich, 99.5+%) and Se (Aldrich, 99.5+%) in liquid ammonia. The mixture was loaded under Ar, sealed under 10^{−4} Torr (1 Torr = 133.322 Pa) in a fused-silica tube, heated in a furnace to 1123 K at 1 K min^{−1}, kept at 1123 K for 70 h, cooled at 0.05 K min^{−1} to 573 K, and finally cooled to room temperature. The reaction mixture was washed with water and acetone. It contained some purple–blue crystals of CsTiP₂O₇. Analysis of these crystals with an energy dispersive X-ray diffraction-equipped Hitachi S-4500 SEM showed the presence of Cs, Ti and P in the ratio of 1:1:2, and the presence of oxygen, which came from silica. The same compound can be obtained from the reaction of a mixture of Ti (0.67 mmol), S (2.0 mmol, Alfa, 99.8%), P₂S₅ (0.5 mmol, Aldrich, 99%), and Cs₂S₃ (0.5 mmol).

Crystal data

CsTiP ₂ O ₇	$D_x = 3.699 \text{ Mg m}^{-3}$
$M_r = 354.75$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4699 reflections
$a = 7.7247$ (6) Å	$\theta = 2.73$ – 27.01°
$b = 10.2237$ (7) Å	$\mu = 7.464 \text{ mm}^{-1}$
$c = 8.3429$ (6) Å	$T = 153$ (2) K
$\beta = 104.788$ (1) $^\circ$	Plate, purple–blue
$V = 637.05$ (8) Å ³	$0.232 \times 0.200 \times 0.090 \text{ mm}$
$Z = 4$	

Data collection

Bruker Smart 1000 CCD diffractometer	1279 independent reflections
ω scans	$R_{\text{int}} = 0.028$
Absorption correction: numerical face indexed (SHELXTL/PC; Sheldrick, 1997)	$\theta_{\text{max}} = 27.01^\circ$
$T_{\text{min}} = 0.198$, $T_{\text{max}} = 0.520$	$h = -9 \rightarrow 10$
4699 measured reflections	$k = -12 \rightarrow 12$
	$l = -10 \rightarrow 10$
	Intensity decay: <2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R(F) = 0.023$	$\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$
$wR(F^2) = 0.068$	$\Delta\rho_{\text{min}} = -1.14 \text{ e \AA}^{-3}$
$S = 1.417$	Extinction correction: SHELXTL/PC
1279 reflections	Extinction coefficient: 0.0082 (7)
101 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0400F_o^2)^2]$	

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL/PC (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1997); software used to prepare material for publication: SHELXTL/PC.

Table 1

Selected geometric parameters (Å).

Cs—O2 ⁱ	2.9840 (18)	Ti—O2	2.0499 (19)
Cs—O6 ⁱⁱⁱ	2.9859 (19)	Ti—O6	2.058 (2)
Cs—O2 ⁱⁱⁱ	3.105 (2)	Ti—O7 ⁱⁱ	2.0810 (19)
Cs—O1 ^{iv}	3.1544 (18)	Ti—O1	2.091 (2)
Cs—O7 ⁱⁱ	3.1577 (18)	P1—O3 ^{vii}	1.503 (2)
Cs—O1 ⁱⁱⁱ	3.2186 (19)	P1—O1 ^{viii}	1.5155 (19)
Cs—O7 ^v	3.267 (2)	P1—O2	1.5201 (19)
Cs—O5 ^{vi}	3.2843 (18)	P1—O4	1.612 (2)
Cs—O4 ^{vi}	3.3105 (19)	P2—O7	1.511 (2)
Cs—O3 ⁱ	3.452 (2)	P2—O5	1.517 (2)
Ti—O3	1.974 (2)	P2—O6	1.517 (2)
Ti—O5 ^{vii}	1.994 (2)	P2—O4	1.615 (2)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1285). Services for accessing these data are described at the back of the journal.

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