$Cs_3Ti_5P_7O_{29}$: A Titanium(IV) Phosphate containing TiO_5 Trigonal Bipyramids*

Kwang-Hwa Lii
Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

---

A new ternary titanium phosphate, $Cs_3Ti_5P_7O_{29}$, has been synthesized and structurally characterized by single-crystal X-ray diffraction. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.307(1)$, $b = 10.330(2)$, $c = 20.230(3)$ Å, $\alpha = 88.65(1)$, $\beta = 84.83(1)$, $\gamma = 72.37(1)°$, $Z = 2$ and $R = 0.0396$. The structure consists of tunnels where the caesium cations are located. The framework is composed of two types of corner-sharing dimers of compositions Ti_2O_{11} formed by two octahedra and Ti_2O_{10} by an octahedron and a trigonal bipyramid, discrete TiO_6 octahedra, PO_4 tetrahedra and P_2O_7 groups. The structural formula is $Cs_3Ti(Ti_2O)_2(PO_4)_5(P_2O_7)$. Five-co-ordinate titanium with trigonal-bipyramidal geometry is unusual in phosphates.

Alkali-metal titanium phosphates are of interest for their technological applications. For example, $NaTi_2(PO_4)_3$ belongs to the Nasicon family of compounds which exhibit fast ion conduction[1] and low thermal expansion.[2] Potassium titanyl phosphate ($KTiOPO_4$) is a superior non-linear optical material for second harmonic generation at 1064 nm due to the high-power conversion efficiencies, high damage threshold, large angular acceptance, and the low sensitivity of its phase matching condition to temperature.[3,4] Although alkali-metal titanium phosphates have been extensively studied, few compounds are known in the caesium–titanium–phosphate system. To our knowledge, $Cs_2TiOP_2O_7$,[5] α- and β-$CsTi_3P_5O_{19}$[6,7] are the only structurally characterized compounds in the system. The structure of $Cs_2TiOP_2O_7$, which is isotypic with that of $Rb_2VOP_2O_7$,[8] consists of sheets of TiO_5 square pyramids and P_2O_7 groups with the Cs atoms between the sheets. The two polymorphs of $CsTi_3P_5O_{19}$ have different three-dimensional networks of vertex-sharing octahedra and tetrahedra. Both frameworks have infinite tunnels where the Cs atoms are located. Although Airapetyan *et al.*[9] reported the crystallization of $CsTiPO_5$ from melt solutions, the compound was not structurally characterized and its X-ray powder pattern cannot be indexed based on the $KTiOPO_4$ structure. As part of our continuing study on the structural chemistry of transition-metal phosphates, we have recently examined the caesium–titanium–phosphate system. We have identified $Cs_3Ti_5P_7O_{29}$ as a new member of this system and describe here its synthesis and crystal structure. The structure consists of unusual TiO_5 trigonal bipyramids.

Experimental

Synthesis.—Crystals of $Cs_3Ti_5P_7O_{29}$ were obtained by a flux-growth method. A mixture of CsH_2PO_4 (2.215 g), $NH_4H_2PO_4$ (0.277 g) and TiO_2 (0.160 g) (Cs:P mole ratio = 0.8 : 1) was placed in a 15 cm^3 platinum crucible and heated from room temperature to 1000 °C over a period of 10 h. It was then maintained at 1000 °C for 30 min, cooled to 800 °C at a rate of 2 °C h^{-1}, followed by quenching to room temperature on removal of the crucible from the furnace. The flux was dissolved with hot water and the solid product was obtained by suction filtration. The product contained a small amount of pale purple crystalline chunks of an unknown compound and colourless rod-like crystals of $Cs_3Ti_5P_7O_{29}$. The crystalline chunk is a cubic phase with $a = 30.18$ Å. A structural study on the chunk is in progress. Energy dispersive X-ray fluorescence analysis on a colourless rod crystal showed that the Cs : Ti : P mole ratio was 0.54 : 1 : 1.44, which is close to the results from the single-crystal X-ray diffraction. Subsequently, a mixture containing a stoichiometric quantity of the starting materials was slowly heated to 1000 °C, maintained at 1000 °C for 30 min, cooled to 800 °C at a rate of 2 °C h^{-1}, and then quenched to room temperature. Based on powder X-ray diffraction the product was contaminated with a small amount of unidentified impurities. The intensity of the most intense reflection of the impurities was about 15% that of the major phase, and all other reflections in the diffraction pattern corresponded very well with that calculated from the single-crystal data. The product was slightly coloured probably due to partial reduction of Ti^{IV}. A single-phase product was not obtained, although several different reaction conditions were tested.

Single-crystal X-Ray Diffraction.—A colourless crystal of dimensions 0.05 × 0.05 × 0.25 mm was selected for indexing and intensity data collection on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. Axial oscillation photographs were taken to check the unit-cell parameters. Octants collected: $+h, \pm k, \pm l$. The intensity data were corrected for Lorentz polarization and absorption effects. The latter were based on ψ scans of several suitable reflections with χ values close to 90° using the NRCVAX program package.[10] The agreement index R_{merge} for $\pm(0\,kl)$ reflections was 0.017. On the basis of statistical analysis of the intensity distribution and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (no. 2). The structure was solved by the direct method and successive Fourier syntheses, and was refined by full-matrix least-squares refinement based on *F* values. We initially refined the structure with Cs(4) at an inversion centre. The Cs atom showed a large thermal parameter and a large nearby residual electron density. A difference synthesis based on the atomic coordinates of all the atoms except Cs(4) revealed two major sites for the Cs atom which are related by an inversion centre and are too closely spaced (0.846 Å) to be simultaneously occupied. The occupancy factor for Cs(4) was initially refined and the resultant value was 0.487(3). In the final cycles of refinement, the occupancy factor for Cs(4) was fixed at 0.5. The very anisotropic thermal parameters of Cs(4) ($U_{11} \approx 6\ U_{22} \approx 1.5\ U_{33}$) is probably related to the incomplete modelling

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

of the disordered Cs atom. The final cycle refinement, including atomic coordinates, isotropic thermal parameters for oxygen atoms, anisotropic thermal parameters for all other atoms and a secondary extinction coefficient, converged at $R = 0.0396$. The largest residual electron density in the final difference map is 1.73 e Å^{-3}, 0.04 Å from Cs(1). Structure solution and least-squares refinement were performed by using programs from the SHELXTL PLUS program package.[11] Neutral-atom scattering factors were used and correction for anomalous dispersion was applied.[12] The crystallographic data are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Structure refinement in the non-centrosymmetric space group $P1$ was also performed. The refinement resulted in slightly higher R factors and unrealistic thermal parameters for quite a few Ti and P atoms. The refinement results also showed that the standard deviations of the bond lengths were about three times that of those from the refinement in $P\bar{1}$ and the Ti–O polyhedra in both cases distorted to the same extent.

Table 1 Crystal data and intensity data collection parameters for $Cs_3Ti_5P_7O_{29}$

Formula	$Cs_3O_{29}P_7Ti_5$
M	1319.02
Space group	$P\bar{1}$ (no. 2)
a/Å	6.307(1)
b/Å	10.330(2)
c/Å	20.230(3)
α/°	88.65(1)
β/°	84.83(1)
γ/°	72.37(1)
U/Å^3	1251.0(4)
Z	2
D_c/g cm^{-3}	3.502
F(000)	1224
λ(Mo-Kα)/Å	0.709 30
μ(Mo-Kα)/cm^{-1}	64.0
T/°C	23
Scan rate/° min^{-1}	8.24
Scan mode	θ–2θ
Scan width/°	0.60 + 0.35 tan θ
2θ range/°	2–50
No. of independent reflections	4405
Observed reflections [$I > 2.5\sigma(I)$]	3524
Refined parameters	259
R^a	0.0396
R'^b	0.0451
Goodness of fit	1.32
$(\Delta\rho)_{max,min}$/e Å^{-3}	1.73, −1.14

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Weighting scheme, $w^{-1} = 1/[\sigma^2(F) + 0.003\,20\,F^2]$.

Results and Discussion

Atomic coordinates and selected interatomic distances for $Cs_3Ti_5P_7O_{29}$ are listed in Tables 2 and 3, respectively. Atom Cs(1) is located at an inversion centre and all other atoms are at general positions. Titanium atoms are five- or six-co-ordinated. The phosphorus atoms are tetrahedrally co-ordinated to oxygen atoms. The co-ordination numbers of caesium cations were determined on the basis of the maximum gap in the Cs–O distances ranked in increasing order. The maximum Cs–O distance in Table 3 agrees with the 3.60 Å cut-off of Donnay and Allmann.[13] The caesium atoms are eight-, nine- or ten-co-ordinated.

A perspective view of the structure along the [100] direction (Fig. 1) shows that the structure consists of infinite tunnels where the caesium cations are located, and the framework consists of two types of corner-sharing dimers of compositions $Ti(2)Ti(3)O_{11}$ formed by two octahedra, and $Ti(4)Ti(5)O_{10}$ by an octahedron and a trigonal bipyramid, discrete $Ti(1)O_6$ octahedra, PO_4 tetrahedra, and P_2O_7 groups. Five-co-ordinate titanium with trigonal-bipyramidal geometry is unusual in phosphates. The structural formula is $Cs_3Ti(Ti_2O)_2(PO_4)_5(P_2O_7)$. Each $Ti(1)O_6$ octahedron shares its six corners with three P_2O_7 groups and two PO_4 tetrahedra. One of the three diphosphate groups is co-ordinated to Ti(1) as a bidentate ligand. Each Ti_2O_{11} unit shares ten corners with two P_2O_7 groups and seven PO_4 tetrahedra. One of the tetrahedra, $P(2)O_4$, forms a bridge over two Ti atoms. Each Ti_2O_{10} unit shares nine corners with nine different PO_4 tetrahedra. All phosphate oxygens except O(29) and the bridging atom of a diphosphate group, O(19), are co-ordinated to Ti atoms. Atoms O(19) and O(29) are co-ordinated to Cs atoms only. As shown in Fig. 2, each $P(2)O_4$ bridges over two Ti atoms within a

Table 2 Positional parameters for $Cs_3Ti_5P_7O_{29}$

Atom	x	y	z
Cs(1)	0.5	0	0.5
Cs(2)	0.325 8(1)	0.551 14(6)	0.860 23(3)
Cs(3)	0.445 9(1)	0.350 77(7)	0.664 28(4)
Cs(4)*	0.069 8(4)	−0.007 5(3)	−0.003 5(2)
Ti(1)	0.221 0(3)	0.363 3(2)	0.397 63(8)
Ti(2)	0.064 5(3)	0.045 5(2)	0.660 52(8)
Ti(3)	0.920 4(3)	0.240 0(2)	0.806 40(8)
Ti(4)	0.323 4(3)	0.308 9(2)	0.011 03(8)
Ti(5)	0.619 1(3)	0.847 2(2)	0.830 46(8)
P(1)	0.236 7(4)	−0.278 0(2)	0.576 5(1)
P(2)	0.091 6(4)	0.911 3(2)	0.806 3(1)
P(3)	0.175 4(4)	0.638 5(2)	0.034 6(1)
P(4)	0.387 1(4)	0.052 1(2)	0.331 8(1)
P(5)	0.432 2(4)	0.188 0(2)	0.845 0(1)
P(6)	−0.023 8(4)	0.306 5(2)	0.542 5(1)
P(7)	−0.140 5(4)	0.556 0(2)	0.756 2(1)
O(1)	0.315(1)	0.836 8(7)	0.831 1(3)
O(2)	0.223(1)	0.241 4(7)	0.811 7(3)
O(3)	0.235(1)	−0.034 9(7)	0.350 1(3)
O(4)	0.867(1)	0.289 4(7)	0.899 9(3)
O(5)	0.381(1)	0.036 3(6)	0.655 5(3)
O(6)	−0.072(1)	0.835 6(7)	0.833 8(3)
O(7)	0.087(1)	0.639 5(6)	0.608 0(3)
O(8)	0.385(1)	0.246 8(7)	0.920 5(4)
O(9)	0.504(1)	0.035 3(7)	0.857 0(3)
O(10)	−0.010(1)	0.698 0(7)	0.991 4(3)
O(11)	0.009(1)	0.054 7(7)	0.835 4(3)
O(12)	0.323(1)	0.175 5(7)	0.379 3(3)
O(13)	0.174(1)	−0.132 4(7)	0.593 1(3)
O(14)	0.389(1)	0.652 5(7)	0.998 1(3)
O(15)	0.393(1)	0.192 7(7)	0.072 9(3)
O(16)	0.111(1)	−0.088 0(6)	0.730 4(3)
O(17)	−0.285(1)	0.659 7(7)	0.809 1(3)
O(18)	0.477(1)	0.641 3(7)	0.586 0(3)
O(19)	0.226(1)	−0.292 5(7)	0.497 7(3)
O(20)	0.610(1)	0.238 0(7)	0.811 0(3)
O(21)	0.624(1)	0.901 4(7)	0.739 8(3)
O(22)	−0.028(1)	0.179 6(6)	0.717 8(3)
O(23)	0.807(1)	0.511 7(7)	0.954 3(4)
O(24)	0.815(1)	0.421 5(7)	0.778 2(3)
O(25)	0.878(1)	0.435 4(7)	0.583 9(3)
O(26)	0.041(1)	0.179 3(7)	0.583 2(3)
O(27)	0.165(1)	0.317 2(7)	0.493 2(3)
O(28)	0.256(1)	0.406 8(7)	0.309 5(3)
O(29)	0.099(1)	0.547 0(7)	0.748 2(4)

* Occupancy factor for Cs(4) is 0.5.

Table 3 Selected interatomic distances (Å) for $Cs_3Ti_5P_7O_{29}$

Cs(1)–O(5)	3.171(6) (2 ×)	Cs(1)–O(12)	3.091(7) (2 ×)	Cs(3)–O(29)	2.931(6)	Cs(4)–O(4)	3.557(7)*
Cs(1)–O(13)	3.246(8) (2 ×)	Cs(1)–O(26)	3.266(6) (2 ×)	Cs(4)–O(4)	3.492(8)	Cs(4)–O(10)	3.237(8)
Cs(1)–O(27)	3.325(6) (2 ×)	Cs(2)–O(1)	2.978(7)	Cs(4)–O(10)	3.117(8)	Cs(4)–O(11)	3.339(8)
Cs(2)–O(6)	3.304(6)	Cs(2)–O(8)	3.271(7)	Cs(4)–O(11)	3.437(8)	Cs(4)–O(14)	3.480(7)
Cs(2)–O(10)	3.327(6)	Cs(2)–O(14)	3.103(8)	Cs(4)–O(15)	3.530(7)	Ti(1)–O(7)	1.964(8)
Cs(2)–O(17)	3.086(8)	Cs(2)–O(20)	3.315(6)	Ti(1)–O(12)	1.884(7)	Ti(1)–O(18)	1.950(8)
Cs(2)–O(24)	3.276(7)	Cs(2)–O(29)	2.795(8)	Ti(1)–O(25)	2.015(7)	Ti(1)–O(27)	2.006(7)
Cs(3)–O(2)	3.492(7)	Cs(3)–O(3)	3.277(6)	Ti(1)–O(28)	1.838(7)	Ti(2)–O(3)	1.958(8)
Cs(3)–O(5)	3.406(7)	Cs(3)–O(7)	3.396(7)	Ti(2)–O(5)	1.963(7)	Ti(2)–O(13)	2.212(7)
Cs(3)–O(18)	3.410(7)	Cs(3)–O(20)	3.302(7)	Ti(2)–O(16)	1.930(7)	Ti(2)–O(22)	1.751(7)
Cs(3)–O(22)	3.510(7)	Cs(3)–O(25)	3.379(8)	Ti(2)–O(26)	2.049(7)	Ti(3)–O(2)	1.926(8)
Ti(3)–O(4)	1.945(7)	Ti(3)–O(11)	1.918(7)	P(2)–O(11)	1.527(7)	P(2)–O(16)	1.529(7)
Ti(3)–O(20)	1.955(8)	Ti(3)–O(22)	1.880(7)	P(3)–O(4)	1.497(8)	P(3)–O(10)	1.497(7)
Ti(3)–O(24)	1.883(7)	Ti(4)–O(8)	1.921(7)	P(3)–O(14)	1.521(8)	P(3)–O(23)	1.533(8)
Ti(4)–O(10)	2.001(8)	Ti(4)–O(14)	1.965(8)	P(4)–O(3)	1.518(8)	P(4)–O(5)	1.512(7)
Ti(4)–O(15)	1.705(7)	Ti(4)–O(23)	1.907(7)	P(4)–O(12)	1.545(7)	P(4)–O(21)	1.516(8)
Ti(5)–O(1)	1.952(8)	Ti(5)–O(6)	1.923(8)	P(5)–O(2)	1.540(8)	P(5)–O(8)	1.532(8)
Ti(5)–O(9)	1.928(7)	Ti(5)–O(15)	1.989(7)	P(5)–O(9)	1.511(7)	P(5)–O(20)	1.525(8)
Ti(5)–O(17)	1.894(7)	Ti(5)–O(21)	1.906(7)	P(6)–O(19)	1.613(8)	P(6)–O(25)	1.522(7)
P(1)–O(7)	1.528(8)	P(1)–O(13)	1.492(7)	P(6)–O(26)	1.501(7)	P(6)–O(27)	1.514(8)
P(1)–O(18)	1.513(7)	P(1)–O(19)	1.613(7)	P(7)–O(17)	1.551(7)	P(7)–O(24)	1.548(8)
P(2)–O(1)	1.511(7)	P(2)–O(6)	1.533(8)	P(7)–O(28)	1.557(7)	P(7)–O(29)	1.478(8)

* Atom Cs(4) is disordered in two sites. Only one set of bond distances is given. The other set is identical to this one.

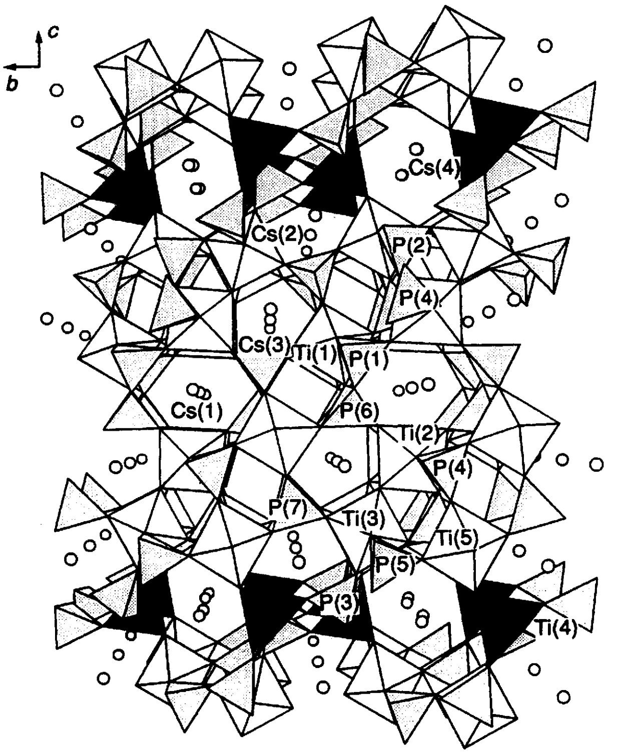

Fig. 1 Polyhedral view of the $Cs_3Ti_5P_7O_{29}$ structure along the [100] direction. In this representation the corners of the polyhedra are O atoms and the Ti and P atoms are at the centres of the polyhedra. Open circles are Cs atoms

Ti_2O_{11} unit and co-ordinates to two adjacent Ti atoms. The same connectivity has been observed in α-$CsTi_3P_5O_{19}$ and $Cs_3Ti_3As_5O_{20}$.[14] The framework of $Cs_3Ti_5P_7O_{29}$ has two hexagonal and four pentagonal tunnels per unit cell, all of which are filled with Cs atoms. One type of hexagonal tunnel, which has the largest windows formed by the edges of two octahedra, two trigonal bipyramids and two tetrahedra, is filled with Cs(4). The disordering of Cs(4) can be correlated with the large window of the tunnel. The other type of hexagonal tunnel is filled with Cs(1) and the pentagonal tunnels with Cs(2) and Cs(3). In α-$CsTi_3P_5O_{19}$, the framework has pentagonal tunnels only. The tunnel formed by the edges of three octahedra and two tetrahedra is filled with Cs atoms, but the other type of tunnel, which is formed by the edges of two octahedra and three tetrahedra, is empty. In $Cs_3Ti_5P_7O_{29}$ one type of pentagonal window is formed by the edges of two octahedra, one trigonal bipyramid and two tetrahedra, and the other type of tunnel, formed by three octahedra and two tetrahedra. Both pentagonal tunnels are large enough to accommodate Cs atoms. In $Cs_3Ti_3As_5O_{20}$ the smaller pentagonal tunnel, which is formed by the edges of two octahedra and three arsenate tetrahedra, is also filled with Cs atoms. The larger size of AsO_4 relative to PO_4 allows the tunnel to accommodate Cs atoms.

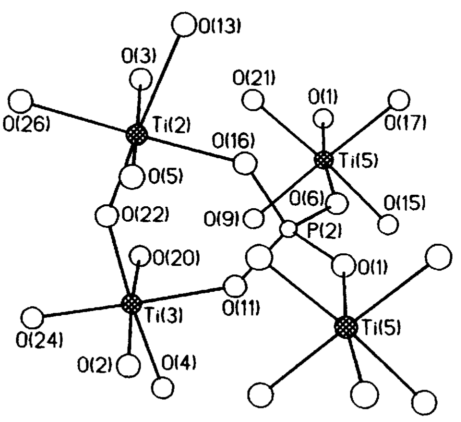

Fig. 2 Structure of $Cs_3Ti_5P_7O_{29}$ showing the connectivity of a $P(2)O_4$ group to TiO_6 octahedra

Each Ti atom in the dimeric Ti_2O_{11} unit is in a distorted octahedral co-ordination of one bridging oxide ion, O(22), and five phosphate oxygens. The titanium-oxide (bridging) distance is shorter than the other Ti–O distances. The bond *trans* to the titanyl bridge is considerably longer. The two TiO_6 octahedra are in an eclipsed configuration. The Ti–O–Ti bond angle is 149.3°. The monomeric octahedron, $Ti(1)O_6$, is considerably more distorted than the monomeric unit in α-$CsTi_3P_5O_{19}$. The distortion is even more pronounced than that of $Ti(3)O_6$ in the dimeric Ti_2O_{11} unit. The octahedral distortion can be estimated by using the equation $\Delta = \frac{1}{6}\Sigma[(R_i - \bar{R})/\bar{R}]^2$, where R_i =

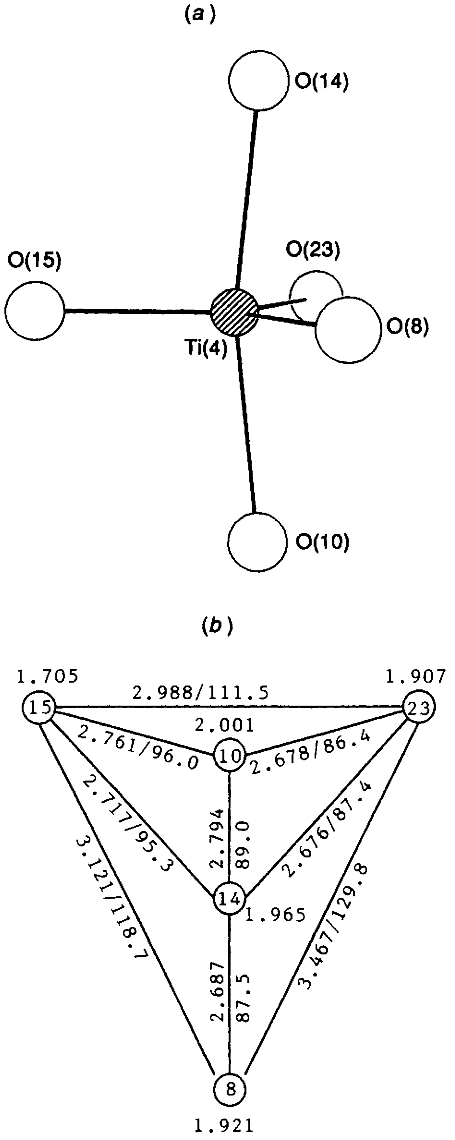

Fig. 3 (*a*) The TiO_5 trigonal bipyramid in $Cs_3Ti_5P_7O_{29}$. (*b*) Schlegel projection of a TiO_5 trigonal bipyramid. The central Ti atom is not included in the projection. The Ti–O distances (Å) are given at the terminal positions of the projection. The O $\cdots$ O distances and their corresponding angles (°) with respect to the central atom are indicated next to the edges

individual bond length and $\bar{R}$ = average bond length.[15] The values of Δ for Ti(1) and Ti(3) are 10.7×10^{-4} and 2.2×10^{-4}, respectively. The large distortion in $Ti(1)O_6$ is probably because one of the diphosphate groups is co-ordinated to the Ti atom as a bidentate ligand. The dimeric Ti_2O_{10} unit is formed by a corner-sharing $Ti(5)O_6$ octahedron and a $Ti(4)O_5$ trigonal bipyramid. The $Ti(5)O_6$ octahedron is only slightly distorted ($\Delta = 2.6 \times 10^{-4}$). Five-co-ordinate titanium is quite unusual in phosphates. To my knowledge, prior to this work, $Cs_2TiOP_2O_7$ was the only phosphate which contains a TiO_5 unit. It has a square-pyramidal structure in which the metal atom lies above the plane of four basal oxygen atoms. However, the geometry of $Ti(4)O_5$ in $Cs_3Ti_5P_7O_{29}$ should be viewed as a distorted trigonal bipyramid (Fig. 3). The axial Ti(4)–O bonds (1.965, 2.001 Å) are longer than the equatorial bonds (1.705–1.921 Å). The Ti atom and three equatorial oxygen atoms are nearly coplanar. The shortest Ti(4)–O bond involves the bridging oxide ion, O(15). In contrast, Ti(5)–O(15) in the octahedron of the dimeric Ti_2O_{10} unit is the longest bond. The Ti(4)–O(15)–Ti(5) bond angle is 148.2°. The PO_4 tetrahedra of the P_2O_7 group are in a staggered configuration. The P atoms are displaced away from the bridging oxygen, O(19), so that one longer and three shorter P–O bonds are formed. The P(1)–O(19)–P(6) bond angle is 129.4°. All phosphate oxygen atoms except O(19) and O(29) are co-ordinated to Ti atoms. The P(7)–O(29) bond is considerably shorter than other P–O bonds because O(29) is co-ordinated to Cs atoms only.

Four ternary phases have been synthesized and structurally characterized in the Cs_2O–TiO_2–P_2O_5 system. The structure of $Cs_2TiOP_2O_7$ is isotypic with that of the vanadium analogue, α-$CsTi_3P_5O_{19}$ is structurally related to $Cs_3Ti_3As_5O_{20}$ or $K_3Ti_3P_5O_{20}$,[16] and the other two phases, β-$CsTi_3P_5O_{19}$ and $Cs_3Ti_5P_7O_{29}$, adopt new structures. Although many $KTiOPO_4$ or Nasicon isostructures have been synthesized in the alkali-metal titanium phosphate system, the caesium analogues $CsTiOPO_4$ and $CsTi_2P_3O_{12}$ have not been reported. Further synthetic work is now in progress to prepare other new compounds in the Cs_2O–TiO_2–P_2O_5 system.

Acknowledgements

Financial support of this investigation by the National Science Council and the Institute of Chemistry, Academia Sinica is gratefully acknowledged.

References

1 J. B. Goodenough, H. Y.-P. Hong and J. Kafalas, *Mater. Res. Bull.*, 1976, **11**, 203.
2 R. Roy, D. K. Agrawal, J. Alamo and R. A. Roy, *Mater. Res. Bull.*, 1984, **19**, 471.
3 F. C. Zumsteg, J. D. Bierlein and T. E. Gier, *J. Appl. Phys.*, 1976, **47**, 4980.
4 G. D. Stucky, M. L. F. Phillips and T. E. Gier, *Chem. Mater.*, 1989, **1**, 492.
5 J. Protas, B. Menaert, G. Marnier and B. Boulanger, *Acta Crystallogr., Sect. C*, 1991, **47**, 698.
6 A. Ono, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3039.
7 K.-H. Lii, T. E. Gier and G. D. Stucky, *J. Solid State Chem.*, in the press.
8 K.-H. Lii and S.-L. Wang, *J. Solid State Chem.*, 1989, **82**, 239.
9 A. G. Airapetyan, G. S. Damazyan, A. L. Manukyan and A. S. Vagansaryan, *Zh. Neorg. Khim.*, 1987, **32**, 1789.
10 E. J. Gabe, Y. Le Page, J. P. Charland and F. L. Lee, *J. Appl. Crystallogr.*, 1989, **22**, 384.
11 G. M. Sheldrick, SHELXTL PLUS Crystallographic System, Release 4.11, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
13 G. Donnay and R. Allmann, *Am. Mineral.*, 1970, **55**, 1003.
14 K.-H. Lii, *J. Chem. Soc., Dalton Trans.*, 1994, 2289.
15 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
16 P. G. Nagornyi and A. A. Kapshuk, *Russ. J. Inorg. Chem.*, 1993, **38**, 7.

Received 19*th July* 1994; *Paper* 4/04408H