

P(1)O ₄ tetrahedron			
P(1)—O(1)†	1.471 (9)	O(1)—P(1)—O(16)	116.6 (4)
P(1)—O(16)	1.521 (5)	O(1)—P(1)—O(11)	117.5 (5)
P(1)—O(11)	1.536 (7)	O(1)—P(1)—O(14)	111.4 (3)
P(1)—O(14)‡	1.613 (5)	O(16)—P(1)—O(11)	106.7 (4)
		O(16)—P(1)—O(14)	103.6 (3)
		O(11)—P(1)—O(14)	98.8 (3)
P(2)O ₄ tetrahedron			
P(2)—O(18)	1.516 (9)	O(18)—P(2)—O(17)	110.7 (5)
P(2)—O(17)	1.522 (5)	O(18)—P(2)—O(3)	112.0 (5)
P(2)—O(3)	1.538 (6)	O(18)—P(2)—O(2)	104.9 (4)
P(2)—O(2)	1.542 (9)	O(17)—P(2)—O(3)	108.0 (3)
		O(17)—P(2)—O(2)	110.1 (5)
		O(3)—P(2)—O(2)	111.1 (5)
P(3)O ₄ tetrahedron			
P(3)—O(7)	1.513 (6)	O(7)—P(3)—O(5)	109.6 (5)
P(3)—O(5)	1.533 (4)	O(7)—P(3)—O(4)	109.7 (5)
P(3)—O(4)	1.543 (4)	O(7)—P(3)—O(6)	112.9 (2)
P(3)—O(6)	1.545 (6)	O(5)—P(3)—O(4)	106.3 (2)
		O(5)—P(3)—O(6)	109.8 (5)
		O(4)—P(3)—O(6)	108.3 (5)
P(4)O ₄ tetrahedron			
P(4)—O(9)	1.501 (6)	O(9)—P(4)—O(19)	110.4 (5)
P(4)—O(19)	1.531 (9)	O(9)—P(4)—O(20)	111.8 (4)
P(4)—O(20)	1.533 (6)	O(9)—P(4)—O(8)	111.5 (5)
P(4)—O(8)	1.554 (9)	O(19)—P(4)—O(20)	108.9 (5)
		O(19)—P(4)—O(8)	103.6 (3)
		O(20)—P(4)—O(8)	110.4 (5)
P(5)O ₄ tetrahedron			
P(5)—O(10)†	1.496 (9)	O(10)—P(5)—O(12)	115.1 (7)
P(5)—O(12)	1.521 (7)	O(10)—P(5)—O(15)	116.1 (4)
P(5)—O(15)	1.529 (6)	O(10)—P(5)—O(14)	110.7 (4)
P(5)—O(14)‡	1.600 (5)	O(12)—P(5)—O(15)	109.1 (4)
		O(12)—P(5)—O(14)	102.2 (3)
P(1)—O(14)‡—P(5)	135.7 (3)	O(15)—P(5)—O(14)	102.0 (3)
Environment around Rb(1) with CN = 10			
Rb(1)—O(7)	2.763 (6)	Rb(1)—O(11)	3.148 (9)
Rb(1)—O(1)	2.864 (8)	Rb(1)—O(9)	3.238 (8)
Rb(1)—O(14)	2.955 (5)	Rb(1)—O(3)	3.238 (8)
Rb(1)—O(19)	3.045 (8)	Rb(1)—O(17)	3.323 (9)
Rb(1)—O(10)	3.074 (8)	Rb(1)—O(5)	3.361 (13)
Environment around Rb(2) with CN = 9			
Rb(2)—O(10)	2.811 (8)	Rb(2)—O(13)	3.198 (4)
Rb(2)—O(19)	2.932 (8)	Rb(2)—O(2)	3.210 (8)
Rb(2)—O(1)	2.935 (7)	Rb(2)—O(11)	3.217 (9)
Rb(2)—O(5)	3.162 (4)	Rb(2)—O(8)	3.398 (8)
Rb(2)—O(15)	3.179 (6)		
Environment around Rb(3) with CN = 11			
Rb(3)—O(6)	2.784 (6)	Rb(3)—O(5)	3.285 (13)
Rb(3)—O(10)	2.923 (8)	Rb(3)—O(17)	3.337 (7)
Rb(3)—O(12)	2.981 (10)	Rb(3)—O(14)	3.387 (5)
Rb(3)—O(2)	3.013 (8)	Rb(3)—O(9)	3.409 (10)
Rb(3)—O(1)	3.021 (7)	Rb(3)—O(20)	3.457 (8)
Rb(3)—O(16)	3.101 (6)		

* Bridging atom between Ti(1)O₆ and Ti(3)O₆.

† Terminal atom from a PO₄ group (not connected to Ti).

‡ Bridging atom between two PO₄ groups.

Data collection, cell refinement and data reduction were carried out using Stoe software. Precise cell refinement was performed by double-step-scan technique. The structure was solved using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). To avoid the strong correlations between nine pairs of positional (y) and displacement parameters for atoms related by pseudo-symmetry, the parameters within these pairs were refined riding on one another. The Flack enantiopole parameter (Flack, 1983) was refined to 0.94 (1). Weights $w = 1/[\sigma^2(F) + kF^2]$ were used until the last few cycles when robust-resistant weights (Tukey, 1974) were applied (parameters used 9.07, -7.01 and 7.16).

I thank Drs Mike Glazer and David Watkin for helpful discussions, Dr Pam Thomas, Warwick University, England, for giving me access to their furnace, and Anthony Fitzmaurice for the Kurtz test run. This work was supported by a grant from the Optoelectronics Research Centre at Southampton University/University College London.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
 Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
 Stucky, G. D., Phillips, M. L. F. & Gier, T. E. (1989). *Chem. Mater.* **1**, 492–509.
 Thomas, P. A., Glazer, A. M. & Watts, B. E. (1990). *Acta Cryst.* **B46**, 333–343.
 Tukey, J. W. (1974). *Critical Evaluation of Chemical and Physical Structural Information*, pp. 3–14. Washington, DC: National Academy of Sciences.
 Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS Users Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1994). **C50**, 1525–1527

RbTi₂(PO₄)₃

RUMEN DUHLEV†

*Clarendon Laboratory, University of Oxford,
 Parks Road, Oxford OX1 3PU, England*

(Received 20 September 1993; accepted 27 January 1994)

Abstract

Rubidium titanium monophosphate forms trigonal crystals, isostructural with its lithium, sodium and potassium analogues. The structure consists of a three-dimensional framework of corner-shared TiO₆ octahedra and PO₄ tetrahedra with the Rb atoms alternating along the $\bar{3}$ axis with Ti₂P₃O₁₈ units, composed of two TiO₆ octahedra linked through three PO₄ tetrahedra.

† Present address: World Scientific Publishing Co. Ltd, 73 Lynton Mead, Totteridge, London N20 8DH, England.

Comment

A large number of compounds with general formula $M^I M^{IV}_2(\text{PO}_4)_3$, where M^I is Li, Na, K, Rb, Cs, NH₄, H₃O, Ag, Tl or Cu and M^{IV} is Ti, Zr, Hf, Th or U, are known to crystallize as the Nasicon type (space group $R\bar{3}c$). RbTi₂(PO₄)₃ was first reported and characterized by Masse (1970), who determined the cell parameters from a Guinier photograph as $a = 8.308$, $c = 23.59$ Å, and assigned the space group $R\bar{3}c$.

Single crystals of RbTi₂(PO₄)₃ were obtained by high-temperature growth. Rb₂CO₃, TiO₂ and NH₄H₂PO₄ in the molar ratio 2.25:1:3.3 were mixed in a platinum crucible, heated to 1373 K, kept at that temperature for 10 h, then cooled slowly (5° h⁻¹) to 923 K and removed from the furnace. After recovering the crystals from the solidified flux, their powder pattern showed that they consisted of a mixture of RbTi₂(PO₄)₃ (Masse, 1970) and a new compound which was identified by structure determination as Rb₃Ti₃P₅O₂₀ (Duhlev, 1994).

The bond lengths and angles (Table 2) are within the commonly observed range. The structure consists of a framework of corner-shared TiO₆ octahedra and PO₄ tetrahedra, with the Rb atoms situated in the tunnels within the framework (Fig. 1). A Ti₂P₃O₁₈ unit composed of two TiO₆ moieties linked through three PO₄ groups can be identified within the structure. These units alternate with Rb atoms along the $\bar{3}$ axis. Rb has six nearest O(2) neighbours [Rb—O(2) = 2.854 (2) Å, bond strength = 0.20 v.u.], three from each TiO₆ group above

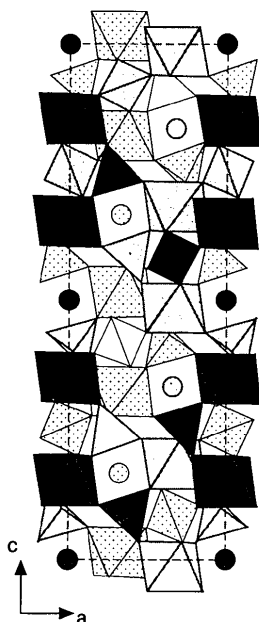


Fig. 1. Projection of the structure of RbTi₂(PO₄)₃ along $[0\bar{1}0]$. The TiO₆ and PO₄ polyhedra and Rb spheres centred at $y=0$ are dark, those at or around $y=\frac{1}{3}$ are lighter, $y=\frac{2}{3}$ are dotted and $y=1$ are empty.

and below. Bond–valence calculations (Brown & Altermatt, 1985) indicate that the six next-nearest neighbours, O(1), from the same two TiO₆ octahedra [Rb—O(1) = 3.366 (2) Å, bond strength = 0.05 v.u.], could be considered also, thus resulting in a coordination number for Rb of 12.

As initially found from the powder patterns (Masse, 1970), RbTi₂(PO₄)₃ is isostructural with NaTi₂(PO₄)₃ (Ivanov, Belokoneva, Egorov-Tismenko, Simonov & Belov, 1980) and KTi₂(PO₄)₃ (Lunezheva, Maksimov, Mel'nikov & Muradyan, 1989). The length and strength (Brown & Altermatt, 1985) of the main bonds in these structures is given in Table 3. Several structural characteristics change in a monotonic way with the increase of the ionic radius of the alkali metal from Na to Rb. While the c -axis length and the volume increase, the a axis shrinks. O(1) comes closer to the metal; the bond strength of the M —O(1) bond increases from 0 (no interaction) to 0.05, which could be considered as a bond, though rather weak. At the same time the severe distortion of the environment of Ti relaxes to form an almost regular octahedron.

Experimental

Crystal data

RbTi₂(PO₄)₃
 $M_r = 466.14$
 Trigonal
 $R\bar{3}c$
 $a = 8.2896$ (8) Å
 $c = 23.530$ (4) Å
 $V = 1400.3$ (3) Å³
 $Z = 6$
 $D_x = 3.32$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 72 reflections
 $\theta = 13$ – 19°
 $\mu = 7.78$ mm⁻¹
 Room temperature
 Rhombohedron
 $0.11 \times 0.11 \times 0.11$ mm
 Colourless

Data collection

Stoe Stadi-4 diffractometer
 2θ – ω scans
 Absorption correction:
 none ($\mu_r = 0.44$)
 1543 measured reflections
 660 independent reflections
 319 observed reflections
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 35^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -37 \rightarrow 37$
 3 standard reflections
 frequency: 50 min
 intensity variation: 5%

Refinement

Refinement on F
 $R = 0.0277$
 $wR = 0.0276$
 319 reflections
 30 parameters
 $w = 1/[\sigma^2(F) + 0.001114F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.02$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.80$ e Å⁻³

Extinction correction:
 Larson (1967)
 Extinction coefficient:
 0.0025 (1)
 Atomic scattering factors
 from *International Tables
 for X-ray Crystallography*
 (1974, Vol. IV) (for
 neutral atoms)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Rb	0	0	0	0.0165 (4)
Ti	0	0	0.15141 (4)	0.0023 (4)
P	0.71964 (17)	0	1/4	0.0022 (5)
O(1)	0.2126 (4)	0.1469 (4)	0.30069 (10)	0.0057 (10)
O(2)	0.4659 (4)	0.3029 (4)	0.23157 (10)	0.0080 (10)

Table 2. Selected geometric parameters (\AA , $^\circ$)

TiO ₆ octahedron				
Ti—O(1)	× 3	1.927 (3)	O(1)—Ti—O(1)	89.2 (1)
Ti—O(2)	× 3	1.944 (3)	O(1)—Ti—O(2)	97.2 (1)
			O(1)—Ti—O(2)	86.5 (1)
			O(1)—Ti—O(2)	172.3 (1)
			O(2)—Ti—O(2)	87.6 (1)
PO ₄ tetrahedron				
P—O(2)	× 2	1.517 (3)	O(2)—P—O(2)	110.7 (2)
P—O(1)	× 2	1.530 (3)	O(2)—P—O(1)	109.0 (2)
			O(2)—P—O(1)	107.1 (2)
			O(1)—P—O(1)	113.9 (2)
Environment around Rb				
Rb—O(2)	× 6	2.854 (2)	O(2)—Rb—O(2)	56.3 (1)
Rb—O(1)	× 6	3.366 (2)	O(1)—Rb—O(1)	65.0 (1)
			O(2)—Rb—O(1)	45.5 (1)
			O(2)—Rb—O(1)	79.0 (1)
			O(2)—Rb—O(1)	86.4 (1)

Table 3. Comparison of cell parameters (\AA), bond lengths (\AA) and bond strengths (v.u.) for isostructural MTi₂(PO₄)₃ compounds

	NaTi ₂ (PO ₄) ₃ *		KTi ₂ (PO ₄) ₃ †		RbTi ₂ (PO ₄) ₃	
	Length	Strength	Length	Strength	Length	Strength
a	8.502	—	8.367	—	8.290	—
c	21.833	—	23.074	—	23.530	—
M—O(2)	2.290	0.27	2.745	0.19	2.857	0.20
M—O(1)	3.788	0	3.418	0.03	3.366	0.05
Ti—O(1)	1.896	0.80	1.918	0.76	1.927	0.74
Ti—O(2)	2.107	0.45	1.942	0.71	1.944	0.71
P—O(2)	1.530	1.27	1.524	1.29	1.517	1.31
P—O(1)	1.533	1.25	1.530	1.27	1.530	1.27

* Ivanov, Belokoneva, Egorov-Tismenko, Simonov & Belov (1980).

† Lunezheva, Maksimov, Mel'nikov & Muradyan (1989).

Data collection, cell refinement and data reduction were carried out using Stoe software. Precise cell refinement was performed by double-step-scan technique. The atomic coordinates for KTi₂(PO₄)₃ (Lunezheva, Maksimov, Mel'nikov & Muradyan, 1989) were used as an initial model. The structure was refined using *SHELX76* (Sheldrick, 1976).

I thank Dr Pam Thomas, Warwick University, England, for providing me with the facilities for growing the crystals. This work was supported by a grant from the Optoelectronics Research Centre at Southampton University/University College London.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B41, 244–247.
 Duhlev, R. (1994). *Acta Cryst.* C50, 1523–1525.
 Ivanov, Yu. A., Belokoneva, E. L., Egorov-Tismenko, Yu. K., Simonov, M. A. & Belov, N. B. (1980). *Dokl. Akad. Nauk SSSR*, 252, 1122–1125; *Sov. Phys. Dokl.* 252, 420–422.
 Larson, A. C. (1967). *Acta Cryst.* 23, 664–665.
 Lunezheva, E. S., Maksimov, B. A., Mel'nikov, O. K. & Muradyan, L. A. (1989). *Kristallografiya*, 34, 611–614; *Sov. Phys. Crystallogr.* 34, 363–365.
 Masse, R. (1970). *Bull. Soc. Fr. Mineral. Cristallogr.* 93, 500–503.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Acta Cryst. (1994). C50, 1527–1529

Ammonium Heptachlorooxodiantimonate(III), (NH₄)₃[Sb₂Cl₇O]

ROBIN D. ROGERS* AND MARY L. JEZL

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA

(Received 14 September 1993; accepted 14 February 1994)

Abstract

Each Sb atom of the title compound is formally ψ -tetrahedral (AB_3E) with covalent bonds to two terminal Cl atoms and one bridging O atom. Three directed secondary interactions to three additional symmetrically bridging Cl atoms give each Sb atom a roughly octahedral coordination geometry. The bridging arising from the secondary interactions produces chains of [Sb₂Cl₄O]₂ units which propagate along the unit-cell *c* axis. The O, Cl(3) and Cl(4) atoms lie on crystallographic mirror planes, while Cl(5) resides on a twofold axis. The ammonium cations are hydrogen bonded to the Cl and O atoms.

Comment

The title compound was unintentionally isolated during the reaction of SbCl₃ with tetraethylene glycol in a 3:1 acetonitrile–methanol solution containing stoichiometric amounts of NH₄OH. The covalent Sb—Cl(1,2) and Sb—O distances are normal (Begley, Hall, Nunn & Sowerby, 1986; Hall & Sowerby, 1979; Rheingold, Landers, Dahlstrom & Zubieta, 1979). There are two types of bridging interaction produced by the secondary Sb—Cl contacts (Sawyer & Gillespie, 1986). The Cl(3) and the O atoms bridge two Sb atoms with an Sb...Sb separation of 3.582 (1) \AA . The Cl(5) and Cl(4) atoms form