

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

The unit cell is similar to that of the monoclinic mineral suanite. Hence, at the beginning of the refinement, the Mg, O and B atomic positions from the previously studied structure [which was determined using rotation and Weissenberg photography by trial-and-error and Fourier series methods (Takeuchi, 1952)] were used, but the refinement failed. The structure was then solved by direct methods (Gilmore, 1983). The positions of the Mg atoms were located by direct methods and those of other atoms from successive Fourier syntheses. The structure was refined anisotropically using full-matrix least-squares techniques.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *GCIF*, local program.

This work was financially supported by the National Science Foundation of China, the State Key Laboratory of Structural Chemistry, and the Nature Science Foundation of Fujian Province.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Block, S., Burley, G., Perloff, A. & Mason, R. D. (1959). *J. Res. Natl Bur. Stand.* **62**, 95–100.
- Davis, H. M. & Knight, M. A. (1945). *J. Am. Ceram. Soc.* **28**, 97–102.
- Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, Univ. of Glasgow, Scotland.
- Guo, G.-C., Cheng, W.-D., Chen, J.-T., Huang, J.-S. & Zhang, Q.-E. (1995). *Acta Cryst.* **C51**, 351–353.
- Kuzel, H. J. (1964). *Neues Jahrb. Mineral. Monatsh.* **12**, 357–360.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *CONTROL. An Automatic Package for Rigaku AFC Single-Crystal Diffractometers*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
- Mrose, M. E. & Fleischer, M. (1963). *Am. Miner.* **48**, 915–924.
- Mutluer, T. & Timucin, M. (1975). *J. Am. Ceram. Soc.* **116**, 196–197.
- Nefedov, E. I. (1961). *Mater. Vses. Nauchno Issled. Geol. Inst.* **45**, 243–247.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Takeuchi, Y. (1952). *Acta Cryst.* **5**, 574–581.
- Toropov, N. A. & Konovalov, P. F. (1940). *Zh. Fiz. Khim.* **14**, 1103–1109.

Acta Cryst. (1995). **C51**, 2471–2473

Tripraseodymium Chloride Bis-(orthosilicate), Pr₃(SiO₄)₂Cl

GUO-CONG GUO

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

YIN-GUI WANG AND JUN-NING ZHUANG

Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

JIU-TONG CHEN, JIN-SHUN HUANG AND QIAN-ER ZHANG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

(Received 7 November 1994; accepted 22 June 1995)

Abstract

Pr₃(SiO₄)₂Cl is isostructural with La₃(SiO₄)₂Cl. The Pr(1)O₇Cl polyhedron is irregular. The Pr(2)O₈Cl₂ polyhedron is a distorted square antiprism with the Cl atom capping distorted square faces. The site of Pr(2) can also be described as at the centre of a Pr(2)(SiO₄)₄Cl₂ octahedron. The structure comprises layers of Pr(2)(SiO₄)₄Cl₂ octahedra separated in the *a* direction by Pr(1) cations occupying the Pr(1)O₇Cl polyhedral sites. The Cl atom is four-coordinate forming a distorted square.

Comment

Few lanthanide chlorosilicates have been prepared. The structure of the rare earth chlorosilicate orthorhombic Yb₃(SiO₄)₂Cl was the first to be determined (Ayasse & Eick, 1973). Yamada, Kano & Tanabe (1978) reported the isostructural phases Y₃(SiO₄)₂Cl and Gd₃(SiO₄)₂Cl, and their luminescent properties when doped with Ce³⁺. Gravereau, Es-Sakhi & Fouassier (1988) reported the crystal structure of monoclinic La₃(SiO₄)₂Cl, and an X-ray structural study on a single crystal of orthorhombic La₃(SiO₄)Cl₅ (Gravereau, Es-Sakhi & Fouassier, 1989). The crystal structure of monoclinic La₃(Si₂O₇)Cl₃ was recently determined (Chen, Guo, Huang & Zhang, 1995). The present paper reports the crystal structure of Pr₃(SiO₄)₂Cl.

Pr(1) and Pr(2) have O₇Cl and O₈Cl₂ environments, respectively. The Pr(1)O₇Cl polyhedron is irregular (Fig. 1). The Pr(2)O₈Cl₂ polyhedron is a distorted

square antiprism with the Cl atoms capping the distorted square faces. The site of Pr(2) can also be described as being at the centre of a Pr(2)(SiO₄)₄Cl₂ octahedron, in which the SiO₄ ions are bidentate and chelate the Pr(2) ions (see Fig. 2). The SiO₄ tetrahedra are more regular.

The Pr(2)(SiO₄)₄Cl₂ octahedra share corners *via* the Cl atoms in the *b* direction, and edges composed of the two O(3) atoms in the *c* direction, forming layers of Pr(2)(SiO₄)₄Cl₂ octahedra.

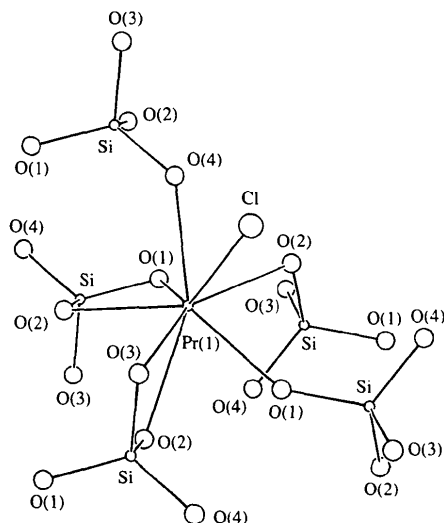


Fig. 1. The Pr(1)(SiO₄)₅Cl polyhedron.

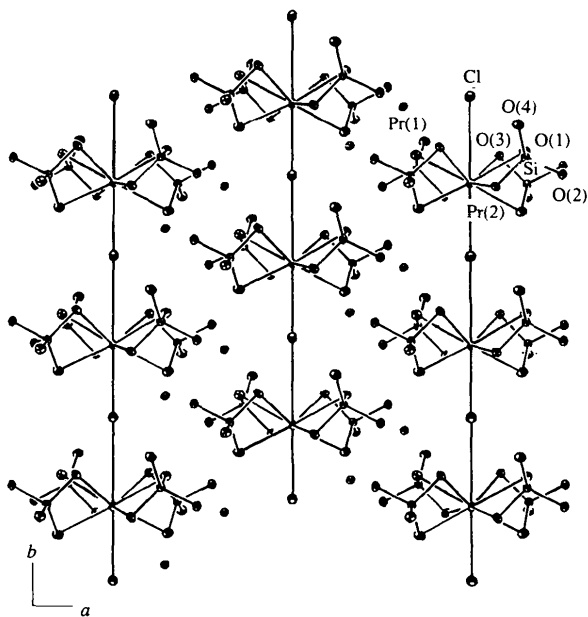


Fig. 2. Projection of the structure of Pr₃(SiO₄)₂Cl along the *c* direction [omitting the Pr(1)—O and Pr(1)—Cl bonds]. Displacement ellipsoids are drawn at the 50% probability level.

The structure is three-dimensional and comprises layers of Pr(2)(SiO₄)₄Cl₂ octahedra separated in the *a* direction by Pr(1) cations occupying the Pr(1)O₇Cl polyhedral sites (Fig. 2).

Two Pr(2)SiO₄ groups and two Pr(1) atoms form tunnels along the *c* direction, which accommodate the Cl atoms (see Fig. 2). The Cl atoms are coordinated to two Pr(1) and two Pr(2) atoms to form a distorted square, with Cl—Pr distances ranging from 2.8611 (7) to 3.510 (3) Å. The accommodation of Cl atoms in tunnels running in the *c* direction leads to strong thermal vibration of the Cl atoms along the *c* direction.

Experimental

The starting material was prepared from the powders PrOCl, Nb (99.5% purity; Shanghai Chemical Corporation) and Te (99.99% purity; Shanghai Chemical Corporation) (1:1:1) in an evacuated and sealed quartz ampoule. The reactants were progressively heated to 1223 K for 7 d, then air-quenched to room temperature. Pale green crystals, which are stable in air, were obtained. EDAX analysis of a single crystal for X-ray diffraction analysis showed that it contained the elements Pr, Cl and Si, and no Te.

Crystal data

Pr₃(SiO₄)₂Cl

M_r = 642.34

Monoclinic

C2/c

a = 14.300 (2) Å

b = 6.430 (1) Å

c = 8.754 (2) Å

β = 98.36 (2)°

V = 796.4 (5) Å³

Z = 4

D_x = 5.36 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 10–20°

μ = 18.67 mm⁻¹

T = 293 K

Rectangle

0.60 × 0.10 × 0.10 mm

Pale green

Data collection

Rigaku AFC-5R diffractometer

ω/2θ scans

Absorption correction:

ψ scan, spherical (see below)

T_{min} = 0.080, *T_{max}* =

0.117

1948 measured reflections

1820 independent reflections

1438 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.028

θ_{max} = 35.0°

h = 0 → 22

k = 0 → 10

l = -14 → 13

3 standard reflections

monitored every 200

reflections

intensity decay: 4.4%

Refinement

Refinement on *F*

R = 0.0323

wR = 0.0400

S = 1.06

1438 reflections

65 parameters

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.0212

Δρ_{max} = 1.63 e Å⁻³

Δρ_{min} = -2.64 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

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

	x	y	z	U_{eq}
Pr(1)	0.18380 (2)	0.10391 (5)	0.16958 (4)	0.00889 (6)
Pr(2)	1/2	0.07297 (8)	1/4	0.00996 (9)
Cl	0	0.0271 (4)	1/4	0.0305 (6)
Si	0.3420 (1)	-0.0553 (3)	-0.0251 (2)	0.0087 (3)
O(1)	0.1549 (3)	0.3854 (8)	0.3440 (5)	0.0124 (9)
O(2)	0.2389 (3)	-0.0572 (8)	0.4174 (5)	0.0105 (8)
O(3)	0.0781 (3)	0.3754 (8)	0.0295 (6)	0.0131 (9)
O(4)	0.1420 (4)	-0.2614 (8)	0.1443 (6)	0.015 (1)

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

Pr(1)—Cl	2.8611 (7)	Pr(2)—O(1 ⁱ)	2.551 (5)
Pr(1)—O(1)	2.442 (5)	Pr(2)—O(3 ^{iv})	2.686 (5)
Pr(1)—O(1 ⁱ)	2.718 (5)	Pr(2)—O(3 ^v)	2.686 (5)
Pr(1)—O(2)	2.430 (4)	Pr(2)—O(3 ^{vi})	2.559 (5)
Pr(1)—O(2 ⁱⁱⁱ)	2.607 (5)	Pr(2)—O(3 ^{vii})	2.559 (5)
Pr(1)—O(2 ⁱⁱⁱⁱ)	2.468 (5)	Pr(2)—O(4 ^v)	2.581 (5)
Pr(1)—O(3)	2.509 (5)	Pr(2)—O(4 ⁱⁱ)	2.581 (5)
Pr(1)—O(4)	2.426 (5)	Si—O(1 ⁱ)	1.625 (5)
Pr(2)—Cl ^{iv}	3.510 (3)	Si—O(2 ⁱⁱⁱ)	1.654 (5)
Pr(2)—Cl ^v	2.920 (3)	Si—O(3 ^{vi})	1.631 (5)
Pr(2)—O(1 ^{iv})	2.551 (5)	Si—O(4 ^{viii})	1.612 (5)
O(1 ⁱ)—Si—O(2 ⁱⁱⁱ)	107.2 (3)	Cl ^v —Pr(2)—Si	105.12 (3)
O(1 ⁱ)—Si—O(3 ^{vi})	105.7 (3)	Cl ^{iv} —Pr(2)—Si ^{ix}	105.12 (3)
O(1 ⁱ)—Si—O(4 ^{viii})	118.3 (3)	Cl ^v —Pr(2)—Si ^x	92.03 (3)
O(2 ⁱⁱⁱ)—Si—O(3 ^{vi})	106.2 (3)	Cl ^v —Pr(2)—Si ^{xi}	92.03 (3)
O(2 ⁱⁱⁱ)—Si—O(4 ^{viii})	109.1 (3)	Si—Pr(2)—Si ^{ix}	149.76 (5)
O(3 ^{vi})—Si—O(4 ^{viii})	109.7 (3)	Si—Pr(2)—Si ^x	90.72 (5)
Cl ^{iv} —Pr(2)—Cl ^v	180.00 (6)	Si—Pr(2)—Si ^{xi}	88.22 (5)
Cl ^{iv} —Pr(2)—Si	74.88 (3)	Si ^{ix} —Pr(2)—Si ^x	88.22 (5)
Cl ^{iv} —Pr(2)—Si ^{ix}	74.88 (3)	Si ^{ix} —Pr(2)—Si ^{xi}	90.72 (5)
Cl ^{iv} —Pr(2)—Si ^x	87.97 (3)	Si ^x —Pr(2)—Si ^{xi}	175.95 (5)
Cl ^{iv} —Pr(2)—Si ^{xi}	87.97 (3)		

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

The positions of the Pr atoms were located in space group $C2/c$ by direct methods (Gilmore, 1983). The coordinates of the remaining atoms were found in succeeding difference Fourier syntheses. To apply the radial part of the absorption correction, it was assumed that the crystal is spherical with a radius equal to the effective size of the crystal in the direction in which the ψ scans give a transmission factor of 1.0. The structure was refined by full-matrix least-squares methods.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF*, local program.

This work was funded by the National Nature Science Foundation of China, the State Key Laboratory of Structure Chemistry and the Natural Science Foundation of Fujian Province.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Ayasse, C. & Eick, H. A. (1973). *Inorg. Chem.* **12**, 1140–1143.
 Chen, J.-T., Guo, G.-C., Huang, J.-S. & Zhang, Q.-E. (1995). In preparation.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
 Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, Univ. of Glasgow, Scotland.
 Gravereau, P., Es-Sakhi, B. & Fouassier, C. (1988). *Acta Cryst.* **C44**, 1884–1887.
 Gravereau, P., Es-Sakhi, B. & Fouassier, C. (1989). *Acta Cryst.* **C45**, 1677–1679.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Molecular Structure Corporation (1988). *CONTROL. An Automatic Package for Rigaku AFC Single-Crystal Diffractometers*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Yamada, H., Kano, T. & Tanabe, M. (1978). *Mater. Res. Bull.* **13**, 101–108.

Acta Cryst. (1995). **C51**, 2473–2476

Potassium Vanadium Selenite, $\text{K}(\text{VO}_2)_3(\text{SeO}_3)_2$

WILLIAM T. A. HARRISON, LAURIE L. DUSSACK AND
ALLAN J. JACOBSON

*Department of Chemistry, University of Houston,
Houston, TX 77204-5641, USA*

(Received 15 March 1995; accepted 22 June 1995)

Abstract

The hydrothermal synthesis and single-crystal structure of potassium vanadium(V) selenite, $\text{K}(\text{VO}_2)_3(\text{SeO}_3)_2$, are reported. $\text{K}(\text{VO}_2)_3(\text{SeO}_3)_2$ is a layered phase based on a hexagonal tungsten-oxide-like array of corner-sharing VO_6 octahedra capped by Se atoms, and is isostructural with $\text{NH}_4(\text{VO}_2)_3(\text{SeO}_3)_2$.

Comment

$\text{K}(\text{VO}_2)_3(\text{SeO}_3)_2$, which is isostructural with $\text{NH}_4(\text{VO}_2)_3(\text{SeO}_3)_2$ (Vaughey, Harrison, Dussack & Jacobson, 1994), is another example of a phase built up from sheets of vertex-sharing VO_6 octahedra like those of hexagonal tungsten oxide (HTO) (Figlarz, 1989). This layer configuration results in octahedral 'three-rings' and 'six-rings' (Fig. 1). Half the three-rings on each side of the V/O layer are capped by Se atoms (as $[\text{SeO}_3]^{2-}$ selenite groups), *i.e.* capping occurs on both faces of the infinite VO_6 sheets (Fig. 2). The K cations, which occupy six-coordinate sites in the inter-layer region, provide charge balancing.