Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

The diphyllosilicate $Rb_2(VO)_2[Si_8O_{19}]$

Sebastian Prinz,* Karine M. Sparta and Georg Roth

Institut für Kristallographie der RWTH Aachen, Jägerstrasse 17-19, 52066 Aachen, Germany
Correspondence e-mail: prinz@xtal.rwth-aachen.de

Received 7 December 2007
Accepted 21 December 2007
Online 16 February 2008

Dirubidium divanadyl phyllooctasilicate, $Rb_2(VO)_2[Si_8O_{19}]$, is the first known anhydrous diphyllosilicate containing V^{IV}. The structure consists of silicate double layers which are separated by $[V_2O_8]^{8-}$ dimers and is related to that of the compounds $A_2Cu_2[Si_8O_{19}]$ (A = Rb or Cs), although the title compound crystallizes in a noncentrosymmetric orthorhombic space group. The silicate double layers contain four tetrahedrally coordinated Si sites in general positions and 12 O sites, nine in general positions and the other three on mirror planes. The vanadyl dimers have two square-pyramidally coordinated V sites (site symmetry m). There are two different 10- and 12-fold coordinated Rb sites with site symmetry m, one of which is a split position located between the dimers in the interlayer space, while the other is in a channel within the silicate layer.

Comment

Low-dimensional V^{IV} and mixed-valent $V^{IV,V}$ compounds are of great interest because of their peculiar magnetic properties, as evidenced by the two-dimensional spin-gap compound CaV_4O_9 (Taniguchi *et al.*, 1995) or the spin-Peierls system α-NaV_2O_5 (Smolinski *et al.*, 1998). Among the few known silicates containing V^{IV}, $Li_2(VO)SiO_4$ has been considered an ideal example of a frustrated two-dimensional square-lattice antiferromagnet (Millet & Satto, 1998). Likewise, few anhydrous double-layer silicates have been reported, among them the Cu^{II}-bearing compounds of general formula $A_2Cu_2[Si_8O_{19}]$ (A = Rb or Cs) (Heinrich & Gramlich, 1982; Watanabe & Kawahara, 1993). These two isomorphous compounds crystallize in the space group $P2_1/m$. The staggered silicate double layers consist of corner-sharing SiO_4 tetrahedra, with $[Cu_2O_6]^{8-}$ dimers (formed by two tetrahedrally distorted square-planar edge-sharing CuO_4 units) interleaved between adjacent double layers.

The title vanadyl compound (Figs. 1–3) is related to the copper phases but differs in certain key respects. Firstly it crystallizes in the noncentrosymmetric space group $Pmc2_1$, and secondly the silicate double layers of the vanadyl compound are linked differently from those in the copper compounds. In both structures, each single sheet can be described in terms of rings of six corner-sharing SiO_4 tetrahedra which link adjacent single sheets into a double layer (Figs. 1 and 3). Two crystallographically distinct silicate rings can be distinguished in the title compound. In the first kind of silicate ring, five of the six SiO_4 tetrahedra are bonded to neighbouring SiO_4 tetrahedra in the bc plane; only the $Si4O_4$ tetrahedra of adjacent silicate layers share corners and link the sheets into a double layer. In the second kind of silicate ring,

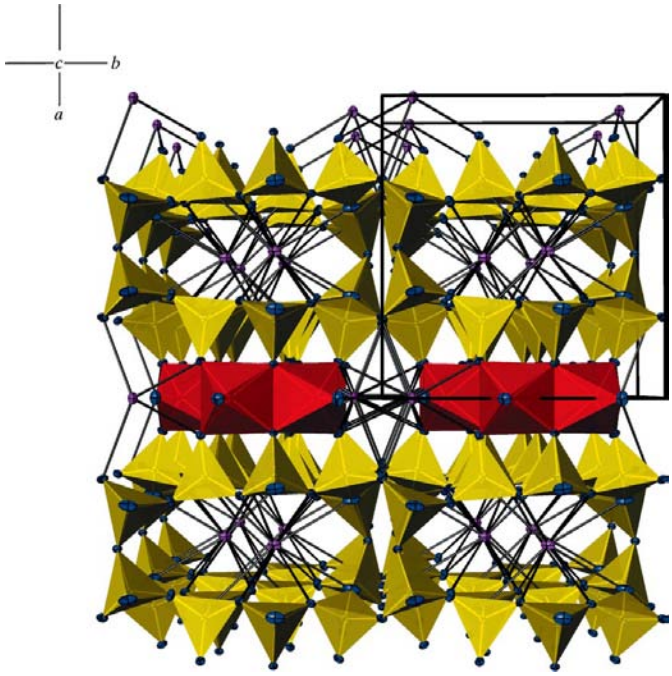

Figure 1
A view of the $Rb_2(VO)_2[Si_8O_{19}]$ structure in a perspective ab projection. Displacement ellipsoids are drawn at the 50% probability level and the unit cell is indicated by black lines. VO_5 square pyramids are dark and SiO_4 tetrahedra are light. Note the Rb filled channels along c.

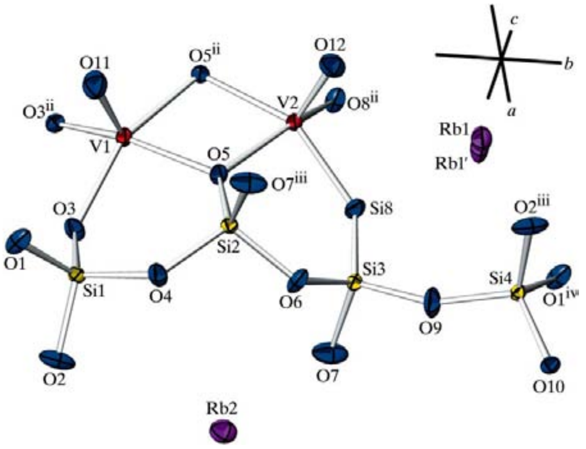

Figure 2
A view of the Si and V polyhedra that make up the framework of $Rb_2(VO)_2[Si_8O_{19}]$. Displacement ellipsoids are drawn at the 50% probability level. The $[V_2O_8]^{8-}$ dimer is linked to the $Si1O_4$, $Si2O_4$ and $Si3O_4$ tetrahedra *via* corner sharing, while the $Si4O_4$ tetrahedra interlink the separate silicate layers of a double layer by sharing atom O10. [Symmetry codes: (ii) $-x, y, z$; (iii) $x, -y + 1, z + \frac{1}{2}$; (iv) $x, y + 1, z$.]

DOI: 10.1107/S0108270107068205

there are two Si4O_4 tetrahedra per ring that link adjacent silicate sheets. In the copper compounds, in contrast, there is only one type of six-membered ring, with two linking SiO_4 tetrahedra in neighbouring positions.

In the title compound, $[V_2O_8]^{8-}$ dimers of edge-sharing VO_5 pyramids, replacing the $[Cu_2O_6]^{8-}$ dimers, link adjacent silicate double layers (Fig. 1). The two independent V atoms occupy special positions of site symmetry *m*. The square-pyramidal oxygen coordination, with one short vanadyl bond and four basal V—O bonds that are almost equal in length, is typical of V^{IV} (Schindler *et al.*, 2000). The pyramidal bases are inclined with respect to each other around the common O5–O5^{ii} edge [symmetry code: (ii) $-x, y, z$]; the apices show a *syn*-orthogonal arrangement (Plass, 1996), *i.e.* they both point to the same side of the dimeric unit (Fig. 2), which has rarely been observed in other substances. The V1—O12^{i} and V2—O12^{i} distances [symmetry code: (i) $-x, -y+1, z-\frac{1}{2}$] between the apical O atom of the V2O_5 pyramid and its next V1 and V2 neighbours along *c* are longer than the value of 2.6 Å usually considered the upper limit for a valid V—O distance of the *trans* bonds in [1+4+1] coordination (Schindler *et al.*, 2000). Therefore, the V coordination is discussed in terms of VO_5 pyramids sharing edges rather than distorted VO_6 octahedra sharing faces.

The disordered Rb1/Rb1′ ions are located in between the dimers in channels parallel to *c*, while the Rb2 ions are enclosed within the double layers. In a projection on to the *bc* plane, they can be seen to occupy the channels formed by the six-tetrahedron silicate rings parallel to *a* in a zigzag manner (Fig. 3). Rb1/Rb1′ are partially disordered sites that are 10-fold coordinated by oxygen, with Rb—O distances ranges of 2.849 (4)–3.585 (4) and 2.837 (7)–3.366 (6) Å, respectively. The Rb2 site is 12-fold coordinated by oxygen (distorted hexagonal prism), with Rb—O distances in the range 3.087 (3)–3.352 (3) Å.

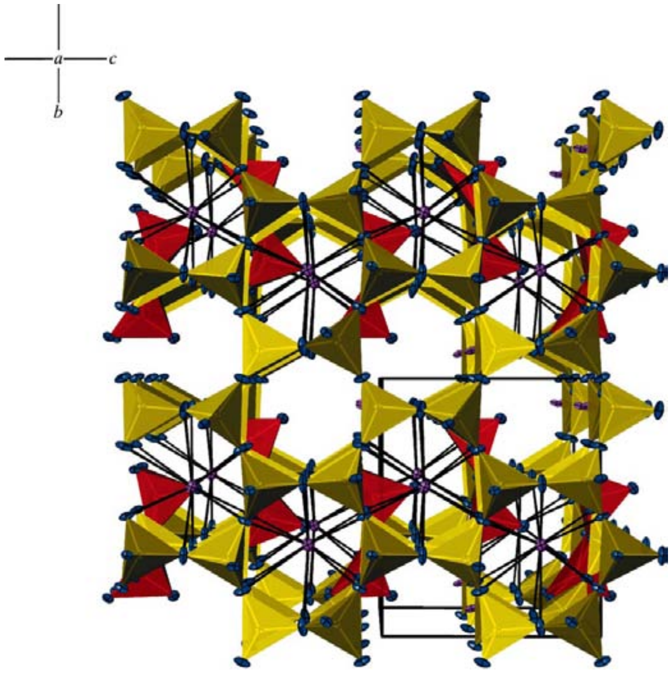

Figure 3
A view of the $Rb_2(VO)_2[Si_8O_{19}]$ structure in a perspective *bc* projection. Displacement ellipsoids are drawn at the 50% probability level and the unit cell is indicated by black lines. VO_5 square pyramids are dark and SiO_4 tetrahedra are light. Note the zigzag pattern of channels occupied by Rb2 and the empty channels with two linking Si4O_4 tetrahedra per six-tetrahedron ring.

Experimental

$RbVO_3$ was prepared by the decomposition of stoichiometric amounts of Rb_2CO_3 in the presence of V_2O_5 in air. The resulting single-phase $RbVO_3$ powder and V_2O_3 were mixed in the molar ratio 2:1 and an excess amount of SiO_2 was added. The mixture was sealed in an evacuated SiO_2 glass ampoule and heated in a furnace at 1123 K for 5 d, followed by subsequent furnace cooling. From the dark-grey powder obtained, blue–green plate-shaped crystals were isolated, which were suitable for analysis by single-crystal X-ray diffraction.

Crystal data

$Rb_2(VO)_2[Si_8O_{19}]$
$M_r = 833.54$
Orthorhombic, $Pmc2_1$
$a = 11.0513\ (9)$ Å
$b = 10.2765\ (6)$ Å
$c = 8.7052\ (6)$ Å
$V = 988.64\ (12)$ Å^3
$Z = 2$
Mo *Kα* radiation
$\mu = 6.43$ mm^{-1}
$T = 301\ (2)$ K
0.3 × 0.2 × 0.08 mm

Data collection

Stoe IPDSII image-plate diffractometer
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
$T_{min} = 0.251$, $T_{max} = 0.648$
37398 measured reflections
4022 independent reflections
3669 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.065$
$S = 1.10$
4022 reflections
165 parameters
2 restraints
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}
Absolute structure: Flack (1983), with 2128 Friedel pairs
Flack parameter: −0.004 (6)

Table 1
Selected geometric parameters (Å, °).

V1—O11	1.590 (4)	V1—V2	3.1525 (9)
V1—O3	1.949 (2)	V2—O12	1.595 (4)
V1—O5	2.029 (2)	V2—O8	1.941 (2)
V1—O12^{i}	2.836 (4)	V2—O5	2.021 (2)
O11—V1—O3	104.31 (13)	O12—V2—O8	104.83 (12)
O11—V1—O5	101.99 (13)	O12—V2—O5	105.33 (12)
O3—V1—O5	92.17 (9)	O8—V2—O5	88.86 (8)

Symmetry code: (i) $-x, -y+1, z-\frac{1}{2}$.

During refinement, high maximum and minimum residual electron densities of *ca* ±1.5 e Å^{-3} were observed. The highest peak was located very close to the Rb1 site. When a split position Rb1′ was introduced, expressing the partial disorder of the Rb1 site, the residual electron density was reduced substantially to *ca* ±0.6 e Å^{-3}. The sum of the occupancies of the Rb1 and Rb1′ sites was restrained to be equal to 1 and they refined to values of 0.809 (4) and 0.191 (4), respectively. The anisotropic displacement parameters of the two sites were restrained to be equal.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors gratefully acknowledge the financial support of this work by the Deutsche Forschungsgemeinschaft (DFG).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3119). Services for accessing these data are described at the back of the journal.

References

Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Heinrich, A. & Gramlich, V. (1982). *Naturwissenschaften*, **69**, 142–143.

Millet, P. & Satto, C. (1998). *Mater. Res. Bull.* **33**, 1339–1345.

Plass, W. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 627–631.

Schindler, M., Hawthorne, F. C. & Baur, W. H. (2000). *Chem. Mater.* **12**, 1248–1259.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Smolinski, H., Gros, C., Weber, W., Peuchert, U., Roth, G., Weiden, M. & Geibel, C. (1998). *Phys. Rev. Lett.* **80**, 5164–5167.

Stoe & Cie (1996). *X-SHAPE* and *X-RED*. Stoe & Cie GmbH, Darmstadt, Germany.

Stoe & Cie (2002). *X-AREA*. Stoe & Cie GmbH, Darmstadt, Germany.

Taniguchi, S., Nishikawa, T., Yasui, Y., Kobayashi, Y., Sato, M., Nishioka, T., Kontani, M. & Sano, K. (1995). *J. Phys. Soc. Jpn*, **64**, 2758–2761.

Watanabe, I. & Kawahara, A. (1993). *Acta Cryst.* C**49**, 854–856.