inorganic compounds

Ba$_3$Li$_2$V$_2$O$_7$Cl$_4$, a new vanadate with a channel structure

Thomas Reeswinkel,‡ Karine M. Sparta* and Georg Roth

Institut für Kristallographie der RWTH Aachen, Jägerstrasse 17–19, 52056 Aachen, Germany

Correspondence e-mail: sparta@xtal.rwth-aachen.de

The tribarium dilithium divanadate tetrachloride Ba$_3$Li$_2$-V$_2$O$_7$Cl$_4$ is a new vanadate with a channel structure and the first known vanadate containing both Ba and Li atoms. The structure contains four non-equivalent Ba^{2+} sites (two with m and two with $2/m$ site symmetry), two Li$^+$ sites, two nonmagnetic V^{5+} sites, five O^{2-} sites (three with m site symmetry) and four Cl$^-$ sites (m site symmetry). One type of Li atom lies in LiO$_4$ tetrahedra (m site symmetry) and shares corners with VO$_4$ tetrahedra to form eight-tetrahedron Li$_3$V$_5$O$_{24}$ rings and six-tetrahedron Li$_2$V$_4$O$_{18}$ rings; these rings are linked within porous layers parallel to the ab plane and contain Ba^{2+} and Cl$^-$ ions. The other Li atoms are located on inversion centres and form isolated chains of face-sharing LiCl$_6$ octahedra.

Comment

Porous crystalline structures containing large cages or channels have been widely investigated, since they are good candidates for shape-selective molecular sieves, as in the well known case of zeolites, or can exhibit interesting ionic transport properties. The title compound contains channels delimited by LiO$_4$ and VO$_4$ tetrahedra and shows an unusual linkage pattern of tetrahedron rings, not observed previously in silicates due to the very rare T:O ratio of 3:7 (where T is the number of cations in tetrahedral coordination and O is the number of O atoms).

The structure contains Li1O$_4$ and VO$_4$ tetrahedra (Fig. 1), which share corners to form eight-tetrahedron Li$_3$V$_5$O$_{24}$ heterorings connected into infinite layers parallel to the ab plane (Fig. 2). These layers are stacked in pairs along the c direction, giving rise to puckered chains of four-tetrahedron Li$_2$V$_2$O$_{12}$ rings parallel to b and six-tetrahedron Li$_2$V$_4$O$_{12}$ rings within the ac plane (Fig. 3). Thus, the linkage of the LiO$_4$ and VO$_4$ tetrahedra produces porous LiV$_2$O$_7$ double layers parallel to the ab plane. The only occurrence of six-tetra-

‡ Present address: Lehrstuhl für Werkstoffchemie der RWTH Aachen, Kopernikusstrasse 16, 52074 Aachen, Germany.

hedron rings in V^{5+} compounds has been reported for LiZnVO$_4$ (Capsoni *et al.*, 2006), but in that case the central cations of the tetrahedra do not lie on the same plane. From the directedness of the tetrahedra and the ordering of the Li1
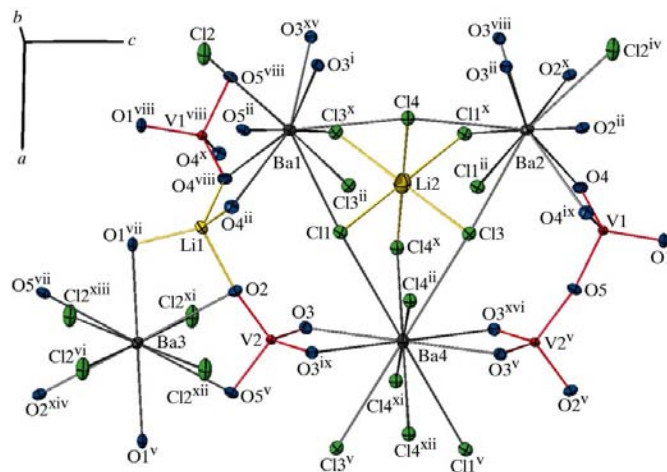

Figure 1
A view of the asymmetric unit of Ba$_3$Li$_2$V$_2$O$_7$Cl$_4$, projected on to the ac plane. Displacement ellipsoids are drawn at the 50% probability level. Symmetry-related atoms have been added to show the coordination environments and some polyhedral connectivities. [Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (iv) $-x, -y, -z + 1$; (v) $-x + 1, -y, -z + 1$; (vii) $x, y, z - 1$; (viii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ix) $x, -y, z$; (x) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (xi) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (xii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (xiii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (xiv) $-x + 1, y, -z$; (xv) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (xvi) $-x + 1, y, -z + 1$.]
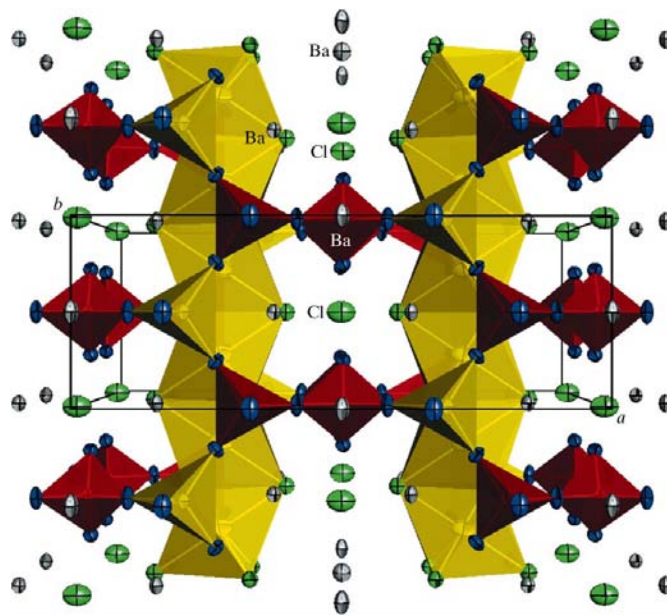

Figure 2
A perspective polyhedral representation of the crystal structure of Ba$_3$Li$_2$V$_2$O$_7$Cl$_4$, projected on to the ab plane. Displacement ellipsoids are drawn at the 80% probability level. Within the eight-tetrahedron rings, the VO$_4$ tetrahedra are the darker polyhedra and the LiO$_4$ tetrahedra the lighter polyhedra. The chains of face-sharing LiO$_6$ octahedra can be seen in the background.

and V atoms, the six-tetrahedron $Li_2V_4O_{12}$ rings bear a resemblance to the $Al_2Si_4O_{18}$ rings found in ordered cordierites (Knorr *et al.*, 1999; Malcherek *et al.*, 2001).

Two channels can be distinguished that are parallel to the monoclinic *b* axis. The smaller channel is delimited by the puckered $Li_2V_2O_{10}$ chain of four-tetrahedron $Li_2V_2O_{12}$ rings within an LiV_2O_7 layer and is empty. The larger channel is formed by the six-tetrahedron $Li_2V_4O_{18}$ rings and is filled by atoms Ba3 and Cl2. The interlayer space is filled by atoms Ba1, Ba2 and Ba4 and infinite chains of face-sharing Li_2Cl_6 octahedra. No other instance of such infinite Li_2Cl_6 chains has been found in the literature.

Within the largest channel, the Ba3 atoms have a planar sixfold coordination of O atoms in the *ac* plane (Fig. 4*a*). Along the direction of the channels, four Cl2 atoms surround Ba3 in a rectangular planar coordination. This is the first occurrence of a BaO_6Cl_4 group with a planar hexagonal arrangement of O atoms to date; the only known compound with a similar environment for Ba is $Ba_9Cu_7O_{15}Cl_2$ (Kipka & Müller-Buschbaum, 1976), containing a BaO_6Cl_2 group, where the two Cl atoms are located on opposite sides of the BaO_6 plane. The displacement ellipsoid of Ba3 is elongated in the *b* direction, towards the Cl atoms. The other three Ba atoms fill the interlayer space and surround the Li_2O_6 chains. The environments of atoms Ba1 and Ba2 are very similar to each other; both are surrounded by six O atoms and five Cl atoms. However, while Ba1 is connected *via* O atoms to two VO_4 tetrahedra of an $Li_2V_4O_{18}$ ring, Ba2 is linked to a $V2O_4$ tetrahedron and an $Li1O_4$ tetrahedron of a neighbouring ring. BaO_6Cl_5 groups have also been observed in verplanckite (Kampf *et al.*, 1973). On the other hand, Ba4 is surrounded by four O atoms in a rectangular planar coordination parallel to the *bc* plane and is also eightfold coordinated by Cl atoms.

This environment is similar to that of the Ba1 atom in Ba_5-$(Mg_{0.4}Mn_{0.6})Mn(V_2O_7)_2Cl_6$ (Müller-Buschbaum & Rettich, 1997). The displacement ellipsoids of Ba1, Ba2 and Ba4 are also elongated along the monoclinic *b* direction; within the *ac* plane, they all point towards the Li_2Cl_6 chain.

The $V1O_4$ and $V2O_4$ tetrahedra possess very similar bond lengths, although their connectedness is different. The $V1O_4$ tetrahedron shares all its corners with one $V2O_4$ and three $Li1O_4$ tetrahedra, while two O atoms in the $V2O_4$ tetrahedron point towards the Ba4 atom in the interlayer space. The $Li1O_4$ tetrahedron shares all its corners solely with VO_4 tetrahedra. The Li_2Cl_6 octahedron possesses four Li2—Cl bonds with similar lengths, pointing towards the Ba1 and Ba2 atoms, and two longer Li2—Cl4 bonds pointing towards Ba4. The equivalent isotropic displacement parameter for the Li2 atoms within the Li_2Cl_6 chains is twice as large as for the tetrahedrally coordinated Li1 atoms.

The displacement ellipsoids of atoms O1, O2 and O4 at the corners of the $Li1O_4$ tetrahedron show a pronounced elongation perpendicular to the Li1—O bonds, indicating a possible rigid body rotation of the $Li1O_4$ tetrahedron within the $Li_2V_4O_{18}$ ring. Atoms Cl1, Cl3 and Cl4 have quasi-isotropic displacement parameters; they are sixfold coordinated by four Ba and two Li2 atoms. The displacement ellipsoid of Cl2 is strongly elongated in the *a* direction, with an equivalent isotropic displacement parameter almost twice as large as for the other Cl atoms, due to a weaker interatomic potential and repulsive forces from the closest anions (Fig. 4*b*) rather than from a possible ionic conductivity. Atom Cl2 is tetrahedrally coordinated by four Ba atoms. There are two V2 atoms close to Cl2, but their influence is screened by atoms O2, O3 and O5 of the $V2O_4$ tetrahedron between V2 and Cl2. These O atoms should force the largest axis of the displacement tensor of Cl2 towards the middle of the oxygen-free faces of $Cl2Ba_4$ (parallel to *a*). The $Cl2Ba_4$ tetrahedron shares an edge with a second $Cl2Ba_4$ group along *c*, resulting in a short Cl2···Cl2 distance of 3.3133 (17) Å.
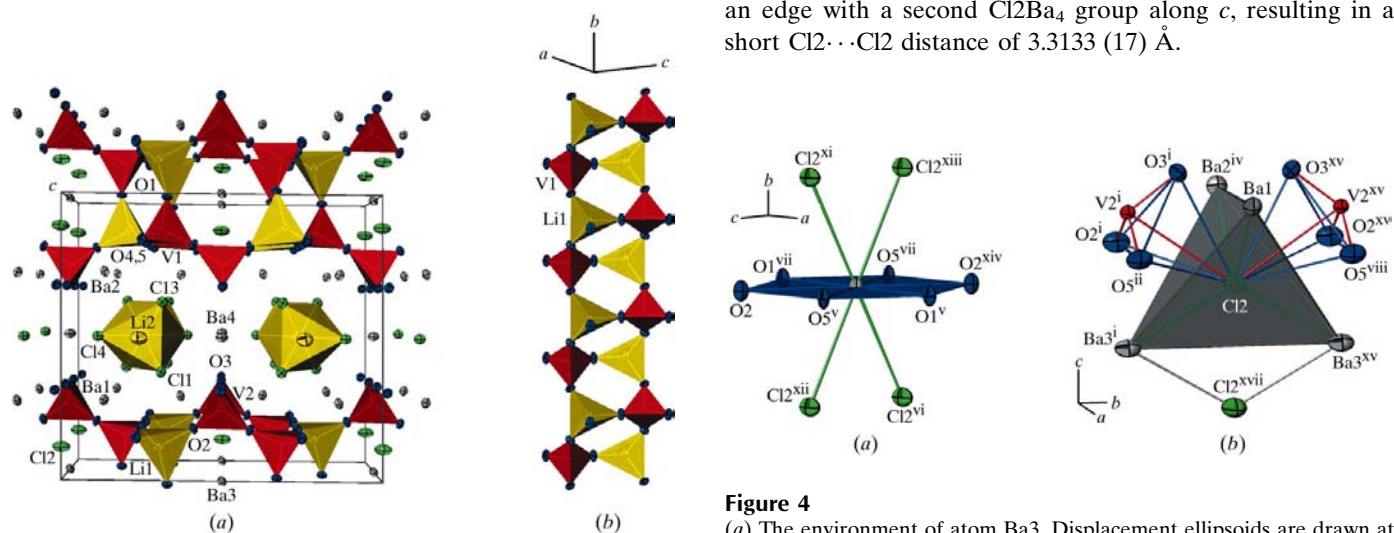

Figure 3
(*a*) A perspective polyhedral representation of the crystal structure of $Ba_3Li_2V_2O_7Cl_4$, projected on to the *ac* plane. Displacement ellipsoids are drawn at the 80% probability level. (*b*) A view of the puckered chains of four-tetrahedron $Li_2V_2O_{12}$ rings parallel to *b*.

Figure 4
(*a*) The environment of atom Ba3. Displacement ellipsoids are drawn at the 50% probability level. (*b*) The environment of atom Cl2. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (iv) $-x, -y, -z + 1$; (v) $-x + 1, -y, -z + 1$; (vi) $-x + \frac{1}{2}, -y - \frac{1}{2}, -z$; (vii) $x, y, z - 1$; (viii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (xi) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (xii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (xiii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (xiv) $-x + 1, y, -z$; (xv) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (xvii) $-x, y, -z$.]

inorganic compounds

Experimental

$Ba_3Li_2V_2O_7Cl_4$ was prepared *via* a molten salt reaction as a by-product during the synthesis of the V^{4+} compound BaV_4O_9 (Reeswinkel *et al.*, 2007). A mixture of LiCl, RbCl and $BaCl_2$ was first prepared by drying the components separately at 413 K and mixing them in the molar ratio 2:1:1. VO_2 powder was added to the mixture in a flux to a VO_2 molar ratio of 10:1. The sample was ground, placed in an Al_2O_3 crucible and dried briefly to remove water from the hygroscopic $BaCl_2$. The crucible was then placed in a glass test tube within a glass gas-washing bottle. The sample was heat treated at 713 K for 24 d in a vertical tube furnace. During that time, argon gas (Ar 5.0) was flushed through the bottle. At the end of the growth process, the sample was cooled slowly to room temperature.

Crystal data

$Ba_3Li_2V_2O_7Cl_4$
$M_r = 781.58$
Monoclinic, $C2/m$
$a = 16.1215 (14)$ Å
$b = 5.7630 (3)$ Å
$c = 14.3795 (13)$ Å
$\beta = 90.592 (7)°$

$V = 1335.90 (18)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 10.87$ mm^{-1}
$T = 293 (2)$ K
$0.19 \times 0.15 \times 0.12$ mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: numerical
(X-$SHAPE$; Stoe & Cie, 1996)
$T_{min} = 0.141$, $T_{max} = 0.295$

22838 measured reflections
3141 independent reflections
2763 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.035$
$S = 1.61$
3141 reflections

106 parameters
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -1.27$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ba1—O3^i	2.7589 (16)	Ba3—Cl2^{vi}	3.3238 (5)
Ba1—O4^{ii}	2.8377 (18)	Ba4—O3	2.8838 (16)
Ba1—Cl2	3.1660 (9)	Ba4—Cl4^{iii}	3.4269 (4)
Ba1—Cl1	3.1824 (8)	Ba4—Cl3	3.4624 (8)
Ba1—Cl4	3.2108 (8)	Ba4—Cl1	3.4927 (8)
Ba1—O5^{iii}	3.3067 (11)	V1—O1	1.670 (2)
Ba1—Cl3^{iii}	3.3179 (4)	V1—O4	1.6945 (16)
Ba2—O3^{ii}	2.7325 (16)	V1—O5	1.802 (2)
Ba2—O4	2.8439 (16)	V2—O2	1.677 (2)
Ba2—Cl2^{iv}	3.1971 (11)	V2—O3	1.6891 (16)
Ba2—Cl4	3.2490 (8)	V2—O5^v	1.810 (2)
Ba2—O2^{iii}	3.2616 (12)	Li1—O1^{vii}	1.918 (6)
Ba2—Cl3	3.2759 (8)	Li1—O4^{ii}	1.942 (4)
Ba2—Cl1^{iii}	3.3625 (4)	Li1—O2	2.005 (6)
Ba3—O1^v	2.746 (2)	Li2—Cl1^{viii}	2.4803 (6)
Ba3—O5^v	2.918 (2)	Li2—Cl3^{viii}	2.4840 (6)
Ba3—O2	2.999 (2)	Li2—Cl4^{viii}	2.6094 (6)

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

Despite the fact that the unit-cell metric and the positions of the Ba, Li, Cl and O atoms suggest the orthorhombic space group *Cmmm*, the structure has to be described in the monoclinic crystal system. The internal R value of the data set before absorption correction is 9% for the $2/m$ Laue class and 24.9% for the *mmm* Laue class. Furthermore, the *Cmmm* symmetry would not allow the ordering of the V ($Z = 23$) and Li ($Z = 3$) atoms within the six-tetrahedron $Li_2V_4O_{18}$ rings, although it is clearly visible in the monoclinic symmetry.

Structure solution using direct methods gave the positions of the Ba, V, O and Cl atoms. The Li atoms were located subsequently from a residual electron-density analysis after refinement of the structure. All atoms could be refined with anisotropic displacement parameters. A possible presence of rubidium from the salt mixture on the barium sites was tested by site-occupancy refinement and proved to be insignificant.

Data collection: X-$AREA$ (Stoe & Cie, 2000); cell refinement: X-$AREA$; data reduction: X-RED (Stoe & Cie, 1996); program(s) used to solve structure: $SIR2002$ (Burla *et al.*, 2003); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 2008); molecular graphics: $ATOMS$ (Dowty, 2000); software used to prepare material for publication: $WinGX$ (Version 1.70.01; Farrugia, 1999).

References

Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
Capsoni, D., Bini, M., Massarotti, V., Mustarelli, P., Belotti, F. & Galinetto, P. (2006). *J. Phys. Chem. B*, **110**, 5409–5415.
Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kampf, A. R., Khan, A. A. & Baur, W. H. (1973). *Acta Cryst.* B**29**, 2019–2021.
Kipka, R. & Müller-Buschbaum, H. (1976). *Z. Naturforsch. Teil B*, **31**, 1067–1069.
Knorr, K., Meschke, M. & Winkler, B. (1999). *Phys. Chem. Miner.* **26**, 521–529.
Malcherek, T., Domeneghetti, M. C., Tazzoli, V., Ottolini, L., McCammon, C. & Carpenter, M. A. (2001). *Am. Mineral.* **86**, 66–79.
Müller-Buschbaum, H. & Rettich, R. (1997). *Z. Naturforsch. Teil B*, **52**, 457–461.
Reeswinkel, T., Prinz, S., Sparta, K. M. & Roth, G. (2007). *Acta Cryst.* B**63**, 270–276.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (1996). *X-SHAPE* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2000). *X-AREA*. Stoe & Cie, Darmstadt, Germany.