

Li(VO₂)₃(TeO₃)₂

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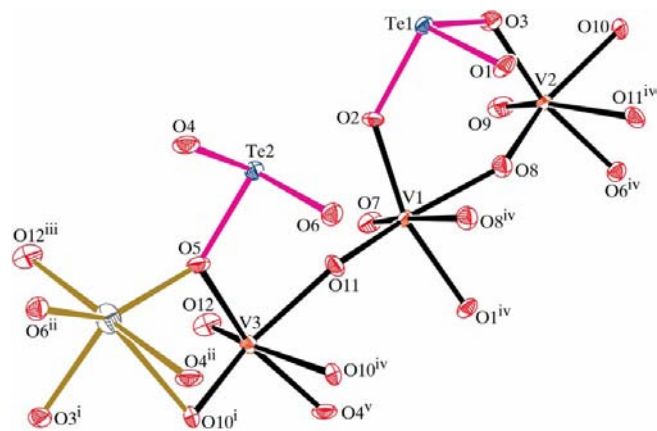
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The title compound, lithium tris[dioxidovanadium(V)] bis[trioxidotellurium(IV)], contains chains of edge-sharing distorted VO₆ octahedra. The pyramidal TeO₃ groups crosslink the chains into sheets. Finally, an Li⁺ cation adopting an unusual capped trigonal-bipyramidal LiO₆ geometry bridges the layers to complete a three-dimensional structure.

Comment

The title compound, (I), is the second lithium vanadium tellurite to be characterized by single-crystal diffraction, complementing LiVO₂(TeO₃) (Darriet, 1973). Although vanadium can occur in the III, IV and V oxidation states in inorganic solids (see, for example, Hung *et al.*, 2002; Calin *et al.*, 2003), both these compounds contain only vanadium(V) ions.

The constituent polyhedra for (I) are shown in Fig. 1 and selected geometric data are listed in Table 1. Atom V1 adopts a distorted octahedral coordination with respect to its six O-atom neighbours, with one characteristic short formal double V=O 'vanadyl' bond [V–O = 1.582 (5) Å], four V–O bonds of intermediate length, and one longer V–O bond [2.325 (5) Å] *trans* to the V=O bond. Atoms V2 and V3 also

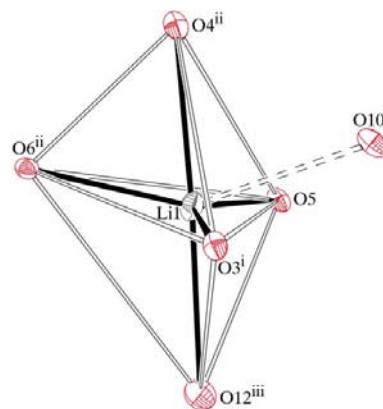
**Figure 1**

The asymmetric unit of (I), expanded to show the metal coordination polyhedra. Displacement ellipsoids are drawn at the 70% probability level. Symmetry codes are as in Table 1.

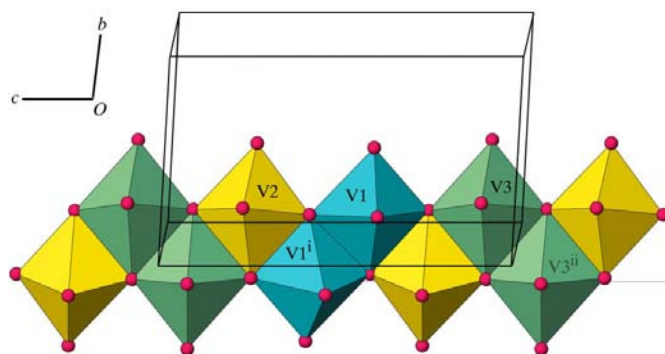
possess vanadyl links, with V=O < 1.6 Å and four V–O bonds in the range 1.75–2.03 Å. The sixth bond, *trans* to the vanadyl link, which completes the distorted octahedron for these atoms (V–O > 2.5 Å), is substantially longer than the equivalent bond for V1.

These very distorted coordination polyhedra are highly characteristic of vanadium(V) and can be correlated theoretically with a second-order Jahn–Teller distortion (Kunz & Brown, 1995) for this *d*⁰ metal ion. The bond-valence sums (BVS), in valence units, for V1, V2 and V3, calculated by the Brown (1996) method, are 5.10, 5.10 and 5.02, respectively (expected 5.00).

Both Te^{IV} atoms in (I) display pyramidal geometries with respect to their three closest O-atom neighbours, with Te–O < 2.00 Å, and it is usually assumed that an unseen stereochemically active lone pair of electrons occupies the fourth tetrahedral vertex about Te (Wells, 1962). Te1 is displaced from the O1/O2/O3 plane by 0.946 (3) Å, and Te2 is displaced from the O4/O5/O6 plane by 1.042 (3) Å. However, as is typical for tellurium(IV) (Feger *et al.*, 1999; Irvine *et al.*, 2003), there are further O atoms with Te⋯O < 3.00 Å in the coordination spheres of both Te1 and Te2. The shortest Te⋯O distance, *viz.* Te2–O11 = 2.557 (5) Å, might justify describing the Te2 coordination as 3+1 (Feger *et al.*, 1999). The BVS for Te1 are 3.74 (for the three close O atoms) and 4.10 (all O

**Figure 2**

The Li coordination in (I), drawn with 50% probability displacement ellipsoids. Symmetry codes are as given in Table 1.

**Figure 3**

Polyhedral representation of an [001] chain of edge-sharing VO₆ octahedra in (I). Symmetry codes are as given in Table 1.

atoms within 3.0 Å). For Te2, BVS values of 3.83 (three Te—O bonds < 2.0 Å), 4.03 (four Te—O bonds < 2.6 Å) or 4.24 (six Te—O bonds < 3.0 Å) arise.

Atom Li1 is surrounded by six O atoms within 2.5 Å. If the LiO₆ polyhedron is not simply regarded as irregular, then a possible description is a monocapped trigonal bipyramid (Fig. 2), with the longest bond to O10ⁱ capping through the O3ⁱ/O4ⁱⁱⁱ/O5 face [symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z$]. If the five O atoms forming the trigonal bipyramid are considered, a BVS of 0.88 arises for Li1 (expected = 1.00). If O10ⁱ is included in the calculation, BVS(Li1) rises to 0.95. Thus, the Brown (2002) criterion that a ligand should contribute 4% of the metal valence to be considered as bonded is fulfilled.

The polyhedral connectivity in (I) results in edge-sharing chains of VO₆ octahedra propagating along [001] (Fig. 3). Crystal symmetry requires that the V1 and V3 octahedra form inversion dimers, while the V2 polyhedron shares an edge with one V1 and one V3 octahedron. The edge-sharing V...V separations are: V1...V1^{iv} = 3.4207 (16) Å, V1...V2^{iv} = 3.3169 (16) Å, V2...V3^{iv} = 3.7016 (17) Å and V3...V3^{viii} = 3.4858 (18) Å [symmetry codes: (iv) $1 - x, -y, 1 - z$; (viii) $1 - x, -y, -z$]. The O—V—O bond angles for the O atoms involved in the edge-shared links show substantial compression from 90°, falling in the range 70.51 (7)–77.58 (19)°.

When the Te atoms are considered as well as the V and O atoms, (010) sheets arise (Fig. 4) in the structure of (I). It is notable that Te1 bonds to, or caps, a triangle of three vanadium polyhedra in the same edge-shared chain. A different triangular capping mode for a Te^{IV} atom was observed in Cs(VO₂)₃(TeO₃)₂ (Harrison & Buttery, 2000), in which the three VO₆ groups share corners. Although the title compound

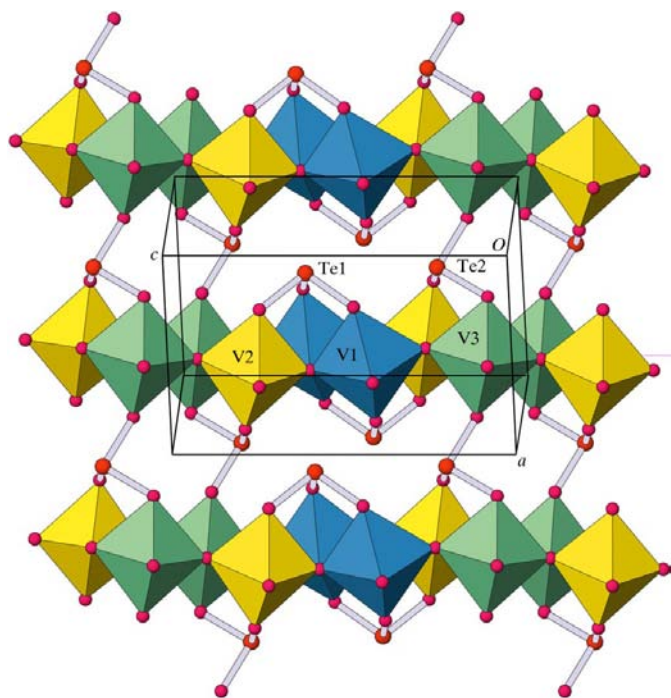


Figure 4
Polyhedral representation of an (010) sheet in (I).

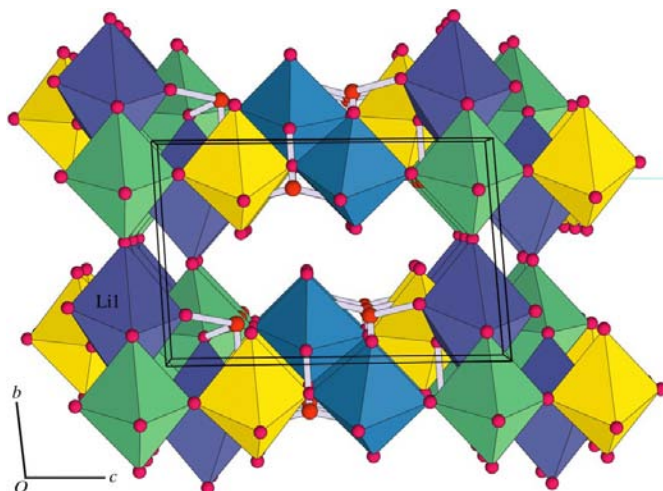


Figure 5
The unit-cell packing for (I), in polyhedral representation for the VO₆ and LiO₆ moieties.

and Cs(VO₂)₃(TeO₃)₂ share the same stoichiometry and a ‘capping’ Te atom, they are otherwise structurally quite dissimilar.

Finally, when the Li atoms in (I) are also considered, a three-dimensional network arises (Fig. 5), with LiO₆ groups bridging the (010) sheets, the key bond being Li1—O12ⁱⁱⁱ [symmetry code: (iii) $1 - x, 1 - y, -z$]. Significant [100] pseudo-channels are apparent in the structure, which probably accommodate the Te^{IV} lone pairs. Thus, any free space accessible by other chemical species is limited.

Experimental

A mixture of V₂O₅ (0.7276 g, 4 mmol), TeO₂ (0.3249 g, 3 mmol) and 1 M aqueous LiOH (7 ml) was placed in a 23 ml Teflon-lined hydrothermal bomb and heated at 438 K for 4 d, followed by cooling to room temperature over a period of a few hours. Upon opening the bomb, the solids were recovered by vacuum filtration, resulting in orange plates and shards of the title compound, accompanied by an as-yet unidentified orange–brown powder, in about a 50:50 ratio.

Crystal data

Li(VO₂)₃(TeO₃)₂
M_r = 606.96
 Triclinic, *P* $\bar{1}$
a = 6.2370 (4) Å
b = 7.2005 (5) Å
c = 10.7066 (8) Å
 α = 92.868 (4)°
 β = 92.743 (5)°

γ = 105.524 (4)°
V = 461.77 (6) Å³
Z = 2
 Mo *K* α radiation
 μ = 9.23 mm⁻¹
T = 120 (2) K
 0.12 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2003)
T_{min} = 0.404, *T_{max}* = 0.769

3858 measured reflections
 1730 independent reflections
 1499 reflections with *I* > 2σ(*I*)
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.089$
S = 1.02
 1730 reflections

163 parameters
 18 restraints
 $\Delta\rho_{\max} = 1.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.93 \text{ e \AA}^{-3}$

Table 1
Selected bond lengths (Å).

Li1—O5	1.899 (12)	V3—O12	1.588 (5)
Li1—O3 ⁱ	2.049 (13)	V3—O10 ^f	1.755 (4)
Li1—O6 ⁱⁱ	2.119 (12)	V3—O4 ^v	1.885 (5)
Li1—O4 ⁱⁱ	2.277 (13)	V3—O5	1.980 (5)
Li1—O12 ⁱⁱⁱ	2.411 (13)	V3—O11	2.014 (5)
Li1—O10 ^f	2.447 (14)	V3—O10 ^{iv}	2.634 (5)
V1—O7	1.582 (5)	Te1—O2	1.890 (5)
V1—O11	1.790 (5)	Te1—O3	1.892 (5)
V1—O2	1.899 (5)	Te1—O1	1.905 (5)
V1—O1 ^{iv}	1.974 (5)	Te1—O6 ^{vi}	2.741 (5)
V1—O8	1.992 (5)	Te1—O7 ^{vii}	2.764 (5)
V1—O8 ^{iv}	2.325 (5)	Te1—O1 ^{vi}	2.765 (5)
V2—O9	1.581 (5)	Te2—O5	1.873 (5)
V2—O8	1.762 (4)	Te2—O4	1.888 (5)
V2—O10	1.940 (5)	Te2—O6	1.901 (5)
V2—O3	1.943 (5)	Te2—O11	2.557 (5)
V2—O6 ^{iv}	1.964 (5)	Te2—O1 ^{vi}	2.801 (5)
V2—O11 ^{iv}	2.532 (5)	Te2—O9 ^{vii}	2.836 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 1, -y, -z + 1$; (v) $x + 1, y, z$; (vi) $-x, -y, -z + 1$; (vii) $-x + 1, -y + 1, -z + 1$.

The U^{ij} values for Li1 were restrained to approximate isotropic behaviour. The highest difference peak is 0.95 Å from atom Te2 and the deepest difference hole is 0.87 Å from Te1.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3051). Services for accessing these data are described at the back of the journal.

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