

Lithium dioxobis[trioxiodato(V)]-
vanadate, $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$ Xue-An Chen,^{a*} Li Zhang,^a Xin-An Chang,^a He-Gui Zang^a
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The title compound represents a new structure type, in which distorted VO_6 octahedra are bridged by iodate groups to form infinite two-dimensional $[\text{VO}_2(\text{IO}_3)_2]^-$ layers that are separated by octahedrally coordinated Li^+ cations.

Comment

Two types of non-linear optical (NLO) materials are well known. The first kind, such as LiNbO_3 , BaTiO_3 , *etc.*, contain high-valent d^0 transition metals that are readily susceptible to second-order Jahn–Teller (SOJT) distortions, giving rise to distorted MO_6^{n-} octahedra. The second kind, *e.g.* $\alpha\text{-LiIO}_3$ and KIO_3 , contain pyramidal IO_3^- ligands with stereochemically active non-bonding electron pairs (Halasyamani & Poeppelmeier, 1998). If an SOJT-distorted transition metal and anions containing non-bonding electron pairs were combined in the same crystal, and if, furthermore, they were arranged in a manner favourable for producing a large NLO effect, a new class of NLO materials would be expected. Based on this idea, several vanadyl iodates, $A[\text{VO}_2(\text{IO}_3)_2]$ ($A = \text{K}$ or Rb) (Sykora, Ok, Halasyamani, Wells & Albrecht-Schmitt, 2002) and $A[(\text{VO})_2(\text{IO}_3)_3\text{O}_2]$ ($A = \text{NH}_4$, Rb or Cs), have recently been synthesized, among which the last three compounds show large second-harmonic generation (SHG) responses of about 500 times that of $\alpha\text{-SiO}_2$ (Sykora, Ok, Halasyamani, Wells & Albrecht-Schmitt, 2002). However, Li-containing vanadyl iodates have not been reported to date. The current interest in these materials has enabled us to discover $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$, which does not exhibit SHG effects but which crystallizes in a unique structural type different from those of the K and Rb analogues. We report its crystal structure here.

$\text{Li}[\text{VO}_2(\text{IO}_3)_2]$ represents a new structure type (Pearson symbol $mP48$; Villars & Calvert, 1991) and is characterized by VO_6 octahedra that are bridged by iodate groups to form an infinite two-dimensional $[\text{VO}_2(\text{IO}_3)_2]^-$ layer parallel to the $(\bar{1}02)$ plane, as shown in Fig. 1. The anionic layers are stacked approximately along the $[10\bar{2}]$ direction, with the interlayer

void spaces filled by Li^+ cations to balance charge. Each Li^+ ion is coordinated by six O atoms in a slightly distorted octahedral geometry, with $\text{Li}—\text{O}$ distances in the range 2.021 (9)–2.228 (9) Å. The average $\text{Li}—\text{O}$ bond distance of 2.099 Å is close to Shannon's crystal radii sum of 2.11 Å (Shannon, 1976) and is also comparable with those found in LiIO_3 (2.111 Å; Svensson *et al.*, 1983) and $\text{LiH}_4\text{IO}_6\cdot\text{H}_2\text{O}$ (2.135 Å; Kraft & Jansen, 1994), all featuring octahedrally coordinated Li^+ .

There is one crystallographically unique V atom, which occupies a distorted octahedron, with two short vanadyl $\text{V}=\text{O}$ bonds to O7 and O8, and four $\text{V}—\text{O}—\text{I}$ links *via* atoms O2, O3, O5 and O6 (Fig. 2). The *cis* $\text{O}—\text{V}—\text{O}$ octahedral angles vary from 77.19 (15) to 100.4 (2)°, and the *trans* angles are in the range 158.36 (17)–169.25 (19)°, deviating significantly from the expected values of 90 and 180°, respectively. The V atoms are susceptible to SOJT distortion and are displaced out of the centre of an idealized VO_6 octahedron along a C_2 axis of the octahedron by about 0.406 Å, thus resulting in the formation of two short [$\text{V}—\text{O}7 = 1.632$ (4) Å and $\text{V}—\text{O}8 = 1.649$ (4) Å], two intermediate [$\text{V}—\text{O}6 = 1.992$ (4) Å and $\text{V}—\text{O}3 = 1.998$ (4) Å] and two long [$\text{V}—\text{O}2 = 2.196$ (4) Å and $\text{V}—\text{O}5 = 2.239$ (4) Å] bonds. This is very similar to the situation for octahedral Mo^{VI} atoms observed in $\text{AMoO}_3(\text{IO}_3)$ ($A = \text{K}$, Rb or Cs ; Sykora, Ok, Halasyamani & Albrecht-Schmitt, 2002), but slightly different from the situation for V^{V} atoms in the previously reported vanadyl iodates $A[(\text{VO})_2(\text{IO}_3)_3\text{O}_2]$ ($A = \text{NH}_4$, Rb or Cs), where the distortion of the VO_6 group toward one O atom leads to a 'one short plus two intermediate plus three long' $\text{V}—\text{O}$ bonding scheme (Sykora, Ok, Halasyamani, Wells & Albrecht-Schmitt, 2002). The $\text{V}—\text{O}$ bond distances observed in $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$ compare well with those found in $A[(\text{VO})_2(\text{IO}_3)_3\text{O}_2]$ ($A = \text{NH}_4$, Rb or Cs) [1.620 (9)–2.227 (8) Å] and $(\text{NH}_4)(\text{VO}_2)_3(\text{SeO}_3)_2$ [1.637 (10)–2.198 (11) Å; Vaughey *et al.*, 1994].

The I atoms occupy two different crystallographic sites. They are both coordinated by three O atoms, forming trigonal–pyramidal geometries. Each IO_3^- group acts as a

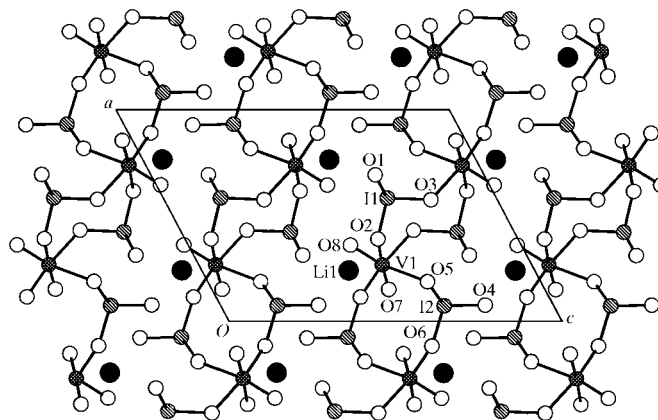


Figure 1

The crystal structure of $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$, projected along the $[010]$ direction. Black circles denote Li atoms, cross-hatched circles V atoms, shaded circles I atoms and open circles O atoms.

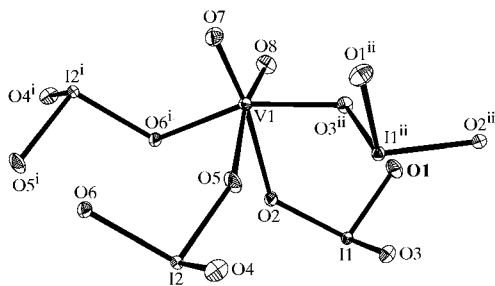


Figure 2

The local coordination geometries of V and I in $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$, with displacement ellipsoids drawn at the 50% probability level and the Li^+ ion omitted. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.]

bidentate ligand bonded to two V^{5+} centres *via* two μ_2 -O atoms, with the third O atom terminal. The I—O bond lengths for the O atoms bound to the V^{5+} centres [1.810 (4)–1.855 (4) Å] are slightly longer than those for the terminal O atoms [1.793 (4) and 1.798 (4) Å; Table 1], as expected, and both are in good agreement with the values observed in $A[\text{VO}_2(\text{IO}_3)_2]$ ($A = \text{K}$ or Rb). The O—I—O bond angles are normal, lying in the range 96.8 (2)–101.27 (19)°. The refined structural model was further supported by bond-valence sum (BVS) calculations (Brown & Altermatt, 1985), which gave reasonable values of 1.10, 4.95 and 4.92–4.95 for Li, V and I atoms, respectively.

In the family of compounds $A[\text{VO}_2(\text{IO}_3)_2]$ ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ or Cs), only the K and Rb phases have been structurally characterized to date. Their crystal structures contain five-coordinate V^{V} atoms that are bound by two terminal O atoms, and by one monodentate and two bridging iodate anions, to create a fundamental $[\text{VO}_2(\text{IO}_3)_3]^{2-}$ building unit. Adjacent $[\text{VO}_2(\text{IO}_3)_3]^{2-}$ units are linked together through bridging iodate anions to generate a one-dimensional $[\text{VO}_2(\text{IO}_3)_2]^-$ chain. These chains are further separated by nine-coordinate K^+ and 11-coordinated Rb^+ cations, giving rise to different space-group symmetries ($P2_1/n$ for the K phase and $P\bar{1}$ for the Rb phase) (Sykora, Ok, Halasyamani, Wells & Albrecht-Schmitt, 2002). The structural differences between $A[\text{VO}_2(\text{IO}_3)_2]$ ($A = \text{Li}, \text{K}$ or Rb) are related not only to the variation in the coordination environments around the V atoms, but also to the cation size effect: six-coordinate octahedral geometry is preferred by the smaller Li^+ ions, a nine-coordinate environment is observed for the K^+ ions, and a higher coordination number of 11 is required for the larger Rb^+ cations.

Experimental

Li_2CO_3 (0.487 mmol), V_2O_5 (0.489 mmol), I_2O_5 (0.983 mmol) and H_2O (2 ml) were weighed and sealed in a 15 ml Teflon-lined stainless steel vessel. This was heated in an oven at 443 K for one week under autogenous pressure and then cooled slowly to room temperature. The product consisted of yellow block-like crystals of $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$, the largest having dimensions of $0.6 \times 0.6 \times 0.4$ mm, in a pale-yellow mother liquor. The crystals, in about 50% yield (based on V), were isolated by washing the reaction product with deionized water and anhydrous ethanol, followed by drying with anhydrous acetone. The

powder X-ray diffraction pattern of the ground crystals is in good agreement with that calculated from the single-crystal data. The IR spectrum of $\text{Li}[\text{VO}_2(\text{IO}_3)_2]$ exhibits three sets of bands characteristic of VO_6 and IO_3^- groups. They are the VO_6 stretching vibrations occurring at 920.0 and 872.5 cm^{-1} , the IO_3^- symmetric (ν_1) and antisymmetric (ν_3) stretching modes in the range 712.0–819.2 cm^{-1} , and the IO_3^- bending modes between 418.4 and 481.7 cm^{-1} .

Crystal data

$\text{Li}[\text{VO}_2(\text{IO}_3)_2]$	$Z = 4$
$M_r = 439.68$	$D_x = 4.623 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.994$ (2) Å	$\mu = 11.35 \text{ mm}^{-1}$
$b = 5.2020$ (10) Å	$T = 290 \text{ K}$
$c = 13.798$ (3) Å	Block, yellow
$\beta = 118.28$ (3)°	$0.2 \times 0.2 \times 0.1 \text{ mm}$
$V = 631.7$ (3) Å ³	

Data collection

Rigaku AFC-7R diffractometer	2681 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.008$
Absorption correction: ψ scan (Kopfmann & Huber, 1968)	$\theta_{\text{max}} = 35.0^\circ$
$T_{\text{min}} = 0.125, T_{\text{max}} = 0.313$	3 standard reflections every 150 reflections
3029 measured reflections	intensity decay: 1.8%
2777 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 13.2592P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.25$	$\Delta\rho_{\text{max}} = 2.58 \text{ e } \text{Å}^{-3}$
2777 reflections	$\Delta\rho_{\text{min}} = -2.60 \text{ e } \text{Å}^{-3}$
104 parameters	

Table 1

Selected bond lengths (Å).

I1—O1	1.798 (4)	I2—O4	1.793 (4)
I1—O2	1.810 (4)	I2—O5	1.814 (4)
I1—O3	1.846 (4)	I2—O6	1.855 (4)

All atoms were refined anisotropically, except for Li, which was refined isotropically.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1994); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *Rigaku/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *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: EM3001). Services for accessing these data are described at the back of the journal.

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