Table 4. *Selected geometric parameters (Å, °) at 150 K*

Co1—N3	1.958 (2)	N4—O2	1.217 (3)
Co1—N4	1.960 (2)	N4—O1	1.224 (3)
Co1—N2	1.9691 (15)	N5—O4	1.235 (3)
Co1—N1	1.989 (2)	N5—O3	1.256 (2)
O2—N4—O1	123.3 (2)	O4—N5—O3	120.35 (11)
O2—N4—Co1	118.9 (2)	O3—N5—O3^{i}	119.3 (2)

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

Since lattice parameters of cobalt(III) nitroammine complexes are known to vary slightly from crystal to crystal of the same compound, comparative studies at the two temperatures were carried out using the same crystal without removing the crystal from the diffractometer. All experiments were carried out in the dark to prevent possible photochemical linkage isomerization. The temperature was maintained and controlled using a Cryosystem (Oxford Cryosystems) open-flow gas cryostat (Cosier & Glazer, 1986).

In order to improve the statistics, the reflections were deliberately collected in a reciprocal volume double the minimum required by crystal symmetry, and equivalent reflections were merged.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989); software used to prepare material for publication: *SHELXL93*.

The study was carried out at the Chemistry Department (Crystallography Group) of Durham University, where EB and JK were spending some research time as guests of JAKH. The authors gratefully acknowledge financial support from the Royal Society (EB), the Academy of Finland and the British Council (JK).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Electrochemically Lithiated Vanadium Oxide, $Li_2V_6O_{13}$

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Abstract

Single crystals of V_6O_{13} were grown by chemical vapour transport and then electrochemically lithiated. The title compound, dilithium hexavanadium tridecaoxide, was the first phase formed during electrochemical lithiation at 2.65 V *versus* Li/Li^+. The $Li_2V_6O_{13}$ structure can be described as layers of VO_6 octahedra stacked perpendicular to the *c* direction. Lithiation causes a 7.6% expansion along the *c* axis. The lithium ions occupy positions with fivefold square-pyramidal oxygen coordination between the layers.

Comment

The title compound is the first lithiated phase obtained during discharge of a lithium battery containing the well known lithium intercalation host compound V_6O_{13}. An essential basis for understanding the relationship between structure and electrochemical properties in modern lithium-battery electrodes is a precise knowledge of the crystal structures of the various lithiated phases formed during cycling. Earlier work on lithiated V_6O_{13} has used X-ray and neutron diffraction techniques on powder samples: phases $Li_xV_6O_{13}$ for *x* between 0.5 and 1.0 (Lampe-Önnerud, Nordblad & Thomas, 1996; West, Zachau-Christiansen, Jacobsen & Atlung, 1985) have been reported as the first lithiated phase. Powder diffraction techniques seem inadequate in revealing the subtleties of the lithiation process. In this single-crystal X-ray study on an electrochemically lithiated sample we are able to determine the detailed lithiated structure.

The structure of V_6O_{13} can be described as layers of VO_6 octahedra parallel to the *ab* plane. There are two types of layers in the structure: one containing V1 centred around $z = 0$ and one containing V2 and V3 centred around z = 0.5. The two layers are connected *via* corner sharing of O5 and O6. The main effect of the lithiation is a 7.6% expansion perpendicular to these layers. Lithium enters a five-coordinate square-pyramidal 4*i* site between the layers. The V1—O6 bond is elongated by 0.65 Å and the V1—O5 bond is contracted by 0.5 Å. This can be seen as a displacement of V1, possibly caused by the coulombic repulsion from the lithium ion.

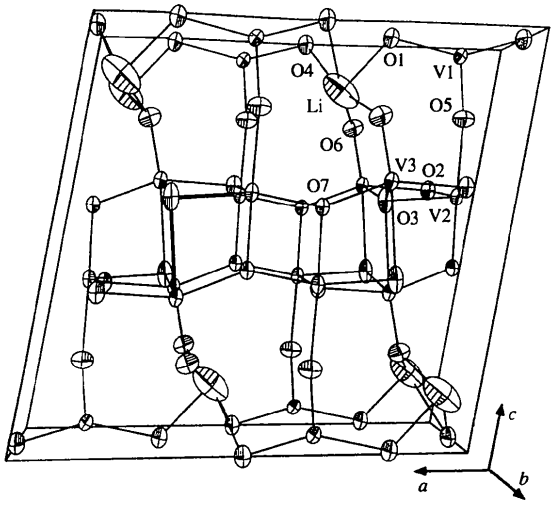

Fig. 1. The structure of $Li_2V_6O_{13}$. Displacement ellipsoids are drawn at the 90% probability level.

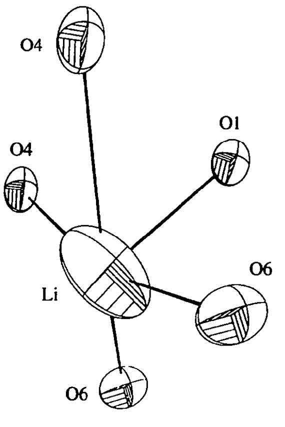

Fig. 2. The square-pyramidal coordination of the lithium ion. Displacement ellipsoids are drawn at the 90% probability level.

Experimental

Single-crystal V_6O_{13} was grown by a chemical vapour transport process (Saeki *et al.*, 1973); the starting material was a powder mixture of crystallographically phase-pure V_6O_{13} [synthesis described by Lampe-Önnerud & Thomas (1995)] and $TeCl_4$ (Merck: as received), in the mass ratio 20:1. Electrochemical lithiation was performed by mixing the obtained single crystals into the cathode of a <Li|polymer electrolyte|V_6O_{13}> battery. The battery was maintained at a slightly elevated temperature (323 K) in a sand bath to enhance reaction kinetics and the lithium-ion diffusion rate. The battery was discharged from an initial 3 V *versus* Li/Li$^+$ down to 2.65 V over 6 weeks. At this voltage, V_6O_{13} has been found to have reached its first lithiated phase in our earlier studies with *in situ* techniques (Gustafsson, Thomas, Koksbang & Farrington, 1992). A single crystal was then located and mounted on a goniometer within an argon-filled drybox.

Crystal data

$Li_2V_6O_{13}$
M_r = 527.52
Monoclinic
$C2/m$
a = 11.857 (6) Å
b = 3.660 (2) Å
c = 10.909 (6) Å
β = 100.43 (4)°
V = 465.6 (6) Å^3
Z = 2
D_x = 3.76 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 14 reflections
θ = 10.36–11.50°
μ = 5.67 mm^{-1}
T = 293 K
Plate
0.17 × 0.12 × 0.07 mm
Black

Data collection

Stoe diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian
T_{min} = 0.323, T_{max} = 0.679
5730 measured reflections
2876 independent reflections
R_{int} = 0.030

θ_{max} = 52.5°
$h = -26 \rightarrow 26$
$k = -8 \rightarrow 8$
$l = -24 \rightarrow 0$
2 standard reflections
frequency: 240 min
intensity decay: 0.07%

Refinement

Refinement on F^2
$R(F)$ = 0.040
$wR(F^2)$ = 0.055
S = 2.69
5730 reflections
71 parameters
$w = 1/\sigma(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.1
$\Delta\rho_{max}$ = 0.93 e Å^{-3} (at 0.67, 0, 0.19 near V1)
$\Delta\rho_{min}$ = −1.01 e Å^{-3} (at 0.35, 0, 0.08 near O6)

Extinction correction: Becker & Coppens (1974), anisotropic type 1
Extinction coefficients: (anisotropic) 0.12 (1) × 10^{-6}, 0.74 (4) × 10^{-7}, −0.90 (8) × 10^{-7}, −0.100 (7) × 10^{-6}, 0.49 (5) × 10^{-7}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V1	0.35436 (1)	0	0.04678 (1)	0.00543 (3)
V2	0.40922 (1)	0	0.39463 (1)	0.00556 (4)
V3	0.70902 (1)	0	0.36350 (1)	0.00561 (3)
O1	0.18027 (5)	0	0.00799 (5)	0.0074 (2)
O2	0.87936 (5)	0	0.37472 (5)	0.0075 (2)
O3	0.23984 (5)	0	0.40683 (6)	0.0095 (2)
O4	1/2	0	0	0.0111 (3)
O5	0.39003 (6)	0	0.19866 (5)	0.0115 (2)
O6	0.65783 (6)	0	0.21349 (6)	0.0131 (2)
O7	0.56855 (5)	0	0.42661 (5)	0.0070 (2)
Li	0.0855 (3)	0	0.1368 (3)	0.037 (2)

Table 2. *Selected geometric parameters (Å)*

V1—O5	1.634 (1)	V2—V3^{vi}	2.968 (1)
V1—O4	1.887 (1)	V2—V3^{v}	2.968 (1)
V1—O1^{i}	1.946 (1)	V3—O6	1.639 (1)
V1—O1^{ii}	1.946 (1)	V3—O3^{vii}	1.909 (1)
V1—O1	2.031 (1)	V3—O3^{viii}	1.909 (1)
V1—O6^{iii}	2.817 (1)	V3—O7	1.914 (1)
V1—Li^{i}	2.896 (2)	V3—O2	2.001 (1)
V1—Li^{ii}	2.896 (2)	V3—O3^{iv}	2.469 (1)
V2—O7	1.858 (1)	Li—O1	1.952 (3)
V2—O7^{iv}	1.920 (1)	Li—O6^{vi}	2.127 (2)
V2—O2^{v}	1.869 (1)	Li—O6^{v}	2.127 (2)
V2—O2^{vi}	1.869 (1)	Li—O4^{vi}	2.461 (2)
V2—O3	2.037 (1)	Li—O4^{v}	2.461 (2)
V2—O5	2.109 (1)	Li—V1^{i}	2.896 (2)
V2—V2^{iv}	2.851 (1)	Li—V1^{ii}	2.896 (2)

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

The structure was solved by difference Fourier syntheses using the atomic coordinates of V_6O_{13} (Wilhelmi, Waltersson & Kilborg, 1971). Refinement of the occupancy factor for the Li site confirmed that the site was fully occupied.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *STOEDATRED*, *LSQLIN*, *ABSSTOE* (Lundgren, 1983). Program(s) used to solve structure: *FORDUP* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *DISTAN* (Lundgren, 1983).

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Lists of displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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β-$BaTbF_6$

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Abstract

The single-crystal structure of the quenchable high temperature form of barium terbium hexafluoride has been refined. This structure is built from infinite chains of edge-sharing $[TbF_8]^{4-}$ dodecahedra linked together by the Ba^{2+} ions and is isostructural with β-$BaZrF_6$.

Comment

Since their pioneering work on ionic radii determination in which Shannon & Prewitt (1969) claimed that there were no available crystallographic data concerning tetravalent terbium in fluorinated media, no report has appeared on this subject. On the other hand, many fluorinated combinations containing tetravalent terbium have been mentioned (Hoppe, 1985, and references therein). All these compounds, however, have been characterized by X-ray powder diffraction only. Single-crystal studies were needed but there were problems in growing crystals because of the relative thermal instability of TbF_4 (Gibson & Haire, 1988). As these problems have now been at least partially overcome, we have undertaken an extensive study of the single-crystal structures of tetravalent terbium fluorides.

$BaTbF_6$ was originally reported with an unknown structure (Feldner & Hoppe, 1983). It can be inferred now that this still unknown structure is a low temperature form, subsequently called α-$BaTbF_6$, since a recent study has shown that $BaTbF_6$ undergoes a phase transition at high temperature to an orthorhombic form of the β-$BaZrF_6$ type (Mehlhorn & Hoppe, 1976). β-$BaTbF_6$ is the first representative of a high temperature polymorph of a Tb^{IV}-containing fluoride and also one of the first Tb^{IV} fluorinated compounds obtained as a single crystal. It is isostructural with β-$BaZrF_6$.

Each Tb^{4+} ion is surrounded by eight F^- ions, four of which are shared in pairs with adjacent Tb^{4+} ions to form infinite chains running along the [100] direction. These chains are linked together by the Ba^{2+} ions. The Tb—F bond distances are divided into two groups: bonds to bridging F atoms are 2.271 (2) Å and bonds to non-bridging F atoms involved in shared edges within the chains are 2.081 (3) Å. Comparison of the bond

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