For both compounds, program(s) used to solve structures: *SHELXTL* (Siemens, 1995); program(s) used to refine structures: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1213). Services for accessing these data are described at the back of the journal.

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Layered Tetramethylammonium Vanadium Oxide $[N(CH_3)_4]V_3O_7$ by X-ray Rietveld Refinement

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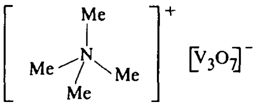
Abstract

Tetramethylammonium trivanadium heptaoxide crystallizes in the monoclinic space group $P2_1/n$ when prepared hydrothermally. Its structure was solved from conventional X-ray powder diffraction with final R(Bragg) = 0.052 and R(prof) = 0.078. Vanadium coordination polyhedra are square pyramids and a tetrahedron which form layers parallel to the *bc* plane. The tetramethylammonium cations are incorporated between the layers.

Comment

Recently, using mild hydrothermal synthesis (Whittingham *et al.*, 1995), we have produced metastable vanadium oxides with the vanadium in a reduced oxidation state: $[N(CH_3)_4]V_4O_{10}$ (Zavalij, Whittingham, Boylan, Pecharsky & Jacobson, 1996), $Li_xV_{2-y}O_{4-y}.H_2O$ (Chirayil, Zavalij & Whittingham, 1996*a*) and $Li_xV_{2-y}O_{4-y}$ (Chirayil, Zavalij & Whittingham, 1996*b*) with open frameworks, as well as a cluster compound $\{[Li(H_2O)_4]_2V_{10}O_{28}.4H_2O\}^{4-}$ (Zavalij, Chirayil, Whittingham, Pecharsky & Jacobson, 1997) with vanadium in the highest oxidation state. We report here the structure of a new layered vanadium oxide $[N(CH_3)_4]V_3O_7$, (I).



(I)

Two V atoms have square-pyramidal (SP) coordination with double-bonded O atoms in the vertex, while a third V atom has a tetrahedral coordination. The square pyramids form a VO_3 chain along the *b* axis by sharing the two edges of their base (Fig. 1). The middle square pyramid (V1) shares two opposite edges of the base and the corner pyramid (V2) shares two neighbor-

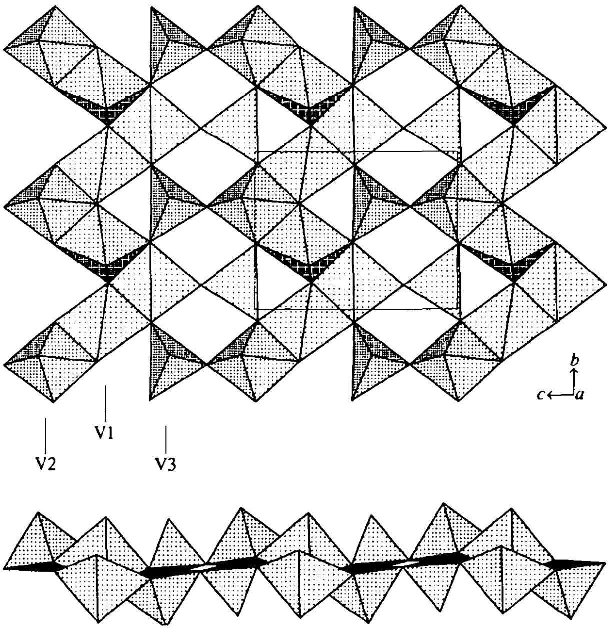


Fig. 1. V_3O_7 layer shown by square pyramids (middle, V1; corner, V2) and tetrahedra (V3).

ing edges. This type of VO_3 chain can be described by the symbolic formula *UuDd* (Zavalij & Whittingham, 1996), where *U* is the corner SP and *u* the middle SP directed up, *D* is the corner SP and *d* the middle SP directed down. The tetrahedra link these chains into a layer by sharing two O atoms with one chain and one O atom with another chain. Tetramethylammonium cations fill the space between the layers (Fig. 2).

Recently the same type of V_3O_7 layer was found in $[NH(CH_2CH_2)_3NH]V_6O_{14}.H_2O$ (II) (Nazar, Koene & Britten, 1996) and similar layers exist in $[M(en)_2]V_6O_{14}$, (III) (Zhang *et al.*, 1996), where *M* is Cu^{2+} and Zn^{2+}. The layers in (I) and (II) are distinguishable only by conformation. In the case of (I), the layer is almost flat, whereas in (II), this layer is crimped because of the different orientations of tetrahedra. This leads to a substantial change in cell dimension [*c* axis in (I)] from 8.43 to 7.55 Å. The layers of (III) are formed from the same *UuDd* chains linked by VO_4 tetrahedra, but the orientation of neighboring chains is opposite, leading to double cell dimensions of 15.7 Å.

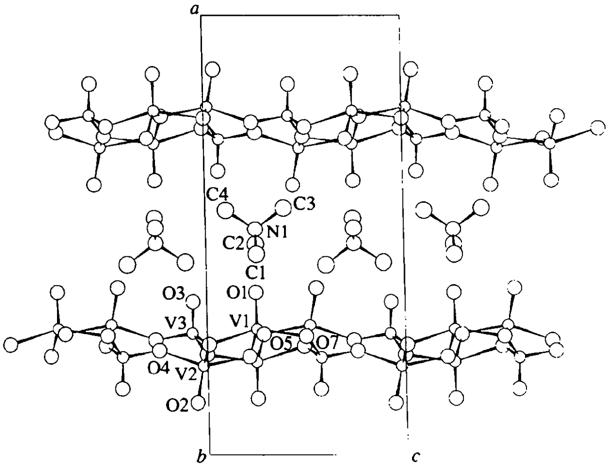


Fig. 2. *INSIGHT*II (Biosym Technologies, 1995) printout of the $[N(CH_3)_4]V_3O_7$ structure along the *b* axis.

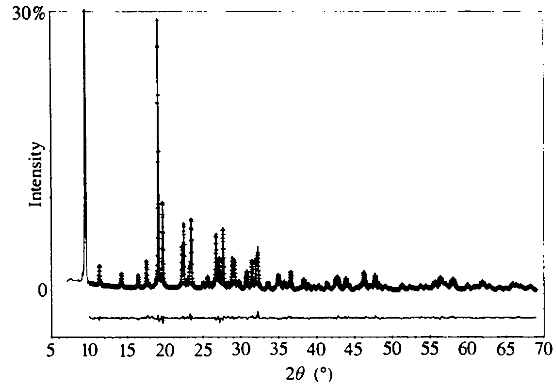


Fig. 3. Comparison of observed (—) and calculated (+++) intensities for $[N(CH_3)_4]V_3O_7$. The difference pattern appears below.

Experimental

The title compound was prepared by hydrothermal treatment of V_2O_5, $[N(CH_3)_4]OH$ and LiOH in a 1:2:1 molar ratio acidified to pH 6.5 with acetic acid. The reaction mixture was heated in a Teflon-lined Parr reactor for three days at 458 K. A black crystalline powder resulted. The same compound is also produced in the absence of LiOH, as well as when HNO_3 is used instead of acetic acid.

Crystal data

$(C_4H_{12}N)[V_3O_7]$
$M_r = 338.97$
Monoclinic
$P2_1/n$
$a = 18.4783\,(5)$ Å
$b = 6.5523\,(2)$ Å
$c = 8.4268\,(3)$ Å
$\beta = 91.132\,(2)^\circ$
$V = 1020.1\,(1)$ Å^3
$Z = 4$
$D_x = 2.207$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
$\mu = 24.24$ mm^{-1}
$T = 293$ K
Specimen shape: flat sheet
25 × 25 × 1 mm
Specimen prepared at 458 K
Black

Data collection

Scintag XDS2000 diffractometer
ω/θ scans
Specimen mounting: packed powder pellet 25 mm in diameter and 1 mm thick

Specimen mounted in reflection mode
$T = 293$ K
$2\theta_{\min} = 7$, $2\theta_{\max} = 69^\circ$
Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on $I_{\rm net}$
$R_p = 0.078$
$R_{wp} = 0.094$
$R_B = 0.052$
$2\theta_{\min} = 10$, $2\theta_{\max} = 69^\circ$
Increment in $2\theta = 0.02^\circ$
Excluded region(s): the region from 7 to 10° 2θ was excluded because of the great value of both intensity and its error for the low angle 002 reflection which caused unstable refinement
Profile function: pseudo-Voigt

424 reflections
60 parameters
H atoms not refined
$w = 1/[Y_i + \sigma(Y_i)]$
$(\Delta/\sigma)_{\max} = 0.12$
$\Delta\rho_{\max} = 0.4$ e Å^{-3}
$\Delta\rho_{\min} = -0.6$ e Å^{-3}
Extinction correction: none
Preferred orientation correction: $I_{\rm corr}(hkl) = I_{\rm obs}(hkl)[1 + (\tau^2-1)\sin^2\varphi]^{-1/2}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected bond lengths (Å)*

V1—O1	1.69 (1)	V2—O5$^{\rm i}$	1.97 (1)
V1—O5	1.85 (1)	V2—O6	1.80 (1)
V1—O5$^{\rm i}$	1.94 (1)	V2—O7$^{\rm i}$	1.83 (1)
V1—O6	2.07 (1)	V3—O3	1.53 (1)
V1—O7	2.07 (1)	V3—O4$^{\rm ii}$	1.64 (1)
V2—O2	1.65 (1)	V3—O6	1.91 (1)
V2—O4	2.03 (1)	V3—O7$^{\rm iii}$	1.93 (1)

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

The powder diffraction pattern was indexed in a monoclinic system using the Ito method from *CSD* software (Akselrud *et* *al.*, 1993). Space group $P2_1/n$ was clearly assigned from the absences of the $0k0$ and $h0l$ reflections. Unfortunately, the integrated intensities from the automatic decomposition method of LeBail (GSAS) were not good enough to solve this structure because of highly overlapped peaks in the presence of α_1 and α_2 lines. Therefore, manual decomposition from *CSD* was used. First, the 2θ range from 7 to 50° was taken where position, shape and intensity were refined for each reflection. Then, the obtained accurate unit-cell dimensions and linear extrapolated peak-shape parameters were used to evaluate integral intensities up to $2\theta = 70°$. Integrated intensities of 286 peaks of the 425 possible reflections were used in direct methods to solve the structure. The intensities of $00l$ reflections were arbitrarily corrected by a factor of 0.67 to reduce the effect of preferred orientation. First, three V and five O atoms were located from the *E* map and then the two O and tetramethylammonium atoms were found from difference Fourier maps. Final full-profile refinement (Fig. 3) was carried out to R(Bragg) = 0.052. The correction given by *CSD* approximation of the preferred orientation $I_{\rm corr}(hkl) = I_{\rm obs}(hkl)[1 + (\tau^2 - 1)\sin^2\varphi]^{-1/2}$ (Pecharskii, Akselrud & Zavalij, 1987) was applied. The resultant preferred orientation correction coefficient was in the range 0.4 for $h00$ reflections to 1.0 for $0kl$ reflections.

Data collection: *DMS Software* (Scintag Inc., 1994). Cell refinement: *CSD*. Data reduction: *CSD*. Program(s) used to solve structure: *CSD*. Program(s) used to refine structure: *CSD*. Molecular graphics: *POLIEDRI* (Pilati, 1990) and *INSIGHT*II (Biosym Technologies, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1166). Services for accessing these data are described at the back of the journal.

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Bis(η^6-toluene)thallium(I) 7,8,9,10,11,12-Hexabromo-*closo*-1-carbadodecaborate: a Halocarborane-Bridged Dimer with Heavy Metal–Arene Interactions

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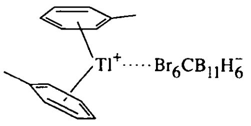
Abstract

The title compound, $[\mathrm{Tl}(\mathrm{C_7H_8})_2](\mathrm{CB_{11}H_6Br_6})$, shows Tl^+ having η^6 interactions with two toluene molecules and dative interactions with two Br atoms of one carborane anion and one Br atom of a neighboring anion.

Comment

The icosahedral carborane anions are an important new class of weakly coordinating anions finding increasing utility in the synthesis of electron-deficient species. The most useful of these are the hexahalogenated derivatives $\mathrm{CB_{11}H_6}X_6^-$ (X = Cl, Br, I), perhaps the most chemically inert and least coordinating anions known to date. They have recently been used to synthesize a salt exhibiting the closest approach to the silylium ion, $R_3\mathrm{Si}^+$ (Reed, Xie, Bau & Benesi, 1993; Xie *et al.*, 1996), an isolable salt of the discrete hydronium ion, $\mathrm{H_9O_4^+}$ (Xie, Bau & Reed, 1995), and the first isolable all-carbon carbocation, the fullerene cation $\mathrm{C_{76}^{+}}$ (Bolskar, Mathur & Reed, 1996).

A frequently used reaction in this synthetic chemistry is halide abstraction *via* silver salt metathesis. In a number of cases, however, the reaction of a labile metal halide with the silver salt of a weakly coordinating anion does not proceed or is incomplete because of Lewis acid/base adduct formation (Liston, Lee, Scheidt & Reed, 1989). We are therefore investigating the corresponding thallium chemistry and have prepared the thallium(I) salt of the hexabromocarborane $\mathrm{CB_{11}H_6Br_6^-}$ as a new potentially superior halide metathesis reagent, (I). It crystallizes from toluene as a bis(toluene) complex.



(I)