

The Crystal Structure of the Neptunium Metavanadate $\text{Np}(\text{VO}_3)_4$

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Abstract

$\text{Np}(\text{VO}_3)_4$ is tetragonal, space group $I4_1/a$, with $Z = 8$, $a = 8.481(3)$, $c = 28.723(8)$ Å. The structure was refined to $R = 0.08$ for 1297 counter intensities with $I > 3\sigma(I)$. The structure contains VO_4 tetrahedra linked by sharing corners; these form parallel endless $(\text{VO}_3)_n$ chains. The Np atoms which hold these groups of chains together have eight O-atom neighbours at an average distance of 2.32 Å.

Introduction

The study of solid-state reactions of ThO_2 with V_2O_5 was performed by Le Flem & Hagenmuller (1964) who found three thorium vanadates. The structures of thorium pyro- and orthovanadates were solved by Quarton (1975). However, the study of the V_2O_5 – NpO_2 system (Freundlich & Pagès, 1969) showed a single phase with 2/1 stoichiometry, similar to thorium metavanadate but of unknown structure.

A structural investigation of single crystals of the $\text{NpO}_2/2\text{V}_2\text{O}_5$ phase (Quarton, Pagès & Freundlich, 1978) led to the cell parameters and the space group $I4_1/acd$. We felt it appropriate to undertake a complete crystal structure analysis of this compound.

Experimental

All preparations were performed in glove boxes, under weak vacuum, from quantities of less than 50 mg. The isotope used was ^{237}Np , which is an α emitter with a half-life of 2.14×10^6 years.

Single crystals were prepared by fusion (1173 K) of the $\text{NpO}_2/2\text{V}_2\text{O}_5$ mixture followed by slow cooling (6 K h^{-1}) to 773 K; they appeared in the form of thin orange plates. Single crystals were stuck on a thin glass rod, and then sealed in a Lindemann capillary to avoid external contamination.

Photographs of several crystals taken by Weissenberg and precession techniques established the symmetry. Cell dimensions are based on $\lambda = 1.5405$ Å for Cu $K\alpha_1$ radiation and were refined by least squares from a powder pattern: $a = 8.481(3)$, $c = 28.723(8)$ Å; possible reflexions: hkl : $h + k + l = 2n$; $hk0$: $h, (k) = 2n$; hhl : $2h + l = 4n$; $0kl$: $k, (l) = 2n$. An additional condition: $2k + l = 4n$, observed on the films, enabled us to locate Np atoms in positions $8(a)$ or $8(b)$ of $I4_1/acd$ and confirmed the preliminary study.

Diffraction intensities were measured with the Nonius CAD-4 four-circle diffractometer of the Centre de Mesures Physiques de Clermont Ferrand. Data-collection conditions were: Mo $K\alpha$ radiation with graphite monochromator, ω – 2θ scan, $\theta_{\text{max}} = 40^\circ$, scanning range: $(1 + 0.35 \tan \theta)^\circ$, variable scan rate from 5 to $1.54^\circ \text{ min}^{-1}$. We used sub-program *FLAT*, which optimizes the measurements for plate-shaped crystals. The row normal to this plate is $[001]$. The intensities of three standard reflexions were checked hourly and the orientation every 100 reflexions. The relative e.s.d. is 0.02. After Lorentz–polarization correction, 3048 positive reflexions remained. Absorption corrections were made by de Meulenaer & Tompa's (1965) analytical method, with the program *AGNOST* (Ahmed, 1974): $\mu(\text{Mo } K\alpha) = 11.06 \text{ mm}^{-1}$.

Structure determination and refinement

Attempts to solve the structure in either $I4_1/acd$ or $I4_1/amd$ were fruitless.

We then considered the possibility that some of the symmetries observed on Weissenberg and precession films were, in fact, only pseudosymmetries due to a particularly high Np contribution. We turned our attention to space group $I4_1/a$, which seemed possible because the extinction conditions are repeated and Np stays on sites close to $8(a)$ of $I4_1/acd$; only the Laue class was altered ($4/m$ for $I4_1/a$).

This hypothesis, with Np atoms in positions $8(e)$ ($0, \frac{1}{4}, z$ lying close to $\frac{1}{2}$), was confirmed by refinement on © 1979 International Union of Crystallography

z, since a difference synthesis yielded the positions of the 32 V atoms on the general positions 16(*f*), and of 16 O atoms on two 8(*e*) sites. A subsequent difference synthesis revealed the positions of the other O atoms.

The structure was refined by least squares with *AFFINE*, a modification of *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). For Np and V, anomalous dispersion was taken into account.

Refinement was carried out on the heavy atoms only, the scale factor, the coordinates and the individual isotropic temperature factors successively. The calculations were monitored by the variation of $R = \sum (|F_o| - K|F_c|) / \sum |F_o|$ and $R_w = [\sum w(|F_o| - K|F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where K is the scale factor and $w = 1/\sigma^2(F_o)$; $\sigma(F_o) = \sigma(F_o^2)/2F_o$.

Refinement was continued on Np, V(1), V(2), O(1) and O(2), each given an individual isotropic temperature factor, then anisotropic factors [for Np, V(1) and V(2) only]. We then introduced the five remaining O atoms, and, after eliminating 1751 planes [with $I \leq 3\sigma(I)$], obtained $R = 0.080$ and $R_w = 0.081$.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34496 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors (B_{eq} for the Np and V atoms)

	Position	x	y	z	B (\AA^2)
Np	8(<i>e</i>)	0 (0)	2500 (0)	3749 (0)	0.4
V(1)	16(<i>f</i>)	1429 (3)	1057 (3)	510 (1)	0.9
V(2)	16(<i>f</i>)	3568 (3)	6064 (3)	511 (1)	0.9
O(1)	8(<i>e</i>)	0 (0)	2500 (0)	373 (8)	1.8 (0.3)
O(2)	8(<i>e</i>)	0 (0)	2500 (0)	5368 (8)	1.9 (0.3)
O(3)	16(<i>f</i>)	2517 (24)	621 (19)	22 (7)	2.5 (0.2)
O(4)	16(<i>f</i>)	9403 (24)	5577 (24)	709 (8)	2.6 (0.3)
O(5)	16(<i>f</i>)	2412 (25)	6736 (23)	917 (7)	2.6 (0.2)
O(6)	16(<i>f</i>)	2622 (21)	1800 (21)	892 (7)	2.3 (0.2)
O(7)	16(<i>f</i>)	5649 (20)	567 (21)	730 (7)	2.2 (0.2)

Table 2. Interatomic distances (\AA)

	Number at this distance	$\sigma(\text{\AA})$		Number at this distance	$\sigma(\text{\AA})$
Np—O(7)	2	2.287 0.018	O(2)—O(5)	2	2.779 0.024
Np—O(4)	2	2.307 0.021	O(2)—O(7)	2	2.855 0.020
Np—O(6)	2	2.342 0.018	O(2)—O(3)	2	2.869 0.021
Np—O(5)	2	2.348 0.020	O(3)—O(6)	1	2.693 0.028
V(1)—O(6)	1	1.620 0.019	O(3)—O(4)	1	2.753 0.029
V(1)—O(4)	1	1.657 0.020	O(3)—O(7)	1	2.846 0.027
V(1)—O(3)	1	1.718 0.020	O(3)—O(5)	1	2.859 0.028
V(1)—O(1)	1	1.767 0.006	O(4)—O(6)	1	2.700 0.027
V(2)—O(5)	1	1.627 0.020	O(4)—O(5)	1	2.799 0.029
V(2)—O(7)	1	1.658 0.018	O(4)—O(5)	1	2.814 0.029
V(2)—O(2)	1	1.768 0.006	O(4)—O(6)	1	2.833 0.030
V(2)—O(3)	1	1.811 0.020	O(5)—O(7)	1	2.609 0.027
O(1)—O(6)	2	2.742 0.022	O(5)—O(7)	1	2.757 0.028
O(1)—O(4)	2	2.822 0.022	O(5)—O(6)	1	2.814 0.028
O(1)—O(3)	2	2.848 0.021	O(6)—O(7)	1	2.712 0.025
			O(6)—O(7)	1	2.811 0.025

The results show, on the one hand, the importance of parameter c (28.723 \AA), since a large volume is needed to place eight Np atoms in a cell and, on the other, the $4/mmm$ pseudo Laue class, since the heavy atom almost occupies the 8(*a*) positions of $I4_1/acd$.

Only the absorption due to the Lindemann capillary could affect noticeably the measurement of intensities, which would not be disturbed by the α radiation of ^{237}Np , although its specific activity ($1 \text{ mCi} = 1.418 \text{ g}$) is high.

Description

The structure has respectively one, two and seven independent atoms of Np, V and O. Atomic parameters are listed in Table 1, interatomic distances in Table 2. *ORTEP* (Johnson, 1965) was used to draw Figs. 1 and 2.

Np atoms have eight O-atom neighbours at an average distance of 2.32 \AA ; the individual distances differ by little more than the experimental error. These eight O atoms, O(4) to O(7), are located at the corners of irregular polyhedra (strongly distorted Archimedean antiprisms) with twelve triangular faces (Fig. 1), each sharing a V atom: O(4), or O(6), is shared by Np and V(1) whereas O(5), or O(7), is shared by Np and V(2).

The O-atom environment of the two different V atoms is tetrahedral with distances between 1.620 and 1.811 \AA . Four O atoms surround each V(1), or V(2), at the corners of distorted tetrahedra whose edges range from 2.61 to 2.81 \AA . These distances, together with the interatomic angles (O—V—O range between 105 and 113°) show that the tetrahedra are only weakly deformed. The V—O distances are in agreement with those given by Clark (1973) for a VO_4 configuration (1.71 \AA , four-coordination). Each VO_4

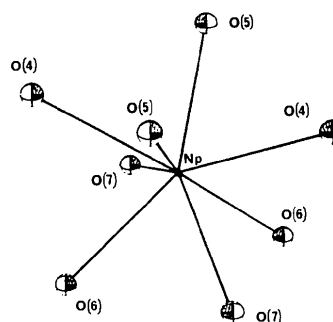


Fig. 1. The neptunium polyhedron.



Fig. 2. Stereoscopic view of two $(\text{VO}_3)_n$ chains.

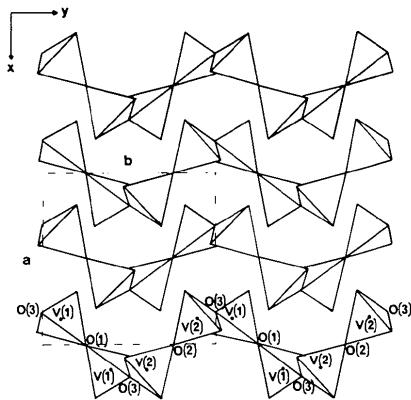


Fig. 3. Projection of the $(\text{VO}_3)_n$ chains on the xy plane (with only V atoms in $z \sim 0.2$ and 0.3).

tetrahedron is linked by two of its corners to two different Np polyhedra and shares the two remaining O atoms with two other VO_4 . Endless chains of tetrahedra are formed running parallel to the xy direction (Figs. 2 and 3). The orientation of the tetrahedra in a chain repeats itself every fourth VO_4 . The $(\text{VO}_3)_n$ chains are bound together in the crystal by the Np atoms.

The piling up of the polyhedra, linked only by the shared corners, confers great stability to this structure.

Conclusion

This structure determination shows $\text{Np}(\text{VO}_3)_4$ to be very different from the isostructural compounds of Nb^{V} (or Ta^{V}) with the formulation $A_{0.25}^{\text{IV}}\square_{0.75}B^{\text{V}}\text{O}_3$ [$A = \text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}$, $B = \text{Nb}, \text{Ta}$ (Keller, 1965); $A = \text{Th}$, $B = \text{Nb}$ (Labeau & Joubert, 1978)]. These compounds have a perovskite vacancy structure in which the O atoms are placed at the centres of the twelve cube edges, giving corner-shared strings of BO_6 octahedra which extend infinitely in three dimensions.

Although original, the $\text{Np}(\text{VO}_3)_4$ structure can nevertheless be considered classical for its cation

coordination. We recognize the VO_4 tetrahedra, as well as the dodecahedron encountered in other oxygen phases of lanthanides [e.g. $\text{Eu}_2(\text{WO}_4)_3$ (Templeton & Zalkin, 1963)] and tri- or tetravalent actinides [e.g. $\text{Am}_2(\text{WO}_4)_3$ (Tabuteau & Pagès, 1978); $\alpha\text{-ThV}_2\text{O}_7$ (Quarton, 1975)].

This structure can also be related to certain silicates in which the anions form endless chains of tetrahedra sharing two O atoms. The stability of this chain structure is due to the natural tendency of oxygen to form two covalent bonds.

Finally, the value of the ionic radius given by Shannon (1976) for Np^{4+} (0.98 Å, eight-coordination) shows that the Np–O distances (2.287 to 2.348 Å), here measured for the first time, are as expected.

References

- AHMED, F. R. (1974). *Crystallographic Computing Methods*. Copenhagen: Munksgaard.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CLARK, R. H. J. (1973). *Comprehensive Inorganic Chemistry*, 3rd ed., p. 522. New York: Pergamon.
- FREUNDLICH, W. & PAGÈS, M. (1969). *C. R. Acad. Sci. Sér. C*, **269**, 392–394.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KELLER, C. (1965). *J. Inorg. Nucl. Chem.* **27**, 1233–1246.
- LABEAU, M. & JOUBERT, J. C. (1978). *J. Solid State Chem.* **25**, 347–356.
- LE FLEM, G. & HAGENMULLER, P. (1964). *Rev. Hautes Temp. Refract.* **1**, 149–152.
- MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- QUARTON, M. (1975). Thèse de Doctorat ès Sciences, Paris.
- QUARTON, M., PAGÈS, M. & FREUNDLICH, W. (1978). *C. R. Acad. Sci. Sér. C*, **286**, 369–371.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- TABUTEAU, A. & PAGÈS, M. (1978). *J. Solid State Chem.* **26**, 153–160.
- TEMPLETON, D. H. & ZALKIN, A. (1963). *Acta Cryst.* **16**, 762–766.