# Crystal Structure of Potassium Dithorium Orthovanadate

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## Abstract

The crystal structure of $KTh_2(VO_4)_3$ was determined from three-dimensional X-ray diffraction data. The crystal symmetry is monoclinic, space group $C2/c$, with four formula units per cell and the lattice constants $a = 18.564$ (7), $b = 7.157$ (3), $c = 8.077$ (4) Å, $\beta = 101.05$ (5)°; $d_m = 5.38 \pm 0.04$, $d_x = 5.348$ Mg m$^{-3}$. The structure was solved by Patterson and Fourier analyses and refined by least-squares methods to a final $R$ value of 0.047, with full corrections for absorption and anomalous dispersion for cations. The V atoms have an irregular tetrahedral coordination. The $VO_4$ and $ThO_9$ polyhedra build the framework of the structure while the K atoms are weakly bound to their eight nearest oxygen neighbours.

## Introduction

A systematic investigation of double orthovanadates, $M^{I}Th_2(VO_4)_3$ and $M^{II}Th(VO_4)_3$, has revealed a number of structures isotypic with those of zircon, scheelite and monazite (Quarton, 1975*a*). With $M^I$ = K, Rb, Cs, however, the analogous compounds belong to a new structure type (Quarton, 1975*b*); their X-ray diffraction patterns are similar to those of double ortho-phosphates, such as $M^{I}Th_2(PO_4)_3$ with $M^I$ = Li, Na, Cu, Ag (Ranby & Hobbs, 1963; Schmid & Mooney, 1964), and of double arsenates $M^{I}Th_2(AsO_4)_3$ with $M^I$

= Li, Na (Freundlich, Erb & Pagès, 1974). Crystal data for double orthovanadates $M^{I}Th_2(VO_4)_3$ are shown in Table 1.

## Experimental

The morphology of a single crystal of $KTh_2(VO_4)_3$, isolated from the melt, was examined by optical goniometry (Fig. 1). The crystallographic features are consistent with the holehedry of the monoclinic system $2/m$.
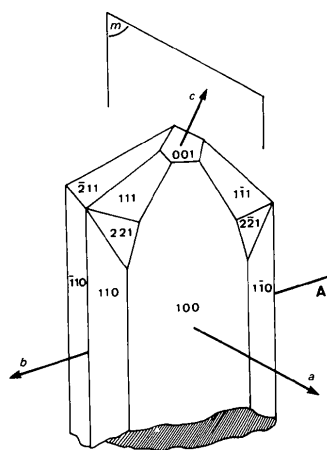


Fig. 1. Morphology of a $KTh_2(VO_4)_3$ single crystal.

Table 1. *Crystallographic parameters of double orthovanadates of* Th *and* K, Rb, Cd

Values were determined from powder diffraction patterns. Estimated standard deviations are given in parentheses.

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | $V$ (Å$^3$) |
|---|---|---|---|---|---|
| $KTh_2(VO_4)_3$ | 18.564 (7) | 7.157 (3) | 8.077 (4) | 101.05 (5) | 1053 (1) |
| $RbTh_2(VO_4)_3$ | 18.662 (4) | 7.183 (2) | 8.096 (2) | 101.63 (2) | 1063 (1) |
| $CsTh_2(VO_4)_3$ | 18.778 (9) | 7.217 (5) | 8.144 (4) | 102.23 (7) | 1078 (1) |

The crystal is a prismatic needle with the long axis parallel to the **c** direction and its dimensions are 25 × 35 × 200 μm. Weissenberg and Buerger diffraction patterns confirm the monoclinic symmetry. The conditions of possible reflections, $hkl$, $h + k = 2n$; $h0l$, $l = 2n$, lead to two possible space groups ($C2/c$ and $Cc$).

Density measurements ($d_m = 5\cdot38 \pm 0\cdot04$ Mg m$^{-3}$) correspond to four elementary KTh$_2$(VO$_4$)$_3$ groups per unit cell ($d_x = 5\cdot348$ Mg m$^{-3}$).

The intensities were collected for 1696 reflections using a Nonius CAD-3 diffractometer and Mo $K\alpha$ radiation selected by a graphite monochromator.

Reflections within the $\theta$ range 3–30° were measured, $h, k, l$ ranging, respectively, from $-24$ to 24, 0 to 9 and 0 to 10. The 040 reflection was measured every twenty reflections as a standard. The high value of the linear absorption coefficient, $\mu$(Mo $K\alpha$) = 32·1 mm$^{-1}$, required that a correction for absorption be made; this was performed by the Fortran program *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965).

The extreme values of the correction coefficients were 0·1744 and 0·3459. Simultaneously, the observed intensities were corrected for Lorentz and polarization effects.

## Structure determination

On a three-dimensional Patterson map the peaks corresponding to Th—Th vectors were easily found and hence the Th atoms are located on general $8(f)$ Wyckoff positions of the space group. These atoms contribute 49·5% of the electron density. A difference map, excluding the Th contribution, allows the V and K atoms to be located: V(1) on $8(f)$ Wyckoff positions of space group $C2/c$, V(2) and K on the binary axis, corresponding to $4(e)$ positions. Entering these sets of positions in a least-squares refinement (Busing, Martin & Levy, 1962) provided an agreement factor $R = 0\cdot20$.

On a new difference map, excluding the cationic contributions, we were able to locate the O atoms, which were then entered in two steps in the least-squares refinement. The $R$ value was then 0·08, with isotropic thermal parameters.

Finally, we introduced anisotropic temperature factors and anomalous-dispersion factors ($f'$ and $f''$

from *International Tables for X-ray Crystallography*, 1962) for the cations, and the final value of the $R$ factor was 0·047.*

The corresponding atomic coordinates and temperature factors are listed in Tables 2 and 3. Atomic scattering factors were taken from Cromer & Waber (1965).

## Description of the structure

The main feature of this structure is the groups of VO$_4$ tetrahedra, which are also found in the orthovanadates of zircon, scheelite, monazite and fergusonite types. Indeed, the absorption IR spectra of KTh$_2$(VO$_4$)$_3$ reveal some lines characteristic of O—V bonds in VO$_4$ tetrahedra; they are observed in the range 900–700 cm$^{-1}$ (Quarton, 1975a).

### Thorium environment

Nine O atoms surround the Th at an average distance of 2·48 Å. They are located on the corners of a polyhedron with 14 triangular faces and 21 edges (Fig. 2). This set of O atoms correctly surrounds the thorium, although it is slightly distorted, as is evident from Table 4. However, the variations are strongly connected to the specific environment of each O atom: besides the central Th, each O is bound to one or several other cations.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34626 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional and thermal parameters of the O atoms*

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·1447 (6) | 0·2261 (16) | 0·0563 (14) | 0·9 (3) |
| O(2) | 0·2801 (5) | 0·4597 (13) | 0·1794 (12) | 1·2 (3) |
| O(3) | 0·2032 (5) | 0·3523 (13) | 0·3896 (12) | 1·1 (3) |
| O(4) | 0·1371 (5) | 0·6190 (13) | 0·1583 (12) | 1·5 (3) |
| O(5) | 0·0769 (5) | 0·9771 (13) | 0·2505 (12) | 0·6 (2) |
| O(6) | 0·0296 (6) | 0·2361 (17) | 0·4278 (14) | 1·4 (3) |

Table 2. *Atomic coordinates and anisotropic thermal coefficients for the cations*

The $\beta_{ij}$ factors are from the thermal function of the form: $\exp[(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13}) \times 10^{-4}]$; zero values arise from symmetry considerations (Levy, 1956; Peterse & Palm, 1966).

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{23}$ | $\beta_{13}$ |
|---|---|---|---|---|---|---|---|---|---|
| Th | 0·15449 (2) | 0·90867 (6) | 0·03464 (5) | 1 (1) | 18 (1) | 4 (1) | 0 (1) | 0 (1) | 2 (0) |
| V(1) | 0·1886 (1) | 0·4203 (3) | 0·1832 (2) | 2 (1) | 25 (6) | 8 (2) | 1 (2) | −1 (2) | −2 (1) |
| V(2) | 0 | 0·1136 (4) | 0·25 | 4 (1) | 13 (8) | 28 (9) | 0 | 0 | 6 (3) |
| K | 0 | 0·6181 (6) | 0·25 | 10 (2) | 10 (5) | 39 (9) | 0 | 0 | 21 (5) |

## Table 4. *Interatomic distances (Å) and angles (°) relative to the thorium environment*

| | | | |
|---|---|---|---|
| Th—O(1.2)* | 2·29 (1) | Th—O(4.2) | 2·35 (1) |
| O(2.1) | 2·48 (1) | O(5.2) | 2·51 (1) |
| O(2.3) | 2·42 (1) | O(5.4) | 2·60 (1) |
| O(3.3) | 2·63 (1) | O(6.4) | 2·53 (1) |
| O(3.4) | 2·47 (1) | | |
| | | | |
| O(1.2)—O(2.1) | 2·89 (2) | O(3.3)—O(3.4) | 2·68 (2) |
| O(2.3) | 3·00 (2) | O(4.2) | 3·49 (2) |
| O(3.3) | 3·85 (2) | | |
| O(5.2) | 2·82 (2) | O(3.4)—O(4.2) | 2·70 (2) |
| O(5.4) | 2·93 (2) | O(5.4) | 3·60 (2) |
| O(6.4) | 3·80 (2) | O(6.4) | 3·40 (2) |
| | | | |
| O(3.3) | 2·84 (2) | O(4.2)—O(5.2) | 2·95 (2) |
| O(3.4) | 2·89 (2) | O(6.4) | 2·66 (2) |
| O(5.4) | 2·61 (2) | | |
| | | | |
| | | O(5.2)—O(6.4) | 3·00 (2) |
| O(2.3)—O(3.3) | 2·54 (1) | | |
| O(4.2) | 3·04 (2) | O(5.4)—O(6.4) | 2·60 (2) |
| O(5.2) | 2·61 (2) | | |
| | | | |
| O(1.2)—Th—O(2.1) | 74·5 (2) | O(3.3)—Th—O(3.4) | 63·3 (3) |
| O(2.3) | 79·1 (1) | O(4.2) | 88·8 (1) |
| O(3.3) | 103·0 (1) | | |
| O(5.2) | 71·9 (2) | O(3.4)—Th—O(4.2) | 68·1 (2) |
| O(5.4) | 73·5 (2) | O(5.4) | 90·6 (1) |
| O(6.4) | 110·5 (3) | O(6.4) | 85·6 (1) |
| | | | |
| O(2.1)—Th—O(3.3) | 67·4 (2) | O(4.2)—Th—O(5.2) | 74·5 (1) |
| O(3.4) | 71·6 (1) | O(6.4) | 66·0 (3) |
| O(5.4) | 61·8 (3) | | |
| | | | |
| | | O(5.2)—Th—O(6.4) | 73·0 (1) |
| O(2.3)—Th—O(3.3) | 60·2 (4) | | |
| O(4.2) | 79·2 (2) | O(5.4)—Th—O(6.4) | 60·8 (4) |
| O(5.2) | 63·8 (3) | | |

\* Oxygen indices are deduced from each other by the following symmetry operations:

$$(n.1) \xrightarrow{\ i\ } (n.2); \qquad (n.1) \xrightarrow{c\ mirror} (n.3);$$

$$(n.1) \xrightarrow{\ A_{2_1}\ } (n.4); \qquad (n.1) \xrightarrow{\ A_2\ } (n.5).$$
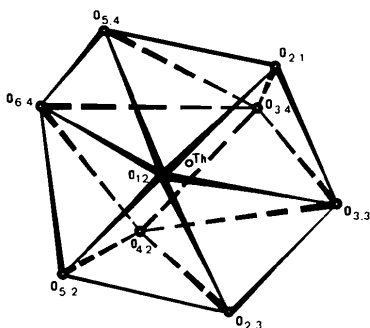


Fig. 2. First-nearest neighbour O atoms of the thorium atom.

With O atoms which do not belong to another Th environment, Th—O bonds are shorter [O(1.2) and O(4.2) for instance]. Such a coordination polyhedron is rarely encountered, for eightfold coordination is the most common for Th.

### Vanadium environment

The two independent atoms V(1) [8(*f*)] and V(2) [4(*e*)] have a slightly distorted tetrahedral environment; the angles and distances (Table 5) are consistent with those found in the literature; the mean V—O distances are 1·741 Å in V(1)O₄ and 1·706 Å in V(2)O₄.

### Potassium environment

The K atom is surrounded by eight O atoms, with the following bond lengths: K—O(4.1) 2·78 (1), K—O(5.1) 2·94 (1), K—O(6.1) 3·09 (2), K—O(6.3) 2·95 (2) Å.

This coordination is quite classical, but the corresponding polyhedron is not at all regular. The mean value of the K—O bonds (2·940 Å) is greater than that found in the literature (2·83 Å). So, K—O(4.1) excepted, the other atomic bonds are relatively weak.

## Discussion

Of particular interest is the bonding of the O atoms which are shared by the Th and V coordination poly-

## Table 5. *Interatomic distances (Å) and angles (°) relative to the vanadium environment*

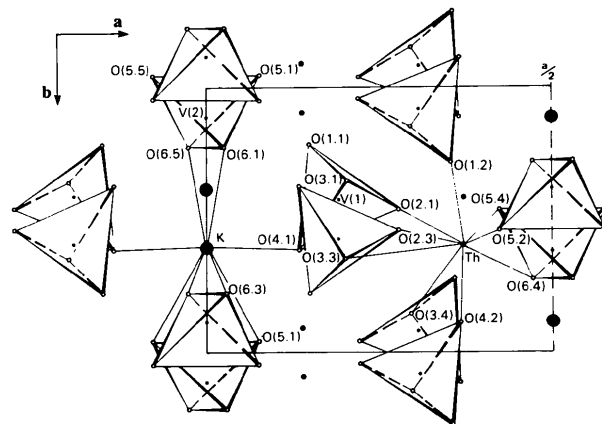| | | | |
|---|---|---|---|
| V(1)—O(1.1) | 1·824 (10) | V(1)—O(3.1) | 1·708 (8) |
| O(2.1) | 1·728 (8) | O(4.1) | 1·704 (8) |
| | | | |
| O(1.1)—O(2.1) | 3·02 (2) | O(2.1)—O(3.1) | 2·54 (1) |
| O(3.1) | 2·85 (2) | O(4.1) | 2·86 (2) |
| O(4.1) | 2·94 (2) | O(3.1)—O(4.1) | 2·79 (2) |
| | | | |
| O(1.1)—V(1)—O(2.1) | 116·7 (3) | O(2.1)—V(1)—O(3.1) | 95·2 (1) |
| O(3.1) | 107·6 (1) | O(4.1) | 113·1 (2) |
| O(4.1) | 112·9 (2) | | |
| | | O(3.1)—V(1)—O(4.1) | 109·5 (2) |
| | | | |
| V(2)—O(5.1) | 1·729 (8) | V(2)—O(6.1) | 1·682 (10) |
| | | | |
| O(5.1)—O(6.1) | 2·60 (2) | O(5.1)—O(5.5) | 2·85 (2) |
| O(6.5) | 2·89 (2) | O(6.1)—O(6.5) | 2·87 (2) |
| | | | |
| O(5.1)—V(2)—O(6.1) | 99·1 (1) | O(5.1)—V(2)—O(5.5) | 111·2 (2) |
| O(6.5) | 115·5 (3) | O(6.1)—V(2)—O(6.5) | 117·2 (3) |



Fig. 3. Projection of the structure along the *c* axis.

hedra. The 'Th complex' is formed by seven '$VO_4$' tetrahedra, of which five are bound to the central Th by a corner while two others are on opposite sides of, and each share an edge with, the polyhedron around the Th (Fig. 3). It can be assumed from the regular Th—O and V—O distances that the framework of the structure is made up of these three kinds of atoms. The O atoms bound to a K ion belong to six $VO_4$ tetrahedra. The K ions do not have their usual cubic environment and appear only to fasten the stacking of $VO_4$ tetrahedra within the planes perpendicular to the a direction. This may be related to the orientation of the crystal growth along the b or c axes.

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