Short Communications

The Crystal Structure of $K_3V_5O_{14}$ *

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As a part of a study of the system $K_2O-V_2O_5-H_2O$ at the U.S. Geological Survey, Washington, D.C., the crystal structure of $K_3V_5O_{14}$ has been worked out. $K_3V_5O_{14}$ crystallizes in red hexagonal prisms by rapid evaporation of dilute solutions of V_2O_5 and K_2O above $40^\circ C$. (R. Marvin, U.S. Geological Survey, written communication.) The crystals, which are often twinned, show strong dichroism, brown to dark red, with absorption $\epsilon < \omega$; ω = dark red and ϵ = greenish

yellow. They are optically uniaxial, negative, with refractive indices $\omega = 2.42$ and $\epsilon = 1.748$. The habit clearly indicates that the point group symmetry is ditrigonal pyramidal, C_{3v} .

From photographs of the $(hk0)$, (hhl) , and $(h0l)$ zones, made with a Buerger precession camera and $MoK\alpha$ radiation, and the habit of the crystal, the space group was established as $P31m$ (C_{3v}^2). The cell dimensions were determined with an x-ray single crystal goniometer using a scintillation counter. The following values were obtained:

$$\begin{array}{ll} a = 8.6796 \pm 0.0020 \text{ \AA} & MoK\alpha_1 = 0.70926 \text{ \AA} \\ c = 4.9914 \pm 0.0008 & MoK\alpha_2 = 0.71354 \\ V = 325.65 \text{ \AA}^3 & MoK\beta = 0.63225 \end{array}$$

$$\text{Density (observed)} = 3.01 \text{ g cm}^{-3}$$

$$\text{Density (calculated)} = 3.03 \text{ g cm}^{-3}.$$

Intensities were recorded for $(hk0)$, $(hk1)$, and $(h0l)$ zones on a Weissenberg camera using unfiltered MoK radiation. The multiple film technique was used and intensities were measured by visual comparison with a calibrated strip.

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Fig. 1. Electron density projection of $K_3V_5O_{14}$, $\rho(x, y)$. Dotted contour, 4 electrons/ $\text{\AA}^2$; contour interval 4 electrons/ $\text{\AA}^2$.

Fig. 2. View of the crystal structure of $K_3V_5O_{14}$, showing triangular and square pyramids linked into a sheet. Scale in Angstrom units.

Owing to difficulties involved in getting a pure sample for chemical analysis, the cell content was uncertain at the outset. Thus, all attempts to interpret the Patterson function $P(u,v)$ in terms of 3K and 6V atoms failed. A solution was readily found for 3K and 5V atoms, however, and the resulting model was confirmed by the Patterson $P(u,w)$. The oxygen locations were then found mainly by space reasoning. From the preliminary positions of the atoms, electron density maps of the functions $\rho(x,y)$ and $\rho(x,z)$ were prepared, and by successive steps of refinement, the following coordinates were determined:

Atom	x	y	z
3 K in (c)	0.605	0	0
2 V_1 in (b)	$1/3$	$2/3$	0.471
3 V_2 in (c)	0.231	0	0.472
2 O_1 in (b)	$1/3$	$2/3$	0.796
3 O_2 in (c)	0.240	0	0.782
3 O_3 in (c)	0.838	0	0.367
6 O_4 in (d)	0.469	0.177	0.366

For these coordinates the reliability factors and temperature coefficients have been found as follows:

($hk0$) (63 obs. data) $R = 0.116$, $B = 1.59 \text{ \AA}^2$;
 (hkl) (51 obs. data) $R = 0.145$, $B = 0.77$;
 ($h0l$) (93 obs. data) $R = 0.164$, $B = 0.90$.

In Fig. 1 the electron density projection $\rho(x,y)$ is illustrated.

The five vanadium atoms lie very nearly in the same z -plane forming almost regular pentagons. The fourteen oxygen atoms are bound to the vanadium atoms in rather an unusual way, reminiscent of the bonding in V_2O_5 (Byström *et al.*¹) and $KVO_3 \cdot H_2O$ (Christ *et al.*²). They form nearly square pyramids around the V_2 atoms and trigonal pyramids around the V_1 atoms, the pyramids all with apices pointing in the same direction along the c -axis and joined by sharing neighboring basal corners. Each hollow space resulting from the five-ring configuration is occupied by a potassium atom, placed about half way between the layers. Each potassium is surrounded by 10 oxygens, five from the apex oxygens of the polyhedra in the lower layer and five from basal corners of polyhedra in the layer above.

The V—O bonds in the c -direction of $K_3V_5O_{14}$ may be compared with the situation along the b -axis in V_2O_5 (Byström *et al.*¹). In both cases there is a short V—O distance of 1.5–1.6 Å within the layer and then a long distance to the neighboring layer. In V_2O_5 the long distance is still short enough, V—O = 2.81 Å, to act as a weak bond, giving the structure a three dimensional network character. In $K_3V_5O_{14}$ the corresponding distance is considerably prolonged, of the order of 3.4 Å, too long for a bond. The vanadium-oxygen polyhedra thus form a two dimensional network, now held together by the interfoliated potassium ions. The nine V—O distances range from 1.55 to 1.87 Å and the K—O distances from 2.72 to 3.36 Å.

A pictorial view of the structure is given in Fig. 2, where the V—O polyhedra have been especially emphasized.

The work on the structure is being continued and a full report will appear at a later date.

1. Byström, A., Wilhelmi, K.-A. and Brotzen, O. *Acta Chem. Scand.* 4 (1950) 1119.
2. Christ, C. L., Clark, J. R. and Evans, H. T., Jr. *Acta Cryst.* 7 (1954) 801.

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