Acta Chemica Scandinavica, 1994: 48: 533–536
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Crystal Structure of Potassium Pentavanadate

Howard T. Evans, Jr.[a,†] and Ann Marie Brusewitz[b]

[a]US Geological Survey, National Center 959, Reston, Virginia 22092, USA and [b]Lappkärrsvägen 45, S-10405 Stockholm, Sweden

Evans, H. T. Jr. and Brusewitz, A. M., 1994. Crystal Structure of Potassium Pentavanadate. – Acta Chem. Scand. 48: 533–536 © Acta Chemica Scandinavica 1994.

Potassium pentavanadate, $K_3V_5O_{14}$, is trigonal, space group $P31m$, with $a = 8.6901(5)$ and $c = 5.0063(4)$ Å. The crystal structure has been refined with 359 three-dimensional intensity data to $R = 0.056$. The structure consists of layers of corner-linked square and trigonal pyramids, with all pyramid apices oriented in the same direction parallel to the c-axis, and interlayered with K^+ ions. In the final structure model, 8% of the layers are oriented randomly in the opposite direction.

Few references to the compound potassium pentavanadate, $K_3V_5O_{14}$, have been recorded in the literature. The first definite report of its existence was given by Byström and Evans,[1] who derived a crystal structure based on projections obtained from film data. Three modes of preparation of the compound (as verified by X-ray powder diffractometry) have been described: (1) The crystals used by Byström and Evans were obtained from aqueous solution; (2) Kelmers[2] found this phase in a study of the system KVO_3–V_2O_5, in which he cooled melts of charges with varying ratios of the end members; and (3) Žúrková *et al.*[3] found that the pentavanadate was formed by heating the decavanadate, $K_6V_{10}O_{28}\cdot 10\ H_2O$ until all water was driven off at 300°C. (The last authors also found an analogous thallium compound, $Tl_3V_5O_{14}$, by similar means.) Holzberg *et al.*[4] studied the system K_2CO_3–V_2O_5 in an O_2 atmosphere and found five compounds, with K_2O:V_2O_5 ratios 1:4, 1:1, 16:9, 2:1 and 3:1, melting in the range 500–1300°C, but they did not find the phase 3:5. Pouchard,[5] in his study of sodium and potassium vanadates(IV, V), prepared 'phase D', namely the pentavanadate, citing the data of Byström and Evans,[1] and listing the X-ray powder data. He states that the compound melts congruently at 390°C. Hagenmuller,[6] following Pouchard,[5] places $K_3V_5O_{14}$ on a K_2O–V_2O_5–V_2O_4 phase diagram, but does not mention it in his review paper. Thus, the phase represents a definite, well established compound, but its conditions of stability are not yet clear. Most recently, Ozeki *et al.*[7a] reported (in an abstract) a crystal structure refinement of $K_3V_5O_{14}$ in $P31m$ with $a = 8.6909(4)$ and $c = 4.9973(3)$ Å, in which R reached 0.031.

Experimental

Trigonal crystals were obtained from an aqueous solution of KVO_3 acidified to ca. pH 6 with acetic acid. The unit cell and space group were determined by precession photography. The trigonal, acentric symmetry of the crystal is clearly apparent from the external habit (Fig. 1). The crystal structure was first determined from the analysis of Weissenberg photographs of $hk0$ and $h0l$ data, which revealed the unique, polar, layer structure consisting of corner-linked square and triangular pyramids.[1] Crystallo-

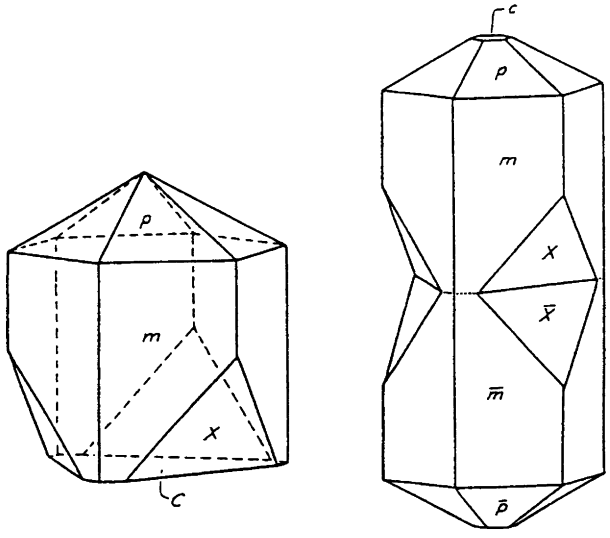

Fig. 1. Crystal forms of potassium pentavanadate: $c\{0001\}$, $C\{000\bar{1}\}$, $m\{10\bar{1}0\}$, $p\{10\bar{1}1\}$, $X\{xx\bar{2}\bar{x}\bar{1}\}$. X is often irregular, with $x \approx 5$.

† To whom correspondence should be addressed.

Table 1. Physical properties of potassium pentavanadate.

Formula: $K_3V_5O_{14}$ Formula weight: 596.06
Density (X-ray): 3.025 g cm^{-3}
Crystallography:
System: Hexagonal–trigonal
Space group: $P31m$, No. 157
Unit cell (from Guinier–Hägg data, see Table 2):
a=8.6899 (6) Å, c=5.0028 (6) Å
V=327.17 (5) $Å^3$, Z=1
Optical properties:
Uniaxial positive, ω=1.748 (2), ε=2.42 (2)
Color garnet red; X red, Z yellow
Luster adamantine
Crystal habit (Fig. 1):
Stubby, prismatic $m\{10\bar{1}0\}$;
Positive terminus pyramid $p\{10\bar{1}1\}$, base $c\{0001\}$
Negative terminus base $C\{000\bar{1}\}$, pyramid $X\{xx2\bar{x}\bar{1}\}$ ($x\approx 5$; $C \wedge X \approx 82°$)
Dominant forms: $m\{10\bar{1}0\}$, $p\{10\bar{1}1\}$, $C\{000\bar{1}\}$
Twinning, on $C\{000\bar{1}\}$, common (base-to-base doublets)
Cleavage $c\{0001\}$, perfect; fracture conchoidal

graphic data for $K_3V_5O_{14}$ are given in Table 1, and powder data, obtained by the Guinier–Hägg method with Cu$K\alpha_1$ radiation, in Table 2.

A thermal study of $K_3V_5O_{14}$ was carried out with a Guinier–Lenne heating powder camera (NONIUS) over the temperature range 25–550°C. The sample melts incongruently at 400°C to a liquid plus an unidentified phase which melts at 520°C. In the temperature range 20–400°C the a-axis does not change significantly, while the c-axis expands linearly and substantially ($\alpha = 3.0 \times 10^{-4}$ Å $°C^{-1}$). The melting temperature is in accord with that reported by Pouchard,[5] although he stated that melting is congruent. A differential scanning calorimetric experiment from 25 to 330°C showed no evidence of any thermal anomaly.

We have made several attempts since 1959 to refine the structure using three-dimensional counter data, but results have not been considered satisfactory ($R > 0.12$, odd electron density effects). Recently, using a NONIUS CAD4 automatic diffractometer, a new data set has been obtained, which has been analyzed with the XTAL2.4 program system[8] at a SUN 4/110 workstation. The ease of use and speed of this computer made it possible to find a proper solution to the structure problem.

Table 2. X-ray powder data for potassium pentavanadate.[a]

h k l	d(meas)	d(calc)	I(rel)
0 0 1	5.002	4.999	58
1 1 0	4.345	4.345	6
1 0 1	4.165	4.166	9
2 0 0	3.763	3.763	15
1 1 1	3.280	3.280	100
2 0 1	3.007	3.008	45
2 1 0	2.845	2.844	64
3 0 0	2.510	2.509	30
0 0 2	2.500	2.501	30
2 1 1	2.472	2.473	30
2 2 0	2.172	2.172	4
1 1 2	2.166	2.168	13
3 1 0	2.088	2.087	22
2 2 1	1.9927	1.9932	3
3 1 1	1.9268	1.9265	10
2 1 2	1.8782	1.8784	24
3 0 2	1.7691	1.7713	8
4 0 1	1.7610	1.7610	8
3 2 0	1.7258	1.7265	8
4 1 0	1.6422	1.6422	23
3 2 1	1.6319	1.6320	19
3 1 2	1.6024	1.6016	5
4 1 1	1.5604	1.5603	29
1 1 3	1.5565	1.5569	8
2 0 3	1.5247	1.5246	14
5 0 0	1.5055	1.5051	8
3 3 0	1.4482	1.4483	9
2 1 3	1.4386	1.4386	11
4 2 0	1.4218	1.4222	6
3 3 1	1.3908	1.3912	3
3 0 3	1.3887	1.3898	3
4 1 2	1.3728	1.3731	9
4 2 1	1.3686	1.3681	9
5 1 0	1.3516	1.3516	4
3 1 3	1.3023	1.3028	5
5 0 2	1.2897	1.2899	4
3 3 2	1.2534	1.2535	7
4 2 2	1.2363	1.2366	6
5 2 0	1.2050	1.2051	3
3 2 3	1.1995	1.1995	4
4 1 3	1.1704	1.1701	7
2 1 4	1.1451	1.1449	7
6 1 1	1.1185	1.1186	4

[a] Data measured on Guinier–Hägg pattern, Si internal standard (a=5.4308 Å), Cu $K\alpha_1$ radiation (λ=1.54056 Å). Note: a weak line (10.0) at 7.59 Å reported by Pouchaud[5] was not observed.

Structure analysis

In the entire sphere bounded by $2\theta = 60°$, 3590 reflections were measured and averaged to 359 independent F-values (Friedel pairs averaged together). Of these only 6 had $|F| < 3\sigma(F)$, but all were used for the structure analysis. The crystal had dimensions of 0.010 cm prism diameter and 0.012 cm height. The absorption of Mo$K\alpha$ X-rays ranged from 35 to 40% ($\mu = 42.6$ cm^{-1}), and has been neglected in all subsequent calculations. The usual Lorentz-polarization and anomalous dispersion corrections have been applied. An isotropic extinction factor was refined with the structure parameters.

Starting with the parameters given by Byström and Evans,[1] least-squares analysis led to the conventional reliability index $R = 0.11$. An electron density map confirmed the main features of the structure, but several small peaks suggested the possibility that some layers were inverted in a disordered manner. When such a layer was introduced into the model to the extent of 8%, the structure then refined (based on unit weights) to $R = 0.056$, ($R_w = 0.067$), with a goodness of fit 1.67. (Ozeki *et al.*[7a] did not find any such disorder in their structure analysis.[7b])

Table 3. Structure parameters for potassium pentavanadate: RMS thermal displacement, u (in Å); occupancy fraction, p; anisotropic thermal parameters, U_{ij} (in Å).
Coordinates:

Atom	Eqpt.	Sym.	x	y	z	u	p	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	3*c*	*m*	0.6080(4)	0	0.0001(7)	0.159(8)	1.00	0.029(1)	0.017(1)	0.029(1)	0.009(1)	0.001(1)	0
V(11)	2*b*	3	1/3	2/3	0.5194(6)	0.099(10)	0.92	0.009(1)	$=U_{11}$	0.012(1)	$=1/2U_{11}$	0	0
V(21)	3*c*	*m*	0.2292(2)	0	0.5160*	0.106(6)	0.92(2)	0.009(1)	0.012(1)	0.017(1)	0.006(1)	0.001(1)	0
O(11)	2*b*	3	1/3	2/3	0.194(2)	0.16(2)	0.92	0.030(4)	$=U_{11}$	0.017(5)	$=1/2U_{11}$	0	0
O(21)	3*c*	*m*	0.250(2)	0	0.190(2)	0.19(2)	0.92	0.052(6)	0.050(8)	0.007(4)	0.025(4)	−0.004(4)	0
O(31)	3*c*	*m*	0.831(1)	0	0.566(3)	0.16(2)	0.92	0.013(3)	0.025(6)	0.060(8)	0.013(3)	0.005(4)	0
O(41)	6*d*	1	0.461(1)	0.169(1)	0.637(1)	0.15(2)	0.92	0.019(3)	0.021(3)	0.027(3)	0.004(3)	0.000(3)	0.004(3)
V(12)			1/3	2/3	0.4806	0.10	0.08						
V(22)			0.2292	0	0.4840	0.11	0.08						
O(12)			1/3	2/3	0.806	0.16	0.08						
O(22)			0.250	0	0.810	0.19	0.08						
O(32)			0.831	0	0.434	0.16	0.08						
O(42)			0.461	0.169	0.363	0.15	0.08						

*z-Parameter fixed for least-squares analysis.

A final test was made with the data set averaged with the Friedel pairs kept separate (703 observations), to determine, if possible, the sense of polarity of the crystal. The refined model, on further least-squares processing with the separated data set (unit weights), led to $R = 0.059$; an inverted model (x, y, z reversed) led to $R = 0.057$. As this change in R results from the addition of a single parameter, the anomalous dispersion of the vanadium atoms shows that there is a strong probability[9] that the pyramid apices point downward in the crystal with respect to the morphology (Fig. 1), rather than upward.

The layers are separated by K^+ ions, which fit equally well on both sides of the V_5O_{14} layer. No further extra features appeared on the ΔF-map, and the disordered model was considered to be a satisfactory solution to the structure problem. A list of observed and calculated structure factors are available from the authors.

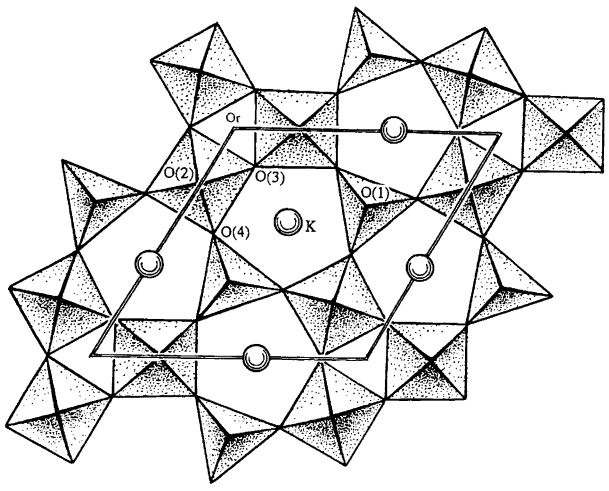

Fig. 2. The $V_5O_{14}^{3-}$ vanadate layer network viewed along the c-axis. O(1) and O(2) are bonded to V(1) and V(2), respectively.

Description of the structure

A plan view of the layer structure is shown in Fig. 2, and detail of a portion of the layer in Fig. 3. The layer character of this structure is very flat and strongly polarized, with all the pyramid apices pointed in the same direction parallel to c. Interatomic distances in the structure are summarized in Table 4. The apical bond length is the same for both the square and triangular pyramids, 1.64(1) Å. In the square pyramid, the basal V–O bonds linked to adjacent square pyramids are 1.903(8) Å, and those linked to triangular pyramids are 1.806(4) Å. The V–O bonds in the triangular base are 1.741(7) Å. The dimensions of the pyramidal base (O–O distances) are 2.55(1) Å in both the square and triangular pyramids.

The partial inversion of the layers found in the structure analysis was assumed to be random, about one layer in 12 being reversed, always with the K^+ layers in common. It is possible that inversion may be in aggregates, corresponding to lamellar microtwinning (not visible optically), but to determine how the inversion actually occurs will require examination with the high-resolution electron microscope.

The K^+ ion is ten-coordinated, contacting two triangular and three square pyramidal apices on one side and five pyramidal base atoms on the other. The average of the former is 3.026 Å, of the latter 2.924 Å, and the average of all ten contacts is 2.975 (Fig. 4). Square pyramidal coordination with oxygen by vanadium(V), first clearly demonstrated by Byström *et al.*[10] in V_2O_5, is now

Table 4. Interatomic distances in potassium pentavandate.

Atoms	d/Å	Atoms	d/Å
V(1)–O(11)	1.630(12)	K–O(41)′(×2)	2.992(8)
V(1)–O(41) (×3)	1.741(7)	V(2)–O(2)	1.643(9)
K–O(11) (×2)	2.850(4)	V(2)–O(31) (×2)	1.806(4)
K–O(21) (×2)	3.136(5)	V(2)–O(41) (×2)	1.903(8)
K–O(21)′	3.257(15)	V(11)–V(21)	3.440(1)
K–O(31)	2.907(13)	V(21)–V(21)′	3.449(3)
K–O(41) (×2)	2.926(8)		

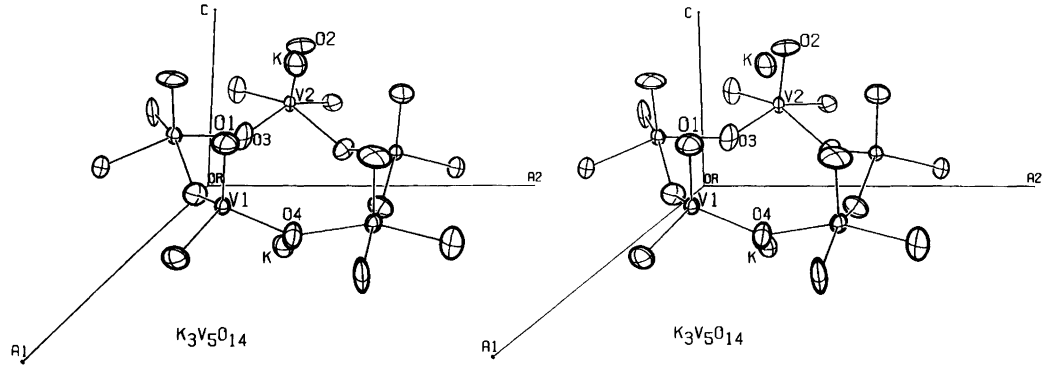

Fig. 3. Detail of the structure of potassium pentavanadate in perspective, showing 50% probability thermal ellipsoids.

known to be common. In alkaline solutions tetrahedral VO_4^{3+} ions analogous to PO_4^{3+} prevail, and as pH is reduced these tend to link into chains or rings[11] (metavanadates). On the acid side of neutrality (pH 4–6) the well known orange complex $V_{10}O_{28}^{6+}$ appears in several hydrogenated states, consisting of condensed, distorted octahedra.[12,13] Thus $K_3V_5O_{14}$ in one sense is intermediate between the metavanadate and polyvanadate states, containing both tetrahedral and five-fold coordination. If weakly acidic decavanadate solutions are allowed to stand for several days, eventually slightly soluble potassium trivanadate (KV_3O_8) precipitates,[12] which contains both octahedral and square pyramid (V_2O_8 groups) polyhedra. Thus vanadium coordination tends to increase with lowered pH, and the whole range of configurations is represented by various compounds.

The structure of $K_3V_5O_{14}$ bears a close resemblance to that of $K_3Ta_3B_2O_{12}$, which has a similar layered trigonal topology.[14] The unit cell is in space group $P\bar{6}2m$ with $a = 8.7816$ and $c = 3.8990$ Å.[15] In this case the trigonal pyramid is replaced by a BO_3 triangle, and the square pyramids are joined directly to the adjacent layer forming TaO_6 octahedra (hence the shortened c-axis).

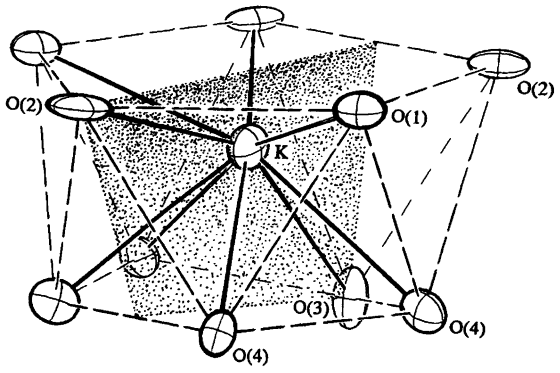

Fig. 4. Coordination of the K^+ ion in potassium pentavanadate. The intersection of the crystallographic mirror plane is shown shaded. The dashed lines show the pentagonal antiprismatic coordination.

Acknowledgments. We particularly thank Yongshan Dai, who collected our last and best intensity data set on the CAD4 diffractometer at the Smithsonian Institution. We are grateful to Tomoji Ozeki, who also recently refined this structure, for his generous exchange of information. Thanks are also due to Bruce S. Hemingway of the US Geological Survey for performing the differential scannig calorimetry experiment.

References

1. Byström, A. M. and Evans H. T., Jr. *Acta Chem. Scand. 13* (1959) 377.
2. Kelmers, A. D. *J. Inorg. Nucl. Chem. 17* (1961) 168.
3. Žúrková, L., Sucha, V., Vargova, C. and Corba, J. *Coll. Czech. Chem. Commun. 39* (1974) 387.
4. Holzberg, F., Reisman, A., Berry M. and Berkenblit, M. *J. Am. Chem. Soc. 78* (1956) 1536.
5. Pouchard, M. *Sur quelques nouvelles phases des systèmes vanadium-oxygène-sodium et vanadium-oxygène-potassium: etude cristallographique, magnetique et électrique*, Thesis, Bordeaux University, Bordeaux 1967.
6. Hagenmuller, P. In: Trotman-Dickinson, A. F., Ed., *Comprehensive Inorganic Chemistry* Pergamon Press, New York 1973, Vol. 4, pp. 541–605.
7. (a) Ozeki, T., Ichida, K. and Sasaki, Y. *Acta Crystallogr., Sect. A43 Supplement* (1987) C148; (b) Ozeki, T. *Personal communication.*
8. Hall, S. R. and Stweart, J. M., Eds., *XTAL User's Manual, Version 2.4* University of Western Australia and University of Maryland 1989.
9. Hamilton, W. C. *Acta Crystallogr. 18* (1965) 502.
10. Byström, A., Wilhelmi, K.-A. and Brotzen, O. *Acta Chem. Scand. 4* (1950) 1119.
11. Pettersson, L., Hedman, B., Andersson, I. and Ingri, N. *Chem. Scr. 22* (1983) 254.
12. Evans, H. T., Jr. and Block, S. *Inorg. Chem. 5* (1966) 1808.
13. Ingri, N. and Brito, F. *Acta Chem. Scand. 13* (1959) 1971.
14. Choisnet, J., Groult, D., Raveau, B. and Gasparin, M. *Acta Crystallogr., Sect. B33* (1977) 1841.
15. Abrahams, S. C., Zyontz, J. L., Berstein, J. L., Remeika, J. P. and Cooper, A. S. *J. Chem. Phys. 75* (1981) 5456.

Received August 31, 1993.