

ungeordnet. Es würden nur die diffusen Stäbe auftreten.

Fig. 2 stellt die beobachteten und die berechneten Profile der diffusen Reflexe dar. Daß die Reflexe ξ , 1/2, 5 auffallend schwach sind, rührt davon her, daß das Pb-Atom dicht neben dem Punkt (0, 0, 0,4) sitzt und der Strukturfaktor $F(\xi, 1/2, 5)$ infolgedessen beinahe verschwindet. Ferner ersieht man, daß die Maxima bei $\xi \equiv 0 \pmod{1}$ diejenigen bei $\xi \equiv 1/2 \pmod{1}$ überragen. Dies hängt damit zusammen, daß die Wahrscheinlichkeiten A und D größer als B und C sind. Wären B und C größer als A und D , so wäre das Intensitätsverhältnis umgekehrt. Daß die Maxima bei $\xi \equiv 1/2 \pmod{2}$ stärker sind als diejenigen bei $\xi \equiv -1/2 \pmod{2}$, ist auf die Tatsache $A > D$ zurückzuführen.

Obwohl sich die wesentlichen Merkmale des Intensitätsverlaufs relativ gut durch die Berechnung reproduzieren lassen, gibt es in einigen Stellen sehr große Abweichungen. Sie sind wahrscheinlich eher auf die experimentellen Schwierigkeiten zurückzuführen als auf irgendwelche Mängel des Strukturmodells. Die ersteren bestehen hauptsächlich darin, daß die Messung mit einer Spaltöffnung erfolgen mußte, die viel größer als der Querschnitt der diffusen Stäbe war. Das Auflösungsvermögen sowie die beobachtete Intensität hängen deshalb von dem Winkel ab, der zwischen dem gebeugten Strahl und dem zu messenden reziproken Gitterstab gebildet wird. Die Auflösung ist am schlechtesten und die Intensität wird am schwersten verfälscht, falls dieser Winkel 90° beträgt. Problematisch ist auch die Frage, ob den

Meßwerten eine Lorentzkorrektur angebracht werden soll oder nicht. Müller (1979) schlug ein Meßverfahren vor, in dem eine ähnliche Korrektur berücksichtigt wird. Des weiteren könnte es eventuell zu einer geringen Unterschätzung der Wahrscheinlichkeiten geführt haben, daß den experimentell bedingten, zusätzlichen Verschmierungen des Reflexprofils keine Rechnung getragen wurde.

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Structure of K_{0.5}V₂O₅

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Abstract. Potassium divanadate, K_{0.5}V₂O₅, $M_r = 201.43$, orthorhombic, *Cmcm*, $a = 3.6784$ (2), $b = 11.6120$ (7), $c = 18.6332$ (9) Å, $V = 795.88$ (8) Å³, $Z = 8$, $D_x = 3.362$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 49.74$ cm⁻¹, $F(000) = 764$, room temperature, final $R = 0.041$ for 632 unique observed reflections. Distorted octahedra of VO₆ are linked together to form V₂O₅ layers parallel to (001). K ions are situated between the layers, surrounded by eight O atoms (CsCl-like coordination), and are in a mirror plane parallel to (001).

Introduction. In the course of a phase-equilibrium study on the KV₂O₅–V₂O₄–V₂O₅ system (Kanke, Takayama-Muromachi & Kato, 1990), we found a new phase (K_{0.5}V₂O₅, orthorhombic). This composition is close to those of the three phases whose structures are unknown, μ (K_{0.42–0.44}V₂O₅, crystal system unknown), ν (K_{0.51}V₂O₅, monoclinic) and ν' (K_{0.61–0.65}V₂O₅, monoclinic), reported previously (Pouchard & Hagenmuller, 1967).

As we successfully prepared single-crystal samples, we have determined the crystal structure.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2), $x = 0$ for all atoms

	y	z	B_{eq}
V(1)	0.43426 (7)	0.42090 (6)	0.61 (1)
V(2)	0.73111 (8)	0.42018 (6)	0.67 (1)
K	0.0800 (3)	0.25	2.15 (4)
O(1)	0.5810 (4)	0.0470 (2)	0.81 (6)
O(2)	0.4519 (4)	0.3355 (3)	1.44 (8)
O(3)	0.7121 (4)	0.3351 (3)	1.24 (8)
O(4)	0.2589 (4)	0.4421 (2)	0.89 (6)
O(5)	0.8989 (3)	0.0651 (2)	0.66 (6)

Table 2. Interatomic distances (\AA)

V(1)—O(2)	1.605 (5)	V(2)—O(3)	1.600 (5)
V(1)—O(1 ^a)	1.805 (4)	V(2)—O(1 ^a)	1.847 (5)
V(1)—O(5 ^{iv})	1.902 (1)	V(2)—O(4 ^{vi})	1.911 (1)
V(1)—O(5 ^v)	1.902 (1)	V(2)—O(4 ^{vii})	1.911 (1)
V(1)—O(4)	2.075 (5)	V(2)—O(5 ^{viii})	1.967 (4)
V(1)—O(1 ^{ix})	2.357 (4)	V(2)—O(4 ^{ix})	2.570 (5)
K—O(2 ^{iv,v,viii,ix})	2.852 (4)	K—O(1 ^{vi,viii,ix})	2.872 (4)

Symmetry code: (i) $x, y, 1/2 - z$; (ii) $x, 1 - y, 1/2 + z$; (iii) $x, 1 - y, 1 - z$; (iv) $1/2 + x, -1/2 + y, 1/2 - z$; (v) $-1/2 + x, -1/2 + y, 1/2 - z$; (vi) $1/2 + x, 1/2 + y, z$; (vii) $-1/2 + x, 1/2 + y, z$; (viii) $1/2 + x, -1/2 + y, z$; (ix) $-1/2 + x, -1/2 + y, z$.

Experimental. In the early stage of our phase equilibrium study on the $\text{K}_x\text{V}_2\text{O}_5$ system, the composition of the title phase was regarded as $\text{K}_{0.525}\text{V}_2\text{O}_5$, so that the powdered sample having this composition was synthesized from KVO_3 , V_2O_4 and V_2O_5 at 873 K. Single crystals were prepared by chemical-transport methods using HCl gas as transport medium. As there was a possibility of the crystals being hygroscopic, the crystal was sealed in a thin-walled (0.01 mm) glass capillary. Lath-like crystal elongated in [100] and flat in (010), size $0.205 \times 0.03 \times 0.02$ mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from 21 reflections ($54^\circ < 2\theta < 64^\circ$), intensity collection by ω - θ scan with $\Delta\omega = (0.7 + 0.35\tan\theta)^\circ$, $(\sin\theta/\lambda) \leq 0.904 \text{ \AA}^{-1}$, $0 \leq h \leq 6$, $-16 \leq k \leq 16$ when $(\sin\theta/\lambda) \leq 0.704 \text{ \AA}^{-1}$ and $0 \leq k \leq 21$ when $(\sin\theta/\lambda) > 0.704 \text{ \AA}^{-1}$, $-33 \leq l \leq 33$, 4016 reflections measured, 1121 unobserved, 1627 reflections with $I > 3\sigma(I)$, 632 unique observed reflections, R_{int} for F 0.027. Three standard reflections 600, 020 and 002 measured every 2 h, decrease of intensity 1.3% during the total exposure time of 142.6 h, linear decay correction applied. Computed absorption correction, correction factor for F from 1.034 to 1.091. Structure solved by direct methods, refined by least-squares methods based on F , anisotropic temperature factors,* atomic

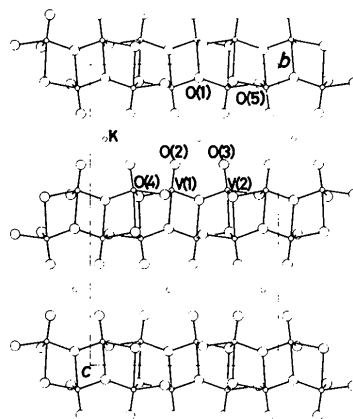
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52884 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). $R = 0.041$, $wR = 0.045$, $w = 1/\sigma^2(F)$, $\Delta/\sigma < 0.005$ in final refinement cycle, $\Delta\rho = -1.2$ – 2.3 e \AA^{-3} . Computer programs used were *SDP* (B. A. Frenz & Associates Inc., 1985), and *ORTEPII* (Johnson, 1976).

Discussion. The atomic fractional coordinates and the equivalent isotropic thermal parameters are listed in Table 1. Important interatomic distances are shown in Table 2. Fig. 1 shows the structure viewed along [100]. Distorted VO_6 octahedra are linked together by sharing edges and corners, and form a V_2O_7 column parallel to [100]. The columns are connected to each other by edge-sharing to form a V_2O_5 slab parallel to (001). The slabs are turned over alternately. Between the slabs, there is a mirror plane parallel to (001). K ions are located in the plane and are surrounded by eight O atoms (CsCl-like coordination). The coordination polyhedra of V(1), V(2) and K have a mirror plane parallel to (100) in which the metal ions are situated. The V_2O_5 slab of the title phase is similar to that of $\delta\text{-Ag}_{1-x}\text{V}_2\text{O}_5$ (Andersson, 1965), $\text{Na}_{0.56}\text{V}_2\text{O}_5$ (Kanke, Kato, Takayama-Muromachi & Isobe, 1990) and $\epsilon\text{-Cu}_x\text{V}_2\text{O}_5$ (Galy, Lavaud, Casalot & Hagenmuller, 1970). However, the slabs are not turned over alternately in the latter three phases.

The K—O distances, 2.852 (4) and 2.872 (4) \AA (Table 2), agree with those calculated between eight-coordinated K^+ and three-coordinated O^{2-} , 2.87 \AA (Shannon, 1976).

The single crystal analyzed in the present study was grown from the powdered sample with a nominal composition $\text{K}_{0.525}\text{V}_2\text{O}_5$. However, EPMA measurement using standard materials, KTaO_3 and LaVO_4 , indicated that the K/V molar ratio of the single crystal was $[0.495(5)]/2$. Therefore, its composition was regarded as $\text{K}_{0.50}\text{V}_2\text{O}_5$.

Fig. 1. Projection of the structure of $\text{K}_{0.50}\text{V}_2\text{O}_5$ onto (100).

The phase-equilibrium study (Kanke, Takayama-Muromachi & Kato, 1990) showed that the present phase has a homogeneity region represented by $K_xV_2O_5$ ($0.49 \leq x \leq 0.54$). Therefore, it is not appropriate to formulate this compound as the stoichiometric compound KV_4O_{10} . The above-mentioned structure cannot contain K ions in excess of $K_{0.50}V_2O_5$. Detailed study is needed to determine the sites of the excess K ions in a potassium-rich compound.

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Structure of Nonasodium α -Triniobatopentadecawolframodiphosphate–Acetonitrile–Water (1/2/23), $Na_9[P_2W_{15}Nb_3O_{62}] \cdot 2CH_3CN \cdot 23H_2O$

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Abstract. $Na_9[P_2W_{15}Nb_3O_{62}] \cdot 2C_2H_3N \cdot 23H_2O$, $M_r = 4974$, triclinic, $P\bar{1}$, $a = 13.341$ (5), $b = 15.890$ (6), $c = 21.395$ (7) Å, $\alpha = 87.85$ (3), $\beta = 77.18$ (3), $\gamma = 71.87$ (3)°, $V = 4200$ (5) Å³, $Z = 2$, $D_x = 3.79$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 214.6$ cm⁻¹, $F(000) = 4264$, $T = 295$ K, $R = 0.062$ for 6966 independent data [$I \geq 3\sigma(I)$]. The anion has the well-known α - $(P_2W_{18}O_{62})^{6-}$ structure with three Nb atoms substituting for the W atoms in one of the two W_3O_{13} caps consisting of three edge-linked WO_6 octahedra. Despite orientational disorder (*ca* 28:72) which partly exchanges the caps, small differences in corresponding bond lengths in the two ends are apparent.

Introduction. This work stems from the continuing studies in this laboratory of trisubstituted heteropolytungstate anions as soluble metal oxide analogues, and in particular of the chemistry of derivatives formed by covalent attachment of catalytically active organometallic groups to surface O atoms of these polyoxoanions. The complete structural characterization of, *e.g.*, $(Bu_4N)_7[(C_5Me_5)Rh.P_2W_{15}Nb_3O_{62}]$ and $(Bu_4N)_7[(C_6H_6)Ru.P_2W_{15}Nb_3O_{62}]$ (Edlund, Saxton, Lyon & Finke,

1988), which are soluble in non-protic polar organic solvents, has been hindered by the failure to obtain single crystals suitable for X-ray work. We have therefore attempted to grow single crystals of mixed-cation (tetraalkylammonium + alkali metal) salts of these complexes. The compound whose structure we report was obtained unexpectedly in the course of this work. This is fortunate since the $(P_2W_{15}Nb_3O_{62})^{9-}$ anion has proved to be the best of the polyoxoanions examined to date for covalently attaching ('supporting') organometallic catalyst precursors, *e.g.* $[(1,5\text{-cod})Ir.P_2W_{15}Nb_3O_{62}]^{8-}$ (Finke, Lyon, Nomiya, Sur & Mizuno, 1990).

Experimental. A solution of $(Bu_4N)_9(P_2W_{15}Nb_3O_{62})$ (Edlund, Saxton, Lyon & Finke, 1988) in MeCN was treated with a solution of $NaBF_4$ in MeCN, and ethyl acetate was then added to precipitate $(Bu_4N)_{6-x}Na_{3+x}(P_2W_{15}Nb_3O_{62})$ ($x = 0$ or 1). A solution of the latter (1.0 g) in 1:1 CD_3CN/CH_3CN (4 ml) to which 3 drops of water had been added deposited a few well-formed colorless prisms of the title compound on standing in an NMR tube for 48 h at 293 K. The amount of material (*ca* 20 mg) precluded a full elemental analysis. Calc. for $Na_9(P_2W_{15}Nb_3O_{62}) \cdot 2CH_3CN \cdot 23H_2O$: Na 4.32, W 57.5%; found: Na 4.24, W 57.5% (Mikroanalytisches Labor Pascher, Remagen, Federal Republic

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