

2,038 (2) à 2,058 (3) Å et leur longueur moyenne [2,052 (3) Å] est pratiquement identique à celle de ses homologues dans CrPS<sub>4</sub> (2,045 Å) (Toffoli, Khodadad & Rodier, 1977a), dans Li<sub>3</sub>PS<sub>4</sub> (2,050 Å) (Mercier, Malugani, Fahys & Robert, 1982), ou dans Pd<sub>3</sub>(PS<sub>4</sub>)<sub>2</sub> (2,05 Å) (Simon, Peters, Peters & Hahn, 1983).

Les distances Ag—S sont relativement homogènes puisqu'elles vont de 2,535 (2) à 2,645 (2) Å [moyenne 2,578 (2) Å] et sont légèrement plus courtes que dans d'autres thiophosphates d'argent. Ainsi, la longueur moyenne des distances Ag—S est de 2,68 Å dans la variété orthorhombique de Ag<sub>4</sub>P<sub>2</sub>S<sub>6</sub> (Toffoli, Khodadad & Rodier, 1983), de 2,63 Å dans la variété monoclinique du même composé (Toffoli, Michelet, Khodadad & Rodier, 1982) et de 2,64 Å dans Ag<sub>4</sub>P<sub>2</sub>S<sub>7</sub> (Toffoli, Khodadad & Rodier, 1977b). Les valeurs extrêmes des angles S—Ag—S sont de 104,19 (6) et 114,93 (6)° [moyenne 109,37 (6)°]. Le tétraèdre AgS<sub>4</sub> est donc peu déformé contrairement à ce qui a été observé dans les thiophosphates précédemment cités et dans Ag<sub>7</sub>(PS<sub>4</sub>,P<sub>2</sub>S<sub>7</sub>) (Toffoli, Khodadad & Rodier, 1982). En effet, dans ces composés l'écart entre les valeurs maximale et minimale des angles S—Ag—S dépasse parfois 80°.

L'environnement de l'atome de zinc est aussi presque régulier. Les angles S—Zn—S sont compris entre 99,54 (8) et 120,91 (8)° [moyenne 109,34 (8)] et les distances Zn—S entre 2,337 (2) et 2,371 (2) Å [moyenne 2,353 (2) Å]. Celles-ci sont comparables à leurs homologues dans ZnS (2,34 Å) (Wyckoff, 1963) ou dans Zn<sub>4</sub>(P<sub>2</sub>S<sub>6</sub>)<sub>3</sub> (2,36 Å) (Bouchetière, Toffoli, Khodadad & Rodier, 1978).

La Fig. 2 représente la projection des atomes sur la face (010). Elle montre que la structure peut être considérée comme formée de deux couches dont les positions moyennes sont approximativement les plans  $z = 0$  et  $z = \frac{1}{2}$ . Cela est dû au fait que les atomes de phosphore, de zinc et d'argent sont situés dans ces plans ou dans leur voisinage immédiat. Chacune des ces couches contient des anions (PS<sub>4</sub>)<sup>3-</sup> et des cations Ag<sup>+</sup> et Zn<sup>2+</sup>.

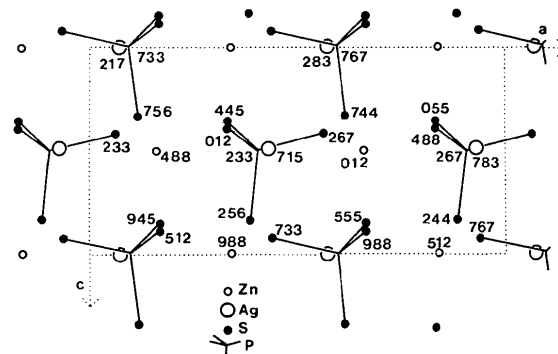


Fig. 2. Représentation de la structure vue parallèlement à l'axe  $b$ . Les nombres indiquent en millièmes les coordonnées  $y$  des atomes auprès desquels ils sont placés.

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## Pentapotassium Trivanadate, K<sub>5</sub>V<sub>3</sub>O<sub>10</sub>

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**Abstract.**  $M_r = 508.31$ , tetragonal,  $P4_12_12$ ,  $a = 8.1757$  (6),  $c = 18.7313$  (7) Å,  $V = 1252.0$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.697$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha_1) = 1.540562$ ,

$\lambda(\text{Cu } K\alpha_2) = 1.544390$  Å for lattice constants,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å for intensity measurement,  $\mu = 3.7$  mm<sup>-1</sup>,  $F(000) = 976$ ,  $T = 298$  K. Final  $R =$

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0.064 for 1124 unique observed reflections. The  $V_3O_{10}$  group has a twofold rotation symmetry and is bent at the central V atom. V—O—V angle  $154.5(6)^\circ$ . One  $K^+$  ion is surrounded nearly octahedrally by six O atoms, the other two  $K^+$  ions in the asymmetric unit are coordinated irregularly by six and seven O atoms, respectively.

**Introduction.** In the binary system  $K_2O-V_2O_5$ , a compound ' $K_{32}V_{18}O_{61}$ ' was believed to exist (Holtzberg, Reisman, Berry & Berkenblit, 1956). As its structure was not known and the formula appeared somewhat doubtful, the present authors decided to determine the structure. A literature survey revealed, however, that Touboul, Ganne, Cuche & Tournoux (1974) had already established in their phase-equilibrium study of the system  $Tl_2O-V_2O_5$  that the corresponding thallium compound must be formulated as  $Tl_5V_3O_{10}$  and crystallizes in the tetragonal space group  $P4/nmm$  with unit-cell dimensions  $a = 8.16(2)$  and  $c = 19.34(2)$  Å. They synthesized  $K_5V_3O_{10}$  and indexed its powder diagram based on a tetragonal lattice with  $a = 8.15(1)$  and  $c = 18.76(2)$  Å, indicating the probable isotypism with  $Tl_5V_3O_{10}$ . The latter structure is not known. The present structure determination verifies the claim of Touboul *et al.* (1974); the space group, however, is  $P4_12_12$ .

**Experimental.** Crystal of irregular shape,  $0.3 \times 0.3 \times 0.15$  mm, hygroscopic, enclosed in thin-wall (0.01 mm) glass capillary. Lattice constants from 18  $h0l$  reflections with  $2\theta > 110^\circ$  recorded on Weissenberg photograph with film radius 57.3 mm. Intensity measurement by Rigaku four-circle diffractometer up to  $(\sin\theta)/\lambda = 0.809 \text{ \AA}^{-1}$ ;  $2\theta/\omega$ -scanning for  $2\theta \geq 30^\circ$ ,  $\omega$ -scanning for  $2\theta < 30^\circ$ , scanning range  $\Delta\omega = 1.2^\circ + 0.5^\circ \tan\theta$  and speed  $2^\circ \text{ min}^{-1}$ . Standard reflections 400, 040 and 008; their intensity variation throughout experiment  $s(F)/\bar{F} = 0.0048 \sim 0.0052$ . 1670 reflections measured, 546 unobserved [ $I < \sigma(I)$  or too weak to be scanned], 1124 considered observed, index range  $0 \leq k \leq h \leq 12$ ,  $0 \leq l \leq 30$ . No absorption correction. Structure solved by trial-and-error and Patterson methods. Atomic coordinates, anisotropic thermal parameters, a scale factor and a free parameter for extinction correction refined by least squares based on  $F$ ;  $R = 0.064$ ,  $wR = 0.054$ ,  $S = 2.87$ ; weight  $w = 1/\sigma^2$  [ $\sigma = \sigma(I)F/(2I)$ ]. Extinction correction according to Zachariasen (1967, 1968) using a simplified expression

$$F_c = sF[1 + (g/\sin 2\theta)(1 + \cos^2 2\theta)(1 + \cos^2 2\theta)^{-1}F^2]^{-1/4},$$

where  $s = 1.224(4)$ ,  $g = 1.35(7) \times 10^{-6}$ . Ratio of maximum least-squares shift to error in final refinement cycle 0.00002.  $\Delta\rho$  in final difference map =  $-1.4 \sim 2.4 \text{ e \AA}^{-3}$ . Atomic scattering factors of Cromer & Mann (1968), dispersion corrections of Cromer & Liberman (1970). Computer programs used: *RSLC3* in

*UNICS* system (Sakurai, 1967), *ORFFE* (Busing, Martin & Levy, 1964), version 2 of *ORTEP* (Johnson, 1965), and unpublished programs written by one of the authors.

Table 1. Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	$B_{eq}(\text{\AA}^2)$
K(1)	0.2363 (3)	x	0	1.70 (5)
K(2)	0.0000 (3)	-0.0273 (3)	0.1117 (1)	2.30 (5)
K(3)	-0.0231 (4)	0.4886 (3)	0.1175 (1)	2.19 (5)
V(1)*	-0.1910 (2)	-x	0.25	1.26 (4)
V(2)	0.2319 (2)	0.2302 (2)	0.23221 (7)	1.07 (2)
O(1)*	-0.258 (1)	0.275 (1)	0.1777 (3)	3.4 (2)
O(2)	0.0204 (9)	0.229 (1)	0.2606 (5)	4.7 (2)
O(3)	0.2396 (9)	0.2303 (8)	0.1435 (3)	2.1 (1)
O(4)	0.322 (1)	0.0618 (8)	0.2627 (4)	2.9 (2)
O(5)	0.3113 (9)	0.4017 (8)	0.2632 (4)	2.2 (1)

\* The anisotropic thermal parameters relate to the symmetry-transformed coordinates deposited (see deposition footnote).

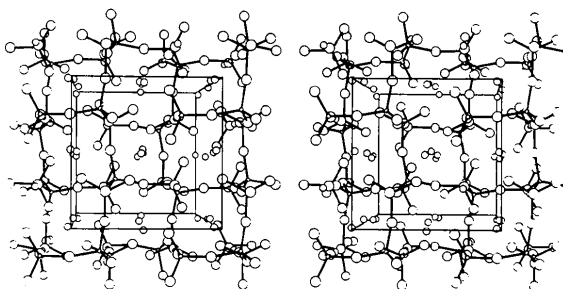


Fig. 1. Stereoview of the  $K_5V_3O_{10}$  structure along [001].

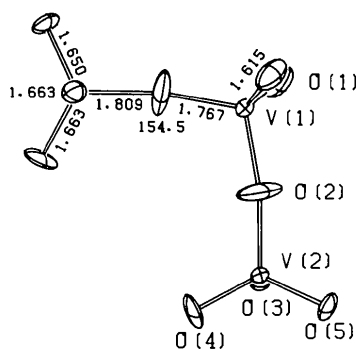


Fig. 2. V—O distances (Å) and V—O—V angle ( $^\circ$ ) in  $V_3O_{10}$  group. E.s.d.'s are 0.006 ~ 0.007 Å and  $0.6^\circ$ . Angles at vanadium are: O(1)—V(1)—O(1')  $114.4(6)$ , O(2)—V(1)—O(2')  $110.9(6)$ , O(1)—V(1)—O(2)  $110.6(4)$ , O(1)—V(1)—O(2')  $105.2(4)$ , O(2)—V(2)—O(3)  $109.3(4)$ , O(2)—V(2)—O(4)  $108.5(4)$ , O(2)—V(2)—O(5)  $106.1(4)$ , O(3)—V(2)—O(4)  $109.1(4)$ , O(3)—V(2)—O(5)  $109.7(3)$ , O(4)—V(2)—O(5)  $114.1(3)^\circ$  where the prime denotes equivalent position  $-y, -x, \frac{1}{2}-z$ .

**Discussion.** The positional and equivalent isotropic thermal parameters are listed in Table 1.\* Fig. 1 shows the structure viewed along [001]. Unlike the triphosphate ions in two phases of  $\text{Na}_5\text{P}_3\text{O}_{10}$  (Corbridge, 1960; Davies & Corbridge, 1958), which take the shape of a linear chain with each  $\text{PO}_4$  tetrahedron being in a staggered position relative to its neighbour(s), the  $\text{V}_3\text{O}_{10}$  group in  $\text{K}_5\text{V}_3\text{O}_{10}$  is bent at the central V(1) atom as illustrated in Fig. 2. It has twofold rotation symmetry, the central V(1) lying on one of the diad axes at  $z = n/4$  and running parallel to  $\langle 110 \rangle$ . The plane defined by the three V atoms of the  $\text{V}_3\text{O}_{10}$  group lies nearly parallel to (001). The two  $\text{VO}_4$  tetrahedra are oriented relative to each other halfway between the eclipsed and staggered conformations. Bond lengths and angles in the  $\text{V}_3\text{O}_{10}$  group are shown in Fig. 2.

The K(1) ion, also placed on the diad axis, is surrounded nearly octahedrally by two O(4) and two O(5) atoms of four trivanadate groups lying at the same level as K(1) itself and by two O(3) atoms of two trivanadate groups in the upper and lower levels, respectively. The K(2) and K(3) ions are coordinated respectively by six and seven O atoms, irregularly, within a K—O distance of 3.1 Å (Table 2).

\* Lists of structure amplitudes, anisotropic thermal parameters and coordinates relative to the anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42014 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. K—O distances (Å) less than 3.1 Å

E.s.d.'s range from 0.006 to 0.010 Å.

Symmetry code:						
(i) $\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{2}+z$			(v) $-\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{2}+z$			
(ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$			(vi) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$			
(iii) $-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$			(vii) $-y, 1-x, \frac{1}{2}-z$			
(iv) $-y, -x, \frac{1}{2}-z$			(viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$			
K(1)	O(3)	2.688	O(4 <sup>i</sup> )	2.714	O(5 <sup>ii</sup> )	2.774
K(2)	O(1 <sup>iii</sup> )	2.659	O(2 <sup>iv</sup> )	3.038	O(3)	2.936
	O(3 <sup>v</sup> )	2.911	O(5 <sup>vi</sup> )	2.862	O(5 <sup>vii</sup> )	2.678
K(3)	O(1)	2.830	O(1 <sup>viii</sup> )	3.066	O(2 <sup>ix</sup> )	2.850
	O(3)	3.051	O(3 <sup>x</sup> )	3.053	O(4 <sup>xi</sup> )	2.745
	O(4 <sup>xii</sup> )	3.001				

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Structure de l'Oxysulfure de Lanthane et d'Etain  $(\text{LaO})_4\text{Sn}_2\text{S}_6$ 

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**Abstract.**  $M_r = 1049.4$ , orthorhombic,  $Pbnm$ ,  $a = 5.841$  (3),  $b = 5.851$  (2),  $c = 19.003$  (3) Å,  $V = 649.4$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 5.37$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71093$  Å,  $\mu = 16.5$  mm<sup>-1</sup>,  $F(000) = 905.2$ ,  $T = 293$  K,  $R = 0.06$  for 1095 independent reflections. The structure is formed of alternating independent layers of  $(\text{LaO})_n$  and  $(\text{SnS}_3)_n$  parallel to the (001) plane. The  $(\text{LaO})_n$  layers are formed of tetrahedra of La with an O atom at their centres. The La—O distances are short. The  $(\text{SnS}_3)_n$  layers contain chains of distorted S octahedra with Sn occupying off-centre positions in the

octahedra. The Sn—S distances indicate a +4 oxidation state. No vacancies were found in the structure.

**Introduction.** Les oxysulfures à deux cations ( $M$  et  $R$ ) dont l'un d'eux est une terre rare, peuvent cristalliser soit selon des structures compactes où les polyèdres de coordination sont imbriqués selon un schéma tri-dimensionnel, soit selon des structures en feuillets dans lesquelles des couches d'oxydes de terre rare  $(RO)_n$  alternent avec des couches de sulfures métalliques  $(M_xS_y)_n$ .