

Preparation and Crystal Structure of Hexapotassium- μ -oxo-hexathiodititanate(IV), $K_6Ti_2OS_6$

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Pale yellow crystals of the title compound were obtained by reacting an intimate mixture of K_2S , $K_2S_2O_4$, Ti and S at 650 °C. $K_6Ti_2OS_6$ is monoclinic, *mP*60, s. g. $P2_1/c$. It is characterized by the formation of bitetrahedral complex anions, $[S_3TiOTiS_3]^{6-}$, which adopt a staggered conformation. The mean Ti-S and Ti-O bond lengths are 2.242(1) and 1.836(2) Å, respectively, the Ti-O-Ti bond angle is 153.8(2)°. Two K^+ ions complete the coordination of the bridging oxygen atom by the cations to a heavily distorted tetrahedral configuration. The anions are arranged in corrugated slabs running parallel to (100). The packing and crystallographic relationship to $K_6Co_2O_7$ are discussed.

Key words: Chalcogenides, Titanium, Complex Oxysulfides

Introduction

Cation rich complex chalcogenides are characterized by a remarkable propensity of Ti(IV) to attain a tetrahedral chalcogen coordination – which is in sharp contrast to the binary chalcogenides where the octahedral coordination of Ti(IV) predominates.

In the course of a study of the ortho-chalcogenometallates, A_4MQ_4 (A = alkali metal or Tl(I), M = Si, Ge, Sn, Ti, Q = S, Se) we have so far been able to characterize several Ti(IV)-compounds which show a surprising structural diversity: Na_4TiS_4 (*oF*1080) [1], Na_4TiSe_4 (*mC*72) [2], Tl_4TiS_4 , Tl_4TiSe_4 (*mP*36) [3], K_4TiSe_4 [4] (*cP*72, Ba_4SiAs_4 type) [5] and Rb_4TiSe_4 [6] (*mP*36, isotypic with Cs_4SnS_4 [7]) contain discrete mononuclear tetrahedral anions. Even after partial or complete substitution of the A^+ cations by Cu(I) the tetracoordination on Ti is retained. Thus edge sharing CuS_4 and TiS_4 tetrahedra build the complex anionic layers of $K_2Cu_2TiS_4$ [8] or the 3D-framework of Cu_4TiS_4 [9].

While Si, Ge, and Sn readily form compounds with binuclear, pyrophosphate type thio- and selenidoanions [10–16] the corresponding Ti-analogues have so far not been obtained. However, small oxygen contaminations due to reaction with the silica tube will readily lead to phases with ternary binuclear anions $[Q_3TiOTiQ_3]^{6-}$. This article deals with $K_6Ti_2OS_6$, a member of these new series.

Table 1. Crystallographic data for $K_6Ti_2OS_6$.

Pearson symbol	<i>mP</i> 60
Unit cell	$a = 13.281(4)$ Å $b = 10.364(1)$ Å $c = 12.963(5)$ Å $\beta = 105.61(2)^\circ$ $P2_1/c$ (No. 14)
Space group	$P2_1/c$ (No. 14)
Z	4
V (Å ³)	1718.5
d_x (gcm ⁻³)	2.85
$\mu_{(Mo-K\alpha)}$ (cm ⁻¹)	30.53
Structure refinement	
<i>hkl</i>	$0 \leq h \leq 16, 0 \leq k \leq 13,$ $-16 \leq l \leq 16$
Reflections measured	4093
Independent reflections	3707
R_{int}	0.019
Observed reflections	$2352 \geq 3.0 \sigma(F_o)$
Refined variables	137
$R = \sum F_o - F_c / \sum F_o $	0.024
$R_w = [\sum w F_o - F_c ^2 / \sum w F_o ^2]^{1/2}$	0.023
$w = [\sigma(F_o)^2 + (0.01F_o)^2]^{-1/2}$	
Residual electron density (eÅ ⁻³)	1.87/–0.30
Extinction coefficient	$1.030 \cdot 10^{-8}$

Experimental Section

Single crystals of the title compound were first accidentally observed during an attempt to prepare K_4TiS_4 [17] where they can be distinguished from the red main product through their pale yellow colour. In order to prepare a single phase product of $K_6Ti_2OS_6$ stoichiometric amounts of

Table 2. Positional parameters, anisotropic and equivalent isotropic temperature factors for $K_6Ti_2OS_6$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>B</i> _{eq}
K(1)	0.08669(6)	0.02380(8)	0.66062(6)	0.0272(4)	0.0279(4)	0.0288(4)	−0.0013(3)	0.0056(3)	−0.0039(3)	2.24(2)
K(2)	0.59399(5)	0.04447(7)	0.17043(6)	0.0231(3)	0.0228(4)	0.0310(4)	−0.0003(3)	0.0094(3)	−0.0032(3)	1.99(1)
K(3)	0.28572(6)	0.21692(8)	0.08392(6)	0.0305(3)	0.0305(4)	0.0237(3)	0.0026(3)	0.0077(3)	0.0059(3)	2.22(2)
K(4)	0.79599(6)	0.23524(9)	0.56510(6)	0.0361(4)	0.0385(5)	0.0245(4)	0.0109(4)	0.0064(3)	0.0039(4)	2.64(2)
K(5)	0.00483(6)	0.15794(8)	0.89574(6)	0.0338(4)	0.0316(4)	0.0402(4)	−0.0037(4)	0.0127(3)	−0.0005(4)	2.74(2)
K(6)	0.46988(6)	0.16751(8)	0.39664(7)	0.0323(4)	0.0336(4)	0.0370(4)	−0.0016(4)	0.0061(3)	−0.0048(4)	2.76(2)
Ti(1)	0.17829(4)	0.13020(5)	0.29310(4)	0.0153(2)	0.0142(3)	0.0165(2)	0.0005(2)	0.0069(2)	−0.0007(2)	1.17(1)
Ti(2)	0.66237(4)	0.39033(5)	0.28365(4)	0.0143(2)	0.0150(3)	0.0156(2)	−0.0013(2)	0.0062(2)	0.0000(2)	1.15(1)
S(1)	0.14187(7)	0.05777(9)	0.44201(7)	0.0347(4)	0.0263(4)	0.0224(4)	−0.0048(4)	0.0132(3)	0.0029(4)	2.11(2)
S(2)	0.03295(7)	0.14701(9)	0.15515(7)	0.0279(4)	0.0306(5)	0.0275(4)	0.0007(4)	−0.0038(4)	−0.0008(4)	2.43(2)
S(3)	0.24731(6)	0.32628(8)	0.33164(7)	0.0261(4)	0.0183(4)	0.0268(4)	−0.0054(4)	0.0048(3)	0.0004(4)	1.91(2)
S(4)	0.62509(6)	0.42787(9)	0.43857(6)	0.0270(4)	0.0286(5)	0.0186(4)	0.0054(4)	0.0107(3)	0.0011(4)	1.88(2)
S(5)	0.51136(7)	0.34933(9)	0.15774(7)	0.0237(4)	0.0304(5)	0.0287(4)	−0.0028(4)	−0.0039(4)	−0.0037(4)	2.35(2)
S(6)	0.77557(6)	0.22555(9)	0.30558(7)	0.0244(4)	0.0272(4)	0.0258(4)	0.0087(4)	0.0045(3)	−0.0035(4)	2.07(2)
O	0.2809(2)	0.0380(2)	0.2559(2)	0.029(1)	0.025(1)	0.034(1)	0.008(1)	0.0143(9)	−0.004(1)	2.24(5)

The anisotropic displacement parameters are defined as: $\exp[-2\pi^2\{h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}\}]$. $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

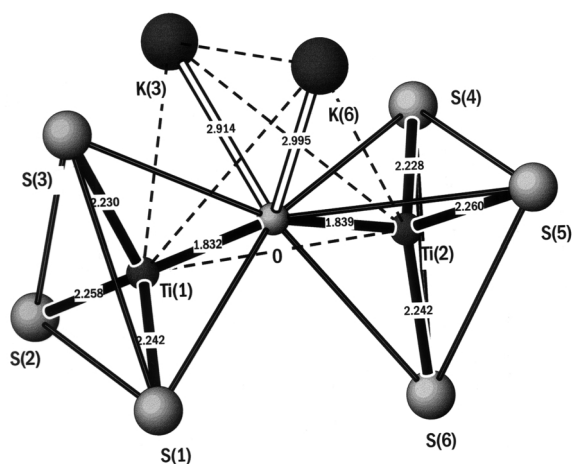


Fig. 1. The structure of $[S_3TiOTiS_3]^{6-}$ and its closest cation environment. The K^+ -ions and the Ti atoms coordinate the bridging O-atom in a distorted tetrahedral configuration. The distances K(1)—O and K(3)—O are distinctly larger than the sum of the ionic radii [$r(K_{CN=6}^+) = 1.52 \text{ \AA}$, $r(O_{CN=4}^{2-}) = 1.24 \text{ \AA}$] [26].

$K_2S_2O_4$ (analytical grade; Merck), K_2S (obtained from the elements in liquid ammonia), Ti (powder 300 mesh, 99.99%; Ventron) and S (recrystallized, 99.99%, Ventron) were intimately mixed in an argon glove box. The mixture was then transferred to an alumina crucible which was sealed in a silica tube under a vacuum of 10^{-2} Pa . The sample was gradually heated to 650°C , annealed for 5d and then brought to ambient temperature at a controlled rate of -3°C/h . The crushed sample consisted of prismatic pale yellow crystals

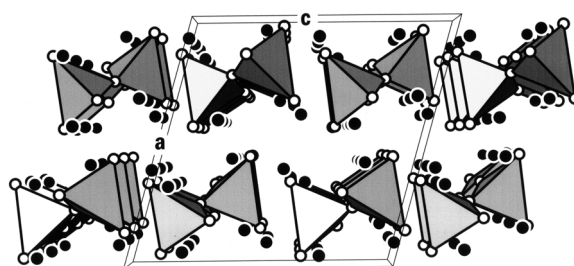


Fig. 2. The crystal structure of $K_6Ti_2OS_6$ in perspective projection along $[010]$. K^+ ions are given as full circles, the anions are in a polyhedral representation.

which were sensitive to air and hence had to be handled under inert conditions.

Preliminary X-ray investigations by Weissenberg and precession film techniques revealed monoclinic symmetry. From the systematic extinctions $h0\ell$: $\ell \neq 2n$ and $0k0$: $k \neq 2n$ the space group was assigned as $P2_1/c$. A crystal with the approximate dimensions $0.2 \times 0.1 \times 0.125 \text{ mm}^3$ – sealed into a thin walled glass capillary – was finally selected for the structure determination and transferred to an automatic kappa-diffractometer (*Nonius Turbo CAD4*) operated with graphite monochromated Mo- $K\alpha$ -radiation ($\lambda = 0.7103 \text{ \AA}$). Intensity data were collected at $21(1)^\circ\text{C}$ over an angular range $2^\circ \leq 2\theta \leq 54^\circ$ applying ω - 2θ scans (scan width $0.80^\circ + 0.35^\circ \tan \theta$, maximum scan time 75s). Crystal, orientational and electronic stability were controlled by three periodically determined control reflections which, however, showed only statistical variations of intensities. Precise lattice constants were obtained by least squares refinement of the setting angles of 25 high angle reflections ($34^\circ \leq 2\theta \leq 42^\circ$) carefully

a) Coordination of the alkali cations

K(1) S(3)	3.055(1)	K(2) S(3)	3.096(1)	K(3) O	2.913(3)
K(1) S(1)	3.086(1)	K(2) S(4)	3.116(1)	K(3) S(5)	3.199(1)
K(1) S(6)	3.128(1)	K(2) S(4)	3.155(1)	K(3) S(3)	3.203(1)
K(1) S(1)	3.132(1)	K(2) S(6)	3.183(1)	K(3) S(1)	3.255(1)
K(1) S(2)	3.482(1)	K(2) S(5)	3.334(1)	K(3) S(4)	3.263(1)
K(1) S(2)	3.661(1)	K(2) S(5)	3.562(1)	K(3) S(3)	3.569(1)
				K(3) S(2)	3.784(1)
K(4) S(4)	3.134(1)	K(5) S(6)	3.191(1)	K(6) S(5)	3.284(1)
K(4) S(1)	3.155(1)	K(5) S(2)	3.240(1)	K(6) S(3)	3.289(1)
K(4) S(6)	3.227(1)	K(5) S(2)	3.284(1)	K(6) S(4)	3.350(1)
K(4) S(2)	3.283(1)	K(5) S(1)	3.430(1)	K(6) S(5)	3.395(1)
K(4) S(6)	3.303(1)	K(5) S(3)	3.539(1)	K(6) S(5)	3.790(1)
K(4) O	3.966(3)	K(5) S(2)	3.818(1)	K(6) O	2.994(3)

b) Geometry of the $[S_3TiOTiS_3]^{6-}$ anion

Ti(1) O	1.832(2)	\angle S(3)	Ti(1) O	104.1(1)
Ti(1) S(3)	2.230(1)	\angle S(1)	Ti(1) S(3)	106.45(4)
Ti(1) S(1)	2.242(1)	\angle S(2)	Ti(1) S(3)	108.63(4)
Ti(1) S(2)	2.258(1)	\angle S(2)	Ti(1) O	111.7(1)
	2.242,33	\angle S(1)	Ti(1) S(2)	111.79(4)
		\angle S(1)	Ti(1) O	113.6(1)
Ti(2) O	1.839(2)	\angle S(5)	Ti(2) O	107.8(1)
Ti(2) S(4)	2.228(1)	\angle S(4)	Ti(2) O	108.2(1)
Ti(2) S(6)	2.242(1)	\angle S(4)	Ti(2) S(5)	108.33(4)
Ti(2) S(5)	2.260(1)	\angle S(4)	Ti(2) S(6)	108.83(4)
		\angle S(6)	Ti(2) O	111.0(1)
		\angle S(5)	Ti(2) S(6)	112.51(4)
Ti(1) Ti(2)	3.575(1)	\angle Ti(1)	O Ti(2)	153.8(2)

c) Shortest interanionic contact

S(3)	S(4)	3.940(1)
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Table 3. Selected interatomic distances (Å) and bond angles for $K_6Ti_2OS_6$.

centred on the diffractometer. They are given in Table 1 together with other crystallographically relevant data.

The crystal structure was solved by direct methods (Multan-82 [18]) and subsequent difference Fourier syntheses. Isotropic refinements (F -refinement) converged at $R = 0.07$. Allowance for anisotropic displacement parameters resulted in $R = 0.024$ ($R_w = 0.023$). A final difference Fourier synthesis was featureless.

Calculations were performed on a VAX 3520 workstation using programs of the MolEN [19] crystallographic software package. Atomic scattering factors for neutral atoms were chosen. An isotropic extinction correction [20] was included in the final refinements. Absorption effects were not accounted for. Further details on the refinement are summarized in Table 1. Positional and anisotropic displacement factors are listed in Table 2. Selected interatomic distances and bond angles are given in Table 3. A list of observed and calculated structure factors has been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, under CSD-nr. 407764.

Results and Discussion

The crystal structure of $K_6Ti_2OS_6$ consists of well separated cations and anions. The anion is the new bitetrahedral $[S_3TiOTiS_3]^{6-}$ moiety which is shown in Fig. 1 together with the corresponding atom labelling scheme while Fig. 2 gives a perspective view of the crystal structure. The binuclear anion does not possess crystallographic symmetry elements. As might be expected from the different polarizabilities the sulfur atoms occupy the terminal positions of the tetrahedra while the oxygen atom occupies the bridging function. The anion is in a staggered conformation, and the Ti-O-Ti bond angle is not linear but adopts a significantly smaller value of $153.8(2)^\circ$. There exists a pseudo mirror plane defined by S(6), Ti(2), Ti(1) and S(3) which is, however, violated by the bridging oxygen atom. The Ti-S-bond lengths in the two tetrahedra are fairly comparable ranging from 2.228(1) to 2.260(1) Å. The av-

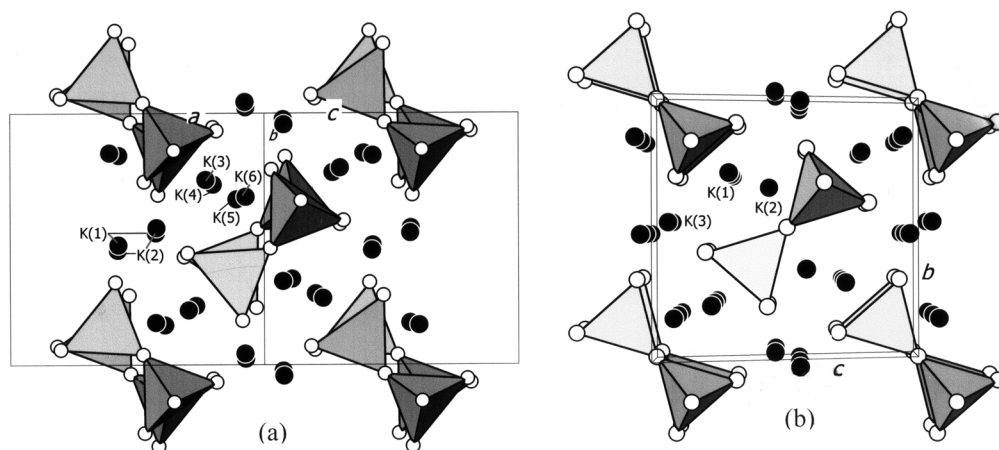


Fig. 3. Projections of the crystal structures of $K_6Ti_2OS_6$ (a) and $K_6Ti_2O_7$ (b) revealing the intimate relationship. The projections may be conceived as a superposition of slices where anions are on the nodes of primitive pseudoquadratic nets while the stacking of the slices generates the characteristic herringbone pattern. Further explanations in the text.

erage value of 2.242(1) Å is identical for both tetrahedra. This value is well within the range found with other thiotitanates(IV) with tetrahedrally coordinated Ti like Na_2TiOS_2 ($\bar{d} = 2.227$ Å) [21], Ti_4TiS_4 ($\bar{d} = 2.263$ Å) [3], Na_4TiS_4 ($\bar{d} = 2.257$ Å) [1] or Cu_4TiS_4 [9] ($\bar{d} = 2.278$ Å). The average Ti-O bond length calculates as 1.836(2) Å. A similar value has been found in Na_2TiOS_2 ($\bar{d} = 1.842$ Å) while in the oxo compound $K_6Ti_2O_7$ [22] the Ti-O bond to the bridging oxygen is distinctly longer ($d = 1.87$ Å).

The anions are arranged in slabs parallel to (100), well separated from each other by the potassium cations. The shortest interanionic contact between the slabs ($d(S(3)-S(4)) = 3.940(1)$ Å) rules out any S—S-bonding interactions between the anionic groups. The potassium cations are irregularly coordinated by 5–7 nonmetal atoms. There are only two close K-O contacts: K(3)-O (2.913(3) Å) and K(6)-O (2.994(3) Å). Together with Ti(1) and Ti(2) they create a heavily distorted tetrahedral cation environment for the bridging O-atom (Figure 1). This asymmetric environment is probably forcing the nonlinearity of the Ti—O—Ti bond angle.

The crystal structure of $K_6Ti_2OS_6$ is related to that of $K_6Ti_2O_7$ (*mp*30, space group $P2_1/c$, $a = 6.582$, $b = 9.318$, $c = 11.269$ Å, $\beta = 123.46^\circ$) [22] which has been assigned to the $K_6Co_2O_7$ [23] structure type. The complex anion in this structure type also shows a staggered configuration. The bridging oxygen atom is located on an inversion centre, the anion adopts C_i symmetry and hence the M—O—M bond angle is strictly linear.

While the crystal structures of $K_6Ti_2OS_6$ and $K_6Ti_2O_7$ belong to the same space group ($P2_1/c$) the cell content of $K_6Ti_2OS_6$ is doubled compared to the oxide. The projections given in Fig. 3 underline the intimate relationship between the two structures. Both can be cut into homologous slices where the anions are arranged in a primitive (pseudo)quadratic pattern. Within each slice the anions are aligned along one of the diagonals, their orientation alternates in the neighbouring slice. An AB-type stacking generates the characteristic herringbone pattern which is apparent in Figure 3. In the structure of $K_6Ti_2O_7$ the slices run along (10 $\bar{1}$), yet along (101) in $K_6Ti_2OS_6$. The identity periods within the slices are **b** and **a**—**c** in $K_6Ti_2O_7$ and calculate as 9.303 and 9.387 Å, reflecting the pseudoquadratic arrangement. In $K_6Ti_2OS_6$ the translation periods are **b** and **a** + **c** (10.364 and 20.906 Å, respectively). In the latter direction the crystallographic identity period has to be doubled to account for the fact that the same slice here contains both enantiomers of the anion.

Another intimately related structure type has been found with $K_6Ge_2O_7$ (s. g. Pc , $a = 6.549$, $b = 9.094$, $c = 11.426$ Å, $\beta = 126.78^\circ$, $Z = 2$) [24]. As in $K_6Ti_2OS_6$, the bitetrahedral anion lacks crystallographic symmetry. While its cell metrics correspond to that of $K_6Ti_2O_7$, the loss of the inversion centre enables the bond angle on the bridging O-atom to become non-linear (it amounts to 157.3° close to the value found in the present compound). In contrast to $K_6Ge_2O_7$ the homologous silicate, $K_6Si_2O_7$, [25] is isotypic with $K_6Ti_2O_7$. In view of the sequence of the radii $r(Si^{4+}) =$

$0.40 \text{ \AA} < r(\text{Ge}^{4+}) = 0.53 \text{ \AA} < r(\text{Ti}^{4+}) = 0.56 \text{ \AA}$ [26] these structural changes appear to be inconsistent and would probably – as has been stated earlier [22] – merit further investigations.

The only other oxothiometallate with binuclear tetrahedral anions known so far is $\text{K}_6\text{Si}_2\text{OS}_6$ (s.g. $P2_1/c$, $a = 8.703$, $b = 11.687$, $c = 8.330 \text{ \AA}$, $\beta = 121.11^\circ$, $Z = 2$) [27]. The anionic group is in a staggered conformation and shows C_i symmetry. The comparison of the two structures does not reveal any further relations-

ships. Thus, at variance with the above-mentioned oxo-compounds, substitution of Ti by Si in the oxysulfides exerts a drastical influence on the crystal structure and leads to an entirely different stacking of the bitetrahedral groups.

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