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Synthesis and characterization of KTh_2SeE_6 , KTh_2Te_6 and $CsTh_2Se_6$

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Abstract

The compounds KTh_2Se_6 , KTh_2Te_6 and CsTh_2Se_6 have been synthesized in the temperature range 873 to 923 K. These compounds are isostructural with the previously synthesized compound CsTh_2Te_6 . They crystallize in the space group D_{2h}^{17} -Cmcm of the orthorhombic system with two formula units in cells: a=4.14(2) Å, b=21.88(4) Å, c=5.64(1) Å, V=511(4) Å³ (T=298 K) for KTh_2Se_6 ; a=4.356(1) Å, b=23.702(7) Å, c=6.141(2) Å, V=634.1(3) Å³ for KTh_2Te_6 (T=113 K); and a=4.14(5) Å, b=23.88(4) Å, c=5.67(5) Å, V=561(13) Å³ (T=298 K) for CsTh_2Se_6 . The structure of KTh_2Te_6 has been determined from single-crystal X-ray data. The structure is composed of $\frac{2}{\pi}$ [Th}_2Te_6⁻] layers that stack perpendicular to [010]. The layers are separated by K⁺ cations that are coordinated to eight Te atoms at the corners of a rectangular parallelepiped. The K site is one-half occupied. Te atoms form infinite chains within the layers along [001] with Te -Te distances between 3.057(3) Å and 3.085(3) Å. KTh_2Se_6 , KTh_2Te_6 and CsTh_2Se_6 are highly resistive along [100].

Keywords: Synthesis; Solid-state compounds

1. Introduction

Solid-state compounds containing actinide metals have been studied extensively because of their interesting magnetic properties and the accessibility of several oxidation states [1,2]. Whereas many ternary chalcogenides containing U have been reported, there are few known ternary chalcogenides containing Th. Ternary Th chalcogenides that have been characterized by single-crystal X-ray studies include ThAsTe. ThGeS and ThP₂S₆ [3–5]. In addition CsTh₂Te₆, the only known ternary Th chalcogenide containing an alkali metal, was previously synthesized and characterized in this laboratory [6]. We have now extended that work to include the new compounds KTh_2Se_6 , KTh_2Te_6 and $CsTh_2Te_6$. All four ATh_2O_6 (A= K. Cs; Q=Se, Te) compounds are isostructural.

2. Experimental

2.1. Syntheses

All of the following reactions (~250 mg) were loaded in a dry box under an Ar atmosphere, transferred into fusedsilica tubes, evacuated to $\sim 10^{-4}$ Torr and sealed. Products were manually extracted from the melts. All products grow as thin needles that have a tendency to twin. All products react slowly with air. Semiquantitative elemental analyses were obtained from EDS measurements performed on a Hitachi S-570 SEM. All A₂Q_x (A=K, Cs; Q=Se, Te; x=1, 3) fluxes were synthesized at 194 K by the stoichiometric reaction of the appropriate elements in liquid ammonia under an N₂ atmosphere.

2.2. KTh₂Se₆

A 2:2:9 molar ratio of K_2 Se (K, Alfa, 99%; Se, Aldrich 99.99%), Th (Alfa, 99.9%) and Se was heated to 923 K over 1 day, held there for 7 days, then cooled to room temperature at 3 K h⁻¹. KTh₂Se₆ crystallizes as black needles.

2.3. KTh ,Te,

A 3:4:9 molar ratio of K_2Te_3 (Te: Aldrich, 99.8%), Th and Te was heated to 873 K over 1 day, kept there for 12 days, then cooled to room temperature at 3 K h⁻¹. KTh₂Te₆ crystallizes as black needles.

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2.4. CsTh₂Se₆

A 4:4:11 molar ratio of Cs_2Se_3 (Cs: Aldrich, 99.5%), Th and Se was heated with the same profile as that used to synthesize KTh_2Se_6 . $CsTh_2Se_6$ crystallizes as dark-green needles.

2.5. Structural analysis of KTh₂Te₆

Cell parameters of a single crystal of KTh₂Te₆ were obtained from 20 reflections in the range $33^{\circ} < 2\theta$ (Mo $K\alpha_1$ <35° automatically centered at 113 K on a Picker diffractometer [7]. Six standard reflections monitored every 100 reflections showed no significant variation in intensity throughout the data collection. The data were processed and corrected for absorption effects [8,9]. Initial positional parameters were obtained from the isostructural compound $CsTh_2Te_6$ [6]. The structure was refined by full-matrix, least-squares techniques with the program SHELXL-96 [10]. The refinement included anisotropic displacement parameters and a secondary extinction coefficient. The MISSYM algorithm as implemented in the PLATON program suite revealed no extra symmetry [11,12]. In arriving at the chemical formula KTh_2Te_6 , we have constrained the occupancy of the K⁺ cation to be 1/2. A refinement with this model leads to agreement indices $R_w(F_0^2) = 0.122$ (20 variables, 491 observations) and $R_1(F) = 0.050$ (410 observations having $F_0^2 > 2\sigma(F_0^2)$), and to $U_{ca}(K)=0.025(4)$ Å². A model that in addition allows the occupancy of the K⁺ cation to vary, converges

Table 1 Crystal data and structure refinement for KTh₃Te₆

Table	2
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Positional parameters and equivalent isotropic displacement parameters for KTh_2Te_6

Atom	x	y	z	Wyckoff notation	U_{eq}^{a} (Å ²)
K ^b	0	0.4957(7)	1/4	4c	0.025(4)
Th	0	0.67818(5)	1/4	4c	0.0057(4)
Te(1)	0	0.27512(9)	1/4	4 <i>c</i>	0.0052(5)
Te(2)	0	0.10292(6)	0.0011(2)	8f	0.0082(4)

 ${}^{a}U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. ^bSite occupancy fixed at 1/2.

to an occupancy of 0.434(2), to the same values of the agreement indices, and to $U_{eq}(K)=0.017(3)$ Å². We will refer to all of the compounds synthesized here as ATh_2Q_6 (A=K, Cs; Q=Se, Te), but keep in mind that the actual composition, which could vary from crystal to crystal, might well be $A_xTh_2Q_6$, x<1.0. The final difference electron map shows no feature with a height greater than 1.3% that of a Th atom. Additional experimental details may be found in Table 1. Table 2 lists final values of the positional parameters and equivalent isotropic displacement parameters, and Table 3 gives selected bond distances and angles.

2.6. Structural analysis of KTh₂Se₆ and CsTh₂Se₆

Crystals of KTh_2Se_6 and $CsTh_2Se_6$ were placed in glass capillaries, which were then sealed under N₂. Oscillation and Weissenberg photographs obtained at 298 K revealed Laue symmetry *mmm* and systematic absences $hk\ell$, h+k=

Compound KTh,Te, 1268.78 Formula weight Space group D¹⁷_{3h}=Cmcm 4.356(1)" a (Å) b (Å) 23.702(7) c (Å) 6.141(2) V (Å') 634.1(3) 2 $\rho_{\rm c}$ (g/cm³) 6.645 T of data collection (K)^h 113 5.6×10⁻⁴ Crystal vol. (mm³) Needle, bounded by {100}, {010}, {001} Crystal shape Graphite monochromated Mo K α_1 (λ (K α_1) =0.7093 Å) Radiation μ (cm⁻¹) 372 Transmission factors" 0.106-0.471 Extinction coefficient 0.0004(2)Data collected $3.42 \le 2\theta \le 56.90, \pm h, -k, -\ell$ No. of unique data including $F_0^2 < 0$ 491 20 No. of variables $R_{\mu}(F^2)^{d}$ 0.122 $R_1(F)$ (on F for $F_0^2 > 2\sigma(F_0^2))^d$ 0.050 Final goodness of fit 1.173

^a Obtained from a refinement with the constraint $\alpha = \beta = \gamma = 90^{\circ}$.

^b The low temperature system is based on a design by Huffman [16].

The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction [9].

 ${}^{d}R_{w}(F_{0}^{2}) = \left[\sum [w(F_{0}^{2} - F_{0}^{2})^{2}]/\sum wF_{0}^{4}\right]^{1/2}; \ w^{-1} = \sigma^{2}(F_{0}^{2}) + (0.04F_{0}^{2})^{2} \ \text{for} \ F_{0}^{2} \ge 0; \ w^{-1} = \sigma^{2}(F_{0}^{2}) \ \text{for} \ F_{0}^{2} \ge 0; \ R_{1}(F) = \sum ||F_{0}| - |F_{0}|/\sum |F_{0}|.$

Table 3		•				
Selected bond	lengths	(Å) and	angles	(deg.)	for	KTh ₂ Te ₆

Bond lengths	
K_Te	3.548(1)×4
K-Te	3.679(1)×4
Th-Te	3.166(2)×2
Th-Te	3.203(1)×4
Th-Te	3.264(1)×2
Te_Te	3.057(3)
Te-Te	3.085(3)
Angles	
Te-Th-Te	86.94(6)
Te-Th-Te	150.68(3)×4
Te-Th-Te	86.35(4)×4
Te-Th-Te	56.99(5)
Te-Th-Te	112.33(6)×2
Te-Th-Te	85.68(5)×2
Te-Th-Te	75.75(3)×4
Te-Th-Te	129.62(3)×4
Te-Th-Te	74.93(4)×4
Te-Th-Te	140.36(8)
Te-Te-Te	180.00(11)

2n+1; $h0\ell$, $\ell=2n+1$ consistent with the orthorhombic space groups $C_{2\nu}^{12}-Cmc2_1$, $C_{2\nu}^{16}-C2cm$ and $D_{2h}^{17}-Cmcm$. The cell parameters obtained are a=4.14(2) Å, b=21.88(4) Å, and c=5.64(1) Å (KTh₂Se₆) and a=4.14(5)Å, b=23.88(4) Å, c=5.67(5) Å (CsTh₂Se₆). The large estimated standard deviations for the latter cell arise from the highly mosaic nature of the crystal. We conclude that KTh₂Se₆ and CsTh₂Se₆ are isostructural to KTh₂Te₆.

2.7. Electrical conductivity

Crystals were removed from the reaction tube and immediately prepared for conductivity measurements. Single crystals ranging in length from 0.4–0.6 mm were mounted with Ag paint on Au wires with graphite extensions. Two-probe dc resistivity measurements were made along the needle axis [100] at 298 K and 77 K. Crystal composition was confirmed later by EDS.

3. Results and discussion

A view of the unit cell of KTh_2Te_6 is shown in Fig. 1. The structure of KTh_2Te_6 comprises ${}^2_x[Th_2Te_6^-]$ layers (Fig. 2) that stack perpendicular to [010]. The layers are separated by K⁺ cations. The K⁺ cations are coordinated by eight Te atoms at the corners of a rectangular parallelepiped with crystallographically imposed *m2m* symmetry. The parallelepipeds share edges along [001]. K-Te interactions range from 3.55(1) Å to 3.68(1) Å, in agreement with those found in the K₄Hf₃Te₁₇ structure (3.49(1) Å to 3.67(1) Å) [13]. As discussed above, the K site is approximately half occupied.

The Th atoms are coordinated to Te atoms in a bicapped



$\mathbf{A} \circ \mathbf{Th} \bullet \mathbf{Q} \bigcirc$

Fig. 1. View of the unit cell of ATh_2Q_6 along [100]. Atoms are drawn as circles of arbitrary size.



Fig. 2. View of one half of the $\sqrt[2]{Th_2Q_n}$ layer of ATh_2Q_n in which the connection of the Th-centred bicapped trigonal prisms is shown. The infinite Q-Q bonds along [001] are drawn as thin lines.

trigonal-prismatic arrangement with imposed symmetry m2m. The prisms share capping Te atoms along the [00'] direction and triangular faces along the [100] direction. Th-Te distances are in the range 3.166(2) Å to 3.264(1) Å, in agreement with those of the CsTh₂Te₆ structure (3.164(3) Å to 3.265(2) Å) [6]. Infinite chains of Te atoms form within the layers along c. The short Te-Te distances within the layers range from 3.057(3) Å to 3.085(3) Å, similar to the Te-Te distances of CsTh₂Te₆ (3.051(4) Å to 3.089(4) Å). Owing to these short Te-Te bonds, we are unable to assign formal oxidation states to the atoms in KTh₂Te₆. Low yields of the products preclude the use of magnetic data to aid in these assignments.

For each of the present three compounds and for $CsTh_2Te_6$ [6] the conductivity along the needle axis ([100]) is below the detection limits of our instrument at 298 K and 77 K. We have not been able to synthesize crystals sufficiently wide to allow the measurement of conductivity along the [001] direction.

Although the ATh_2Q_6 compounds (A=K, Cs; Q=Se, Te) have no structural analogues, there are some related compounds. These two-dimensional structures contain a bicapped trigonal-prismatic framework similar to that of the three-dimensional UTe, structure [14]. In addition, the ATh_2Q_6 compounds share structural similarities with $ACuM_2Q_6$ (A=K, M=La, Q=S; A=Cs, M=Ce, Q=S; A=K, M=Ce, Q=Se) [15]. The ACuCe₂Q₆ structure may be described as the ATh_2Q_6 structure with one-half of the tetrahedral sites within the layers occupied by Cu⁺ cations. The ACuM₂Q₆ compounds do not contain infinite Q-Qchains, but rather discrete sets of Q_2^2 anions; there are no Q-Q bonds within the Cu-centered tetrahedra. In examining these two structure types one can postulate that it may be possible to synthesize the series of compounds $A_x Ce_2 Q_0$ (x=0-2) with the same structure as $ATh_2 Q_0$. In addition, it may be possible to insert a Cu⁺ into the ${}_{\infty}^{2}$ [Th₂Q₀] layers of ATh₂Q₀ to synthesize ACuTh₂Q₀.

Acknowledgments

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