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Syntheses, Crystal Structures, and Physical Properties of the New Thorium Chalcogenides $CuTh_2Te_6$ and $SrTh_2Se_5$

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Single crystals of $CuTh_2Te_6$ form by a stoichiometric reaction of the elements at 1000 °C. The compound crystallizes in the space group $C_{2h}^2-P2_1/m$ with unit cell parameters $a = 6.170(2)$ Å, $b = 4.332(1)$ Å, $c = 10.424(3)$ Å, $\beta = 98.85(1)°$, and $Z = 1$ at 113 K. The structure was solved from single-crystal X-ray data. It consists of layers of ${}^2_\infty[Th_2Te_6^-]$ double chains joined by Cu^+ cations. Each Th atom is coordinated to eight Te atoms in a bicapped trigonal prismatic arrangement. There are three crystallographically unique Te atoms. Each $ThTe_8$ unit is bridged through one distinct Te atom, such that the capping Te atom of one unit forms the vertex of its neighbor. The two nonbridging Te atoms form infinite Te−Te chains along the exterior of the ${}^2_\infty[Th_2Te_6^-]$ layer. Copper atoms are coordinated to these Te atoms in a tetrahedral arrangement. Owing to the existence of Te−Te bonds of intermediate length, the assignment of formal oxidation states in this compound is not possible. Four-probe dc electrical conductivity measurements of a single crystal of $CuTh_2Te_6$ indicate the compound is a semiconductor along [010]. Magnetic susceptibility measurements in the range 2−300 K show $CuTh_2Te_6$ to be paramagnetic with $\mu_{eff} = 2.06\ \mu_B$ at 300 K. Single crystals of $SrTh_2Se_5$ form from the reaction SrSe + Th + 3Sn + 3Se at 1000 °C. EDAX experiments show no tin present in several crystals analyzed. Transparent red blocks of $SrTh_2Se_5$ crystallize in the space group $C_{2h}^5-P2_1/c$ with unit cell parameters $a = 8.704(2)$ Å, $b = 7.861(2)$ Å, $c = 12.458(4)$ Å, $\beta = 90.00(2)°$, and $Z = 4$ at 113 K. The structure, which is related to that of U_3S_5, is a three-dimensional framework with Sr cations located in one-dimensional channels. There are two distinct Th environments, bicapped trigonal prismatic and distorted monocapped octahedral. There are no Se−Se bonds and so formal oxidation states of Sr^{2+}, Th^{4+}, and Se^{2-} may be assigned.

Introduction

Research in the solid-state chemistry of actinide compounds has expanded greatly in the last few decades, motivated not only by the interesting magnetic properties that the actinides afford but also by the potential of such compounds to exhibit superconductivity[1−3] and to be used for radwaste storage.[4]

Though there are many well-characterized uranium chalcogenide compounds in the literature,[5−8] knowledge of the chalcogenide chemistry of thorium is severely lacking. Only recently have attempts been made to synthesize and characterize new thorium compounds. To that end, the focus of our investigation is primarily the synthesis, structural characterization, and measurement of physical properties of thorium chalcogenides. We have previously reported the isostructural compounds ATh_2Q_6 (A = K, Cs; Q = Se, Te);[9,10] there exists one U analogue, $Tl_{0.56}UTe_3$.[11] Although $CuTh_2Te_6$ has the ATh_2Q_6 stoichiometry, it is not isostructural with the earlier compounds but does show striking similarities. $SrTh_2Se_5$ is isostructural with U_3Q_5[12,13] as well as to a class of AU_2Q_5 compounds (A = La−Gd,[14,15] Ca, Ba, Sr,[16,17] Pb;[18] Q = S, Se); it represents the first structurally characterized Th analogue of this series.

Experimental Section

Synthesis. Crystals of $CuTh_2Te_6$ were synthesized from a direct combination of the elements at 1000 °C. Stoichiometric amounts of Cu (Alfa, 99.5% metals basis), Th (Johnson Matthey, 99.8%), and Te (Aldrich, 99.8%) were loaded into fused silica tubes and evacuated to $\sim 10^{-4}$ Torr. The thorium was handled in an argon-filled drybox to prevent exposure to oxygen and moisture. The samples were then

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Table 1. Crystal Data and Structure Refinement for $CuTh_2Te_6$ and $SrTh_2Se_5$

compound	$CuTh_2Te_6$	$SrTh_2Se_5$
fw	1293.22	946.50
space group	$C_{2h}^{2}-P2_1/m$ (No. 11)	$C_{2h}^{5}-P2_1/c$ (No. 14)
a (Å)	6.170(2)	8.704(2)
b (Å)	4.332(1)	7.861(2)
c (Å)	10.424(3)	12.458(4)
β (deg)	98.85(1)	90.00(2)
V (Å^3)	275.3(1)	852.4(4)
Z	1	4
T (K)	113(2)	113(2)
λ (Mo Kα_1)	0.7093	0.7093
d_{calcd} (g/cm^3)	7.800	7.375
linear abs coeff (cm^{-1})	444	623
transm factors	0.008−0.129	0.032−0.104
R(F)^a for $F_o^2 > 2\sigma(F_o^2)$	0.0326	0.0449
R$_w$(F_o^2)^b (all data)	0.0803	0.0999

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

placed in a horizontal tube furnace, reacted at 1000 °C for 6 days, and cooled at 3 °C/h. There was no evidence of attack on the silica tubing by any of the reactants. Single crystals of $CuTh_2Te_6$ grew as thin black plates of approximate dimensions 0.2 mm × 0.2 mm × 0.5 mm. These crystals were manually extracted from the reaction mixture. Several crystals were analyzed on an EDAX-equipped Hitachi SEM. The average Cu:Th:Te elemental ratio of all samples was 1:2:6. Single crystals of $CuTh_2Te_6$ form in high yields.

$SrTh_2Se_5$ formed in the reaction of Th (Johnson Matthey, 99.8%), Sn (Alfa, 99.85%), and Se (Aldrich, 99.5%) with an SrSe (Alfa, 99.5%) flux in a SrSe:Th:Sn:Se ratio of 1:1:3:3. The reactions were carried out, and the samples analyzed by the methods described above. Again, there was no evidence of attack of the silica tubes. Crystals grew as transparent red blocks with dimensions on the order of 0.06 mm. These were manually extracted from the reaction mixture. This reaction produces only minor amounts of crystalline $SrTh_2Se_5$. The majority of products were amorphous unreacted material and spherical droplets of elemental Sn. Attempts to synthesize $SrTh_2Se_5$ in higher yields by a stoichiometric reaction of the elements proved unsuccessful.

Structure Determination. For each compound a single crystal was mounted directly in the cold stream of a Picker diffractometer.[19,20] Final cell parameters were determined from the setting angles of 26 reflections in the range $26 \leq 2\theta(\mathrm{Mo}) \leq 39°$ for $CuTh_2Te_6$ and 27 reflections in the range $30 \leq 2\theta(\mathrm{Mo}) \leq 34°$ for $SrTh_2Se_5$, centered at 113 K. Six standards from a wide range of reciprocal space were checked after every 100 reflections and showed no significant change in intensity throughout data collection. The data were processed[21] and corrected for absorption[22] effects. The structures of both compounds were solved with the use of the direct methods program SHELXS of the SHELXTL PC suite of programs.[23] The structures were refined by full-matrix, least-squares techniques with the program SHELXL-96.[24] The final refinements included anisotropic displacement parameters and secondary extinction coefficients. For the final refinement of the $CuTh_2Te_6$ compound, the occupancy of the copper atom was held at 0.5, as in the penultimate refinement the occupancy refined to 0.453(7) and errors on such occupancies, as derived from X-ray data, are usually deceivingly small.[25] Additional experimental details are given in Table 1 and in Supporting Information. Tables 2 and 3 give final positional parameters and equivalent isotropic displacement parameters. Tables 4 and 5 give selected bond distances and angles.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $CuTh_2Te_6$

atom	x	y	z	$U_{eq}{}^a$
Th(1)	0.293 06(4)	0.7500	0.664 59(3)	0.005 1(2)
Te(1)	0.233 74(8)	0.2500	0.440 54(6)	0.005 3(2)
Te(2)	0.100 37(10)	0.2500	0.839 61(6)	0.011 3(2)
Te(3)	0.594 69(11)	0.2500	0.834 72(7)	0.013 7(2)
Cu(1)^b	0.395 8(4)	0.2500	1.033 7(3)	0.013 0(5)

^{a} U is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b} Cu was assigned an occupancy of 0.5.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $SrTh_2Se_5$

atom	x	y	z	U_{eq}
Th(1)	0.001 97(9)	0.021 42(9)	0.179 31(6)	0.004 2(2)
Th(2)	−0.252 11(8)	−0.076 6(1)	0.509 46(6)	0.004 3(2)
Se(1)	−0.237 5(2)	−0.196 9(3)	0.281 3(2)	0.005 2(4)
Se(2)	−0.457 5(2)	0.174 1(3)	0.411 2(2)	0.006 8(4)
Se(3)	−0.044 2(2)	0.163 2(3)	0.400 2(2)	0.004 9(4)
Se(4)	0.225 0(2)	−0.172 3(3)	0.314 3(2)	0.005 5(4)
Se(5)	0.223 8(2)	0.040 7(3)	−0.001 1(2)	0.004 8(4)
Sr(1)	0.504 7(2)	0.037 5(3)	0.173 5(2)	0.008 7(4)

Table 4. Selected Bond Lengths (Å) for $CuTh_2Te_6$

Th(1)−Te(1)	3.267(1)	Te(2)−Te(3)	3. 058(1)
Th(1)−Te(1)	3.273(1)	Te(2)−Te(3)	3.113(1)
Th(1)−Te(1)	3.165(1) × 2	Cu(1)−Te(2)	2.506(3)
Th(1)−Te(2)	3.178(1) × 2	Cu(1)−Te(3)	2.560(2) × 2
Th(1)−Te(3)	3.207(1) × 2	Cu(1)−Te(3)	2.567(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $SrTh_2Se_5$

Th(1)−Se(1)	2.984(2)	Se(2)−Th(2)−Se(3)	126.75(7)
Th(1)−Se(1)	3.057(2)	Se(2)−Th(2)−Se(2)	77.42(7)
Th(1)−Se(3)	2.996(2)	Se(3)−Th(2)−Se(2)	149.82(6)
Th(1)−Se(3)	3.008(2)	Se(2)−Th(2)−Se(3)	152.40(7)
Th(1)−Se(4)	2.986(2)	Se(3)−Th(2)−Se(3)	77.46(7)
Th(1)−Se(4)	3.116(2)	Se(2)−Th(2)−Se(3)	75.60(6)
Th(1)−Se(5)	2.967(2)	Se(2)−Th(2)−Se(4)	89.48(6)
Th(1)−Se(5)	3.004(2)	Se(3)−Th(2)−Se(4)	78.20(6)
		Se(2)−Th(2)−Se(4)	85.04(6)
Th(2)−Se(1)	2.998(2)	Se(3)−Th(2)−Se(4)	82.55(6)
Th(2)−Se(2)	2.820(2)	Se(2)−Th(2)−Se(1)	106.54(6)
Th(2)−Se(2)	2.929(2)	Se(3)−Th(2)−Se(1)	104.87(6)
Th(2)−Se(3)	2.895(2)	Se(2)−Th(2)−Se(1)	80.90(6)
Th(2)−Se(3)	2.947(2)	Se(3)−Th(2)−Se(1)	74.80(6)
Th(2)−Se(4)	2.951(2)	Se(4)−Th(2)−Se(1)	155.68(6)
Th(2)−Se(5)	3.020(2)	Se(2)−Th(2)−Se(5)	79.32(6)
		Se(3)−Th(2)−Se(5)	72.93(6)
Sr−Se(2)	3.073(3)	Se(2)−Th(2)−Se(5)	134.89(6)
Sr−Se(2)	3.167(3)	Se(3)−Th(2)−Se(5)	124.84(6)
Sr−Se(1)	3.175(3)	Se(4)−Th(2)−Se(5)	132.81(6)
Sr−Se(1)	3.199(3)	Se(1)−Th(2)−Se(5)	69.51(6)
Sr−Se(5)	3.252(3)		
Sr−Se(5)	3.273(3)		
Sr−Se(4)	3.281(3)		
Sr−Se(4)	3.423(3)		

Magnetic Susceptibility. A 230 mg sample of $CuTh_2Te_6$ containing single crystals and microcrystalline powder was ground into a fine powder and used for magnetic susceptibility measurements. Composition of the sample was checked by EDAX. The magnetization was measured between 2 and 300 K with a Quantum Design SQUID magnetometer. All measurements were corrected for core diamagnetism. Insufficient quantities of $SrTh_2Se_5$ were available for magnetic susceptibility measurements.

Electrical Conductivity. The composition of a single crystal of $CuTh_2Te_6$ was established with EDAX measurements. This crystal, of approximate dimensions 0.3 cm × 0.03 cm × 0.002 cm, was mounted with gold paint to four gold wires. Four-probe resistivity

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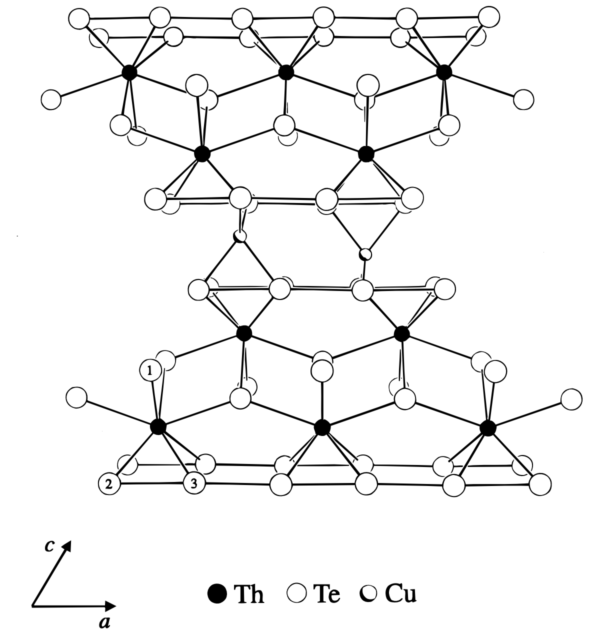

Figure 1. Unit cell of $CuTh_2Te_6$ showing the $[Th_2Te_6^-]$ slabs connected by Cu atoms. Here and in all subsequent figures the atoms are of arbitrary size.

measurements were made as a function of temperature along [010] according to methods published elsewhere.[26] Crystals of $SrTh_2Se_5$ do not grow to a size sufficient for such conductivity measurements.

Results and Discussion

$CuTh_2Te_6$. The structure of $CuTh_2Te_6$ (Figure 1) consists of ${}^{2}_{\infty}[Th_2Te_6^-]$ layers linked in a three-dimensional manner by tetrahedrally coordinated Cu atoms. Each Th atom is coordinated to eight Te atoms in a bicapped trigonal prismatic arrangement. There are three crystallographically unique Te atoms. One unique Te atom bridges each $ThTe_8$ unit such that the capping atom of one unit is the vertex of its neighbor. The two nonbridging Te atoms form infinite Te−Te chains along the exterior of the ${}^{2}_{\infty}[Th_2Te_6^-]$ layer. These chains have alternating Te−Te interactions of 3.058(1) and 3.113(1) Å, which are comparable to the Te−Te interactions of KTh_2Te_6 (3.057(3)−3.085(3) Å) and $CsTh_2Te_6$ (3.052(4)−3.088(3) Å). These distances fall between those of a $(Te-Te)^{2-}$ single bond of 2.76 Å and a van der Waals contact of 4.10 Å and make assignment of formal oxidation states somewhat arbitrary. The Cu atoms situated between the layers are bonded to two Te atoms from each neighboring chain in a tetrahedral arrangement. The Cu−Te bond lengths range from 2.506(3) to 2.567(3) Å, which can be compared to the Cu(I)−Te bond lengths in other solid-state compounds such as KCuTe (2.58(2) Å)[27] and $TlCu_3Te$ (2.593(2)−2.867(3) Å).[28] The Cu atoms are disordered over two crystallographically equivalent sites separated by a distance of 2.6 Å.

In essence the $CuTh_2Te_6$ structure is a simple variant of the ATh_2Q_6 structure type. The ATh_2Q_6 structure consists of the same ${}^{2}_{\infty}[Th_2Q_6^-]$ slabs; however, the metal cations are separated from the exterior chalcogen atoms by distances of over 3.5 Å (A = K; Q = Te) and 3.8 Å (A = Cs; Q = Te). These alkali metals are coordinated by eight Te atoms at the corners of a rectangular parallelepiped. The coordination-number preference[29] of Cu^+ is 4. To achieve this environment, the Cu atom, as distinct from the alkali metals, condenses the layered structure of ATh_2Q_6 into a three-dimensional one. The symmetry of the structure is also lowered, from *Cmcm* to $P2_1/m$. Such effects on the dimensionality of a chalcogenide structure upon substitution of various cations are well-known and have been reviewed previously.[30] The ATh_2Q_6 compounds also have structures similar to that of $ZrSe_3$, which has the same M_2Q_6 slabs separated only by a van der Waals gap; there are no cations holding the slabs together.

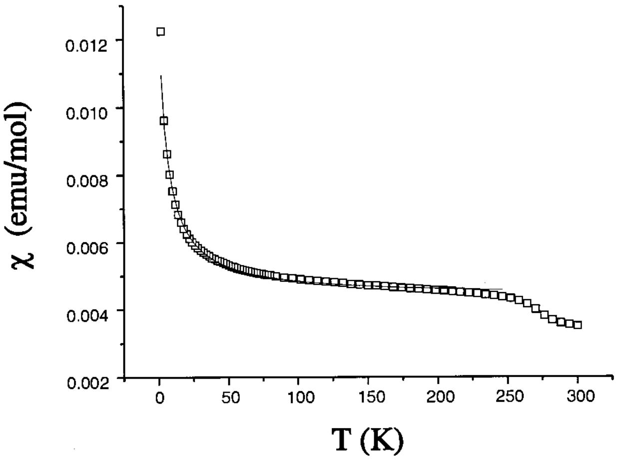

Figure 2. Plot of the molar susceptibility of $CuTh_2Te_6$ vs temperature. The solid line is the least-squares fit.

Magnetic susceptibility measurements were made on a powdered sample of $CuTh_2Te_6$ in the range 2−300 K. A plot of χ vs T is shown in Figure 2. The anomaly occurring at approximately 250 K is too weak to arise from a magnetic transition, nor does the anomaly arise from a structural change, as the crystal structure redetermined at 293 K does not differ significantly from that determined at 113 K. The susceptibility data from 2 to 246 K were fit by least-squares methods to the modified Curie−Weiss equation $\chi = C/(T + \theta) + \chi_o$. The resulting values for χ_o, C, and θ are 4.38(2) × 10^{-3} emu/mol, 4.9(2) × 10^{-2} emu K/mol, and −5.5(4) K, respectively. A value of the effective magnetic moment of 2.06 μ_B at 300 K was calculated from the equation $\mu_{eff} = [(3\chi k_B T)/(N\mu_B^2)]^{1/2}$, where χ is the molar susceptibility at temperate T and N is Avogadro's number. The value of μ_{eff} for $Tl_{0.56}UTe_3$ is 3.27 μ_B.[11]

Conductivity measurements[31] made on $CuTh_2Te_6$ perpendicular to the Te−Te chains show the compound to be a semiconductor. The band gap ϵ, as estimated from log σ vs T^{-1}, where σ is the conductivity, is 0.45 eV. Room-temperature resistivity measurements made on the K and Cs analogues perpendicular to the Te−Te chains show the materials to be weak semiconductors. No resistivity measurements have been made on $Tl_{0.56}UTe_3$.

$SrTh_2Se_5$. The structure of $SrTh_2Se_5$ is rather more complex than that of $CuTh_2Te_6$ or ATh_2Q_6. There are two independent Th atoms, each with a different coordination environment. Atom Th(1) is coordinated to eight Se atoms in a bicapped trigonal prism, and Th(2) is coordinated to seven Se atoms in a highly distorted face-capped octahedron (Table 5). Each Th(1) atom shares all three edges of the trigonal prism with three Th(1)

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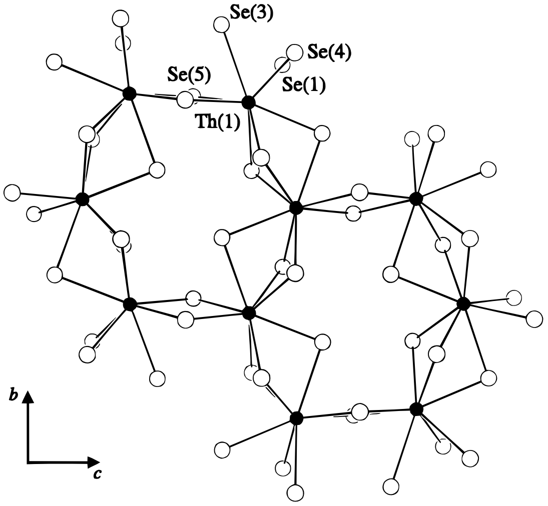

Figure 3. View along [100] showing the coordination of atom Th(1) in $SrTh_2Se_5$.

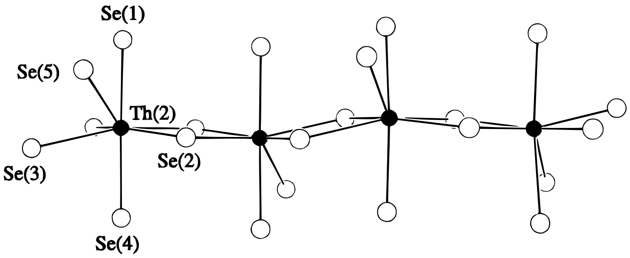

Figure 4. View of the coordination of atom Th(2) in $SrTh_2Se_5$.

neighbors; two of the neighboring atoms share caps as well (Figure 3). Connected in this way the Th(1) atoms form a $^{2}_{\infty}[\mathrm{ThSe}_8^{4-}]$ net perpendicular to the [100] axis with Th(1)−Se bond lengths ranging from 2.967(2) to 3.116(2) Å. Th(2) atoms form chains of edge-shared octahedra that run perpendicular to the $^{2}_{\infty}[\mathrm{ThSe}_8^{4-}]$ layer through the holes of the net (Figure 4). The overall structure is three-dimensional with Sr cations situated in one-dimensional channels along [010] (Figure 5). The Sr atoms are coordinated to eight Se atoms in a bicapped trigonal prism with Sr−Se interactions of 3.073(3)−3.281(3) Å.

$SrTh_2Se_5$ is isostructural with a class of compounds whose structures are derived from that of U_3Q_5 ($Q = S, Se$). In the U_3Q_5 structure the formal charges can be described as $U^{4+}(U^{3+})_2(Q^{2-})_5$, with the U^{3+} cations occupying the capped octahedral and one of the bicapped trigonal prismatic sites. It has been shown that divalent cations can substitute for one of the U^{3+} cations, with subsequent oxidation of the remaining U^{3+} to U^{4+} to give $M^{2+}(U^{4+})_2(Q^{2-})_5$.[14,15] This substitution changes the symmetry of the system from orthorhombic to monoclinic with $\beta = 90°$. Trivalent cations, such as Ln^{3+}−Gd^{3+}, will substitute for both U^{3+} sites to yield $U^{4+}(M^{3+})_2(Q^{2-})_5$[32]

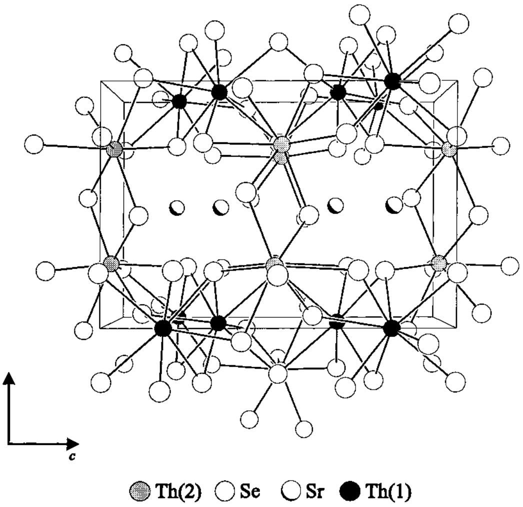

Figure 5. View of the unit cell of $SrTh_2Se_5$ showing the three-dimensional channel structure comprised of the Th(1) net and the Th(2) chains.

while retaining orthorhombic symmetry. The Th compounds of this type[15,33] have not been structurally characterized.

$SrTh_2Se_5$ is a classical metal chalcogenide. It has no short Se−Se contacts and no extended, delocalized Se−Se bonds. Each Se atom can therefore be considered to have a formal charge of 2−. The Sr cations are formally 2+, which leads to an unambiguous assignment of the Th oxidation state as 4+. On the other hand, $CuTh_2Te_6$ is not a classical metal chalcogenide. It contains Te−Te interactions that fall between those of a single bond and of a van der Waals interaction. While such interactions are common,[34,35] they render discussion of formal oxidation states useless.

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Supporting Information Available: Further crystallographic details, anisotropic displacement parameters, and complete metrical details for $CuTh_2Te_6$ and $SrTh_2Se_5$ are available in CIF file format (1 file) on the Internet only. Ordering information is given on any current masthead page. Structure amplitude tables may be obtained directly from the authors.

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