The Related Compounds $MThTe_3$ (M = Mn, Mg) and $ACuThSe_3$ (A = K, Cs): Syntheses and Characterization

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Received August 27, 1999

Single crystals of $MnThTe_3$ (**1**) and $MgThTe_3$ (**2**) grow as small black plates from the stoichiometric reaction of the elements, the former at 1000 °C and the latter at 900 °C with the aid of a Sn flux. Both compounds crystallize in the space group *Cmcm* of the orthorhombic system with four formula units in cells of dimensions a = 4.2783(6) Å, b = 13.8618(11) Å, and c = 9.9568(15) Å for **1** and a = 4.2854(6) Å, b = 14.042(2) Å, and c = 9.9450(14) Å for **2** at T = 153(2) K. $KCuThSe_3$ (**3**) forms as red blocks from a stoichiometric mixture of K_2Se, Cu, Th, and Se at 800 °C, and $CsCuThSe_3$ (**4**) forms as yellow blocks from a stoichiometric mixture of Cs_2Se_3, Cu, Th, and Se at 850 °C. Compounds **3** and **4** also crystallize in the space group *Cmcm* of the orthorhombic system with four formula units in cells of dimensions a = 4.1832(8) Å, b = 14.335(3) Å, and c = 10.859(2) Å for **3** and a = 4.2105(7) Å, b = 15.715(3) Å, and c = 10.897(2) Å for **4** at 153(2) K. Compounds **1** and **2** are isostructural with each other as well as with several uranium analogues and comprise pseudolayered structures with slabs of corner-shared MTe_6 octahedra alternating with slabs of cap- and edge-shared $ThTe_8$ bicapped trigonal prisms. The slabs are bonded together through the sharing of edges and vertices of the various polyhedra to form three-dimensional structures. Compounds **3** and **4** are two-dimensional layered structures that are closely related to **1** and **2**. In **3** and **4**, $ThSe_6$ octahedra form the same slabs as MTe_6 in **1** and **2** and Cu atoms occupy the tetrahedral holes in the layers. Alkali metal cations occupy bicapped trigonal prismatic sites between the layers. Neither structure type has short Q−Q interactions, and therefore the oxidation states of all atoms are straightforwardly assigned on the assumption of Th^{4+}. Magnetic susceptibility measurements on compound **1** show a ferromagnetic transition at 70 K and a magnetic moment of 5.9(2) μ_B per Mn ion, indicating low-spin Mn^{2+}.

Introduction

The chemistry of thorium chalcogenides has only recently become the focus of extensive research.[1−5] There are several detailed structural studies of ternary thorium chalcogenides that indicate they are isostructural with their uranium analogues.[6] However, that uranium and thorium compounds are isostructural has often been assumed and thus the existence of many thorium chalcogenide phases has been reported without the benefit of structural analysis.

We are interested in expanding thorium chalcogenide chemistry beyond that which is known for uranium. As an example reported here, because there are no structurally characterized Mg/U phases and there is a paucity of information on magnesium tellurides, we have synthesized and characterized a Mg/Th/Te phase, $MgThTe_3$. We also report the synthesis and characterization of the isostructural compound $MnThTe_3$.

It is well-known that the actinides prefer larger coordination environments, such as bicapped trigonal prisms and square antiprisms, to smaller six-coordinate octahedral environments.[6] Indeed, octahedral coordination of thorium has only been observed in solid-state chalcogenides for ThS[7] and ThSe.[8] Octahedral uranium sites are somewhat more prevalent in solid-state chalcogenides, e.g., $BaUS_3$[9] and $CsCuUTe_3$.[10] We have synthesized and report here the isostructural quaternary thorium selenides $KCuThSe_3$ and $CsCuThSe_3$; these are isostructural with $CsCuUTe_3$. These latter compounds are two-dimensional layered structures that are closely related structurally to $MThTe_3$ (M = Mg, Mn). Insofar as we can ascertain, no structural data for quaternary thorium chalcogenides have been published.

Experimental Section

General Synthesis. For all compounds, reaction mixtures weighing 0.250 g each were loaded into fused silica tubes and sealed at a pressure of approximately 10^{-4} Torr. The tubes were then placed in furnaces and heated to the appropriate reaction temperatures over a period of several hours. After 6 days, the furnaces were shut off and allowed to cool to room temperature rapidly. Th (99.8%, Alfa Aesar or Strem), Se (99.5+%, Aldrich), Te (99.8%, Aldrich), Mn (99.3%, Alfa Aesar), Mg (99.8%, Alfa Aesar), and Cu (99.999%, Alfa Aesar) were used as starting materials without further purification. K_2Se and Cs_2Se_3 fluxes were synthesized from stoichiometric mixtures of the elements in liquid ammonia. All Th was handled in an argon-filled glovebox to avoid contamination with oxygen. All samples used for single-crystal diffraction and magnetic susceptibility studies were analyzed for elemental content on an EDS-equipped Hitachi 4500 SEM; elemental ratios were found to be approximately M:Th:Te = 1:1:3 and A:Cu:Th:Se = 1:1:1:3.

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10.1021/ic991039b CCC: $19.00
Published on Web 02/02/2000

Table 1. Crystal Data and Structure Refinement Details for $MThTe_3$ and $ACuThSe_3$[a]

	$MnThTe_3$	$MgThTe_3$	$KCuThSe_3$	$CsCuThSe_3$
fw	669.78	639.15	571.56	665.37
a (Å)	4.2783(6)	4.2854(6)	4.1832(8)	4.2105(7)
b (Å)	13.8618(11)	14.042(2)	14.335(3)	15.715(3)
c (Å)	9.9568(15)	9.9450(14)	10.859(2)	10.897(2)
V (Å^3)	590.49(13)	598.44(15)	651.2(3)	721.0(2)
d_{calcd} (g/cm^3)	7.534	7.094	5.830	6.129
linear abs coeff (cm^{-1})	417	392	433	435
transm factors	0.02−0.38	0.13−0.34	0.11−0.44	0.09−0.50
$R(F)^b$ ($F_o^2 > 2\sigma(F_o^2)$)	0.0449	0.0236	0.0358	0.0490
$R_w(F_o^2)^c$ (all data)	0.1082	0.0608	0.0817	0.1127

[a] Space group $Cmcm$, $T = 153(2)$ K, $Z = 4$, $\lambda = 0.710\,73$ Å. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

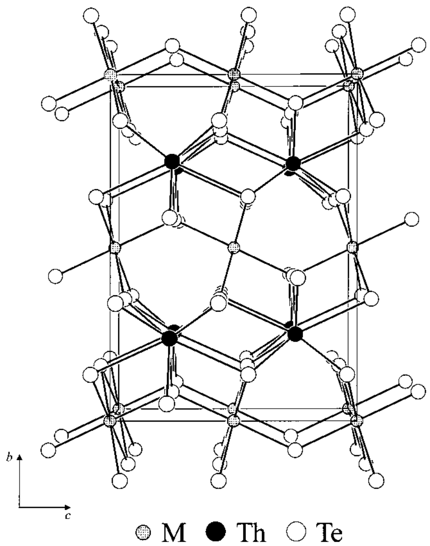

Figure 1. View of the $MThTe_3$ structure along [100]. Though the displacement parameters of all atoms are well-behaved (see Supporting Information), for the sake of clarity here and in Figures 3 and 4 atoms are drawn as circles of arbitrary size.

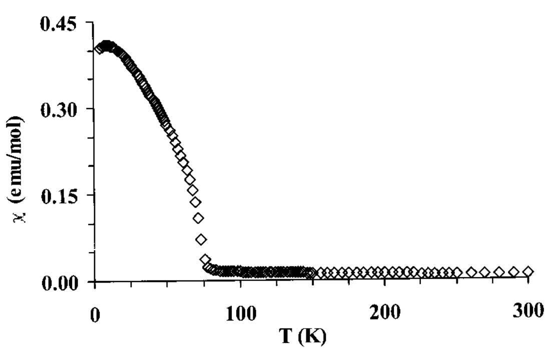

Figure 2. Magnetic susceptibility vs temperature for $MnThTe_3$, showing the ferromagnetic transition at ∼70 K.

$MThTe_3$ (M = Mn, Mg). $MnThTe_3$ (**1**) was synthesized from a stoichiometric reaction of the elements at 1000 °C. $MgThTe_3$ (**2**) was synthesized similarly, but it was necessary to add a Sn flux to aid in crystallization and the reaction was run at 900 °C. Compounds **1** and **2** formed as small black plates and needles in ∼100% yields based on crystalline products. Small droplets of elemental Sn were observed in the product mixture of $MgThTe_3$.

$ACuThSe_3$ (A = K, Cs). Single crystals of $KCuThSe_3$ (**3**) and $CsCuThSe_3$ (**4**) grew from the reactions at 850 °C of K_2Se + 2Cu + 2Th + 5Se and Cs_2Se_3 + 2Cu + 2Th + 3Se, respectively. Compound **3** formed as transparent red blocks in very high yields, ∼100%, whereas **4** crystallized as yellow blocks in somewhat lower yields, ∼50% based on single-crystal products.

Crystallographic Details. Crystal structures of all compounds were obtained in the following manner: A single crystal was manually extracted from the product mixture and analyzed for elemental content. The crystal was then mounted on the end of a glass fiber and placed in the cold stream[11] of a Bruker SMART-1000 X-ray diffractometer equipped with a CCD detector. The crystal was kept at −120 °C throughout the entire data collection. Data were collected with 0.3° ω scans for 20 s per frame for **1**, **2**, and **4** and 25 s per frame for **3**. Final unit cell parameters were obtained by a global refinement of the positions of all reflections, as performed by the processing program SAINT+.[12] A face-indexed absorption correction was applied with the use of XPREP,[13] and subsequently the program SADABS,[12] which relies on redundancy in the data, was used to apply some semiempirical corrections for frame variations. The structure of **1** was solved by Patterson methods, and the structures of **2**−**4** were solved by direct methods with the use of SHELXS[14] of the SHELXTL-97 suite of programs. The structures were refined by full-matrix, least-squares techniques with the program SHELXL-97.[13] Final refinements included anisotropic displacement parameters for all compounds as well as an extinction correction for compound **1**. These displacement parameters are well-behaved for all atoms in all of the compounds except for those of the Se atoms of compound **3**. Though the displacement ellipsoids of these atoms remain positive definite, they are of unexpected shape. Relevant crystallographic parameters are given in Table 1. Additional crystallographic information can be found in the Supporting Information.

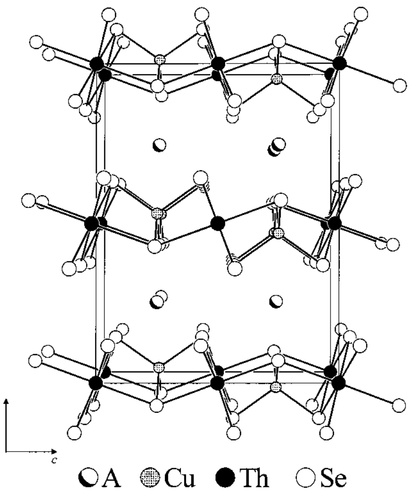

Figure 3. View of the $ACuThSe_3$ structure along [100].

Magnetic Susceptibility. A 0.515 g sample of $MnThTe_3$ was ground into a fine powder and used for magnetic susceptibility measurements. To assess the purity of the sample, an X-ray powder diffraction pattern

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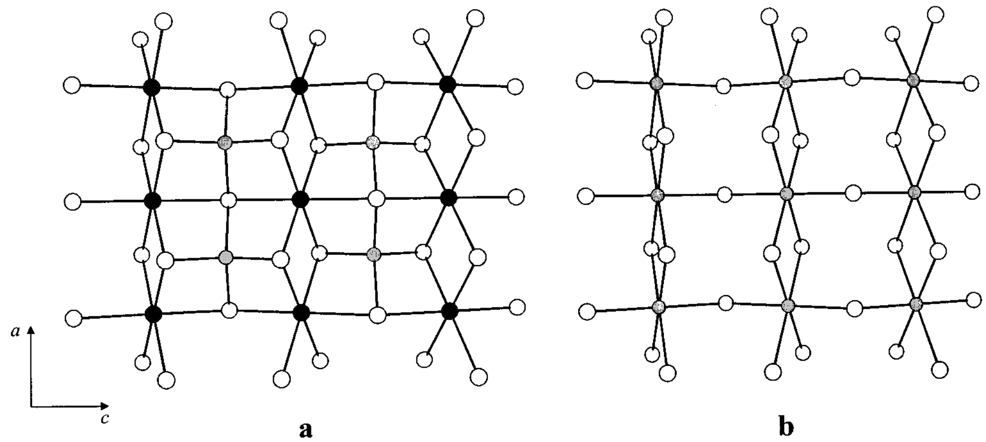

Figure 4. Comparison of the $CuThSe_3$ planes of $ACuThSe_3$ (a) and MTe_3 planes of $MThTe_3$ (b). Note how the Cu atoms of (a) fill the tetrahedral holes that are vacant in (b). Th atoms are dark circles, Q atoms are open circles, Cu atoms are gray circles (a), and M atoms are gray circles (b).

Table 2. Selected Bond Lengths (Å) for $MThTe_3$

	$MnThTe_3$	$MgThTe_3$
Th(1)−Te(2) × 2	3.160(1)	3.157(1)
Th(1)−Te(1) × 4	3.224(1)	3.223(1)
Th(1)−Te(1) × 2	3.374(1)	3.374(1)
M(1)-Te(2) × 2	2.737(1)	2.750(1)
M(1)-Te(1) × 4	2.995(1)	3.033(1)

was obtained and compared with a calculated pattern. The magnetization of the sample was measured as a function of temperature from 5 to 300 K on a Quantum Design SQUID magnetometer.

Results and Discussion

$MThTe_3$. The compounds $MThTe_3$ (M = Mn, Mg) adopt a three-dimensional structure comprising alternating slabs of MTe_6 octahedra and $ThTe_8$ bicapped trigonal prisms, as shown in Figure 1. The MTe_6 octahedra share edges along [100] and corners along [001] to form an infinite buckled sheet reminiscent of the layers found in many distorted perovskite structures. As distinct from the typical perovskite structure, the MTe_6 octahedra do not share corners in the third direction [010] to form a three-dimensional network. Instead, adjacent MTe_6 slabs are linked by $ThTe_8$ bicapped trigonal prisms through edges and caps to form a two-dimensional spacer layer. The MTe_6 octahedra share edges and corners with the $ThTe_8$ prisms to bind the layers together, forming an overall three-dimensional structure. The $MThTe_3$ compounds are isostructural with several MUQ_3 compounds (M = Sc,[15] Mn,[16] Fe;[17] Q = S, Se). Several thorium compounds with the same formulas and analogous unit cell parameters have also been reported;[18] however, no structural data are available. Compounds **1** and **2** are the first Te analogues of the series.

As shown from the bond distance data in Table 2, the MTe_6 octahedra are slightly distorted, with the equatorial bonds M−Te(1) longer than the axial bonds M−Te(2). The isostructural compounds $FeUS_3$[17] and $ScUS_3$[15] also exhibit a similar octahedral distortion. Though the M−Te(1) and M−Te(2) distances are decidedly different, neither is atypical. The Mn−Te(1) distance of 2.995(1) Å falls within the range of those found in $MnIn_2Te_4$[19] (2.889(2)−3.014(2) Å), and the Mn−Te(2) distance of 2.737(1) Å is only slightly shorter than those

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $ACuThSe_3$

	$KCuThSe_3$	$CsCuThSe_3$
Th(1)−Se(2) × 2	2.893(1)	2.878(1)
Th(1)−Se(1) × 4	2.900(1)	2.906(1)
Cu(1)−Se(1) × 2	2.459(2)	2.464(2)
Cu(1)−Se(2) × 2	2.545(2)	2.556(2)
Se(1)−Th(1)-Se(1) × 2	87.70(3)	87.13(5)
Se(2)−Th(1)-Se(1) × 4	89.60(3)	89.45(4)
Se(2)−Th(1)-Se(1) × 4	90.40(3)	90.55(4)
Se(1)−Th(1)-Se(1) × 2	92.30(3)	92.87(5)
Se(1)−Th(1)-Se(1) × 2	180	180
Se(2)−Th(1)-Se(2)	180	180
Se(1)−Cu(1)-Se(1) × 4	108.92(10)	108.29(3)
Se(1)−Cu(1)-Se(2)	109.33(2)	110.88(14)
Se(2)−Cu(1)-Se(2)	110.56(10)	112.83(14)

found in $Cs_2Mn_3Te_4$[20] (2.7442(6)−2.7515(8) Å). The Mg−Te(1) distance of 3.033(1) Å is slightly longer than that in $MgTe_2$[21] (2.95(1) Å), and the Mg−Te(2) distance of 2.750(1) Å is close to that in MgTe[22] (2.76 Å).

The Th−Te distances in **1** and **2** (3.160(1)−3.374(1) Å) are comparable to those in $CuTh_2Te_6$[4] and $CsTh_2Te_6$[2] (3.165(2)−3.364(2) Å). The closest Te···Te distances in **1** and **2** are 3.8−4.3 Å, close to the van der Waals separation of about 4.3 Å. Hence there are no Te−Te bonds, and formal oxidation states may be assigned as Mn^{2+}, Mg^{2+}, and Te^{2-} on the assumption of Th^{4+}. Verification of these assignments comes from the magnetic susceptibility of $MnThTe_3$, shown in Figure 2. The high-temperature data above 210 K were fit to the Curie−Weiss relation $\chi = C/(T + \Theta)$ with $C = 4.34(1)$ emu K/mol and $\Theta = 195(2)$ K to yield an effective magnetic moment (μ_{eff}) of 5.9(1) μ_B/Mn^{2+} ion. This is in excellent agreement with the calculated value of 5.9 μ_B for low-spin Mn^{2+}.[23] The data also show a ferromagnetic transition at approximately 70 K.

$ACuThSe_3$. The quaternary compounds $KCuThSe_3$ (**3**) and $CsCuThSe_3$ (**4**), shown in Figure 3, are substitutional analogues of the $MThTe_3$ structure type described above. Both structure types possess a two-dimensional, metal-centered octahedral

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framework; however, in **3** and **4** it is the Th atom that sits at the center of the octahedron, as opposed to the M atoms in **1** and **2**. In **3** and **4**, Cu atoms fill the tetrahedral sites between adjacent $ThSe_6$ octahedra, forming a ${}^2_\infty[CuThTe_3^-]$ layer. These tetrahedral sites are vacant in the MTe_6 layers of **1** and **2**. Figure 4 shows the relationship between these layers. The larger alkali metals of **3** and **4** occupy the bicapped trigonal prismatic sites in which Th sits in **1** and **2**. These cations force the ${}^2_\infty[CuThTe_3^-]$ layers apart, and the resultant structure is two-dimensional.

Bond distances and angles for **3** and **4** are given in Table 3. The Th−Se distances of 2.893(1) and 2.900(1) Å for **3** and of 2.878(1) and 2.906(1) Å for **4** can be compared to those of ThSe[8] (2.931(2) Å) and the seven-coordinate Th in $SrTh_2Se_5$[4] (2.967(2)−3.116(2) Å). As there are no short Se···Se interactions, formal oxidation states may be assigned as K^+, Cs^+, Cu^+, Th^{4+}, and Se^{2-}.

$KCuThSe_3$ and $CsCuThSe_3$ are isostructural with a variety of compounds with the general formula $AMRQ_3$ (A = alkali or alkaline-earth metal; M = first- or second-row transition metal; R = U,[10] rare-earth element,[24−26] or second- or third-row transition metal;[27,28] Q = S, Se, Te). Attempts to prepare the analogous $ACuThTe_3$ compounds proved unsuccessful, even though $CsCuUTe_3$ is known.[10] Though the binary compounds ThS[7] and ThSe,[8] as well as UQ (Q = S,[7] Se, *and* Te[29]) adopt the cubic rock salt structure with the metal atoms in octahedral coordination, ThTe adopts the CsCl structure with Th in a cubic coordination environment.[30,31] Also, increasing the Th content of mixed monotellurides ($U_xTh_{1-x}Te$)[32] causes a structural change from the rock salt to the CsCl structure type. Apparently, $ThTe_6$ octahedra are unstable in solid-state materials. We have previously reported the mixed Se−Te analogue $CsAgThSe_{3-x}Te_x$ ($x \approx 0.73$).[6] This compound was synthesized in an attempt to determine a site preference for Se and Te in the structure; however, both chalcogens disorder over the two independent anion sites.[33] $CsAgThSe_{3-x}Te_x$ is most likely stabilized by its high selenium content.

Acknowledgment. This research was supported by NSF Grant DMR-9709351. Use was made of the MRL Central Facilities supported by the MSERC program of the National Science Foundation (Grant DMR-9632472) at the Materials Research Center of Northwestern University. We are indebted to Mr. M. Z. Lin for his assistance with the magnetic susceptibility measurements.

Supporting Information Available: X-ray crystallographic files, in CIF format, for $MnThTe_3$, $MgThTe_3$, $KCuThSe_3$, $CsCuThSe_3$, and $CsAgThSe_{2.27}Te_{0.73}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Transparent yellow crystals of $CsAgThSe_{3-x}Te_x$ form in ~50% yield from the reaction of Cs_2Se_3, Ag, Th, and Te (molar ratio = 1:1:2:3) at 700 °C. See Supporting Information for crystallographic details. Se and Te atoms are disordered over the two crystallographically independent sites. The value of $x = 0.73(1)$ is close to the EDS results on the crystal used for the structure determination. Additional EDS analyses of other crystals from the same reaction mixture yielded a range for x of 0.50−1.0.