Uranium Tellurides: New One- and Two-Dimensional Compounds $CsUTe_6$, $CsTiUTe_5$, $Cs_8Hf_5UTe_{30.6}$, and $CsCuUTe_3$

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Received November 8, 1994[®]

The new compounds $CsUTe_6$, $CsTiUTe_5$, $Cs_8Hf_5UTe_{30.6}$, and $CsCuUTe_3$ have been synthesized through the reaction of the metals with a Cs_2Te_n flux. $CsUTe_6$ crystallizes in space group D_{2h}^{16}-*Pnma* of the orthorhombic system with eight formula units in a cell of dimensions $a = 30.801(7)$, $b = 8.143(2)$, and $c = 9.174(2)$ Å and $V = 2301(1)$ Å^3 ($T = 113$ K). $CsTiUTe_5$ crystallizes in space group D_{2h}^{5}-*Pmma* of the orthorhombic system with two formula units in a cell of dimensions $a = 6.130(1)$, $b = 8.240(2)$, and $c = 10.363(2)$ Å and $V = 523.4(2)$ Å^3 ($T = 113$ K). $Cs_8Hf_5UTe_{30.6}$ crystallizes in space group C_{2h}^{5}-$P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions $a = 12.043(3)$, $b = 18.724(4)$, and $c = 30.496(6)$ Å, $\beta = 97.64(3)°$, and $V = 6816(2)$ Å^3 ($T = 113$ K). $CsCuUTe_3$ crystallizes in space group D_{2h}^{17}-*Cmcm* of the orthorhombic system with four formula units in a cell of dimensions $a = 4.327(1)$, $b = 16.661(4)$, and $c = 11.337(3)$ Å, and $V = 817.3(3)$ Å^3 ($T = 113$ K). The structures of all four compounds were determined by single-crystal X-ray methods. $CsUTe_6$ has a one-dimensional structure that contains pairs of U/Te chains coupled by Te–Te bonds and separated by Cs^+ cations. There are many Te–Te distances less than 3.1 Å; if an arbitrary maximum Te–Te single bond distance is taken as 2.98 Å, then the chains may be formulated $^1_\infty[U_2(Te_3)_3(Te_2)(Te)^{2-}]$, with U in the +IV oxidation state. The U atoms are coordinated to nine Te atoms in a tricapped trigonal-prismatic arrangement. Electrical resistivity measurements give conductivities of $1.6(4) \times 10^{-2}$ Ω^{-1} cm^{-1} (298 K) and $1.5(2) \times 10^{-3}$ Ω^{-1} cm^{-1} (77 K). $CsTiUTe_5$ has a layered structure that contains UTe_8 bicapped trigonal prisms sharing a common edge and $TiTe_6$ octahedra sharing faces. Cs^+ cations, located in pentagonal prisms of Te atoms, separate the layers. The structure contains an infinite linear Te–Te chain with a separation of 3.065(1) Å. Assignment from the structural results of formal oxidation states is difficult. Magnetic susceptibility data for $CsTiUTe_5$ give a curvilinear χ^{-1} vs T plot. When fit to a modified Curie–Weiss law, the values $C = 8.8(3) \times 10^{-2}$ emu K/mol, $\Theta = -1.5(2)$ K, and $\chi_o = 2.11(8) \times 10^{-3}$ emu/mol result. The value of μ_{eff} (300 K) is 2.23(1) μ_B for each $CsTiUTe_5$ unit. The resistivity of $CsTiUTe_5$ at 77 K is beyond the detection limits of our instrument, but it is $1.2(9) \times 10^{-3}$ Ω^{-1} cm^{-1} at 298 K. $Cs_8Hf_5UTe_{30.6}$ is a one-dimensional compound with ordered Hf and U atoms and disordered Te atoms in two unique chains that may be formulated $^1_\infty[Hf_3Te_{15.6}{}^{4-}]$ and $^1_\infty[Hf_2UTe_{15}{}^{4-}]$. Cs^+ cations separate the chains. The Hf and Uatoms are coordinated to Te atoms in a distorted trigonal prismatic framework. Since there are many short Te–Te distances the assignment of formal oxidation states is not possible. $CsCuUTe_3$ is a layered compound with no Te–Te bonding. Formal oxidation states are unambiguously Cs^I, Cu^I, U^{IV}, and Te^{II-}. As expected, Cs^+ cations separate the $^2_\infty[CuUTe^{3-}]$ layers, which contain UTe_6 octahedra and $CuTe_4$ tetrahedra. This structure differs markedly from the channel structure of $CsAg_5Te_3$ formed through an analogous synthesis with Cu replaced by Ag.

Introduction

Solid-state compounds of uranium have been studied extensively because of the unusual magnetic properties that arise from the presence of f-electrons and because of the accessibility of several oxidation states.[1,2] The binary U/Te phase diagram is complex; a critical review[3] of all reported structures and powder diffraction patterns includes UTe, U_3Te_4, cubic U_2Te_3, orthorhombic U_2Te_3, U_7Te_{12}, $UTe_{1.78}$, UTe_2, $UTe_{2.5}$, α-UTe_3, β-UTe_3, $UTe_{3.4}$, and UTe_5. The range of magnetic properties is shown in ferromagnetic[4] UQ (Q = S, Se, Te), paramagnetic[5] UQ_3, and antiferromagnetic[6] U_2Te_3.

The propensity for chalcogen compounds to assume non-closest-packed arrangements makes them an ideal system for the study of the structural chemistry of uranium. The large uranium atom can adopt many coordination environments, including UTe_6 octahedra in UTe,[4] regular and distorted USe_8 quadratic antiprisms in α-USe_2,[7] and UTe_9 tricapped trigonal prisms in β-UTe_3.[8] Furthermore, the binary telluride phases[8,9] are structurally interesting because there are many Te–Te distances intermediate between a $(Te-Te)^{2-}$ single bond of 2.76 Å[10] and a $Te^{2-}\cdots Te^{2-}$ van der Waals contact of 4.10 Å.[11] This incomplete reduction of Te can render assignment of formal oxidation states rather arbitrary.

Whereas there are many known ternary uranium sulfides and selenides,[12] the chemistry of ternary uranium chalcogenides

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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0020-1669/95/1334-3165$09.00/0

containing alkali metals or copper is relatively unexplored. The only reported alkali-metal phases are KUS_2[13] and KUS_3.[14] The only reported copper-containing ternary uranium chalcogenide compound, $Cu_2U_6Q_{13}$ (Q = S, Se),[15,16] has trigonal-planar Cu atoms and distorted UQ_8 bicapped trigonal prisms. The existence of a lone quaternary alkali metal/copper/uranium/chalcogenide, $KCuUSe_3$, has been reported.[17]

There are very few known ternary uranium tellurides. Single crystal studies have been carried out on MUTe (M = As, Sb),[18,19] $LnUTe_6$ (Ln = La, Ce, Pr, Nd, Sm, Gd),[20] and $Sb_{0.8}UTe_{0.2}$;[4] X-ray powder patterns have been reported for C_2U_2Te,[21] N_2U_2Te,[22] NUTe,[23] MUTe (M = Bi, Ge, Sn),[19,24] $LnUTe_3$ (Ln = Tb, Dy, Ho),[25] $Ln_{1.5}U_{1.5}Te_5$ (Ln = Tb, Dy, Ho, Er),[25] and $Dy_{0.5}U_{0.5}Te_x$ (x = 2, 3).[26]

By use of the reactive flux method[27] an amazing variety of low-dimensional metal polychalcogenides with novel structures[28-37] has been synthesized. One successful route to the synthesis of new solid-state compounds employs substitutional variations on known compounds in accordance with the principles of coordination chemistry and the known coordination preferences of various metals.[38] However, the most interesting structural variations are found when substitutions do not just involve simple replacement of one atom for another. For example, among the metal chalcogenides we have found that the substitution of Na for K can bring about subtle differences in structure[32,33] in the quaternary A/Cu/Zr/Q (A = alkali metal, Q = S, Se, Te) system. By contrast, substitution of Cs for K in the ternary system A/M/Te (A = alkali metal, M = Zr, Hf) leads to a change in composition from $K_4M_3Te_{17}$[39] to $Cs_4Zr_3Te_{16}$.[40] Because many of the compounds we have recently synthesized contain group IV metals (Ti, Zr, Hf) we sought to expand into entirely unknown areas of solid-state chemistry by including U with these group IV metals in various ternary and quaternary chalcogenides. This effort has been successful; we present here the synthesis and characterization of four new uranium tellurides. A preliminary discussion of the structure of $CsTiUTe_5$[41] has been reported.

Experimental Section

Synthesis. The binary starting material Cs_2Te_3 was synthesized at −79 °C from reaction of stoichiometric amounts of elemental Cs (Aldrich, 99.5%) and Te (Aldrich, 99.8%) in liquid NH_3 under an Ar atmosphere. The composition Cs_2Te_3 was confirmed by X-ray powder diffraction methods.[42,43] All of the following reactions were carried out in fused silica tubes that were evacuated to $\sim10^{-4}$ Torr and sealed. The tubes were charged with the reaction mixtures in a drybox under an Ar atmosphere. All ternary/quaternary products were lustrous, black needles; these were manually extracted from the melts.

Synthesis of $CsUTe_6$. The reaction mixture consisted of Ag (45 mg, 0.42 mmol; Johnson Matthey 99.999%), U (36 mg, 0.15 mmol; Aesar, 99.7%), Te (87 mg, 0.68 mmol; Aldrich, 99.8%), and Cs_2Te_3 (97 mg, 0.15 mmol). The sample was kept at 650 °C for 1 day and then 900 °C for 4 days, before being cooled at 3 °C/h to room temperature. The target quaternary compound of Cs, U, Ag, and Te did not form; other products included binaries and the ternary compound $CsAg_5Te_3$.[44] The products $CsUTe_6$ and $CsAg_5Te_3$ were distinguished by either EDX (energy dispersive X-ray analysis) or by X-ray photographic techniques. Analysis of several crystals of $CsUTe_6$ with an EDX-equipped Hitachi S570 SEM confirmed the presence of Cs, U, and Te in the approximate ratio 1:1:6; no Ag was detected.

Synthesis of $CsTiUTe_5$. The reaction mixture contained Ti (13 mg, 0.26 mmol; Aesar 99.9%), U (45 mg, 0.19 mmol), Te (73 mg, 0.57 mmol), and Cs_2Te_3 (123 mg, 0.19 mmol). The sample was kept at 650 °C for 2.5 days and then 900 °C for 6 days, before being cooled at 3 °C/h to room temperature. This initial synthesis yielded a few crystals of sufficient quality for use in X-ray diffraction studies. Higher yields were obtained through a stoichiometric reaction heated to 900 °C for 6 days and cooled at 5 °C/h to room temperature. EDX analysis of several crystals confirmed the presence of Cs, Ti, U, and Te in the approximate ratio 1:1:1:6. The exact composition of the compound was established from the X-ray structure determination.

Synthesis of $Cs_8Hf_5UTe_{30.6}$. In an attempt to synthesize the Hf analogue of the two-dimensional compound $CsTiUTe_5$, $Cs_8Hf_5UTe_{30.6}$ was prepared in low yield from a loading of the elements Hf (22 mg, 0.12 mmol; Johnson Matthey, 99.6%), U (23 mg, 0.10 mmol), Te (102 mg, 0.80 mmol), and Cs_2Te_3 (124 mg, 0.19 mmol). The reaction tube was held at 700 °C for 4 days and cooled at 3 °C/h to room temperature. EDX analysis of several crystals confirmed the presence of Cs, Hf, U, and Te in the approximate ratio 5.5:4:1:20. The exact composition of the compound was established from the X-ray structure determination.

Synthesis of $CsCuUTe_3$. This compound was prepared from a loading of the elements Cu (25 mg, 0.40 mmol; Alfa, 99.999%), U (100 mg, 0.42 mmol), Te (93 mg, 0.73 mmol), and Cs_2Te_3 (115 mg, 0.18 mmol). The reaction tube was held at 400 °C for 6 days and cooled at 5 °C/h to room temperature, then reheated to 900 °C for 6 days and cooled at 5 °C/h. EDX analysis of several crystals confirmed the presence of Cs, Cu, U, and Te in the approximate ratio 1:1:1:3.5. The exact composition of the compound was established from the X-ray structure determination.

Electrical Conductivity. Single crystals of $CsUTe_6$ or $CsTiUTe_5$ ranging in length from 0.4 to 0.7 mm were mounted with Ag paint on Au wires with graphite extensions. Two-probe dc resistivity measurements along the needle axis were made at 298 and 77 K.

Magnetic Susceptibility. A sample weighing 21.8 mg was obtained by the extraction of single crystals of $CsTiUTe_5$. Magnetic susceptibil-

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(44) $CsAg_5Te_3$: a = 14.576(4) Å, c = 4.5520(10) Å, V = 967.1(4) Å^3 (T = 113 K); $P4_2/mnm$. $R_w(F_o^2)$ = 0.087, $R(F)$ = 0.039.

Table 1. Crystallographic Details on Cs/U/Te Compounds

formula	$CsUTe_6$	$CsTiUTe_5$	$Cs_8Hf_5UTe_{30.6}$	$CsCuUTe_3$
fw	1136.54	1056.84	6095.77	817.28
space group	D_{2h}^{16}-*Pnma*	D_{2h}^{5}-*Pmma*	$C_{2h}^{5}-P2_1/c$	D_{2h}^{17}-*Cmcm*
a, Å	30.801(7)	6.130(2)	12.043(2)	4.3270(10)
b, Å	8.143(2)	8.240(2)	18.724(4)	16.661(4)
c, Å	9.174(2)	10.363(2)	30.496(6)	11.337(3)
β, deg	90	90	97.64(3)	90
V, Å^3	2301(1)	523.4(2)	6816(2)	817.3(3)
Z	8	2	4	4
T, K^a	113	113	113	113
d(calcd), g cm^{-3}	6.568	6.705	5.941	6.642
abs coeff, cm^{-1}	1813	332.2	270.0	371.7
transm factors	0.056−0.258	0.376−0.673	0.493−0.704	0.047−0.148
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^b$	0.0793	0.0237	0.0732	0.0482
$R_w(F_o^2)^b$	0.171	0.059	0.177	0.130

^{a} The low-temperature system is based on a design by Huffman.[45a] ^{b} $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

ity measurements were made as a function of both applied field and temperature with the use of a Quantum Design SQUID magnetometer. Field-dependence measurements made at 5 K over the range 0−10^4 G showed no susceptibility dependence on field. Temperature-dependence measurements were made at 2 × 10^3 G over the range 6−300 K. All measurements were corrected for background and core diamagnetism.

Crystallography of $CsUTe_6$. Initial cell parameters and symmetry information for $CsUTe_6$ were determined from Weissenberg photographs taken at 298 K. Final cell parameters of a = 30.801(7), b = 8.143(2), and c = 9.174(2) Å were determined from a least-squares analysis of the setting angles of 27 reflections in the range 52° < 2θ(Cu Kα_1) < 58° that had been automatically centered at 113 K on a Picker diffractometer operated from a PC.[45b] (Owing to the long *a* axis, Cu radiation was used in this study.) The intensities of six representative reflections monitored every 100 reflections were used to bring observations to a common scale; a 5% increase in intensity was noted after a re-orientation of the crystal, and the data were scaled accordingly. Crystallographic details are listed in Table 1. Additional information is given in Table SI.[46] Intensity data were processed and corrected for absorption[47] on an IBM RS/6000 series computer with programs and methods standard in this laboratory. The data were averaged through the use of the program XPREP.[48]

The observed Laue symmetry and the systematic absences are consistent with the orthorhombic space groups $D_{2h}{}^{16}$-*Pnma* and $C_{2v}{}^{9}$-$Pn2_1a$. Intensity statistics as well as agreement among equivalent reflections favored the centrosymmetric space group *Pnma*. The structure was solved in this space group with the use of the direct methods program SHELXS of the SHELXTL PC program package.[49] The structure was refined by full-matrix least-squares techniques with the use of the program SHELXL-93,[50] the function $\sum w(F_o^2 - F_c^2)^2$ being minimized. Anisotropic thermal motion and an extinction parameter were included in the refinement. The final refinement led to a value of $R_w(F_o^2)$ of 0.171. The conventional *R* index (on *F* for $F_o^2 > 2\sigma(F_o^2)$) is 0.079. The final difference electron density map shows no feature with a height greater than 3.4% of a Te atom. Values of the atomic parameters and equivalent displacement parameters are given in Table 2, and anisotropic displacement parameters are given in Table SII.[46]

Crystallography of $CsTiUTe_5$. Initial cell parameters and symmetry information for $CsTiUTe_5$ were determined from Weissenberg photographs taken at 298 K. Final cell parameters of a = 6.130(1), b = 8.240(2), and c = 10.363(2) Å were determined from a least-squares analysis of setting angles of 25 reflections in the range 30° < 2θ(Mo Kα_1) < 39° that had been automatically centered at 113 K on an Enraf-Nonius CAD4 diffractometer. Six representative standard reflections monitored every three hours of X-ray exposure time showed no significant variations in intensity during data collection. Intensity data were processed and corrected for absorption, as described previously.

For $CsTiUTe_5$ the observed Laue symmetry and the systematic absences are consistent with the orthorhombic space groups $D_{2h}{}^{5}$-*Pmma*, $C_{2v}{}^{2}$-$P2_1ma$, and $C_{2v}{}^{4}$-*Pm*2*a*. Intensity statistics favored the centrosymmetric space group *Pmma*. The structure was solved in this space group with the use of the direct methods program SHELX-86.[51] The solution was refined with the use of the program SHELXL-93, as described previously. The final refinement included anisotropic thermal motion and an extinction parameter. The final value of $R_w(F_o^2)$ is 0.059, whereas the conventional *R* index (on *F* for $F_o^2 > 2\sigma(F_o^2)$) is 0.024. The final difference electron density map shows no feature with a height greater than 0.4% of a Te atom. Values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 3 and anisotropic displacement parameters are given in Table SIII.[46]

Crystallography of $Cs_8Hf_5UTe_{30.6}$. Final cell parameters of a = 12.043(3) Å, b = 18.724(4) Å, c = 30.496(6) Å, and β = 97.64(3)° were determined from a least-squares analysis of setting angles of 25 reflections in the range 14° < 2θ(Mo Kα_1) < 36° that had been automatically centered at 113 K on an Enraf-Nonius CAD4 diffractometer. Six representative standard reflections monitored every 3 h of X-ray exposure time showed no significant variations in intensity during data collection. Peak profile data were collected for $Cs_8Hf_5UTe_{30.6}$.[52] Intensity data were processed and corrected for absorption, as described previously.

The observed Laue symmetry and the systematic absences for $Cs_8Hf_5UTe_{30.6}$ are consistent with the monoclinic space group $C_{2h}{}^{5}$-$P2_1/c$. The structure was solved with the use of the program SHELXS. It was refined with the use of the program SHELXL-93 as described above. In early refinements for $Cs_8Hf_5UTe_{30.6}$, thermal parameters for Te atoms 30, 31, and 32 were much smaller than those of the other Te atoms in the structure. A structural model that included disorder among these Te atoms was used in the structure refinements. Since two of these

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $CsUTe_6$

atom	*x*	*y*	*z*	*U*(eq)^a
Cs(1)	0.03770(14)	1/4	0.4162(5)	0.0180(14)
Cs(2)	0.29384(14)	1/4	0.8960(5)	0.022(2)
U(1)	0.37541(8)	1/4	0.4013(3)	0.0104(8)
U(2)	0.62519(8)	1/4	0.6233(3)	0.0096(8)
Te(1)	0.12247(10)	0.0158(5)	0.1549(3)	0.0125(9)
Te(2)	0.30691(12)	0.0041(5)	0.2613(3)	0.0127(13)
Te(3)	0.44291(12)	0.0081(5)	0.2660(3)	0.0104(13)
Te(4)	0.02813(14)	1/4	0.0067(5)	0.0133(14)
Te(5)	0.15191(14)	1/4	0.5607(5)	0.016(2)
Te(6)	0.19174(14)	1/4	0.1388(5)	0.0123(13)
Te(7)	0.27966(14)	1/4	0.4837(5)	0.0114(14)
Te(8)	0.40643(14)	1/4	0.0709(5)	0.0147(14)
Te(9)	0.45071(14)	1/4	0.6517(5)	0.0102(13)

^{a} *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $CsTiUTe_5$

atom	*x*	*y*	*z*	*U*(eq)
Cs	1/4	1/2	0.78776(5)	0.00985(10)
U	1/4	0	0.33246(3)	0.00569(7)
Ti	0	0	0	0.0071(2)
Te(1)	1/4	0.24557(4)	0.11113(4)	0.00599(8)
Te(2)	0	0.25240(4)	1/2	0.00634(8)
Te(3)	1/4	0	0.77525(5)	0.00698(10)

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Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Cs_8Hf_5UTe_{30.6}$

atom	x	y	z	U(eq)	occupancy
U(1)	0.14880(13)	0.26364(8)	0.48649(5)	0.0175(4)	1
Hf(1)	−0.1184(2)	0.01650(10)	0.25259(6)	0.0191(4)	1
Hf(2)	0.21715(14)	0.02200(9)	0.25933(6)	0.0175(4)	1
Hf(3)	0.5472(2)	0.02301(10)	0.26607(7)	0.0252(5)	1
Hf(4)	0.48668(14)	0.25484(9)	0.49022(5)	0.0141(4)	1
Hf(5)	0.80987(14)	0.25033(9)	0.49295(6)	0.0153(4)	1
Cs(1)	0.4716(2)	0.4945(2)	0.59164(9)	0.0234(6)	1
Cs(2)	0.7395(2)	0.2926(2)	0.33349(8)	0.0202(6)	1
Cs(3)	1.0728(2)	0.5272(2)	0.43797(10)	0.0345(8)	1
Cs(4)	0.8091(3)	0.2384(2)	0.65982(11)	0.0395(8)	1
Cs(5)	−0.0193(3)	−0.0352(2)	0.41965(10)	0.0385(8)	1
Cs(6)	0.2098(2)	0.2632(2)	0.30201(10)	0.0336(8)	1
Cs(70)	0.5251(8)	0.0026(5)	0.4224(3)	0.0282(14)	0.398(8)
Cs(71)	0.4883(5)	0.0120(3)	0.4413(2)	0.0282(14)	0.602(8)
Cs(80)	0.2489(4)	0.2494(2)	0.14849(14)	0.0239(9)	0.632(5)
Cs(81)	0.3449(6)	0.2998(4)	0.1735(2)	0.0239(9)	0.368(5)
Te(1)	−0.3240(2)	0.0802(2)	0.19629(9)	0.0171(6)	1
Te(2)	−0.2210(3)	−0.0354(2)	0.16084(10)	0.0299(8)	1
Te(3)	−0.0788(2)	0.1769(2)	0.26956(9)	0.0207(7)	1
Te(4)	−0.0714(3)	−0.1188(2)	0.30496(12)	0.0471(10)	1
Te(5)	0.0439(2)	0.1040(2)	0.20257(9)	0.0220(7)	1
Te(6)	0.0574(2)	−0.09654(14)	0.23819(8)	0.0133(6)	1
Te(7)	0.0775(2)	0.0782(2)	0.32268(9)	0.0183(6)	1
Te(8)	0.1827(2)	−0.0072(2)	0.16290(9)	0.0186(6)	1
Te(9)	0.2491(2)	−0.0297(2)	0.35112(9)	0.0175(6)	1
Te(10)	0.3594(2)	0.0897(2)	0.20125(9)	0.0221(7)	1
Te(11)	0.3892(2)	−0.0965(2)	0.27314(10)	0.0237(7)	1
Te(12)	0.3935(2)	0.0913(2)	0.32133(9)	0.0185(6)	1
Te(13)	0.5350(3)	−0.0992(2)	0.20990(11)	0.0346(8)	1
Te(14)	0.5162(2)	0.18113(14)	0.26319(10)	0.0237(7)	1
Te(15)	−0.0549(2)	0.20739(14)	0.42416(9)	0.0148(6)	1
Te(16)	−0.0123(2)	0.2496(2)	0.55912(10)	0.0279(7)	1
Te(17)	0.0473(2)	0.3309(2)	0.39769(10)	0.0223(7)	1
Te(18)	0.1906(2)	0.09953(14)	0.48511(9)	0.0203(7)	1
Te(19)	0.2097(2)	0.3854(2)	0.55002(10)	0.0265(7)	1
Te(20)	0.3091(2)	0.19053(14)	0.42690(9)	0.0147(6)	1
Te(21)	0.3328(2)	0.37907(13)	0.48015(9)	0.0128(6)	1
Te(22)	0.3452(2)	0.18157(14)	0.54668(9)	0.0166(6)	1
Te(23)	0.4589(2)	0.30419(14)	0.39794(8)	0.0129(6)	1
Te(24)	0.5249(2)	0.2837(2)	0.58632(9)	0.0163(6)	1
Te(25)	0.6232(2)	0.19535(14)	0.42654(9)	0.0134(6)	1
Te(26)	0.6655(2)	0.36848(14)	0.51140(8)	0.0131(6)	1
Te(27)	0.6607(2)	0.17431(14)	0.54717(9)	0.0164(6)	1
Te(28)	0.7876(2)	0.09605(14)	0.48164(9)	0.0162(6)	1
Te(29)	0.8122(2)	0.38373(14)	0.44873(9)	0.0171(6)	1
Te(30)	−0.2397(5)	0.0683(3)	0.3256(2)	0.0383(10)	0.584(5)
Te(31)	0.6601(5)	−0.0506(3)	0.3528(2)	0.0383(10)	0.584(5)
Te(32)	−0.2827(7)	0.0157(4)	0.3287(3)	0.0383(10)	0.416(5)

atoms (Te(30′) and Te(31)) are separated by a reasonable Te−Te bond of 2.714(8) Å and display coordination similar to atoms Te(4)−Te(6) and Te(11)−Te(13), they were treated as a Te_2 unit. This unit and the third atom (Te(32)) were disordered and the occupancies were refined; the occupancies can be found in Table 4. In this model, alternately atom Te(30′) and atom Te(32′) link atom Hf(1′) and atom Hf(3); atom Te(31) caps the trigonal prism about atom Hf(3). The sum of the partial Te atom occupancies from this disordered model gives rise to the nonstoichiometry of the compound. There is also disorder of two of the Cs^+ atoms (Cs(70)/Cs(71) and Cs(80)/Cs(81)), wherein each atom is randomly distributed over two sites. The final refinement included anisotropic thermal motion. The final values of the agreement indices are $R_w(F_o^2) = 0.177$ and R (on F for $F_o^2 > 2\sigma(F_o^2)$) = 0.073. The final difference electron density map shows no features with a height greater than 11.4% of an ordered Te atom. Values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 4, and anisotropic displacement parameters are given in Table SIV.[46]

Crystallography of $CsCuUTe_3$. Initial cell parameters and symmetry information were determined from Weissenberg photographs taken at 298 K. Final cell parameters of $a = 4.327(1)$, $b = 16.661(4)$, and $c = 11.337(3)$ Å were determined from a least-squares analysis of setting angles of 50 reflections in the range $26° < 2\theta(\mathrm{Mo}\ K\alpha_1) < 35°$ that had been automatically centered at 113 K on a Picker diffractometer operated from a PC.[45] Six representative standard reflections monitored every 100 reflections showed no significant variations in intensity throughout data collection. Intensity data were processed and corrected for absorption, as described previously.

The observed Laue symmetry and the systematic absences are consistent with the orthorhombic space groups D_{2h}^{17}-*Cmcm*, C_{2v}^{12}-*Cmc*2$_1$, and C_{2v}^{16}-*C*2*cm*. Intensity statistics and the agreement among equivalent reflections favored space group D_{2h}^{17}-*Cmcm*. The structure was solved in this space group with the use of the program SHELXS.

The structure was refined as described above. The final refinement for $CsCuUTe_3$ included anisotropic thermal motion and an extinction parameter. The final values of $R_w(F_o^2)$ and R (on F for $F_o^2 > 2\sigma(F_o^2)$) are 0.130 and 0.048, respectively. The final difference electron density map shows no features with heights greater than 1.9% of a Te atom. Values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 5 and anisotropic displacement parameters are given in Table SV.[46]

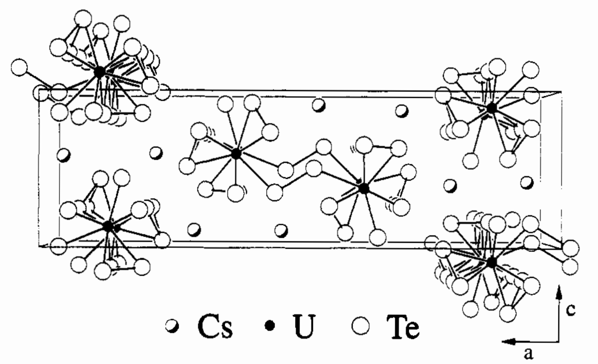

Figure 1. Unit cell of $CsUTe_6$ showing the unusual pairing of $^1_\infty[U_2(Te_3)_3(Te_2)Te^{2-}]$ chains through Te−Te bonds. Here and in all subsequent figures the atoms are of arbitrary size.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $CsCuUTe_3$

atom	x	y	z	U(eq)
Cs	0	0.74340(8)	$^1/_4$	0.0136(3)
Cu	0	0.4662(2)	$^1/_4$	0.0134(5)
U	0	0	0	0.0091(3)
Te(1)	0	0.37733(6)	0.05900(7)	0.0099(3)
Te(2)	0	0.06032(8)	$^1/_4$	0.0098(3)

Results and Discussion

$CsUTe_6$ This compound is the first telluride reported in the A/U/Q (A = alkali metal; Q = chalcogen) family. Its unusual structure (Figure 1) comprises coupled pairs of one-dimensional anionic U/Te chains separated by Cs^+ cations. Several one-dimensional chain structures have been characterized[39,40,53] from reactions utilizing Cs_2Te_n fluxes, but none have been cross-linked. Similar to the other chain structures, the wide range of Te−Te interactions within the chains makes simple bonding descriptions inadequate.

The two independent U atoms are each coordinated to nine Te atoms in a tricapped trigonal prismatic arrangement (Figure 2); the Cs^+ cations are also nine coordinate. The $^1_\infty[U_2Te_{12}^{2-}]$ chains extend along the [010] direction through a common triangular face of the U-atom centered trigonal prisms. Atom U(1) is connected to atom U(2) through atoms Te(1), Te(2), and Te(3). Atoms Te(7), Te(8), and Te(9) cap atom U(1) whereas atoms Te(4), Te(5), and Te(6) cap atom U(2). The chains are coupled through a Te−Te bond (2.795(9) Å) between capping atoms Te(4) and Te(9).

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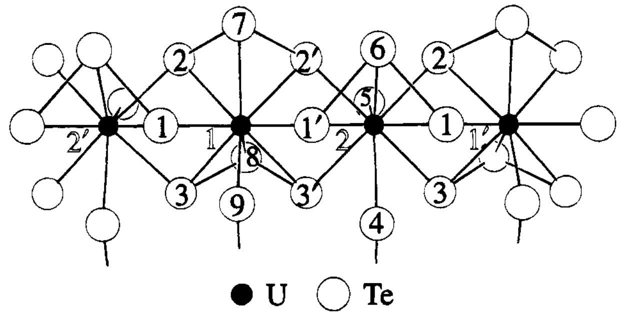

Figure 2. View of the $^{1}_{\infty}[U_2(Te_3)_3(Te_2)Te^{2-}]$ chain of $CsUTe_6$. The atom numbering scheme is given.

Table 6. Selected Bond Lengths (Å) for $CsUTe_6$[a]

U(1)−Te(7)	3.043(5)	U(2)−Te(1)^{8,9} (2)	3.186(4)
U(1)−Te(3)^{1} (2)	3.120(4)	U(2)−Te(4)^{8}	3.217(5)
U(1)−Te(8)	3.177(5)	Te(1)^{1}−Te (6) (2)	2.865(5)
U(1)−Te(1)^{2,3} (2)	3.177(4)	Te(1)−Te(9)^{10} (2)	3.124(5)
U(1)−Te(2)^{1} (2)	3.179(4)	Te(2)^{1}−Te(7) (2)	2.979(5)
U(1)−Te(9)	3.263(5)	Te(2)−Te(5)^{10} (2)	3.045(5)
U(2)−Te(5)^{6}	3.013(5)	Te(3)^{1}−Te(8) (2)	2.889(5)
U(2)−Te(2)^{5,7} (2)	3.126(4)	Te(3)−Te(4)^{2} (2)	3.175(5)
U(2)−Te(3)^{5,7} (2)	3.137(4)	Te(4)−Te(9)^{11} (2)	2.791(6)
U(2)−Te(6)^{8}	3.158(5)		

[a] Symmetry transformations used to generate equivalent atoms: (1) $x, -y + 1/2, z$; (2) $-x + 1/2, -y, z + 1/2$, (3) $-x + 1/2, y + 1/2, z + 1/2$; (4) $-x + 1, -y + 1, -z + 1$; (5) $-x + 1, -y, -z + 1$; (6) $x + 1/2, y, -z + 3/2$; (7) $-x + 1, y + 1/2, -z + 1$; (8) $x + 1/2, y, -z + 1/2$; (9) $x + 1/2, -y + 1/2, -z + 1/2$ (10) $-x + 1/2, -y, z - 1/2$; (11) $x - 1/2, y, -z + 1/2$.

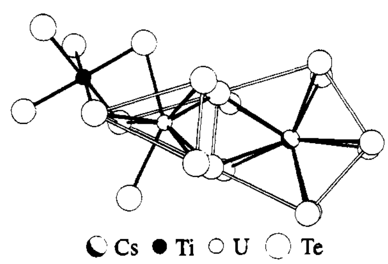

Figure 3. Metal atom coordination environments in $CsTiUTe_5$.

Selected bond distances are given in Table 6. Complete metrical data are given in Table SVI.[46] The range of U−Te distances (3.006(8)−3.265(7) Å) is similar to the range found in UTe_2 (3.080(1)−3.203(1) Å).[54] There are many short Te−Te interactions in $CsUTe_6$. The anion in this structure can be described as $^{1}_{\infty}[U_2(Te_3)_3(Te_2)(Te)^{2-}]$ if an arbitrary maximum Te−Te single bond distance of 2.98 Å is chosen. This arbitrary description is consistent with formal U^{IV} atoms; there is no experimental evidence for this assignment.

Despite the wide range of Te−Te interactions along the chains, the compound is a semiconductor. Two probe dc resistivity measurements at 298 and 77 K indicate conductivities of $1.6(4) \times 10^{-2}$ and $1.5(2) \times 10^{-3}$ Ω^{-1} cm^{-1}, respectively.

$CsTiUTe_5$. $CsTiUTe_5$ is a layered compound that shows a strong correlation between metal-atom radii and coordination number. The Te atoms form coordination environments of 6, 8, and 10 for Ti, U, and Cs, respectively, as shown in Figure 3. The unit cell of $CsTiUTe_5$ viewed down [100] in Figure 4 shows the two-dimensional nature of the structure. Formal $^{2}_{\infty}[TiUTe_5^{-}]$ layers are separated by Cs^+ cations that are coordinated in a regular pentagonal prism of Te atoms. Oxidation state assignment is again complicated by close Te−Te interactions within the layers.

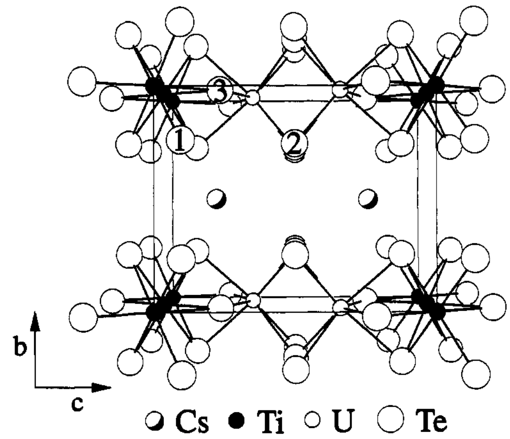

Figure 4. Unit cell of $CsTiUTe_5$ as viewed down [100]. The atom numbering scheme is given.

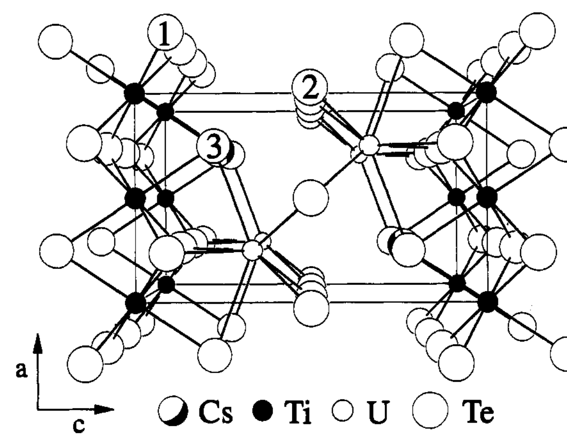

Figure 5. Unit cell of $CsTiUTe_5$ as viewed down [010].

Table 7. Selected Bond Lengths (Å) for $CsTiUTe_5$[a]

U−Te(1)^{1} (2)	3.059(1)	Ti−Te(1)^{1,5,6} (4)	2.787(1)
U−Te(2)^{1,2,3} (4)	3.113(1)	Ti−Te(3)^{3,7} (2)	2.788(1)
U−Te(3)^{3,4} (2)	3.262(1)		

[a]Symmetry transformations used to generate equivalent atoms: (1) $-x + 1/2, -y, z$; (2) $x + 1/2, y, -z + 1$; (3) $-x, -y, -z + 1$; (4) $-x + 1, -y, -z + 1$; (5) $-x, -y, -z$; (6) $x - 1/2, y, -z$; (7) $x, y, -z$.

The anionic layers of $CsTiUTe_5$ shown in Figure 5 contain UTe_8 bicapped trigonal prisms and $TiTe_6$ octahedra. The U-atom centered trigonal prisms comprise four Te(2) atoms and two Te(1) atoms capped by two Te(3) atoms. Selected bond distances are given in Table 7, and complete metrical data are given in Table SVII.[46] The U−Te distances and U-atom coordination environments are similar to those found in UTe_2.[54] In both structures, the UTe_8 bicapped trigonal prisms have a short Te−Te distance at one edge of the triangular face. Whereas the trigonal prisms of UTe_2 share triangular faces, the trigonal prisms of $CsTiUTe_5$ share edges of a rectangular face through Te(2) atoms in the [100] direction. This connectivity creates an infinite, linear chain of Te atoms separated by only 3.065(1) Å. This distance falls in the intermediate range of Te−Te interactions between a full single bond and a nonbonding, van der Waals distance. The edge-sharing of UQ_8 (Q = chalcogen) bicapped trigonal prisms in $CsTiUTe_5$ has been seen previously in the pairs of US_8 bicapped trigonal prisms of FeU_2S_5.[55]

Each $TiTe_6$ octahedron shares faces with two adjacent octahedra to form an unusual $^{1}_{\infty}[TiTe_3^{2-}]$ chain. There are a

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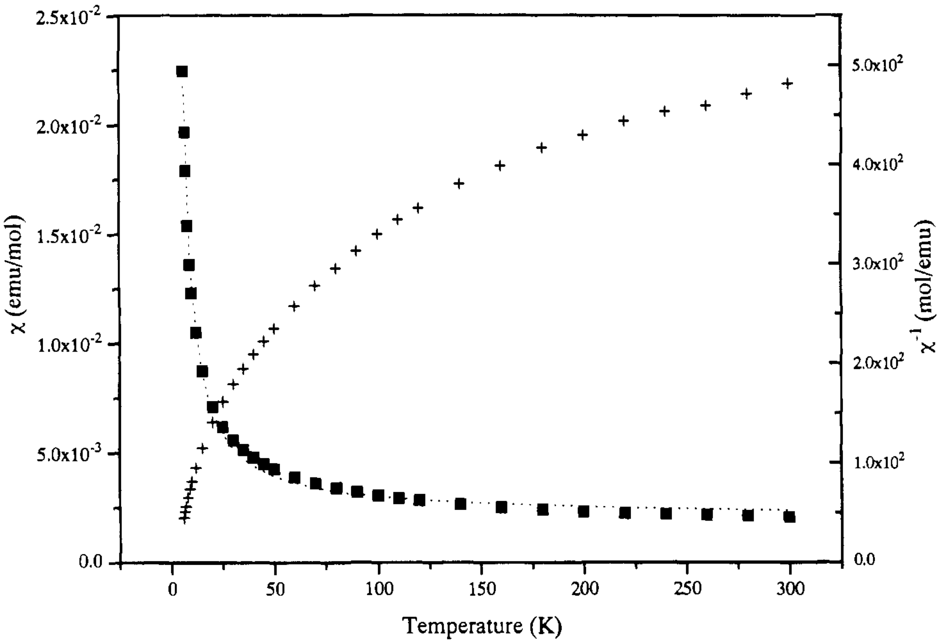

Figure 6. Plot of the molar susceptibility (■) and inverse susceptibility (+) of $CsTiUTe_5$ vs temperature.

few examples of oxides ($BaNiO_3$ and $BaMnO_3$), chlorides ($CsNiCl_3$ and $CsCuCl_3$), and sulfides ($BaTiS_3$, $BaVS_3$, and $BaTaS_3$) that have metal-centered octahedra in face-sharing chains,[56] but we know of no tellurides. Also, whereas other layered compounds contain TiQ_6 octahedra,[32,33] none have face-sharing chains within the layers. The $TiTe_6$ octahedra are nearly regular with Ti-Te distances that agree with those found in $TiTe_2$.[57] They are connected to the U-centered trigonal prisms through atoms Te(1) and Te(3).

With its linear infinite chain of short Te–Te interactions we expected $CsTiUTe_5$ to show high conductivity. However, the two-probe resistivity along the [100] direction (Te–Te chain direction) indicates that $CsTiUTe_5$ is a semiconductor with a room-temperature conductivity of $1.2(9) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. The resistivity at 77 K is beyond the detection limits of our instrument.

The accessibility of several oxidation states for U and the short, infinite Te(2)–Te(2) interaction make assignment of formal oxidation states difficult. To help in this effort, magnetic property measurements were made. A plot of χ vs T (Figure 6) was fit by least-squares methods to the modified Curie–Weiss equation $\chi = C/(T + \Theta) + \chi_o$. The resulting values are $C = 8.8(3) \times 10^{-2}$ emu K/mol, $\Theta = -1.5(2)$ K, and $\chi_o = 2.11(8) \times 10^{-3}$ emu/mol. The value of μ_{eff} at 300 K is 2.23(1) μ_B for each $CsTiUTe_5$ unit, intermediate between that expected for U^{IV} and U^{V}. For $CsTiUTe_5$ the plot of χ^{-1} vs T is curvilinear, as are those for β-US_2[1] and $BaCeCuQ_3$ (Q = S, Se).[58]

$Cs_8Hf_5UTe_{30.6}$. The structure of $Cs_8Hf_5UTe_{30.6}$ comprises one-dimensional, linear M–Te chains separated by Cs^+ cations (Figure 7). The two unique chains, shown in Figure 8, can be formulated $^1_\infty[Hf_3Te_{15.6}{}^{4-}]$ and $^1_\infty[Hf_2UTe_{15}{}^{4-}]$. Disorder among the Te atoms reduces the relative amount of Te. Within the chains, there are many intermediate Te–Te distances. The present structure may be compared with that of $Cs_4Zr_3Te_{16}$[40] (i.e. $Cs_8Zr_6Te_{32}$). The five Hf atoms and one U atom replace the Zr atoms.

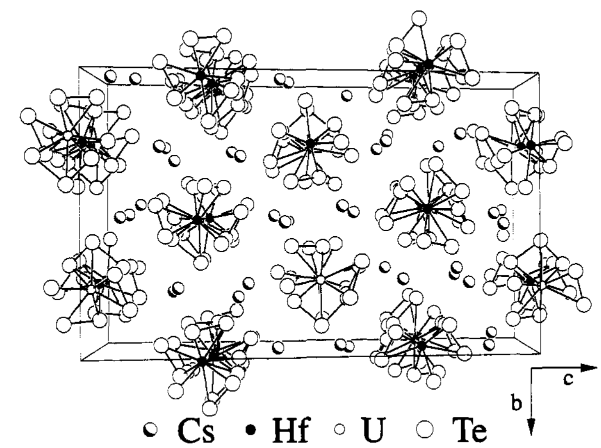

Figure 7. Unit cell of $Cs_8Hf_5UTe_{30.6}$.

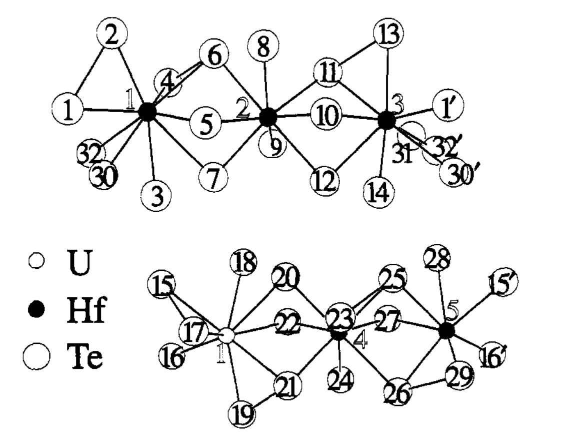

Figure 8. Side view of the $^1_\infty[Hf_3Te_{15.6}{}^{4-}]$ and $^1_\infty[Hf_2UTe_{15}{}^{4-}]$ chains of $Cs_8Hf_5UTe_{30.6}$.

The Hf and U atoms in $Cs_8Hf_5UTe_{30.6}$ are coordinated to seven, eight, or nine Te atoms in linear chains roughly based on a trigonal prismatic framework. Although there is some disorder among Te atoms, the U and Hf atoms are ordered. Indeed, the U–Te distances are consistently longer than the corresponding Hf–Te distances. Selected bond distances are given in Table 8 and complete metrical data are given in Table SVIII.[46]

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Table 8. Selected Bond Lengths (Å) for $Cs_8Hf_5UTe_{30.6}$

U(1)−Te(19)	3.018(3)	Hf(4)−Te(23)	2.938(3)
U(1)−Te(15)	3.082(3)	Hf(4)−Te(20)	2.942(3)
U(1)−Te(17)	3.088(3)	Hf(4)−Te(27)	2.952(3)
U(1)−Te(18)	3.115(3)	Hf(4)−Te(24)	2.955(3)
U(1)−Te(21)	3.119(3)	Hf(4)−Te(21)	2.965(3)
U(1)−Te(20)	3.136(3)	Hf(4)−Te(26)	3.035(3)
U(1)−Te(16)	3.144(4)	Hf(5)−Te(16)^{1}	2.740(3)
U(1)−Te(22)	3.189(3)	Hf(5)−Te(29)	2.840(3)
Hf(1)−Te(30)	2.983(6)	Hf(5)−Te(26)	2.914(3)
Hf(1)−Te(4)	3.008(4)	Hf(5)−Te(28)	2.917(3)
Hf(1)−Te(1)	3.061(3)	Hf(5)−Te(15)^{1}	2.934(3)
Hf(1)−Te(2)	3.063(3)	Hf(5)−Te(27)	2.963(3)
Hf(1)−Te(6)	3.066(3)	Hf(5)−Te(25)	3.001(3)
Hf(1)−Te(3)	3.074(3)	Te(1)−Te(2)	2.783(4)
Hf(1)−Te(5)	3.102(4)	Te(3)−Te(7)	2.962(4)
Hf(1)−Te(7)	3.183(3)	Te(3)−Te(5)	3.004(4)
Hf(1)−Te(32)	3.245(8)	Te(4)−Te(6)	2.750(4)
Hf(2)−Te(10)	2.913(3)	Te(5)−Te(8)	3.021(4)
Hf(2)−Te(7)	2.921(3)	Te(7)−Te(9)	2.936(4)
Hf(2)−Te(9)	2.938(3)	Te(8)−Te(10)	2.920(4)
Hf(2)−Te(12)	2.950(3)	Te(9)−Te(12)	3.066(4)
Hf(2)−Te(6)	2.952(3)	Te(10)−Te(14)	3.018(4)
Hf(2)−Te(5)	2.957(3)	Te(11)−Te(13)	2.776(4)
Hf(2)−Te(8)	2.965(3)	Te(12)−Te(14)	2.975(4)
Hf(2)−Te(11)	3.026(3)	Te(15)−Te(17)	2.789(4)
Hf(3)−Te(32)^{1}	2.613(9)	Te(18)−Te(22)	2.902(4)
Hf(3)−Te(13)	2.850(4)	Te(18)−Te(20)	2.960(4)
Hf(3)−Te(12)	2.955(3)	Te(19)−Te(21)	2.755(4)
Hf(3)−Te(11)	2.963(3)	Te(20)−Te(23)	2.998(4)
Hf(3)−Te(14)	2.984(3)	Te(22)−Te(24)	3.017(4)
Hf(3)−Te(1)^{1}	2.993(3)	Te(23)−Te(25)	2.893(4)
Hf(3)−Te(30)^{1}	3.059(7)	Te(24)−Te(27)	2.970(4)
Hf(3)−Te(10)	3.065(4)	Te(25)−Te(28)	3.052(4)
Hf(3)−Te(31)	3.130(6)	Te(26)−Te(29)	2.785(4)
Hf(4)−Te(22)	2.921(3)	Te(27)−Te(28)	3.048(4)
Hf(4)−Te(25)	2.927(3)	Te(30)−Te(32)^{2}	2.714(8)

^{a} Symmetry transformations used to generate equivalent atoms: (1) $x + 1, y, z$; (2) $x - 1, y, z$.

In the $^{1}_{\infty}[Hf_3Te_{15.6}{}^{4-}]$ chain, atom Hf(1) is connected to atom Hf(2) through atoms Te(5), Te(6), and Te(7). Atom Hf(2) is connected to atom Hf(3) through atoms Te(11), Te(12), and Te(13). Atom Hf(3) is connected to atom Hf(1′) through atoms Te(1), Te(30), and Te(32). Atoms Te(2), Te(3), and Te(4) cap atom Hf(1); atoms Te(8) and Te(9) cap atom Hf(2); atoms Te(13), Te(14), and Te(31) cap atom Hf(3). The modeled disorder between the μ-Te and μ-Te_2 ligands connecting atoms Hf(3) and Hf(1) seems reasonable, the Te−Te bond of the μ-Te_2 ligand being 2.714(8) Å. In the $^{1}_{\infty}[Hf_2UTe_{15}{}^{4-}]$ chain, atom U(1) is connected to atom Hf(4) through atoms Te(20), Te(21), and Te(22) with atoms Te(17), Te(18), and Te(19) as caps. Atom Hf(4) is connected to atom Hf(5) through atoms Te(25), Te(26), and Te(27) with atoms Te(23) and Te(24) as caps. Atom Hf(5) is connected to atom U(1) through atoms Te(15) and Te(16); atoms Te(28) and Te(29) are caps.

As in $Cs_4Zr_3Te_{16}$, $Cs_8Hf_5UTe_{30.6}$ has a wide range of short Te−Te interactions (2.70−3.07 Å). There are seven unambiguous single Te−Te bonds in the range 2.705(8)−2.789(4) Å. There are 16 more Te−Te interactions shorter than 3.07 Å. Simple electron counting and oxidation state formalisms cannot be applied.

$CsCuUTe_3$. The new two-dimensional compound $CsCuUTe_3$ adopts the structure of $KCuZrQ_3$ (Q = S, Se, Te)[32] with Cs atoms substituted for K atoms and U atoms substituted for Zr atoms. A perspective view of the structure down [100] given in Figure 9 shows the layered nature of the structure as well as the labeling scheme. Figure 10 shows an isolated $^{2}_{\infty}[CuUTe_3{}^{-}]$ layer, as viewed down [010]. The layers are separated by Cs^+ ions in bicapped trigonal-prismatic coordination.

The layers of $CsCuUTe_3$ contain $CuTe_4$ tetrahedra and UTe_6 octahedra. The $CuTe_4$ tetrahedra share edges with the four adjacent UTe_6 octahedra; the UTe_6 octahedra are interconnected by edge-sharing two equatorial Te(1) atoms in the [100] direction and corner-sharing through the axial Te(2) atoms in the [001] direction. The UTe_6 octahedra and $CuTe_4$ tetrahedra are only slightly distorted, with bond distances that agree well with the those found in UTe (U−Te 3.078 Å)[4] and $KCuZrTe_3$ (Cu−Te 2.583(1), 2.593(1) Å).[32] Selected bond distances are given in Table 9. Complete metrical data are given in Table SIX.[46]

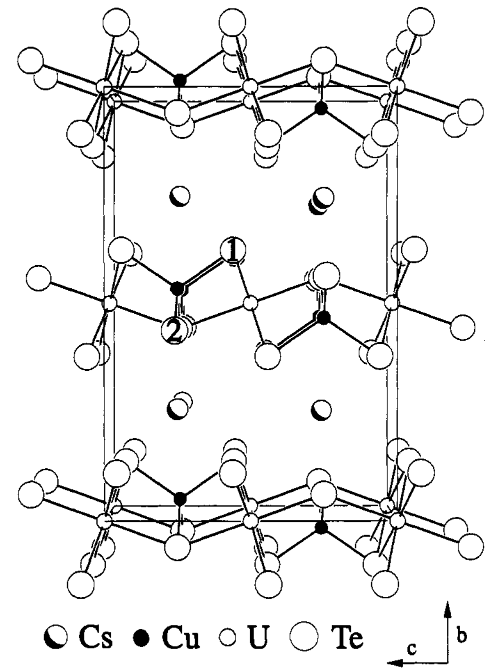

Figure 9. Unit cell of $CsCuUTe_3$ viewed down the [100] direction. The atom numbering scheme is given.

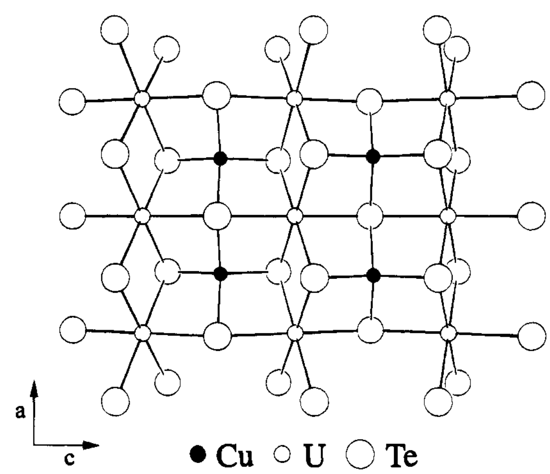

Figure 10. Single $^{2}_{\infty}[CuUTe_3{}^{-}]$ layer of $CsCuUTe_3$ viewed down the [010] direction.

Table 9. Selected Bond Lengths (Å) for $CsCuUTe_3$

Cu−Te(1)^{1,2,3} (4)	2.672(2)	Te(1)−Te(1)^{9}	4.301(2)
U−Te(2)^{4} (2)	3.007(1)	Te(1)−Te(2)^{2}	4.320(1)
U−Te(1)^{5,6,7,8} (4)	3.051(1)	Te(1)−Te(1)^{10}	4.327(1)
Te(1)−Te(2)^{8}	4.246(1)		

Symmetry transformations used to generate equivalent atoms: (1) $x, y, -z + 1/2$; (2) $x + 1/2, y + 1/2, z$; (3) $x - 1/2, y + 1/2, z$; (4) $-x, -y, -z$; (5) $x - 1/2, y - 1/2, z$; (6) $-x + 1/2, -y + 1/2, -z$; (7) $x + 1/2, y - 1/2, z$; (8) $-x - 1/2, -y + 1/2, -z$; (9) $-x, -y + 1, -z$; (10) $x + 1, y, z$.

The closest Te•••Te distance of 4.246(1) Å is indicative of

Scheme 1

van der Waals interactions. Thus, the formal oxidation states of Cs^{I}, Cu^{I}, U^{IV}, and Te^{II-} may be assigned.

The structure of $CsCuUTe_3$ may be visualized in terms of the progressive expansion of the structure of UI_3, as shown in Scheme 1. The structure of UI_3, which contains tetrahedral and octahedral holes, comprises UI_8 bicapped trigonal prisms that share edges. The addition of Fe atoms into vacant octahedral sites in UI_3 coupled with substitution of S atoms for I atoms gives the structure of $FeUS_3$.[59] Insertion of Cu atoms into vacant tetrahedral sites of $FeUS_3$ together with substitution of Zr atoms for Fe atoms and K atoms for U atoms gives the $KCuZrS_3$ structure. Finally, substitution of U atoms for Zr atoms, Cs atoms for K atoms, and Te atoms for S atoms in the structure of $KCuZrS_3$ gives the structure of $CsCuUTe_3$. U atoms reappear in the structure of $CsCuUTe_3$ in the octahedral sites whereas the larger Cs atoms occupy the bicapped trigonal prismatic sites.

The differences in the coordination chemistry of Cu and Ag are clearly demonstrated in this work. Under similar reaction conditions, the reaction of Cs_2Te_3, U, and Te with Cu affords the two-dimensional compound $CsCuUTe_3$ but reaction of the same reagents with Ag gives two ternary compounds, $CsUTe_6$ and $CsAg_5Te_3$ (Figure 11). The regular tetrahedral coordination of Cu with Te atoms in $CsCuUTe_3$ is to be contrasted with two different Ag-atom coordination geometries in $CsAg_5Te_3$. The channel structure of $CsAg_5Te_3$ is built from columns of three-coordinate Ag atoms that are capped by tetrahedrally-coordinated Ag atoms. The columns are further connected by tetrahedral Ag atoms to complete the structure. The structure of $CsAg_5Te_3$ is closely related to that of $CsAg_7S_4$.[60]

(59) Noël, H.; Padiou, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 1593–1595.
(60) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1556–1558.

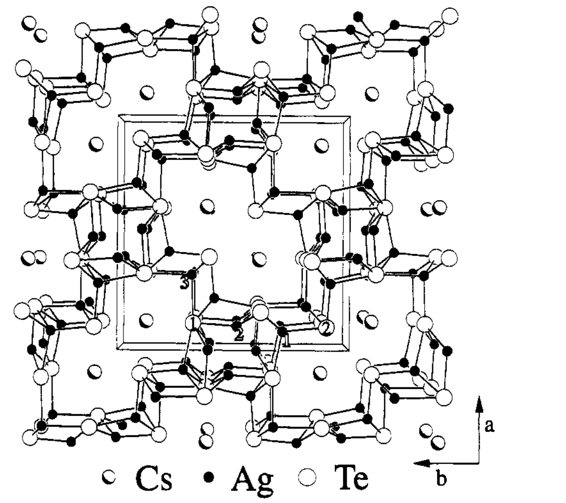

Figure 11. Unit cell of $CsAg_5Te_3$ viewed down the [001] direction. The atom numbering scheme is given. Ag–Ag interactions range from 2.883(1) to 3.148(1) Å, and Ag–Te interactions range from 2.742(1) to 3.006(1) Å.

Clearly, the present work is only the beginning of the exploration of the vast structural chemistry of ternary and quaternary uranium tellurides.

Acknowledgment. This research was supported by the U.S. National Science Foundation through Grant DMR91-14934. This work made use of MRL Central Facilities, supported by the National Science Foundation at the Materials Research Center of Northwestern University under Grant No. DMR91-20521. We acknowledge useful discussions with Prof. A. J. Freeman.

Supplementary Material Available: Tables SI–SIX listing further experimental details, anisotropic displacement parameters, and complete metrical details for $CsUTe_6$, $CsTiUTe_5$, $Cs_8Hf_5UTe_{30.6}$, and $CsCuUTe_3$ (25 pages). Ordering information is given on any current masthead page. Structure amplitude tables may be obtained directly from the authors.

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