



RbAuUSE₃, CsAuUSE₃, RbAuUTE₃, and CsAuUTE₃: Syntheses and structure; magnetic properties of RbAuUSE₃

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ARTICLE INFO

Article history:

Received 9 May 2009

Received in revised form

26 June 2009

Accepted 4 July 2009

Available online 14 July 2009

Keywords:

Uranium

Gold

Solid-state quaternary chalcogenide

Synthesis

Crystal structure

Magnetism

ABSTRACT

The compounds RbAuUSE₃, CsAuUSE₃, and RbAuUTE₃ were synthesized at 1073 K from the reactions of U, Au, Q, and A₂Q₃ (A = Rb or Cs; Q = Se or Te). The compound CsAuUTE₃ was synthesized at 1173 K from the reaction of U, Au, Te, and CsCl as a flux. These isostructural compounds crystallize in the KCuZrS₃ structure type in space group *Cmcm* of the orthorhombic system. The structure consists of ²₃[AuUQ₃] layers that contain nearly regular UQ₆ octahedra and distorted AuQ₄ tetrahedra. The infinite layers are separated by bicapped trigonal prismatic A cations. The magnetic behavior of RbAuUSE₃ deviates significantly from Curie–Weiss behavior at low temperatures. For *T* > 200 K, the values of the Curie constant *C* and the Weiss constant *θ_p* are 1.82(9) emu K mol⁻¹ and $-3.5(2) \times 10^2$ K, respectively. The effective magnetic moment *μ_{eff}* is 3.81(9) *μ_B*. Formal oxidation states of A/Au/U/Q may be assigned as +1/+1/+4/-2, respectively.

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1. Introduction

The investigation of coinage metal/uranium/chalcogenides has been motivated by the interest in physical properties resulting from the combination of *d*- and *f*-electrons. These studies have led to a number of ternary and quaternary compounds. The ternary compounds include Cu₂U₆Q₁₃ (Q = S, Se) [1], Cu₂U₃Q₇ (Q = S, Se) [2], Cu_{0.78}U₂Te₆ [3], Cu_{*x*}UTE₃ (*x* = 0.25, 0.33) [4], and Ag_{3.86}U₅S₁₂ [5]; the quaternary compounds include AMUQ₃ (A = K, Rb, Cs; M = Cu, Ag; Q = S, Se, Te) [6–9], K₂Cu₃US₅ [10], A₆Cu₁₂U₂S₁₅ (A = K, Rb) [11,12], and Ba₂Cu₂US₅ [13].

These coinage metal/uranium/chalcogenides present an interesting variety of oxidation states of uranium. For example, K₂Cu₃US₅ contains U⁵⁺, A₆Cu₁₂U₂S₁₅ (A = K, Rb) contains U⁵⁺ or U⁶⁺, and the remaining compounds contain U⁴⁺. One common feature of all the compounds is that the coinage metal, Cu or Ag, adopts an oxidation state of +1. Here we extend our investigation of coinage metal/uranium/chalcogenides to include Au. There appears to be no structural information in the literature on Au/U/Q compounds. Unlike Cu and Ag, which can adopt oxidation states of +1 or +2, Au prefers an oxidation state of +1 or +3. Gold chalcogenides commonly contain Au¹⁺; however, there are instances, such as AAuSe₂ (A = Na, K) [14] and CrAuTe₄ [15], where Au adopts the +3 oxidation state. We present here the synthesis, characterization, and magnetic properties of four new

gold uranium chalcogenides, and assign the oxidation states for Au and U as +1 and +4, respectively.

2. Experimental

2.1. Syntheses

The following reagents were used as obtained: U turnings (depleted, Oak Ridge National Laboratory), Rb (Strem Chemicals, 99+%), Cs (Strem Chemicals, 99.5%), Se (Cerac, 99.999%), Te (Aldrich, 99.8%), Au (Johnson Matthey, 99.99%), and CsCl (Strem Chemicals, 99.999%). Finely divided U powder was prepared by a modification [16] of the literature procedure [17]. The reactive fluxes [18] A₂Q₃ were prepared by stoichiometric reactions of the elements in liquid NH₃ at 194 K. The remaining reactants were used as obtained. Reactions were carried out in carbon-coated fused-silica tubes. The tubes were charged with reaction mixtures under an Ar atmosphere in a glove box and then they were evacuated to $\sim 10^{-4}$ Torr and flame sealed. Selected single crystals from each reaction were examined with an EDX-equipped Hitachi S-3400 SEM.

2.2. Syntheses of RbAuUSE₃, CsAuUSE₃, and RbAuUTE₃

The reaction mixture consisted of 0.13 mmol of U, 0.13 mmol of Au, 0.25 mmol of A₂Q₃, and 0.63 mmol of Q. The reaction tube was placed in a computer-controlled furnace where it was heated to

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1073 K in 24 h, kept at 1073 K for 120 h, cooled to 473 K in 120 h, and then quickly cooled to 298 K. The products were washed free of flux with *N,N*-dimethylformamide and then dried with acetone. Long black plates of AAuUQ_3 were obtained in about 25 wt% yield (based on U). There were no other crystalline products; the excess A_xQ_y flux contained U/Q and Au/Q binary phases. EDX analysis of selected crystals showed the presence of A, Au, U, and Q. The compounds are stable in air.

2.3. Synthesis of CsAuUTe_3

Single crystals were prepared from the reaction of 0.13 mmol of U, 0.25 mmol of Au, 0.50 mmol of Te, and 1.2 mmol of CsCl as a flux. The reaction tube was placed in a computer-controlled furnace where it was heated to 1173 K in 24 h, kept at 1173 K for 96 h, cooled to 579 K in 198 h, and finally cooled to 298 K in 24 h. Long black plates of CsAuUTe_3 were obtained in about 15 wt% yield (based on U). There were no other crystalline products; the excess CsCl salt flux contained U/Cl, U/Te, and Au/Te binary phases. EDX analysis of selected crystals showed the presence of Cs, Au, U, and Te, but not of Cl. The compound is stable in air.

2.4. Structure determinations

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K on a Bruker APEX2 diffractometer [19] for CsAuUTe_3 , and on a Bruker Smart-1000 CCD diffractometer [20] for the other three compounds. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at φ settings of 0° , 90° , 180° , and 270° . The exposure time was 10 s/frame for CsAuUTe_3 , and 15 s/frame for the other compounds. The collection of intensity data was carried out with the APEX2 software [19] for CsAuUTe_3 , and with the program SMART [20] for the other compounds. Cell refinement and data reduction were carried out with the use of the program SAINT v7.34a in APEX2 [19]. Face-indexed absorption corrections were performed numerically with the use of the program SADABS [20]. This program was also employed to make incident beam and decay corrections. The structure was solved with the direct-methods program SHELXS and refined with the full-matrix least-squares program SHELXL [21]. Each final refinement included anisotropic displacement parameters. A secondary extinction correction was necessary for both RbAuUTe_3 and CsAuUTe_3 . The program STRUCTURE TIDY [22] was employed to standardize the atomic coordinates in each structure. Additional experimental details are given in Table 1 and the Supporting material. Selected metrical details are presented in Table 2.

2.5. Magnetic susceptibility measurement of RbAuUSe_3

Magnetic susceptibility as a function of temperature was measured on a 6.65 mg sample of ground single crystals of RbAuUSe_3 with the use of a Quantum Design MPMS5 SQUID magnetometer. The sample was loaded into a gelatin capsule. Both zero-field cooled (ZFC) and field-cooled (FC) susceptibility data were collected between 2 and 300 K at an applied field of 500 G. All data were corrected for electron core diamagnetism [23], as well as for the diamagnetism of the sample container.

Table 1

Crystal data and structure refinement for RbAuUSe_3 , CsAuUSe_3 , RbAuUTe_3 , and CsAuUTe_3 .^a

	RbAuUSe_3	CsAuUSe_3	RbAuUTe_3	CsAuUTe_3
<i>F</i> _w	757.35	804.79	903.27	950.71
<i>a</i> (Å)	4.142(4)	4.1922(8)	4.374(3)	4.3581(7)
<i>b</i> (Å)	15.025(15)	15.903(3)	16.107(10)	16.787(3)
<i>c</i> (Å)	10.615(11)	10.730(2)	11.338(7)	11.2966(17)
<i>V</i> (Å ³)	660.6(11)	715.3(2)	798.7(9)	826.5(2)
ρ_c (g cm ⁻³)	7.615	7.473	7.512	7.641
μ (mm ⁻¹)	70.377	63.249	55.282	51.913
<i>R</i> (<i>F</i>) ^b	0.037	0.056	0.024	0.043
<i>R</i> _w (<i>F</i> ²) ^c	0.085	0.129	0.069	0.120

^a For all structures, the space group is *Cmcm*, *Z* = 4, *T* = 100(2)K, and $\lambda = 0.71073 \text{ \AA}$.

^b $R(F) = \sum |F_0| - |F_c| / \sum |F_0|$ for $F_0^2 > 2\sigma F(F_0^2)$.

^c $R_w(F_0^2) = \{ \sum [w(F_0^2 - F_c^2)]^2 / \sum w F_0^4 \}^{1/2}$. For $F_0^2 < 0$, $w^{-1} = \sigma^2(F_0^2)$; for $F_0^2 \geq 0$, $w^{-1} = \sigma^2(F_0^2) + (0.04 \times F_0^2)^2$.

Table 2

Selected interatomic distances (Å) and angles (deg) for RbAuUSe_3 , CsAuUSe_3 , RbAuUTe_3 , and CsAuUTe_3 .^a

	RbAuUSe_3	CsAuUSe_3	RbAuUTe_3	CsAuUTe_3
A–Q(1) × 2	3.414(3)	3.604(3)	3.643(2)	3.773(2)
A–Q(2) × 4	3.532(3)	3.696(2)	3.665(2)	3.786(1)
A–Q(2) × 2	3.612(3)	3.719(3)	3.918(2)	3.961(1)
U–Q(1) × 2	2.846(3)	2.863(1)	3.063(2)	3.037(1)
U–Q(2) × 4	2.866(2)	2.893(2)	3.094(2)	3.079(1)
Au–Q(1) × 2	2.650(2)	2.674(2)	2.799(2)	2.786(1)
Au–Q(2) × 2	2.542(2)	2.566(3)	2.741(2)	2.724(1)
Au...Au	4.142(4)	4.192(1)	4.374(3)	4.358(1)
Au...A	3.766(3)	3.960(2)	4.036(2)	4.189(2)
U...A	4.612(4)	4.823(2)	4.886(3)	5.059(1)
Q(1)–U–Q(1)	180	180	180	180
Q(1)–U–Q(2)	95.17(5)	94.92(7)	95.28(3)	95.05(3)
Q(2)–U–Q(2)	87.45(9)	87.13(7)	89.96(5)	89.90(3)
Q(1)–Au–Q(1)	102.8(1)	103.2(1)	102.71(6)	102.92(6)
Q(1)–Au–Q(2)	108.58(4)	108.04(4)	110.37(2)	109.88(2)
Q(2)–Au–Q(2)	118.6(1)	120.2(1)	112.24(6)	113.84(5)

^a The U atom has crystallographic symmetry 2/*m*, and the Au, A, and Q(1) atoms have crystallographic symmetry *m*2*m*.

3. Results and discussion

3.1. Syntheses

Black single crystals of RbAuUSe_3 , CsAuUSe_3 , and RbAuUTe_3 were obtained in 25 wt% yield by the reaction of U, Au, A_2Q_3 , and Q at 1073 K. This method proved unsuccessful for the preparation of CsAuUTe_3 . However, an alternative synthesis from U, Au, Te, and excess CsCl at 1173 K produced CsAuUTe_3 in 15 wt% yield. Efforts to synthesize sulfide analogues by means of either method yielded only binary uranium sulfide crystals.

3.2. Structure

The four isostructural compounds RbAuUSe_3 , CsAuUSe_3 , RbAuUTe_3 , and CsAuUTe_3 crystallize in the KCuZrS_3 structure type [24] in space group *Cmcm* of the orthorhombic system (Fig. 1). The structure contains two-dimensional ${}_\infty[\text{AuUQ}_3]$ layers stacked in the [010] direction, with alkali-metal cations intercalated between the layers. The closest Se...Se and Te...Te interactions in the structures of the present AAuUQ_3 compounds are 3.852(3) and 4.130(1) Å, respectively, which are longer than

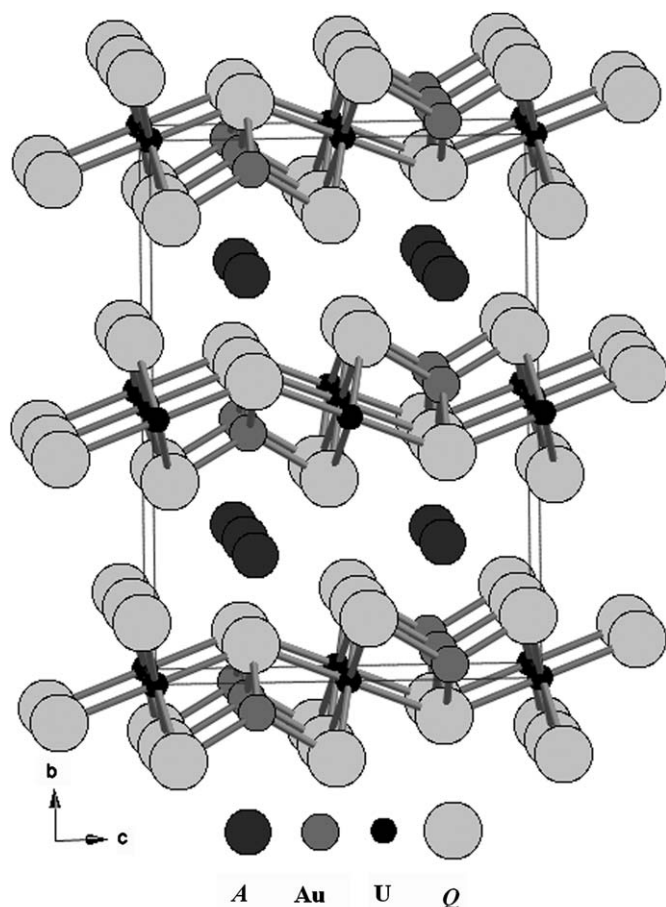


Fig. 1. View down [100] of the crystal structure of the isostructural $AAuUQ_3$ ($A = \text{Rb}, \text{Cs}$; $Q = \text{Se}, \text{Te}$) compounds.

bonding distances. Therefore, the formal oxidation states of $A/Au/U/Q$ may be assigned as $+1/+1/+4/-2$, respectively.

Each U atom sits on a site of symmetry $2/m$ and is octahedrally coordinated to six Q atoms and each Au atom sits on a site of $m2m$ symmetry and is tetrahedrally coordinated to four Q atoms. For the series of compounds $AMUQ_3$ ($A = \text{K}, \text{Rb}, \text{Cs}$; $M = \text{Cu}, \text{Ag}, \text{Au}$; $Q = \text{S}, \text{Se}, \text{Te}$), the geometries of the UQ_6 octahedra and MU_4 tetrahedra become more distorted when Cu is replaced by Ag or Au (Table 2). For example, the $Q-U-Q$ bond angles for $CsMUSe_3$ are: $M = \text{Cu}$, $90.31(1)^\circ$ and $87.19(1)^\circ$; $M = \text{Ag}$, $94.34(2)^\circ$ and $85.48(2)^\circ$; and $M = \text{Au}$, $94.92(7)^\circ$ and $87.13(7)^\circ$. The $Q-M-Q$ bond angles for $CsMUSe_3$ are: $M = \text{Cu}$, $108.02(1)$ – $114.47(1)^\circ$; $M = \text{Ag}$, $105.68(5)$ – $122.54(4)^\circ$; and $M = \text{Au}$, $103.2(1)$ – $120.2(1)^\circ$.

The tetrahedral coordination of chalcogen atoms around Au is exceedingly rare. To the best of our knowledge, the only previous example of this coordination geometry for Au in the solid state is in the structure of $BaAuGdSe_3$ [25], which incidentally also crystallizes in the $KCuZrS_3$ structure type. In chalcogenide compounds, Au^{1+} prefers a two-coordinate linear geometry because of the large $6s$ – $6p$ energy separation, 4.63 eV, as compared to ns – np energy separations of 3.79 and 3.66 eV for Cu and Ag, respectively [26]. To achieve coordination numbers of three or four, Au must utilize its higher-energy p -orbitals for bonding, which makes those coordination numbers less favorable. Nevertheless, there are a few examples of three-coordinate Au^{1+} chalcogenides, including $AAuTe$ ($A = \text{Na}, \text{K}$) [27], where Au adopts a trigonal planar geometry. In contrast, Au^{3+} can assume a four-coordinate environment, such as in $AAuSe_2$ ($A = \text{Na}, \text{K}$) [14],

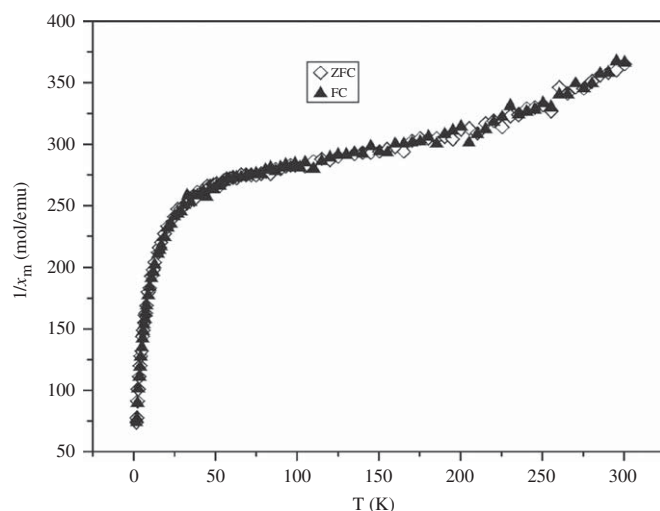


Fig. 2. Inverse magnetic susceptibility ($1/\chi_m$) vs. T for $RbAuUSe_3$.

Na_5AuSe_{12} [28], and $CrAuTe_4$ [15]; however, the geometry is square planar in these examples. There are instances of Au exhibiting tetrahedral coordination to chalcogen-containing ligands in organometallic complexes, such as $[Au(1,4,7\text{-trithiacyclononane})_2][PF_6]$ [29]. But in solid-state extended structures, the present $AAuUQ_3$ compounds, along with the previously known $BaAuGdSe_3$ compound, present the only instances of tetrahedral coordination of Au^{1+} by chalcogens.

In the $AAuUQ_3$ compounds, the UQ_6 octahedra share edges with neighboring octahedra in the [100] direction, and corners in the [001] direction. The AuQ_4 tetrahedra share corners with neighboring tetrahedra in the [100] direction to form infinite chains, as well as four edges with adjacent UQ_6 octahedra. The nearest $Au \cdots Au$ interatomic distance in the $AAuUQ_3$ compounds is $4.142(4) \text{ \AA}$ in $RbAuUSe_3$ (Table 2). This distance is too long to be a d^{10} – d^{10} interaction [30], such as those found in KAu_5 [14] where there are short $Au \cdots Au$ contacts of $2.963(1)$ and $2.950(3) \text{ \AA}$. In the present structures the A cations adopt a bicapped trigonal prismatic coordination. The $Au \cdots A$ interatomic distances are shorter than the corresponding $U \cdots A$ distances. This may indicate an interaction between the d^{10} electron pairs on the Au and the positive charge on the A cation. This would be consistent with the Pauling electronegativity of Au, 2.4, which is the highest of all the transition metals, and is comparable to those of the heavier chalcogens Se (2.4) and Te (2.1) [31]. Examples of compounds exhibiting $Au \cdots A$ interactions include KAu_5 [32], $[PPh_4]_4[KAu_9Te_7]$ [33], and $[NEt_4]_3[NaAu_{12}Se_8]$ [34].

All interatomic distances are normal. Thus: U–Se, $2.846(3)$ – $2.893(2) \text{ \AA}$ vs. $2.840(3)$ – $2.923(3) \text{ \AA}$ in K_4USe_8 [35]; U–Te, $3.037(1)$ – $3.094(2) \text{ \AA}$ vs. $3.018(3)$ – $3.189(3) \text{ \AA}$ in $Cs_8Hf_5UTe_{30.6}$ [6]; Au–Se, $2.542(2)$ – $2.674(2) \text{ \AA}$ vs. $2.576(1)$ – $2.646(1) \text{ \AA}$ in $BaAuGdSe_3$ [25]; Au–Te, $2.724(1)$ – $2.799(2) \text{ \AA}$ vs. $2.702(1)$ in $RbAuTe$ [27]; Rb \cdots Se, $3.414(3)$ – $3.612(3) \text{ \AA}$ vs. $3.416(1)$ – $3.614(1) \text{ \AA}$ in $RbAgUSe_3$ [9]; Cs \cdots Se, $3.604(3)$ – $3.719(3) \text{ \AA}$ vs. $3.536(2)$ – $4.224(2) \text{ \AA}$ in $Cs_2Hg_2USe_5$ [36]; Rb \cdots Te, $3.643(2)$ – $3.918(2) \text{ \AA}$ vs. $3.5510(8)$ – $4.2091(8) \text{ \AA}$ in $Rb_3Ti_3Te_{11}$ [37]; Cs \cdots Te, $3.773(2)$ – $3.961(1) \text{ \AA}$ vs. $3.759(6)$ – $4.045(6) \text{ \AA}$ in $CsUTe_6$ [6].

3.3. Magnetic susceptibility of $RbAuUSe_3$

Fig. 2 shows the temperature dependence of the inverse molar susceptibility ($1/\chi_m$) for $RbAuUSe_3$ for both ZFC and FC data, which are superimposable. The $1/\chi_m$ vs. T plot exhibits only a

minimal straight-line region, and the change in slope is more pronounced at lower temperatures. For $T > 200$ K, the data can be fit to the modified Curie–Weiss law $\chi^{-1} = (T - \theta_p)/C$. The values of the Curie constant C and the Weiss constant θ_p are $1.82(9) \text{ emu K mol}^{-1}$ and $-3.5(2) \times 10^2 \text{ K}$, respectively. The effective magnetic moment, μ_{eff} , as calculated from the equation $\mu_{\text{eff}} = (7.997C)^{1/2} \mu_B$ [38], is $3.81(9) \mu_B$. This value falls within the range of the theoretical free-ion moments for U^{4+} [39], from $3.58 \mu_B$ (LS coupling) to $3.84 \mu_B$ (jj coupling). There are other U^{4+} chalcogenides that have similar values of μ_{eff} , for example K_4USe_8 ($3.82 \mu_B$) [35] and KCuUSE_3 ($3.65 \mu_B$) [7].

Similar magnetic behavior was also observed for the isostructural compound KCuUSE_3 [7], as well as for $\text{Ba}_2\text{Cu}_2\text{US}_5$ [13], where in both cases it was attributed to crystal-field effects of the $5f$ orbitals on U. The previous two compounds, as well as the current RbAuUSE_3 compound, all possess two-dimensional layered structures, where the magnetic ordering is expected to occur between the U atoms within a layer. Calculation of the magnetic ordering for the isostructural compounds CsmUS_3 ($M = \text{Cu, Ag}$) [9] determined that the lowest energy magnetic structure was an antiferromagnetic spin state in which the U atoms within the ${}_{\infty}^2[\text{MUQ}_3^-]$ layers aligned parallel and those between the ${}_{\infty}^2[\text{MUQ}_3^-]$ layers aligned antiparallel. The large negative value of θ_p for RbAuUSE_3 ($-3.5(2) \times 10^2 \text{ K}$) is consistent with local antiferromagnetic ordering, as is also observed in KCuUSE_3 ($\theta_p = -378 \text{ K}$).

In the present investigation only the magnetic properties of RbAuUSE_3 were measured. Previous members of the KCuZrS_3 structure type have exhibited little variation in magnetic phenomena as a function of chalcogen, despite the differences in covalent bonding between the M and Q atoms. For example, both CsHgGdSe_3 [40] and CsCdGdTe_3 [41] display Curie–Weiss paramagnetism, and both BaCuCeQ_3 ($Q = \text{S, Se}$) [42] compounds demonstrate Curie–Weiss paramagnetism with a temperature-independent component.

Supporting material

Crystallographic files in CIF format for RbAuUSE_3 , CsAuUSE_3 , RbAuUTE_3 , and CsAuUTE_3 have been deposited with FIZ Karlsruhe as CSD numbers 420483, 420484, 420485, and 420486. They may be obtained free of charge by contacting FIZ Karlsruhe at +497247808 666 (fax) or crysdata@fiz-karlsruhe.de (e-mail).

Acknowledgments

This research was supported by the US Department of Energy, Basic Energy Sciences Grant ER-15522. Magnetic measurements were made at the Materials Research Science and Engineering Center, Magnet and Low Temperature Facility, supported by the National Science Foundation (DMR05-20513).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [10.1016/j.jssc.2009.07.012](https://doi.org/10.1016/j.jssc.2009.07.012).

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