



Synthesis, structure, and magnetic and electronic properties of $\text{Cs}_2\text{Hg}_2\text{USe}_5$

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ABSTRACT

The compound $\text{Cs}_2\text{Hg}_2\text{USe}_5$ was obtained from the solid-state reaction of U, HgSe, Cs_2Se_3 , Se, and CsI at 1123 K. This material crystallizes in a new structure type in space group $P2_1/n$ of the monoclinic system with a cell of dimensions $a = 10.276(6)\text{Å}$, $b = 4.299(2)\text{Å}$, $c = 15.432(9)\text{Å}$, $\beta = 101.857(6)^\circ$, and $V = 667.2(6)\text{Å}^3$. The structure contains ${}^2_\infty[\text{Hg}_2\text{USe}_5]$ layers separated by Cs atoms. Within the layers are distorted HgSe_4 tetrahedra and regular USe_6 octahedra. In the temperature range of 25–300 K $\text{Cs}_2\text{Hg}_2\text{USe}_5$ displays Curie–Weiss paramagnetism with $\mu_{\text{eff}} = 3.71(2)\mu_{\text{B}}$. The compound exhibits semiconducting behavior in the [010] direction; the conductivity at 298 K is $3 \times 10^{-3}\text{S/cm}$. Formal oxidation states of Cs/Hg/U/Se may be assigned as +1/+2/+4/–2, respectively.

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1. Introduction

The extensive variety of structures and physical properties in binary uranium chalcogenide chemistry [1] has spurred interest in ternary and quaternary compounds [2]. Among the quaternaries, the $A/M/U/Q$ (A = alkali metal; M = transition metal; Q = S, Se, or Te) family of compounds probably has been the most intensively studied. It is somewhat surprising that only five compositionally different quaternary phases have been identified whereas 10 different binary actinide chalcogenides are known, namely U_4Q_3 , UQ , U_3Q_4 , U_2Q_3 , U_3Q_5 , U_7Q_{12} , UQ_2 , U_2Q_5 , UQ_3 , and UQ_5 [1]. The most common quaternary phase observed is that of the AMUQ_3 (A = K, Rb, Cs; M = Cu, Ag) [3–6] family, which adopts the layered KZrCuS_3 [7] structure type. Other reported quaternary compounds in the $A/M/U/Q$ family include CsMUTe_5 (M = Ti, Zr) [3,8], $\text{Cs}_8\text{Hf}_5\text{UTe}_{30.6}$ [3], $\text{A}_6\text{Cu}_{12}\text{U}_2\text{S}_{15}$ (A = K, Rb) [9,10], and $\text{K}_2\text{Cu}_3\text{US}_5$ [11].

Here we continue our investigation of $A/\text{Hg}/\text{U}/\text{Q}$ phases. These are potentially of interest because Hg can adopt different oxidation states (+1 or +2) and because it can display coordination numbers of two, three, or four. Moreover, Hg readily forms quaternary $A/\text{Hg}/\text{Ln}/\text{Q}$ (Ln = rare-earth metal) compounds, for example CsLnHgSe_3 (Ln = La–Nd, Sm, Gd, Y) [12]. The only known quaternary Hg/U chalcogenide is the salt $[\text{Hg}_3\text{Te}_2][\text{UCl}_6]$ [13]. Here we report the synthesis, crystal structure, and magnetic and electronic properties of $\text{Cs}_2\text{Hg}_2\text{USe}_5$.

2. Experimental

2.1. Syntheses

The following reagents were used as obtained: U turnings (depleted, Oak Ridge National Laboratory), Cs (Strem Chemicals, 99.5%), Se (Cerac, 99.999%), HgSe (Alfa Aesar, 99.9%), and CsI (Strem Chemicals, 99.9%). Finely divided U powder was prepared by a modification [13] of the literature procedure [14]. The reactive flux [15], Cs_2Se_3 , was prepared by the stoichiometric reaction of the elements in liquid NH_3 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-3500 SEM.

2.2. Synthesis of $\text{Cs}_2\text{Hg}_2\text{USe}_5$

The reaction mixture consisted of 0.17 mmol of U, 0.17 mmol of HgSe, 0.11 mmol of Cs_2Se_3 , 0.16 mmol of Se, and approximately 90 mg of CsI as a flux. The reaction mixture was placed in a computer-controlled furnace where it was heated to 1123 K in 24 h, kept at 1123 K for 96 h, cooled to 473 K in 96 h, and then quickly cooled to 298 K. The product consisted of long black plates of $\text{Cs}_2\text{Hg}_2\text{USe}_5$ in about 25 wt% yield (based on U) and an amorphous black melt. EDX analysis of selected crystals showed the presence of Cs, Hg, U, and Se, but not of I. The compound is moderately stable in air.

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2.3. Structure determination

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 153 K on a Bruker Smart-1000 CCD diffractometer [16]. 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 20 s/frame. The collection of intensity data was carried out with the program SMART [16]. Cell refinement and data reduction were carried out with the use of the program SAINT v7.23a in APEX2 [17]. Face-indexed absorption corrections were performed numerically with the use of the program SADABS [16]. The program SADABS 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 [18]. Additional experimental details are given in Table 1 and the Supporting material. Selected metrical details are presented in Tables 2 and 3.

2.4. Magnetic susceptibility measurement

Magnetic susceptibility as a function of temperature was measured on a 5.04 mg sample of ground single crystals of Cs₂Hg₂USe₅ with the use of a Quantum Design MPMS5 SQUID magnetometer. The sample was loaded into a gelatin capsule. Both

Table 1
Crystal data and structure refinement for Cs₂Hg₂USe₅.

Fw	1299.83
Space group	<i>P2</i> / <i>n</i>
Z	2
<i>a</i> (Å)	10.276(6)
<i>b</i> (Å)	4.299(2)
<i>c</i> (Å)	15.432(9)
<i>b</i> ($^\circ$)	101.857(6)
<i>V</i> (Å ³)	667.2(6)
<i>T</i> (K)	153(2)
λ (Å)	0.71073
ρ_c (g cm ⁻³)	6.470
μ (mm ⁻¹)	54.02
<i>R</i> (<i>F</i>) ^a	0.026
<i>R</i> _w (<i>F</i> ²) ^b	0.063

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

^b For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (0.0262 \times P)^2 + 4.3335 \times P$; $P = (F_o^2 + 2 \times F_c^2) / 3$.

Table 2
Selected interatomic distances (Å) for Cs₂Hg₂USe₅.^a

Hg–Se(1)	2.526(1)
Hg–Se(1)	2.928(1)
Hg–Se(2)	2.846(1)
Hg–Se(3)	2.526(1)
U–Se(1) $\times 2$	2.872(1)
U–Se(2) $\times 2$	2.892(1)
U–Se(2) $\times 2$	2.902(1)
Cs–Se(1)	3.601(2)
Cs–Se(1)	3.641(2)
Cs–Se(1)	4.224(2)
Cs–Se(2)	3.663(2)
Cs–Se(2)	3.673(2)
Cs–Se(2)	4.171(2)
Cs–Se(3)	3.536(2)
Cs–Se(3)	4.057(2)

^a The U and Se(3) atoms have crystallographic symmetry 2.

Table 3
Selected interatomic angles (deg) for Cs₂Hg₂USe₅.

Se(1)–Hg–Se(1)	103.08(5)
Se(1)–Hg–Se(2)	91.09(4)
Se(1)–Hg–Se(2)	103.25(4)
Se(1)–Hg–Se(3)	90.82(4)
Se(1)–U–Se(1)	175.22(3)
Se(1)–U–Se(2) $\times 2$	85.36(4)
Se(1)–U–Se(2) $\times 2$	88.90(4)
Se(1)–U–Se(2) $\times 2$	91.09(4)
Se(1)–U–Se(2) $\times 2$	94.65(4)
Se(2)–U–Se(2)	84.03(5)
Se(2)–U–Se(2)	84.39(5)
Se(2)–U–Se(2) $\times 2$	95.79(5)
Se(2)–U–Se(2) $\times 2$	179.82(2)

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 [19].

2.5. Single-crystal electrical conductivity measurement

The electrical resistivity of a single crystal of Cs₂Hg₂USe₅ was measured along [010] between 2 and 300 K by standard four-probe ac methods with the use of a Quantum Design PPMS instrument. A crystal, 1.044 mm in length, was mounted with four leads constructed of 15 μ m diameter Cu wire and 8 μ m diameter graphite fibers, and attached with Dow 4929N silver paint.

3. Results and discussion

3.1. Synthesis

Black single crystals of Cs₂Hg₂USe₅ were obtained in about 25 wt% yield by the reaction of U, HgSe, Cs₂Se₃, Se, and CsI (as flux) at 1123 K. Attempts to synthesize the sulfide analog of Cs₂Hg₂USe₅ produced crystals of Cs₂Hg₆S₇ [20]. Efforts to synthesize the telluride analog led just to the recrystallization of HgTe.

3.2. Structure

Cs₂Hg₂USe₅ crystallizes in a new structure type (Fig. 1) in space group *P2*/*n* of the monoclinic system. Its structure comprises two-dimensional ∞ [Hg₂USe₅] layers stacked along *c** that are separated by Cs atoms. Each U atom is octahedrally coordinated to six Se atoms. Every USe₆ octahedron shares its edges along [010] with two other octahedra to form a one-dimensional ∞ [USe₄] chain. The Hg atoms form two short Hg–Se bonds and two long Hg–Se bonds to give a distorted tetrahedral environment. The HgSe₄ tetrahedra share two corners along [010] to form one-dimensional ∞ [HgSe₇] chains. Furthermore, each HgSe₄ tetrahedron shares a corner along [100] with another HgSe₄ tetrahedron to form a Hg₂Se₇ dimer. Finally, the HgSe₄ tetrahedra share edges with two USe₆ octahedra along [100] to form the two-dimensional ∞ [Hg₂USe₅] layers, as shown in Fig. 2. The Cs atoms are eight-coordinate and form bicapped trigonal prisms with Se atoms. Each CsSe₈ prism has two face-sharing neighbors along [010] and four-edge sharing ones along [100] to form a two-dimensional ∞ [CsSe₃] layer, which is illustrated in Fig. 3.

Because there are no Se–Se bonds in the structure of Cs₂Hg₂USe₅, the formal oxidation states of Cs/Hg/U/Se may be assigned most reasonably as +1/+2/+4/–2 or as +1/+1/+6/–2, respectively. The U–Se distances, varying from 2.872(1) to 2.902(1) Å, are comparable to those of 2.8715(4)–2.8723(5) Å for

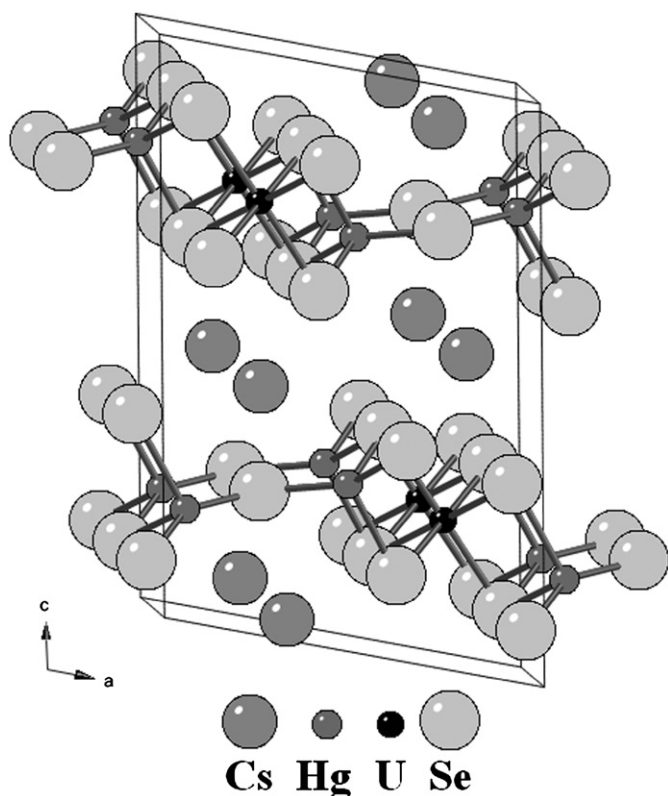


Fig. 1. The crystal structure of $\text{Cs}_2\text{Hg}_2\text{USe}_5$, viewed down [010].

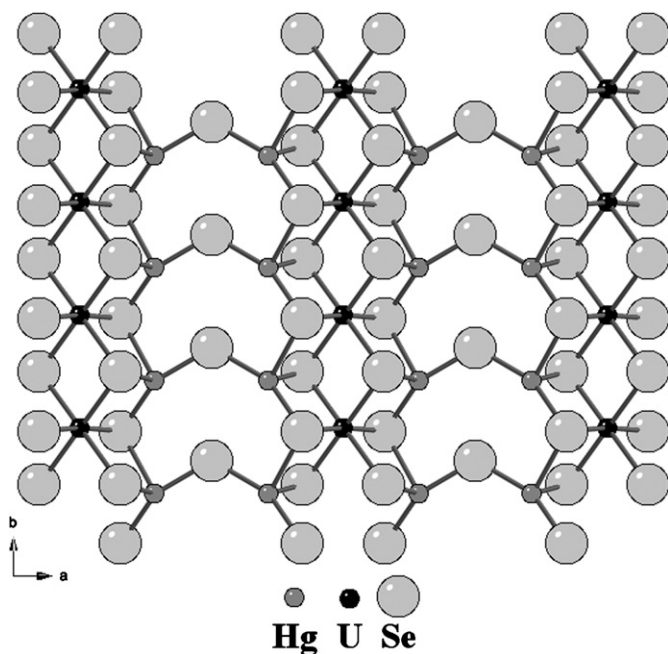


Fig. 2. The two-dimensional ${}^2_{c}[\text{Hg}_2\text{USe}_5]$ layer, viewed down c^* .

CsAgUSe_3 [6], and 2.850(2)–3.126(3) Å for UMnSe_3 [21], both U(IV) compounds. There are no examples of uranium(VI) selenide compounds. However, as the ionic radius decreases from U(IV) to U(V) to U(VI) (0.89–0.76–0.73 Å) [22] the bonding distances should also decrease. Compare the U–S bond distances of 2.714(1)–2.7165(9) Å in KCuUS_3 [6], a compound containing U(IV) S_6 octahedra, to those of 2.587(1)–2.6827(9) in $\text{K}_2\text{Cu}_3\text{US}_5$

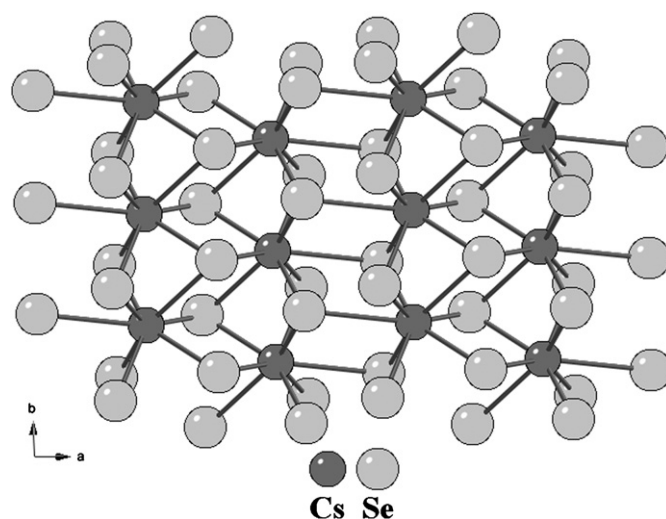


Fig. 3. The two-dimensional ${}^2_{c}[\text{CsSe}_3]$ layer, viewed down c^* .

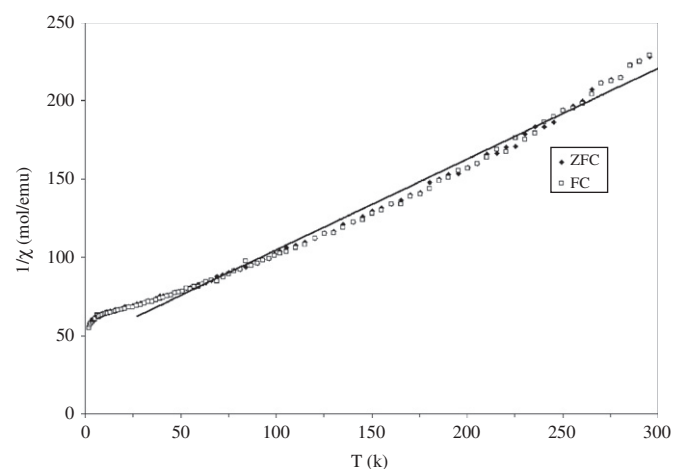


Fig. 4. Inverse magnetic susceptibility ($1/\chi_m$) vs. T for $\text{Cs}_2\text{Hg}_2\text{USe}_5$.

[11], a compound containing U(V) S_6 octahedra. Therefore, the U–Se distances in the present compound strongly support the presence of U(IV). The magnetic data discussed below are also consistent with U(IV) and not with U(VI). Moreover, the Hg–Se distances of 2.526(1)–2.928(1) Å in $\text{Cs}_2\text{Hg}_2\text{USe}_5$ are similar to those of 2.50(1)–2.92(1) Å for Hg_4SiSe_6 [23], a compound containing Hg(II) Se_4 tetrahedra. The Cs \cdots Se distances, ranging from 3.536(2) to 4.223(2) Å, are within the range of 3.498(2)–4.817(2) Å in CsSmGeSe_4 [24].

3.3. Magnetic susceptibility

Fig. 4 shows the temperature dependence of the inverse molar susceptibility ($1/\chi_m$) for $\text{Cs}_2\text{Hg}_2\text{USe}_5$ for both ZFC and FC data, which are superimposable. For $T > 25$ K, the data can be fit to the Curie–Weiss law $\chi^{-1} = (T - \theta_p)/C$. The values of the Curie constant C and the Weiss constant θ_p are 1.720(2) emu K mol^{-1} and $-80.3(4)$ K, respectively. The negative value of θ_p may indicate some local antiferromagnetic ordering. The effective magnetic moment, μ_{eff} , as calculated from the equation $\mu_{\text{eff}} = (7.997C)^{1/2} \mu_B$ [25], of 3.71(2) μ_B is within the range of the theoretical values for U(IV) [26] of 3.58 μ_B (LS coupling) to 3.84 μ_B (jj coupling). The μ_{eff} value of 3.71(2) μ_B for $\text{Cs}_2\text{Hg}_2\text{USe}_5$ is also consistent with the

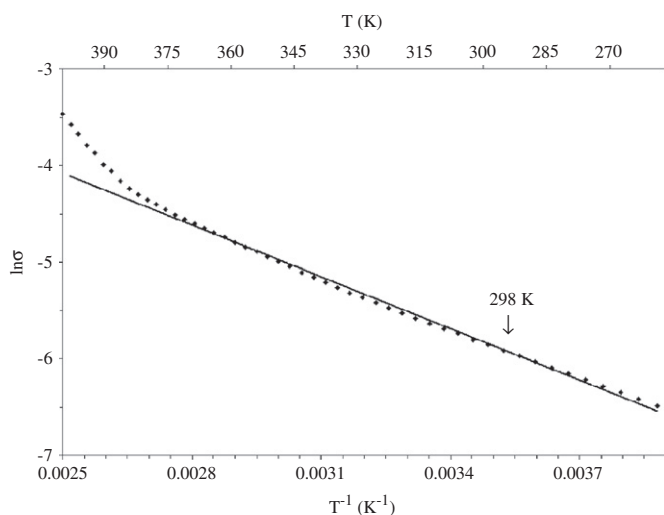


Fig. 5. Plot of $\ln \sigma$ vs. $1/T$ for $\text{Cs}_2\text{Hg}_2\text{USe}_5$.

values of 3.82 and $3.65 \mu_{\text{B}}$, respectively, for the U(IV) chalcogenides K_4USe_8 [27] and KCuUSe_3 [4]. If $\text{Cs}_2\text{Hg}_2\text{USe}_5$ were a compound of Hg(I) and U(VI), then it would be diamagnetic.

3.4. Electrical conductivity

As expected for a stoichiometric U(IV) compound, $\text{Cs}_2\text{Hg}_2\text{USe}_5$ displays semiconducting behavior. The temperature dependence of its electrical conductivity along [010] is shown in Fig. 5. At 298 K the conductivity σ is $3 \times 10^{-3} \text{ S/cm}$. Below 258 K, the sample resistance is beyond the detection limits of the instrument. This semiconductor shows a simple Arrhenius-type thermal activation $\sigma = \sigma_0 \exp(-E_a/(k_B T))$, where k_B is the Boltzmann constant. The calculated thermal activation energy, E_a , is 0.155(1) eV. For intrinsic semiconductors, $E_a \approx \frac{1}{2} E_{\text{gap}}$ [28]; thus the band gap should be approximately 0.3 eV. This value is consistent with both the black color of the present compound as well as with that of 0.3 eV for both CsCuUS_3 [6] and KCuUSe_3 [4], other members of the $A/M/U/Q$ family of compounds.

Supporting material

The crystallographic file in CIF format for $\text{Cs}_2\text{Hg}_2\text{USe}_5$ has been deposited with FIZ Karlsruhe as CSD number 419885. It may be obtained free of charge by contacting FIZ Karlsruhe at +497247808 666 (fax) or crysdata@fiz-karlsruhe.de (e-mail).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2009.01.013.

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