

Synthesis and crystal structure of Cs₂U₃Se₇

Adel Mesbah, George N. Oh, Brian J. Bellott, James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, United States

ARTICLE INFO

Article history:

Received 4 December 2012

Received in revised form

16 January 2013

Accepted 18 January 2013

Available online 28 January 2013

Keywords:

Synthesis

Uranium

Reactive flux method

Single-crystal X-ray structure

Channel structure

ABSTRACT

The compound Cs₂U₃Se₇ has been synthesized at 1273 K by the reaction of U, Se, As, and Cs₂Se₃. The compound crystallizes in a new structure type in the orthorhombic space group $D_{2h}^{16} - Pnma$ with four formula units in a cell of dimensions $a = 22.847(1) \text{ \AA}$, $b = 4.172(1) \text{ \AA}$, $c = 16.639(1) \text{ \AA}$. In the asymmetric unit there are three independent U atoms, each octahedrally coordinated by six Se atoms. These USe₆ octahedra are connected to form a channel structure with the channels running in the [010] direction. Within the unit cell the channel comprises twelve U centers.

© 2013 Elsevier Masson SAS. All rights reserved.

1. Introduction

The actinide chalcogenides display a variety of interesting structures as well as magnetic, electronic, and optical properties [1,2]. In the ternary A/U/Q compounds (A = alkali metal; Q = S or Se or Te) among the compounds known are Li₂US₃ [3], Na₂US₃ [3], K₂UTe₃ [4], Rb₂UTe₃ [4], and KUS₂ [5]. None of these compounds show any Q–Q bonding interactions. In contrast, other actinide compounds do contain Q–Q bonds in their structures, and most of those known belong to the AAn₂Q₆ family (An = U, Th, Np; Q = S, Se, Te) [6–13], but CsUTE₆ [14] and K₄USE₈ [15] are also known.

Because the actinide chalcogenides are little studied compared to other metal chalcogenides, exploratory syntheses frequently reveal previously unknown compounds and structures. Such is the case here where we report the synthesis and structural characterization of the new compound Cs₂U₃Se₇. This compound crystallizes in a new structure type but shows some similarities to the structures of Cr₂Sn₃Se₇ [16] and CaFe₂O₄ [17].

2. Experimental

2.1. Syntheses

Black needles of Cs₂U₃Se₇ have been obtained by the reaction of U (30 mg, 0.126 mmol), Se (13 mg, 0.164 mmol), As (6 mg,

0.080 mmol), and Cs₂Se₃ (34 mg, 0.038 mmol). The ²³⁸U powder was prepared from depleted turnings (Oak Ridge National Laboratory) by hydridization and decomposition under heat and vacuum [18], in a modification of a previous literature method [19]. The Cs₂Se₃ flux was synthesized by the stoichiometric reaction of Cs (Aldrich 99.5%) and Se (Cerac, 99.999%) in liquid NH₃ at 194 K [20]. The other reactants, Se (Cerac, 99.999%) and As (Strem, 2 N), were used as received. The starting mixture was loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was then evacuated to 10^{−4} Torr, and flame sealed. It was then placed in a computer-controlled furnace, heated to 1273 K in 48 h, held there for 4 h, cooled to 1223 K in 12 h, held there for 192 h, then cooled to 298 K at 3 K/h. A few needles were selected and analyzed by EDX. These showed the presence of only Cs, U, and Se in the approximate atomic ratio 2:3:7.

2.2. Structure determination

Single-crystal X-ray diffraction data were collected at 100(2) K on a Bruker APEX II Kappa diffractometer equipped with graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A collection strategy of ω and ϕ scans was obtained by use of an algorithm in COSMO in the APEX II software [21]. The exposure time was 10 s/frame; the step size was 0.5°. Data were indexed, refined, and integrated by SAINT in the APEX II package [21]. Numerical face-indexed absorption corrections were carried out in the program SADABS [22]. The structure was solved and refined with the use of the SHELXTL package [23]. The program STRUCTURE TIDY [24] in

* Corresponding author. Fax: +1 847 491 2976.

E-mail address: ibers@chem.northwestern.edu (J.A. Ibers).

Table 1
Crystallographic data and structure refinement for $\text{Cs}_2\text{U}_3\text{Se}_7$.

	$\text{Cs}_2\text{U}_3\text{Se}_7$
Space group	$D_{2h}^{16} - Pnma$
Fw (g mol ⁻¹)	1532.63
<i>a</i> (Å)	22.847(1)
<i>b</i> (Å)	4.172(1)
<i>c</i> (Å)	16.639(1)
<i>V</i> (Å ³)	1586.0(2)
<i>Z</i>	4
<i>T</i>	100(2) K
λ	0.71073 Å
ρ (g cm ⁻³)	6.419
μ (mm ⁻¹)	51.11
<i>R</i> (<i>F</i>) ^a	0.0378
<i>R</i> _w (<i>F</i> _o ²) ^b	0.0891

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

^b $R_w(F_o^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$. For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ where $q = 0.0452$.

PLATON [25] was used to standardize the atomic positions. Crystal data and refinement details are given in Table 1 and in Supporting material.

3. Results

3.1. Syntheses

Black needles of $\text{Cs}_2\text{U}_3\text{Se}_7$ were obtained in a high yield at 1273 K. An X-ray powder diffraction pattern did not show the presence of other elements or impurities despite the presence of As as a starting reactant. Nevertheless, susceptibility measurements (ZFC = 500 Oe) showed two possible antiferromagnetic transitions at 90 K and 51 K. The transition at 90 K was field dependent (FC = 500 Oe). There was also a field dependence at 298 K that is typical of the presence of ferromagnetic impurities. For these reasons the true magnetic behavior of $\text{Cs}_2\text{U}_3\text{Se}_7$ remains to be determined. Unfortunately, all further attempts to synthesize the compound with or without As led to the formation of the ternary compound CsU_2Se_6 [7].

3.2. Structure

The compound $\text{Cs}_2\text{U}_3\text{Se}_7$ crystallizes in a new structure type in the orthorhombic space group $D_{2h}^{16} - Pnma$, with four formula units

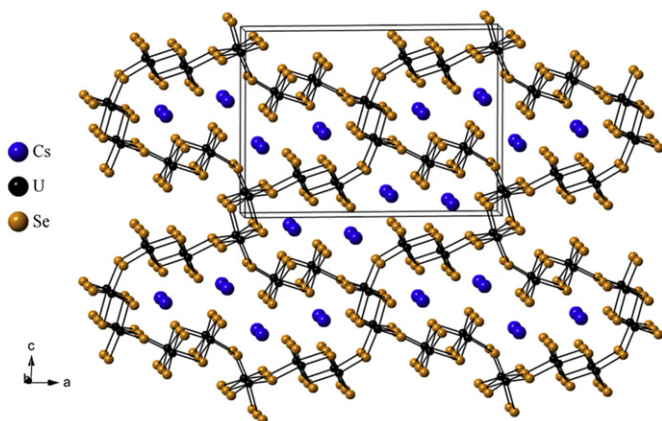


Fig. 1. General view down [010] of the structure of $\text{Cs}_2\text{U}_3\text{Se}_7$.

Table 2
Selected interatomic bond lengths (Å) for $\text{Cs}_2\text{U}_3\text{Se}_7$.

Atom–atom	Distance (Å)	Atom–atom	Distance (Å)
U1–Se6	2.686(2)	U3–Se6	2.761(2)
U1–Se5	2.837(1) × 2	U3–Se1	2.781(1) × 2
U1–Se7	2.861(1) × 2	U3–Se2	2.889(1) × 2
U1–Se7	2.869(2)	U3–Se4	2.896(2)
U2–Se3	2.774(1) × 2	Cs–Se	3.555(1)–3.740(2)
U2–Se2	2.815(2)	U1–U2	4.172(2)
U2–Se5	2.856(2)	U2–U3	5.188(2)
U2–Se4	2.881(1) × 2		

in a cell of dimensions $a = 22.847(1)$ Å, $b = 4.172(1)$ Å, $c = 16.639(1)$ Å. In the structure there are three U, two Cs, and seven Se atoms in crystallographically independent sites all with site symmetry m .

A general view of the structure approximately down [010] is presented in Fig. 1 and selected metrical data are given in Table 2. Each U atom is octahedrally coordinated to six Se atoms. Each U1 atom is surrounded by three Se7, two Se5, and one Se6 atom; each U2 atom is coordinated by two Se3, two Se4, one Se5, and one Se2 atom; each U3 atom is coordinated by two Se1, two Se2, one Se6, and one Se4 atom. There are no Se–Se bonds in the structure. Therefore, formal oxidation states of +1, +4, and –2 may be assigned to Cs, U, and Se, respectively.

Fig. 2 shows the connectivity of the structure along [001]. Fig. 3 shows that $\text{Cs}_2\text{U}_3\text{Se}_7$ is a channel structure with the channels running along [010]. The channels are filled with seven-coordinate Cs atoms with Cs···Se interatomic distances ranging between 3.555(1) Å and 3.740(2) Å.

With the exception of the U1–Se6 distance of 2.685(2) Å, the U–Se distances are typical for six-coordinate U^{4+} ; they range from 2.837(1) Å to 2.896(2) Å. The U1–Se6 distance is unexpectedly short. Given that the EDX analysis did not reveal the presence of oxygen and that the displacement ellipsoids of atom Se6 are not unusual, it seems very unlikely that the atom “Se6” is an admixture of Se and O. Even if the compound were actually $\text{Cs}_2\text{U}_3\text{Se}_{7-x}\text{O}_x$ we would expect that the admixture of O would be spread over multiple sites, and not just the Se6 site. Thus, we believe that the short U1–Se6 distance must arise from steric interactions. With a Se···Cs limit of 4.0 Å, the coordination

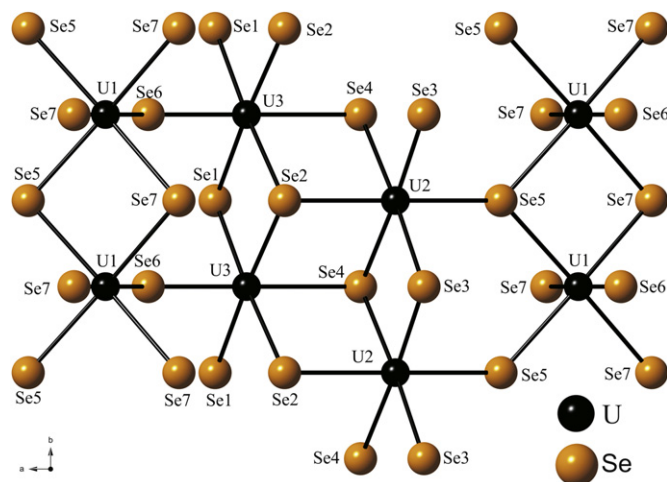


Fig. 2. The connections of USe_6 octahedra viewed down [001] in the $\text{Cs}_2\text{U}_3\text{Se}_7$ structure.

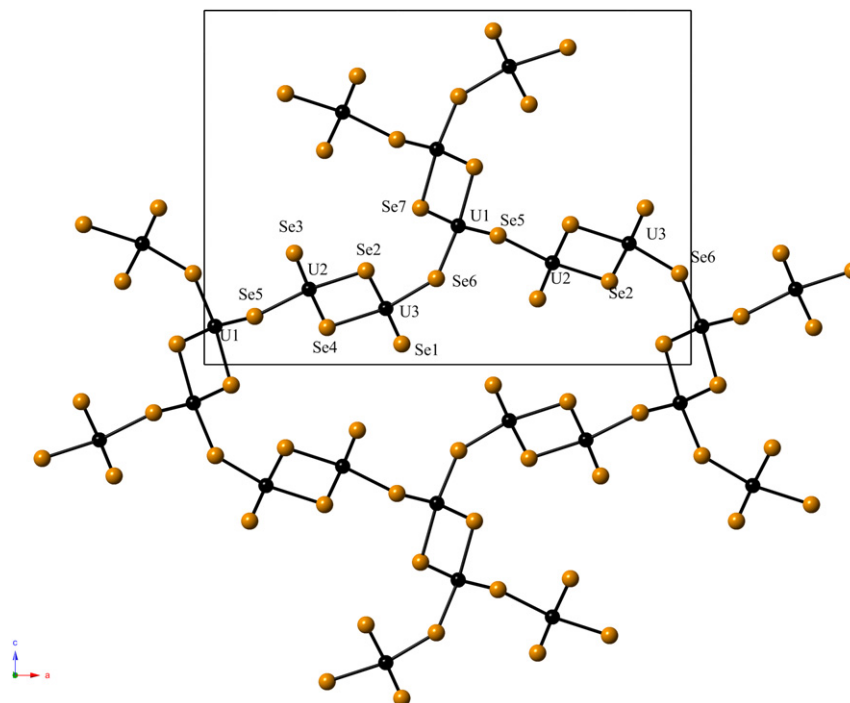


Fig. 3. The connections of USe_6 octahedra to form channels along $[010]$ in the structure of $Cs_2U_3Se_7$.

numbers of atoms Se1 through Se7 are 5,5,5,5,4,4,5, respectively. In general, lower coordination numbers lead to shorter distances. Of the two four-coordinate Se atoms, atom Se5 is connected to two U2 atoms, one U3 atom, and one Cs1 atom with the $Se5 \cdots Cs1$ interaction being 3.740 Å. In contrast, four-coordinate atom Se6 is surrounded by atoms U1 and U2 and two Cs2 atoms with the $Se6 \cdots Cs2$ distance being 3.555(2) Å, the shortest $Se \cdots Cs$ interaction in the structure. We do not offer these observations as a definitive explanation of the short U1–Se6 distance.

Although the structure of $Cs_2U_3Se_7$ represents a new structure type, it shows some similarities to the structures of $Cr_2Sn_3Se_7$ [16] and $CaFe_2O_4$ [17]. All three crystallize in the orthorhombic space group $D_{2h}^{16} - Pnma$ with all the atoms having site symmetry $m..$. All three are channel structures with the channels running in the $[010]$ direction and formed by the connections of USe_6 , $(Cr/Sn)Se_6$, or FeO_6 octahedra, respectively. However, within the unit cells the channel in $Cs_2U_3Se_7$ comprises twelve metal centers (Fig. 3), whereas that in $Cr_2Sn_3Se_7$ (Fig. 4) comprises thirteen, and that in $CaFe_2O_4$ (Fig. 5) comprises six.

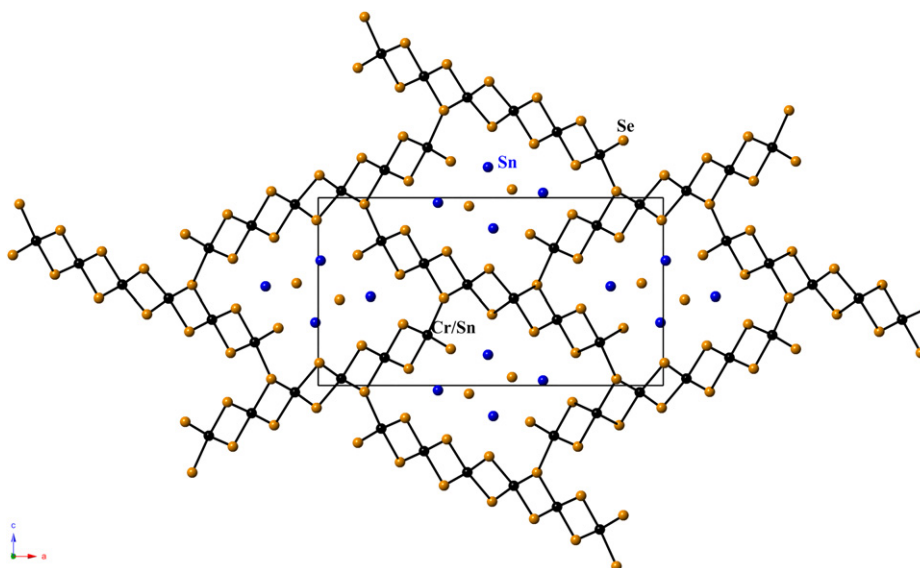


Fig. 4. The structure of $Cr_2Sn_3Se_7$ [16] viewed down $[010]$.

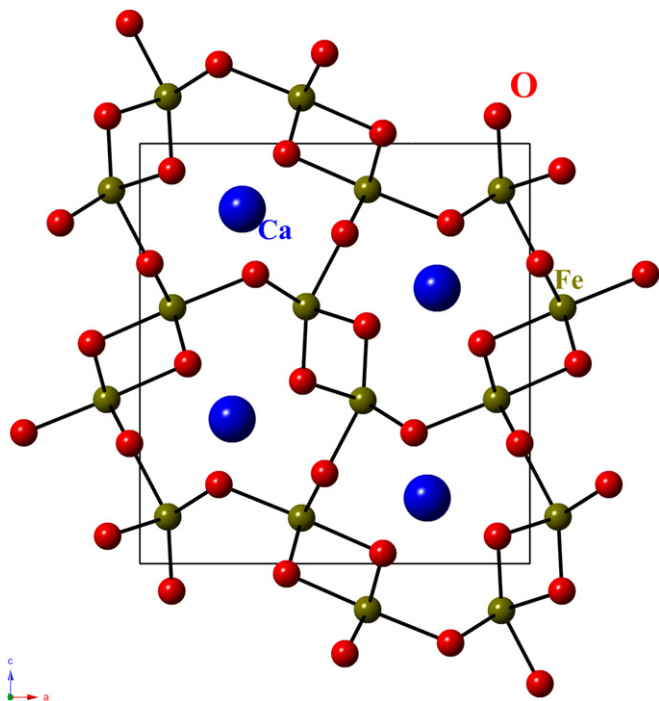


Fig. 5. The structure of CaFe_2O_4 [17] viewed down [010].

4. Conclusions

The new compound $\text{Cs}_2\text{U}_3\text{Se}_7$ was synthesized at 1273 K. It crystallizes in the space group $D_{2h}^{16} - Pnma$ of the orthorhombic system in a new structure type. The crystal structure is composed of channels along the [010] direction that are formed by the connection of USe_6 units. The channels are filled by Cs atoms. The structure of $\text{Cs}_2\text{U}_3\text{Se}_7$ shows similarities to those of $\text{Cr}_2\text{Sn}_3\text{Se}_7$ and CaFe_2O_4 but within the unit cells of each the number of metal centers in the channels differs.

Acknowledgments

This research was kindly supported at Northwestern University by the U.S. Department of Energy, Basic Energy Sciences, Chemical

Sciences, Biosciences, and Geosciences Division and Division of Materials Science and Engineering Grant ER-15522. Use was made of the IMSERC X-ray Facility at Northwestern University, supported by the International Institute of Nanotechnology (IIN).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.solidstatesciences.2013.01.008> and CSD No. 425462.

References

- [1] D.E. Bugaris, J.A. Ibers, Dalton Trans. 39 (2010) 5949–5964.
- [2] E. Manos, M.G. Kanatzidis, J.A. Ibers, in: L.R. Morss, N.M. Edelstein, J. Fuger (Eds.), The Chemistry of the Actinide and Transactinide Elements, fourth ed., vol. 6 Springer, Dordrecht, The Netherlands, 2010, pp. 4005–4078.
- [3] H. Masuda, T. Fujino, N. Sato, K. Yamada, M. Wakeshima, J. Alloys Compd. 284 (1999) 117–123.
- [4] K. Stöwe, S. Appel-Colbus, Z. Anorg. Allg. Chem. 625 (1999) 1647–1651.
- [5] J. Padiou, J. Lucas, C. R. Acad. Sci. Ser. IIc Chim. 263 (1966) 71–73.
- [6] D.E. Bugaris, D.M. Wells, J. Yao, S. Skanthakumar, R.G. Haire, L. Soderholm, J.A. Ibers, Inorg. Chem. 49 (2010) 8381–8388.
- [7] B.C. Chan, Z. Hulvey, K.D. Abney, P.K. Dorhout, Inorg. Chem. 43 (2004) 2453–2455.
- [8] K.-S. Choi, R. Patschke, S.J.L. Billinge, M.J. Waner, M. Dantus, M.G. Kanatzidis, J. Am. Chem. Soc. 120 (1998) 10706–10714.
- [9] J.A. Cody, J.A. Ibers, Inorg. Chem. 35 (1996) 3836–3838.
- [10] H. Mizoguchi, D. Gray, F.Q. Huang, J.A. Ibers, Inorg. Chem. 45 (2006) 3307–3311.
- [11] O. Tougaard, A. Daoudi, M. Potel, H. Noël, Mater. Res. Bull. 32 (1997) 1239–1245.
- [12] E.J. Wu, M.A. Pell, J.A. Ibers, J. Alloys Compd. 255 (1997) 106–109.
- [13] A. Mesbah, J.A. Ibers, Acta Crystallogr. Sect. E Struct. Rep. Online 68 (2012) i76.
- [14] J.A. Cody, J.A. Ibers, Inorg. Chem. 34 (1995) 3165–3172.
- [15] A.C. Sutorik, M.G. Kanatzidis, J. Am. Chem. Soc. 113 (1991) 7754–7755.
- [16] S. Jobic, F. Bodenau, G. Ouvrard, E. Elkaim, J.P. Lauriat, J. Solid State Chem. 115 (1995) 165–173.
- [17] B.F. Decker, J.S. Kasper, Acta Crystallogr. 10 (1957) 332–337.
- [18] D.E. Bugaris, J.A. Ibers, J. Solid State Chem. 181 (2008) 3189–3193.
- [19] A.J.K. Haneveld, F. Jellinek, J. Less-Common Met. 18 (1969) 123–129.
- [20] S.A. Sunshine, D. Kang, J.A. Ibers, J. Am. Chem. Soc. 109 (1987) 6202–6204.
- [21] Bruker APEX2 Version 2009.5-1 and SAINT Version 7.34a Data Collection and Processing Software, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2009.
- [22] G.M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, 2008.
- [23] G.M. Sheldrick, Acta Crystallogr. Sect. A Found. Crystallogr. 64 (2008) 112–122.
- [24] L.M. Gelato, E. Parthé, J. Appl. Crystallogr. 20 (1987) 139–143.
- [25] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2008.