SHORT COMMUNICATION

The $[U_2I_{10}]^{2-}$ Anion: Synthesis and Structure of $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$

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Abstract. The new anion $[U_2I_{10}]^{2-}$ has been isolated in the compound $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$. This compound was synthesized from the elements at 1173 K. It crystallizes in space group *Cccm* of the orthorhombic system with four formula units in a cell of dimensions $a = 21.5134(9)$ Å, $b = 22.1619(9)$ Å, and $c = 16.7834(6)$ Å. The crystal structure comprises infinite $[Ta(Se_2)_2]_n$ cationic chains charge balanced by $[U_2I_{10}]^{2-}$ anions. The new $[U_2I_{10}]^{2-}$ anion is formed by two edge-sharing UI_6 octahedra. The U–I bond lengths are normal for tetravalent uranium. For charge balance, the $[Ta_7(Se_2)_{14}]^{4+}$ cation must contain three Ta^{IV} and four Ta^V atoms. Charge is delocalized over this cation as the Ta···Ta interactions differ minimally.

Introduction

Although some anions of formula $[M_2X_{10}]^{n-}$ (M = metal; X = F, Cl, Br, I) are known, there are none known for M = U and only two confirmed crystallographically for X = I, namely $[Sb_2I_{10}]^{4-}$ [1] and $[Bi_2I_{10}]^{4-}$ [2, 3]. It is well known that metal complexes can be stabilized by large counterions [4]. Consequently, the discovery of a new, large anion, namely $[U_2I_{10}]^{2-}$, is of significance. The synthesis and structure of the compound $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$ are described here.

Experimental Section

Black crystals of $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$ were prepared from tantalum (Aldrich, 99.9 %), selenium (Cerac, 99.99 %), ^{238}U (ORNL), and iodine at 1173 K. A mixture of uranium (0.168 mmol), tantalum (0.336 mmol), iodine (0.504 mmol), and selenium (3.865 mmol) was loaded into a fused-silica tube. Afterwards, the tube was evacuated and flame-sealed. The reaction tube was heated in a computer-controlled furnace to 513 K in 2 h, to 713 K in 99 h, and afterwards to 1173 K in 46 h. Finally, it was slowly cooled at 5 K·h^{-1} to 373 K and crash cooled to 293 K. The presence of all four elements was confirmed by EDS analysis. The material is air sensitive.

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) at 100 K with a Bruker APEXII CCD diffractometer [5]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of 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 per frame. The collection of the intensity data and cell refinement were carried out with the program APEX2 [5]. Data reduction was carried out by using the program SAINT+ [6]. Face-indexed absorption, incident beam, and decay corrections were performed numerically by using the program SADABS [6]. The structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [7]. The program STRUCTURE TIDY [8] was then employed to standardize the atomic coordinates. Further details are given in Table 1 and in the cif file, which has been deposited [9].

Table 1. Crystal data and structural refinement for $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$.

Compound	$[Ta_7(Se_2)_{14}][U_2I_{10}]_2$
Formula	$I_{20}Se_{28}Ta_7U_4$
M /g·mol^{-1}	6967.65
Crystal system	orthorhombic
Space Group	*Cccm*
a /Å	21.5134 (9)
b /Å	22.1619 (9)
c /Å	16.7834 (6)
V /Å^3	8002.0 (5)
Temperature /K	100 (2)
Z	4
ρ_c /g·cm^{-3}	5.784
μ (Mo-K_α) /cm^{-1}	380.55
Crystal size /mm	$0.36 \times 0.21 \times 0.10$
max/min transmission	0.1138/0.0255
$R(F)$ [$I > 2\sigma(I)$]	0.029
$R_w(F_o^2)$[a]	0.069

a) $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{1/2}$.

Results and Discussion

The structure of $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$ can be viewed as a packing of $[Ta_7(Se_2)_{14}]^{4+}$ chains and the $[U_2I_{10}]^{2-}$ anions (Figure 1). The chains extend along [010] and with the $[U_2I_{10}]^{2-}$ anions form alternating layers along [100]. There are two crystallographically independent $[U_2I_{10}]^{2-}$ anions in the asymmetric unit, each with crystallographically imposed $2/m$ symmetry. Each is formed by two edge-sharing UI_6 octahedra (Figure 2). Even though the structure of A_2UX_5 (A = K and

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The [U₂I₁₀]²⁻ Anion: Synthesis and Structure of [Ta₇(Se₂)₁₄][U₂I₁₀]₂

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Rb, X = Cl, Br, and I) contains edge-sharing monocapped trigonal prisms that form chains [10] and the UI_6 species is well known in organometallic chemistry [11, 12], the $[U_2I_{10}]^{2-}$ anion does not appear to have been reported previously. The U–I bond lengths (Figure 2), which range from 2.9026(9) to 3.1270(5) Å, are normal for U^{IV}. For example, the U–I bond length in $Li_2[UI_6]$ is 3.013 Å [13]. The U(1)–U(1) and U(2)–U(2) distances are 4.719 and 4.653 Å, respectively, beyond the Hill limit for direct f–f orbital overlap [14], but slightly shorter than in $K_2[UI_5]$ where low temperature antiferromagnetic ordering was found [10].
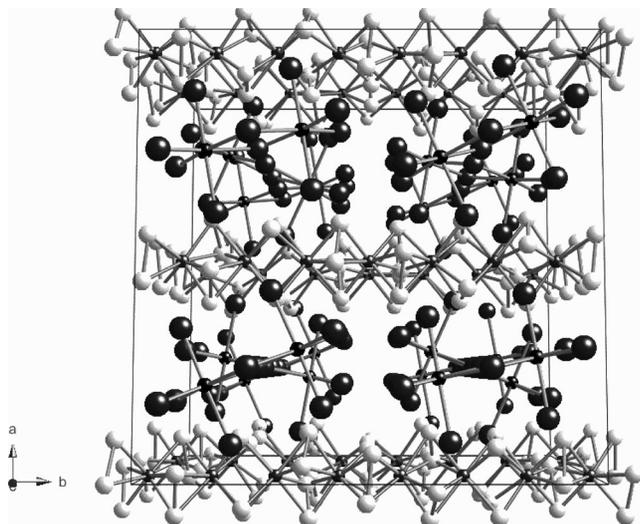

Figure 1. View approximately down [001] of the structure of $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$. The cationic chains (small dark gray balls, tantalum; light large gray balls, selenium) extend along [010]. In the anions the small black balls are uranium, the large black balls are iodine.
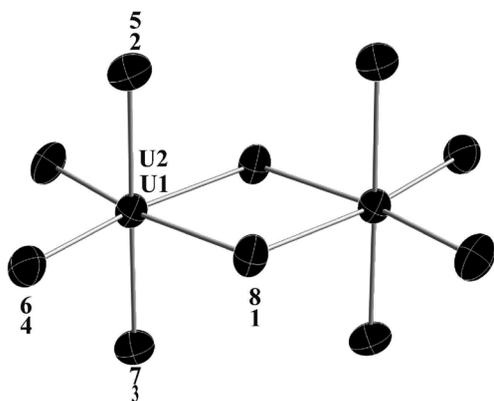

Figure 2. View of the $[U_2I_{10}]^{2-}$ anion in $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$. Each of the crystallographically independent anions has imposed symmetry $2/m$. Distances: U(1)–I(1), 3.1270(5); U(2)–I(8), 3.1108(6); U(1)–I(2), 3.0000(9); U(2)–I(5), 3.0351(8); U(1)–I(3), 2.9039(9); U(2)–I(7), 2.9026(9); U(1)–I(4), 2.9406(6), U(2)–I(6), 2.9307(6) Å.

The $[Ta_7(Se_2)_{14}]^{4+}$ cation (Figure 3) comprises another example of Ta/Q_2 (Q = S, Se, and Te) chains [15–19]. This anion has crystallographically imposed 222 symmetry at atom Ta(4). Each of the four crystallographically independent tanta-

lum atoms is coordinated by four Se_2 groups, the centers of which form a distorted tetrahedron. The Ta–Se distances ranging from 2.5685(8) to 2.7344 (8) Å are normal as are the Se–Se single-bond lengths of 2.356(1) to 2.361(1) Å. For charge balance, the $[Ta_7(Se_2)_{14}]^{4+}$ cation must contain three Ta^{IV} and four Ta^V atoms. Charge is delocalized over this cation as the four Ta···Ta interactions of 3.1521(8) to 3.1760(4) Å differ minimally.
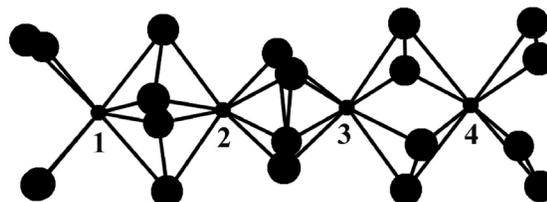

Figure 3. Part of the $[Ta_7(Se_2)_{14}]^{4+}$ anion in $[Ta_7(Se_2)_{14}][U_2I_{10}]_2$ with the tantalum atoms numbered. The rest of the anion is generated by a 222 symmetry operation that is at atom Ta(4). Distances: Ta(1)–Ta(1), 3.1521(8); Ta(1)–Ta(2), 3.1559(6); Ta(2)–Ta(3), 3.1730(6); Ta(3)–Ta(4), 3.1760(4); Ta–Se, 2.5685(8) to 2.7344(8); Se–Se, 2.356(1) to 2.361(1) Å.

Acknowledgement

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[9] The crystallographic file in CIF format for $I_{20}Se_{28}Ta_7U_4$ has been deposited with FIZ Karlsruhe as CSD number 380350. It may be obtained free of charge by contacting FIZ Karlsruhe (Fax: +49-7247-808-666 or E-Mail: crysdata@fiz-karlsruhe.de).

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