Single-crystal structures of uranium and neptunium oxychalcogenides \(\text{AnQ}\) (\(\text{An}=\text{U}, \text{Np}; \text{Q}=\text{S}, \text{Se}\))

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**ABSTRACT**

The compounds UOS, UOSe, NpOS, and NpOSe have been synthesized and their structures determined by means of single-crystal X-ray diffraction methods. The results provide more detailed crystallographic information, including more precise interatomic distances, than earlier determinations from powder diffraction data. These isostructural compounds adopt the PbFCl structure type. Each \(\text{An}\) atom is surrounded by four \(\text{O}\) and five \(\text{Q}\) atoms in a distorted monocapped square-antiprismatic arrangement. © 2009 Elsevier Inc. All rights reserved.

1. Introduction

The actinide oxysulfides \(\text{AnOS}\) (\(\text{An}=\text{Th, U, Np}\)) were first identified and their structures deduced from powder X-ray diffraction data in 1949 [1]. \(\text{AnOS}\) crystallizes in the \(\text{PbFCl}\) structure type in space group \(\text{P4/nmm}\) of the tetragonal system. The structure differs from those of the parent \(\text{AnQ}\) compounds [2–8]. For example, \(\text{UO}_2\) crystallizes in the cubic space group \(\text{Fm3m}\) [9] and \(\alpha\)-\(\text{US}_2\) crystallizes in the tetragonal space group \(\text{P4/ncc}\) [10]. Since then, there have been numerous studies of the \(\text{AnOS}\) and \(\text{AnOSe}\) compounds. These include their syntheses, structures, and magnetic, electronic, and thermal properties [11–29]. Of particular interest are their magnetic properties. The \(\text{AnOS}\) (\(\text{An}=\text{U, Np}\)) compounds undergo antiferromagnetic transitions at low temperatures and exhibit strong uniaxial anisotropy. The \(\text{An}\) moments are aligned along the \(c\) axis in a type 1A stacking order (+ + − −) for \(\text{AnOS}\) and \(\text{AnOSe}\), and in a type 1 stacking order (+ − + −) for \(\text{UOTe}\) [14,16,18,19,22,27,28]. The compound \(\text{NpOTe}\) is not known.

With the exception of UOS [17] and UOSe [22,23], the structures of the \(\text{AnQ}\) compounds were characterized by powder X-ray diffraction analyses. Here we report single-crystal X-ray diffraction structures. They provide more detailed crystallographic information, including more precise interatomic distances, than did the previous studies.

2. Experimental

2.1. Syntheses

\(\text{UO}_2\) (Strem Chemicals, 99.8%), Fe (Aesar, 99.9%), S (Alfa-Aesar, 99.9%), Se (Cerac 99.999%), \(\text{Sb}_2\), \(\text{Se}_2\) (Aldrich, 99.5%), \(\text{SnO}_2\) (Aldrich, 99.8%), \(\text{Pd}\) (Aldrich, 99.9%) and \(\text{CsCl}\) (Strem Chemicals, 99.999%) were used as received. Finely divided \(\text{U}\) powder was prepared from \(\text{U}\) turns (ORNL) by a modification of the literature procedure [30]. Brittle \(237\text{Np}\) chunks were crushed and used as received (99.99%, ORNL). \(\text{Sb}_2\text{S}_3\) and \(\text{Sb}_2\text{Se}_3\) were prepared from the direct reactions of the elements in sealed fused-silica tubes at 1123 K. The purities of \(\text{Sb}_2\text{S}_3\), \(\text{Sb}_2\text{Se}_3\), and UOS (see below) were confirmed by powder X-ray diffraction measurements. For all the reactions, the reactants were loaded into fused-silica ampules in an \(\text{Ar}\)-filled glove box. The ampules were then evacuated to approximately \(10^{-4}\) Torr and flame-sealed. The reaction mixtures were placed in a computer-controlled furnace and heated according to a specific temperature profile. All of the crystals found in these reactions were characterized by single-crystal X-ray diffraction methods and the products of the uranium reactions were also examined with an EDX-equipped Hitachi S-3400 SEM. The \(\text{AnQ}\) compounds are stable in air and are not sensitive to water and common organic solvents. Caution! \(237\text{Np}\) and any ingrown daughter products are \(\gamma\)- and \(\beta\)-emitting radioisotopes and as such are considered a health risk. Their use requires appropriate infrastructure and personnel trained in the handling of radioactive materials. The procedures we use for the syntheses of \(\text{Np}\) compounds have been described [31].
UOS. This compound was prepared through a solid-gas reaction of UO$_2$, C, and S at 1213 K \cite{20}, 0.030 g (0.10 mmol) of the resultant UOS powder was mixed with 0.030 g of Sb$_2$S$_3$ flux (m.p. 823 K) and heated to 1273 K in 24 h, held at 1273 K for 7 days, cooled to 973 K in 4 days, and then cooled to 298 K in 10 h. The reaction products consisted of black square plates of UOS, large black needles of Sb$_2$S$_3$, and polycrystalline powders of both compounds, with approximately 25% of the UOS forming single crystals.

UOSe. In an investigation of the Pd/U/O/Se system UOSe was formed as a byproduct of the reaction of Pd (0.007 g, 0.065 mmol), Se (0.011 g, 0.139 mmol), and CsCl flux (0.090 g). The reaction mixture was heated to 1173 K in 32 h, held at 1173 K for 4 days, cooled to 773 K in 5.5 days, and then cooled to 298 K in 10 h. To form single crystals of UOSe the resultant powder was mixed with 0.030 g Sb$_2$S$_3$ flux (m.p. 879 K) and heated to 1273 K in 24 h, held at 1273 K for 7 days, cooled to 973 K in 4 days, and then cooled to 298 K in 10 h. The products consisted primarily of large black needles of Sb$_2$S$_3$ mixed with Pd and UOSe powders as well as several black square plates of UOSe.

NpOS. In a study of the Np/Fe/S system NpOS resulted as a byproduct of the reaction of Np (0.020 g, 0.084 mmol), Se (0.011 g, 0.139 mmol), and CsCl flux (0.090 g). The reaction mixture was mixed with 0.030 g Sb$_2$S$_3$ flux (m.p. 879 K) and heated to 1173 K in 32 h, held at 1173 K for 4 days, cooled to 773 K in 5 days, held at 773 K for 2 days, and then cooled to 298 K in 6 h. The reaction products were washed with water and dried with acetone. The products included many large black prisms of Np$_3$S$_5$ \cite{32}, a few small black square plates of NpOS, and an unidentified black powder. The yield of Np$_3$S$_5$ was about 30% based on Np.

NpOSe. A few black NpOSe crystals were obtained from the reaction of Np (0.020 g, 0.084 mmol), Se (0.011 g, 0.139 mmol), and CsCl flux (0.090 g). The reaction mixture was heated to 1173 K in 32 h, held at 1173 K for 4 days, cooled to 773 K in 5 days, held at 773 K for 2 days, and then cooled to 298 K in 6 h. The products were washed with water and dried with acetone. Black prisms of Np$_3$Se$_5$ \cite{13} in about 90% yield based on Np were the major product.

2.2. Structure determination

Single-crystal X-ray diffraction data for AnOQ (An=U, Np; Q=S, Se) were collected with the use of graphite-monochromatized MoKα radiation (λ=0.71073 Å) at 100 K on a Bruker APEX2 diffractometer \cite{34}. The crystal-to-detector distance was 5.023 cm for UOQ and 5.106 cm for NpOQ. 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 for UOQ and 600 frames for NpOQ at ϕ settings of 0°, 90°, 180°, and 270°. The exposure time was 20 s/frame for UOQ and 25 s/frame for NpOQ. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2 \cite{34}. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS \cite{35}. The structures were solved with the direct-methods program SHELXS and refined with the full-matrix least-squares program SHELXL \cite{36}. The program STRUCTURE TIDY \cite{37} was used to standardize the positional parameters. Additional experimental details are given in Table 1 and in the Supporting material.

2.3. Powder X-ray diffraction measurements

Powder samples were mounted on zero-background holders, and X-ray diffraction patterns were collected with a Rigaku Geigerflex powder X-ray diffractometer with the use of CuKα radiation (λ=1.5418 Å). The program JADE 8 was used to analyze the data \cite{38}.

3. Results and discussion

3.1. Syntheses

There have been many different methods for the preparation of AnOQ compounds in the literature \cite{2–4,20}. Often these compounds were byproducts \cite{13}. Most of the rational syntheses involve chalcogenization of actinide oxides, which generally results in a powder sample \cite{20}. Single crystals can be grown by using fluxes or chemical transport agents \cite{24}. This is the case for our

![Fig. 1. View down [010] of the structure of AnOQ.](image-url)
synthesis of UOS. In contrast, UOSe, NpOS, and NpOSe crystals were obtained as byproducts during the syntheses of actinide chalcogenides. SeO₂ was the most likely oxygen source for the UOSe reaction whereas the fused-silica ampules, which were etched during the reactions, were the most likely oxygen source for the Np reactions. Pd and Fe metals are not essential for the syntheses of UOSe and NpOS, respectively, as crystals were observed in similar reactions without the presence of these metals.

3.2. Structures

Our results for the AnOQ structures from single-crystal X-ray diffraction analyses are consistent with the previous structural studies but are more precise. The present AnOQ compounds are isostructural and adopt the PbFCl structure type in space group Pn̅m of the tetragonal system (Fig. 1). Because there are no Q–O bonds in the structure, formal oxidation states of +IV/II – II may be assigned to An/O/Q, respectively. The oxidation state for Np of +IV has been confirmed for NpOS and NpOSe by means of 237Np Mössbauer spectroscopy [27,28].

As shown in Fig. 1, each An atom is connected to four O and five Q atoms in a distorted monocapped square antiprism. Each AnO₄Q₅ polyhedron shares one O and two Q atoms with four identical neighbors in the ab plane to form a single layer and further connects to four other units from the adjacent single layer by sharing two O atoms to form a double AnOQ₅ layer. Between those double layers, AnO₄Q₅ polyhedra share two Q atoms with each other.

Selected interatomic distances for AnOQ are listed in Table 2. An–O and An–Q distances are comparable to the values for other An(IV) cations in similar coordination environments. For example, the U–S distances are 2.908(3) and 2.924(1) Å in UOSe, which are comparable to those of 2.750(4)–2.986(4) Å for the eight-coordinate U–S distances range from 2.681(2) to 2.754(1) Å, which are shorter than those of 2.889(2) and 2.9067(8) Å found in NpOS. This is not surprising because Np cations are six-coordinate in AMNpS₅ versus nine-coordinate in NpOS.

Table 2

<table>
<thead>
<tr>
<th>Distance</th>
<th>UOSe</th>
<th>UOSe</th>
<th>NpOS</th>
<th>NpOSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>An–O1 × 4</td>
<td>2.344(2)</td>
<td>2.3540(4)</td>
<td>2.3249(2)</td>
<td>2.3344(2)</td>
</tr>
<tr>
<td>An–Q1 × 4</td>
<td>2.924(1)</td>
<td>3.018(4)</td>
<td>2.9067(8)</td>
<td>3.0053(5)</td>
</tr>
<tr>
<td>An–Q1</td>
<td>2.906(3)</td>
<td>3.087(2)</td>
<td>2.889(2)</td>
<td>3.077(1)</td>
</tr>
</tbody>
</table>

Fig. 2. Comparison of axial lengths for AnOQ (An=Th, U, Np; Q=S, Se).

X-ray diffraction methods to date. In those compounds the Np–S distances range from 2.681(2) to 2.754(1) Å, which are shorter than those of 2.889(2) and 2.9067(8) Å found in NpOS. This is not surprising because Np cations are six-coordinate in AMNpS₅ versus nine-coordinate in NpOS.

Fig. 2 displays the lattice constants for AnOQ (An=U, Np; Q=S, Se) (single-crystal data, 100 K), and for ThOS [1] and ThOSe [12] (powder data, 293 K). The contraction of the actinide radius with Z is evident in these lattice constants. It is also evident in the tabulation of interatomic distances in Table 2.

The present metrical data for the AnOQ (An=U, Np; Q=S, Se) compounds generally agree with those derived previously, mainly from X-ray diffraction powder studies. With two exceptions, those earlier studies either lacked standard deviations on derived interatomic distances or if they were given they were considerably larger than those provided in Table 2. Only for two previous studies of UOSe single crystals can a comparison (Table 3) be made. The possibly significant differences presumably arise from differences in the temperatures at which the data were collected.

Table 3

<table>
<thead>
<tr>
<th>U–O (Å)</th>
<th>U–Se (Å)</th>
<th>U–Se (Å)</th>
<th>T (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3540(4)</td>
<td>3.018(4)</td>
<td>3.087(2)</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>2.346(4)</td>
<td>3.012(5)</td>
<td>3.080(5)</td>
<td>113</td>
<td>23</td>
</tr>
<tr>
<td>2.357(1)</td>
<td>3.026(1)</td>
<td>3.099(2)</td>
<td>293</td>
<td>22</td>
</tr>
</tbody>
</table>

Supporting material

The crystallographic files in CIF format for UOS, UOSe, NpOS, and NpOSe have been deposited with FIZ Karlsruhe as CSD numbers 420131, 420133, 420132, and 420134, respectively. These may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (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 doi:10.1016/j.jssc.2009.12.013.

References
