Single-crystal structures of uranium and neptunium oxychalcogenides *An*OQ (*An*=U, Np; Q=S, 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 *An* atom is surrounded by four O and five Q atoms in a distorted monocapped square-antiprismatic arrangement.

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1. Introduction

The actinide oxysulfides *An*OS (*An*=Th, U, Np) were first identified and their structures deduced from powder X-ray diffraction data in 1949 [1]. *An*OS crystallizes in the PbFCl structure type in space group $P4/nmm$ of the tetragonal system. The structure differs from those of the parent AnQ_2 compounds [2–8]. For example, UO_2 crystallizes in the cubic space group $Fm\bar{3}m$ [9] and α–US_2 crystallizes in the tetragonal space group $P4/ncc$ [10]. Since then, there have been numerous studies of the *An*OQ (*An*=Th, U, Np; Q=S, Se, Te) compounds. These include their syntheses, structures, and magnetic, electronic, and thermal properties [11–29]. Of particular interest are their magnetic properties. The *An*OQ (*An*=U, Np) compounds undergo antiferromagnetic transitions at low temperatures and exhibit strong uniaxial anisotropy. The *An* moments are aligned along the c axis in a type 1A stacking order $(+ + - -)$ for *An*OS and *An*OSe, and in a type 1 stacking order $(+ - + -)$ for UOTe [14,16,18,19,22,27,28]. The compound NpOTe is not known.

With the exception of UOS [17] and UOSe [22,23], the structures of the *An*OQ 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

UO_2 (Strem Chemicals, 99.8%), Fe (Aesar, 99.9%), S (Alfa-Aesar, 99.99%), Se (Cerac 99.999%), Sb (Aldrich, 99.5%), SeO_2 (Aldrich, 99.8%), Pd (Aldrich, 99.9%) and CsCl (Strem Chemicals, 99.999%) were used as received. Finely divided U powder was prepared from [238]U turnings (ORNL) by a modification of the literature procedure [30]. Brittle [237]Np chunks were crushed and used as provided (99.99%, ORNL). Sb_2S_3 and Sb_2Se_3 were prepared from the direct reactions of the elements in sealed fused-silica tubes at 1123 K. The purities of Sb_2S_3, Sb_2Se_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 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 *An*OQ compounds are stable in air and are not sensitive to water and common organic solvents.

Caution! [237]Np and any ingrown daughter products are α- and γ-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 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 [20]. 0.030 g (0.10 mmol) of the resultant UOS powder was mixed with 0.030 g of Sb_2S_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_2S_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), SeO_2 (0.007 g, 0.063 mmol), U (0.030 g, 0.126 mmol), and Se (0.020 g, 0.253 mmol). The starting materials were heated to 1223 K in 24 h, held at 1223 K for 7 days, cooled to 923 K in 4 days, and finally cooled to 298 K in 10 h. To form single crystals of UOSe the resultant powder was mixed with 0.030 g Sb_2Se_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_2Se_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 0.020 g (0.084 mmol) of Np, 0.002 g (0.04 mmol) of Fe, 0.007 g (0.22 mmol) of S, and 0.090 g of CsCl flux. The reaction 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 reaction products were washed with water and dried with acetone. The products included many large black prisms of Np_3S_5 [32], a few small black square plates of NpOS, and an unidentified black powder. The yield of Np_3S_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 5.5 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_3Se_5 [33] 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 Mo$K\alpha$ radiation (λ=0.71073 Å) at 100 K on a Bruker APEX2 diffractometer [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 [34]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [35]. The structures were solved with the direct-methods program SHELXS and refined with the full-matrix least-squares program SHELXL [36]. The program STRUCTURE TIDY [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 Cu$K\alpha$ radiation (λ=1.5418 Å). The program JADE 8 was used to analyze the data [38].

3. Results and discussion

3.1. Syntheses

There have been many different methods for the preparation of AnOQ compounds in the literature [2–4]. Often these compounds were byproducts [13]. Most of the rational syntheses involve chalcogenization of actinide oxides, which generally results in a powder sample [20]. Single crystals can be grown by using fluxes or chemical transport agents [24]. This is the case for our
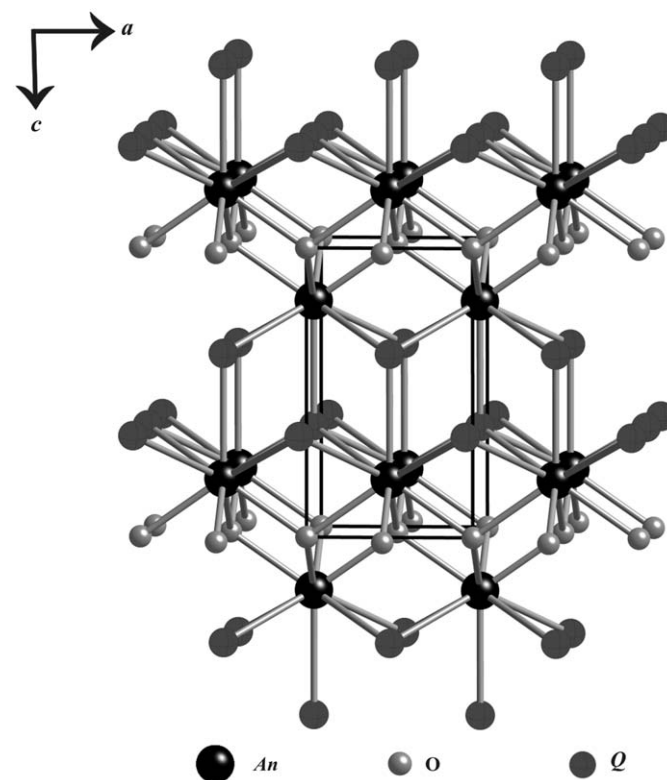
Table 1
Crystal data and structure refinements for AnOQ.[a]

Compound	UOS	UOSe	NpOS	NpOSe
Fw	286.09	332.99	285.06	331.96
a (Å)	3.8360(3)	3.8936(2)	3.8088(3)	3.8725(3)
c (Å)	6.6982(6)	6.9711(3)	6.6491(6)	6.9239(6)
V (Å^3)	98.56(1)	105.683(9)	96.46(1)	103.83(2)
ρ_c (g cm^{-3})	9.640	10.464	9.815	10.618
μ (cm^{-1})	829.2	935.68	544.58	671.13
$R(F)$[b]	0.0132	0.0183	0.0166	0.0156
$R_w(F^2)$[c]	0.0341	0.0414	0.0410	0.0432

[a] For all structures Z=2, space group=$P4/nmm$, λ=0.71073 Å, T=100(2) K.

[b] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o^2>2\sigma(F_o^2)$.

[c] $R_w(F_o^2)=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$ for all data. $w^{-1}=\sigma^2(F_o^2)+(qF_o^2)^2$ for $F_o^2\geq0$; $w^{-1}=\sigma^2(F_o^2)$ for $F_o^2<0$. q=0.0205 for UOS, 0.0125 for UOSe, 0.0260 for NpOS, and 0.0182 for NpOSe.

Fig. 1. View down [010] of the structure of AnOQ.

synthesis of UOS. In contrast, UOSe, NpOS, and NpOSe crystals were obtained as byproducts during the syntheses of actinide chalcogenides. SeO_2 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 $P4/nmm$ of the tetragonal system (Fig. 1). Because there are no Q–Q bonds in the structure, formal oxidations 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 ^{237}Np 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 AnO_4Q_5 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 AnOQ layer. Between those double layers, AnO_4Q_5 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 UOS, which are close to those of 2.750(4)–2.986(4) Å for the eight-coordinate U atom in α-US_2 [10]. There are very few single-crystal Np–Q distances reported. In fact, $AMNpS_3$ (A=K, Rb,Cs; M=Cu, Ag) [31] are the only Np(IV) compounds characterized by single-crystal

Table 2
Selected interatomic distances (Å) for AnOQ.

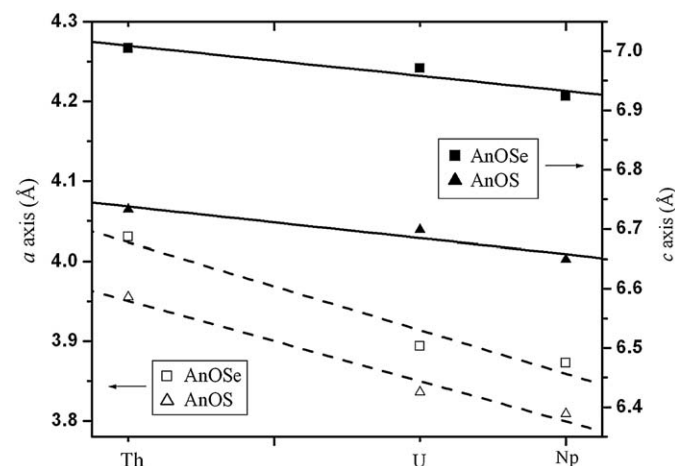| Distance	UOS	UOSe	NpOS	NpOSe
An–O1 × 4	2.3445(2)	2.3540(4)	2.3249(2)	2.3344(2)
An–Q1 × 4	2.924(1)	3.0184(9)	2.9067(8)	3.0055(5)
An–Q1	2.908(3)	3.087(2)	2.889(2)	3.077(1)

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

Table 3
Comparison of three single-crystal X-ray structure determinations of UOSe.

U–O (Å)	U–Se (Å)	U–Se (Å)	T (K)	Reference
2.3540(4)	3.0184(9)	3.087(2)	100	This work
2.346(4)	3.012(5)	3.080(5)	113	23
2.357(1)	3.026(1)	3.099(2)	293	22

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 $AMNpS_3$ 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.

Supporting material

The crystallographic files in CIF format for UOS, UOSe, NpOS, and NpOSe have been deposited with FIZ Karlsruhe as CSD numbers 421031, 421033, 421032, and 421034, respectively. These may be obtained free of charge by contacting FIZ Karlsruhe at +497247808 666 (fax) or crysdata@fiz-karlsruhe.de (e-mail).

Acknowledgments

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.

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