

The Synthesis and Crystal Structure of NpSe₃

Brian J. Bellott,^[a] Richard G. Haire,^[b] and James A. Ibers*^[a]

Keywords: Neptunium triselenide; Synthesis; Single crystal structure analysis; X-ray diffraction

Abstract. Neptunium triselenide, NpSe₃, was synthesized in high yield by the reaction of the elements in a Sb₂Se₃ flux at 1223 K. Its structure has been determined by single-crystal X-ray diffraction methods. The compound crystallizes with two formula units in space group $C_{2h}^2-P2_1/m$ of the monoclinic system in the TiS₃ structure type with cell constants at 100 K of $a = 5.592(3)$ Å, $b = 4.002(2)$ Å, $c = 9.422(5)$ Å,

$\beta = 97.40(1)^\circ$. The asymmetric unit comprises one neptunium and three selenium atoms, each with site symmetry m . Np–Se interatomic distances range from 2.859(2) to 2.927(3) Å; the Se–Se bond length of 2.340(3) Å is typical of a single bond. The compound may thus be charge-balanced and formulated as Np⁴⁺Se²⁻Se₂²⁻.

Introduction

The extensive chemistry of actinide compounds arises from their 5f orbitals; these show varying degrees of localization from bonding to itineracy. In the assessment of their degree of localization neptunium is particularly important as it is at the border between tetravalent thorium and uranium and trivalent lanthanide-like plutonium.^[1] To take the rich chemistry of the binary Np_xQ_y system (Q = chalcogen = S, Se, or Te) as an example,^[1] many of the reported compounds, including Np₃Q₅ (Q = S, Se)^[2] and β -NpS₂,^[3] are isostructural with Th or U analogues, within which Np is in the formal oxidation state of +4. In contrast, Np₂Q₃ (Q = S, Se, Te),^[3–6] NpTe₂,^[6] and NpTe₃^[6] are isostructural with Pu analogues, within which Np is +3. However, many of these Np_xQ_y compounds were characterized decades ago by X-ray powder diffraction methods. Specifically, for NpSe₃ the reports are confusing at best and incorrect at worst. Because the structure is a key to understanding interactions and electron distributions within An_xQ_y systems (An = actinide), it is important to examine such binary systems and here we report the results of a single-crystal X-ray diffraction study of NpSe₃.

Results and Discussion

Table 1. summarizes the early literature on the structure of NpSe₃. All the powder diffraction studies found the space group to be $P2_1/m$ but the earliest found a cell that was doubled along the c axis. At that time a doubled cell was also

assigned to USe₃ and the assumption was that NpSe₃ and USe₃ were isostructural with the trichalcogenides of Ti, Zr, and Hf,^[7] even though the unit cells of the latter were not doubled along c . Nevertheless, *Damien* et al.^[5] indicated that Np was probably +4. Three years later *Blaise* et al. carried out magnetic measurements on USe₃ and NpSe₃ and concluded that Np was +3.^[8] The more definitive ²³⁷Np Mössbauer measurements were first interpreted as favoring the +3 oxidation state,^[9] but were later reinterpreted to favor the +4 oxidation state.^[3] From this brief summary it is clear that these heroic measurements on NpSe₃, which is difficult to prepare and dangerous to handle, led to conflicting results regarding its structure and the formal oxidation state of Np. The single-crystal X-ray study in 1984^[10] established the structure of USe₃ and the U⁴⁺ oxidation state and this present single-crystal study establishes the structure of NpSe₃ and the Np⁴⁺ oxidation state.

Black crystals of NpSe₃ were synthesized in high yield from the combination of the elements in a Sb₂Se₃ flux. A Sb₂Se₃ flux has been successfully employed to synthesize a number of lanthanide selenides as single crystals, including Ln₃LuSe₆ (Ln = La, Ce).^[11] Clearly, Sb₂Se₃ as a flux has shown great potential for the syntheses of single crystals of lanthanide and actinide chalcogenides.

Neptunium triselenide, NpSe₃, crystallizes with two formula units in space group $P2_1/m$ of the monoclinic system in the TiSe₃ structure type.^[7] As shown in Figure 1 and Table 2, NpSe₃ contains one crystallographically unique Np position and three crystallographically unique Se positions. Each has site symmetry m . Each Np atom is coordinated by four Se atoms and two Se–Se pairs. Given the distances shown, NpSe₃ may be written as Np⁴⁺Se²⁻Se₂²⁻, as the Se–Se distance of 2.340(3) Å is a typical Se–Se single bond and the Np–Se distances of 2.859(2) to 2.927(3) Å are consistent with those in other Np_xSe_y compounds, including the eight-coordinate Np⁴⁺ center in Np₃Se₅ (2.7738(5) to 2.9770(7) Å).^[2] The Se atoms are shared among other Np centers to comprise the crystal structure (Figure 2). Given the nature of the structure (Figure 1)

* Prof. Dr. J. A. Ibers
Fax: +1-847-491-2976
E-Mail: ibers@chem.northwestern.edu

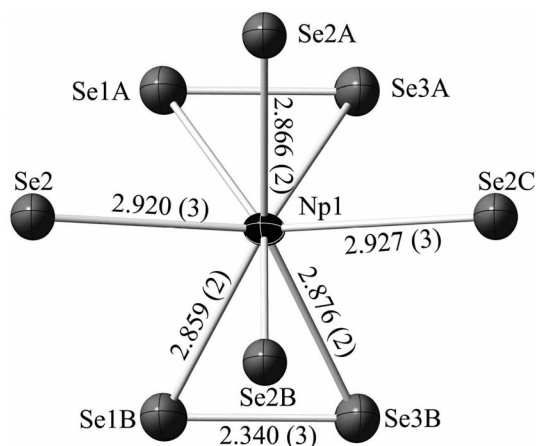
[a] Department of Chemistry
Northwestern University
2145 Sheridan Rd.
Evanston, IL 60208–3113, USA

[b] Chemical Science Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831, USA

Table 1. Summary of crystallographic unit cell determinations of NpSe₃ and USe₃.

| <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å | β /° | Reference | Year | Remarks |
|-------------------|-------------|-------------|------------|-----------|------|--|
| NpSe ₃ | | | | | | |
| 5.64(2) | 4.01(1) | 19.06(7) | 79.6(3) | [5] | 1973 | Similar to early USe ₃ cell (below) |
| 5.63 | 4.03 | 9.43 | 96.9 | [12] | 1980 | Neutron powder 77K |
| 5.63 | 4.03 | 9.57 | 80.5 | [9] | 1982 | X-ray powder |
| 5.592(3) | 4.002(2) | 9.422(5) | 97.40(1) | This work | 2012 | Single crystal 100 K |
| USe ₃ | | | | | | |
| 5.68 | 4.06 | 19.26 | 99.5 | [13] | 1961 | X-ray powder |
| 5.65 | 4.06 | 9.55 | 97.3 | [14] | 1968 | X-ray powder |
| 5.652(2) | 4.056(3) | 10.469(9) | 115.03(6) | [10] | 1984 | Single crystal |
| 5.652(2) | 4.056(3) | 9.564(7) | 97.34(5) | [10] | 1984 | Standard setting |

there is no question that the formal oxidation state of Np in NpSe₃ is +4.

**Figure 1.** The coordination about Np in NpSe₃. The displacement ellipsoids are drawn at the 95% probability level.**Table 2.** Crystal data and structure refinement for NpSe₃.

| | |
|---|---|
| Temperature /K | 100(2) |
| Formula Mass /g·mol ⁻¹ | 947.76 |
| Space Group, <i>Z</i> | <i>P2</i> ₁ / <i>m</i> , 2 |
| Lattice constants /Å | <i>a</i> = 5.592(3) <i>b</i> = 4.002(2) <i>c</i> = 9.422(5) β = 97.40 (1)° |
| Volume /Å ³ | 209.1(2) |
| Density _{calculated} /g·cm ⁻³ | 7.527 |
| Crystal size /mm | 0.216 × 0.071 × 0.037 |
| Diffractometer | Bruker APEX II |
| X-ray radiation, λ /Å | Mo- <i>K</i> _α 0.71073 |
| Monochromator | graphite |
| Absorption coefficient μ /mm ⁻¹ | 50.726 |
| θ range /° | 4.36–26.44 |
| Index range | –6 ≤ <i>h</i> ≤ 7 –5 ≤ <i>k</i> ≤ 4 –11 ≤ <i>l</i> ≤ 11 |
| Independent Reflections | 485 |
| Transmission <i>t</i> _{min} , <i>t</i> _{max} | 0.0464, 0.2910 |
| No. of parameters | 25 |
| <i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²) | 0.0370, 0.0961 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ /e Å ⁻³ | –1.98, 5.34 |

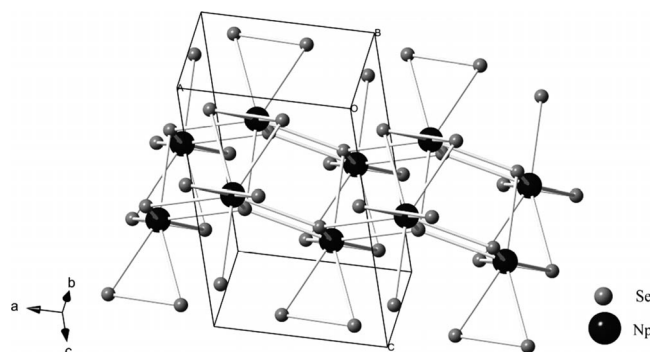
**Figure 2.** Part of the crystal structure of NpSe₃. The black spheres are neptunium; the gray ones are selenium.

Table 3 provides a comparison of interatomic distances in NpSe₃ with those in USe₃. As expected from the actinide contraction of the early actinides, the Np–Se distances are shorter than the U–Se distances by 0.020 to 0.055 Å.

Table 3. Comparison of distances /Å in NpSe₃ and USe₃^{a)}.

| | NpSe ₃ | USe ₃ ^{b)} |
|-------------|-------------------|--------------------------------|
| An–Se(1) 2× | 2.859(2) | 2.914(1) |
| An–Se(2) 2× | 2.866(2) | 2.905(1) |
| An–Se(3) 2× | 2.876(2) | 2.896(1) |
| An–Se(2) | 2.920(3) | 2.952(1) |
| An–Se(2) | 2.927(3) | 2.967(1) |
| Se(1)–Se(3) | 2.340(3) | 2.361(1) |

a) NpSe₃ data were collected at 100 K; USe₃ data were collected at 293 K. b) Ref. [10]. The original numbering of the selenium atoms has been changed; the distances correspond to those distances in Figure 1.

Conclusions

NpSe₃ may be prepared in high yield by the reaction of the elements in a Sb₂Se₃ flux at 1223 K. The compound crystallizes in space group *P2*₁/*m* of the monoclinic system in the TiS₃ structure type. NpSe₃ is isostructural with USe₃. The structure comprises a Np center coordinated by four Se atoms and two Se–Se pairs. The Se–Se distance is 2.340(3) Å, a typical single-bond length. NpSe₃ may be formulated as Np⁴⁺Se^{2–}Se₂^{2–}, the formal oxidation state of Np being +4.

Table 4. Fractional atomic coordinates and anisotropic displacements parameters for NpSe₃.^{a)}

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ |
|------|-------------|----------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Np1 | 0.28326(14) | 0.2500 | 0.15547(9) | 0.0075(4) | 0.0042(4) | 0.0222(5) | 0.000 | 0.0011(3) | 0.000 |
| Se1 | 0.4621(4) | 0.2500 | 0.6685(2) | 0.0097(11) | 0.0100(10) | 0.0241(12) | 0.000 | 0.0011(8) | 0.000 |
| Se2 | 0.7640(4) | 0.2500 | 0.0642(2) | 0.0088(10) | 0.0092(10) | 0.0233(12) | 0.000 | 0.0023(8) | 0.000 |
| Se3 | 0.8783(4) | 0.2500 | 0.6594(2) | 0.0099(11) | 0.0104(10) | 0.0242(12) | 0.000 | 0.0045(8) | 0.000 |

a) All atoms are in Wyckoff site *2e* and have *m* symmetry.

Experimental Section

Caution! ²³⁷Np is a α - and β -emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials. The procedures we use for the synthesis of Np compounds have been described.^[15] Sb (Aldrich, 99.5%) and Se (Cerac, 99.999%) were used as received. Sb₂Se₃ was prepared by the stoichiometric reaction of the elements at 1273 K for 24 h. Brittle ²³⁷Np chunks were crushed and used as provided (ORNL).

Np (17.2 mg, 0.073 mmol), Se (20 mg, 0.253 mmol), and Sb₂Se₃ (100 mg, 0.208 mmol) were loaded into a fused-silica ampule in an Ar-filled glove box and then flame-sealed under vacuum. The reaction mixture was placed in a computer-controlled furnace and heated to 1173 K in 24 h, then to 1223 K in 24 h, kept at 1223 K for 48 h, cooled to 1173 K in 24 h, then cooled to 673 K in 150 h, and finally cooled to 298 K in 24 h. The reaction products included black columnar crystals of Sb₂Se₃ and black columnar single crystals of NpSe₃. A 0.037 × 0.071 × 0.216 mm black column was selected for use in single-crystal X-ray diffraction experiments.

Single crystal X-ray diffraction data for NpSe₃ at 100 K were collected with the use of graphite-monochromatized Mo-*K*_α radiation ($\lambda = 0.71073$ Å) on a Bruker APEX2 diffractometer.^[16,17] The crystal to detector distance was 5.106 cm and 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 30 s per frame. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2.^[16,17] Absorption corrections and incident beam corrections were performed with the use of the program SADABS.^[18] The structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL.^[19] The program STRUCTURE TIDY^[20] was used to standardize the positional parameters. Further details are given in Table 2 and Table 4, and in the cif file, which has been deposited.^[21]

Acknowledgments

This research was supported at Northwestern University by the U.S. Department of Energy, Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division and Division of Materials Sciences and Engineering Grant ER-15522. We thank *Dr. Lynda Soderholm*, Director of the Actinide Facility, Argonne National Laboratory, for providing laboratory facilities for this Np study. We particularly thank *Dr. G. B. Jin* for his assistance.

References

- [1] Z. Yoshida, S. G. Johnson, T. Kimura, J. R. Krsul, in: *The Chemistry of the Actinide and Transactinide Elements*, Third ed. (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer: Dordrecht, **2006**; Vol. 2, pp. 699–812.
- [2] G.-B. Jin, S. Skanthakumar, R. G. Haire, L. Soderholm, J. A. Ibers, *Inorg. Chem.* **2011**, *50*, 1084–1088.
- [3] T. Thévenin, J. Jové, M. Pagès, *Hyperfine Interact.* **1984**, *20*, 173–186.
- [4] J.-P. Marcon, *Commis. Energ. At. [Fr]*, Rapp. **1969**, CEA-R-3919, 1–99.
- [5] D. Damien, N. Damien, J. Jové, J. P. Charvillat, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 649–655.
- [6] D. Damien, *J. Inorg. Nucl. Chem.* **1974**, *36*, 307–308.
- [7] S. Furuse, L. Brattås, A. Kjekshus, *Acta Chem. Scand. Ser. A* **1975**, *29*, 623–631.
- [8] A. Blaise, J. M. Fournier, P. Salmon, A. Wojakowski, in: *5th Int. Conf. Plutonium & Other Actinides* (Eds.: H. Blank, R. Lindner), North-Holland: Amsterdam, **1976**, pp. 635–640.
- [9] T. Thevenin. Ph.D. Dissertation, **1982**.
- [10] A. Ben Salem, A. Meerschaut, J. Rouxel, *C. R. Acad. Sci. Sér. 2* **1984**, *299*, 617–619.
- [11] G. B. Jin, E. S. Choi, R. P. Guertin, J. S. Brooks, C. H. Booth, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2007**, *46*, 9213–9220.
- [12] C. H. de Novion, A. Tabuteau, D. Damien, **1980**, Rapport III, as quoted in Ref. [9].
- [13] P. Khodadad, *Bull. Soc. Chim. Fr.* **1961**, 133–136.
- [14] F. Grønvald, H. Haraldsen, T. Thurmann-Moe, T. Tufte, *J. Inorg. Nucl. Chem.* **1968**, *30*, 2117–2125.
- [15] D. M. Wells, G. B. Jin, S. Skanthakumar, R. G. Haire, L. Soderholm, J. A. Ibers, *Inorg. Chem.* **2009**, *48*, 11513–11517.
- [16] Bruker, *SMART Version 5.054*, Data Collection and *SAINT-Plus Version 6.45a*, Data Processing Software for the SMART System, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, **2003**.
- [17] 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**.
- [18] G. M. Sheldrick. *SADABS*, Department of Structural Chemistry, University of Göttingen, Göttingen, Germany, **2008**.
- [19] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [20] L. M. Gelato, E. Parthé, *J. Appl. Crystallogr.* **1987**, *20*, 139–143.
- [21] The crystallographic file in CIF format for NpSe₃ has been deposited with FIZ Karlsruhe as CSD number 424526. It may be obtained free of charge by contacting FIZ Karlsruhe at +49-724-7808-666 (Fax) or crysdata@fiz-karlsruhe.de.

Received: May 09, 2012
Published Online: August 14, 2012