Black prisms of Np3Q5 (Q = S, Se) have been synthesized by the stoichiometric reactions between Np and Q at 1173 K in a CsCl flux. The structures of these compounds were characterized by single-crystal X-ray diffraction methods. The Np3Q5 compounds are isostructural with U3Q5. The structure of Np3Q5 is constructed from layers of Np₂Q₅ which comprise only two stable phases, NpO₂ and Np₂O₅. The structure of these compounds was characterized by single-crystal X-ray diffraction methods. The space group Pnma with U₃S₅ and U₃Se₅ have antiferromagnetic orderings at 35(1) and 36(1) K, respectively. Above the magnetic ordering temperatures, both Np₂S₅ and Np₂Se₅ behave as typical Curie–Weiss paramagnets. The effective moments obtained from the fit of the magnetic data to a modified Curie–Weiss law over the temperature range 70 to 300 K are 2.7(2) μ₆(Np₂S₅) and 2.9(2) μ₆(Np₂Se₅).

Introduction

Binary actinide chalcogenides An₃Q₈ (An = actinide; Q = S, Se, Te) exist in a variety of crystal structures and chemical compositions with An:Q ratios between 1:1 and 1:5.¹ –³ As a result, they exhibit a wide range of electronic and magnetic properties. Among these, 20 Np₃Q₅ compounds with formulas of NpQ (Q = S, Se, Te), Np₂Q₄ (Q = S, Se, Te), Np₂Q₃ (Q = S, Se, Te), NpQ₂ (Q = S, Te), and NpQ (Q = S, Se, Te) have been identified.² –⁴ Most of these compounds have been characterized only by powder X-ray diffraction analyses, and their physical properties have not been fully studied. It is interesting that binary neptunium chalcogenides exhibit a very rich structural chemistry compared to binary neptunium oxides, which comprise only two stable phases, NpO₂ and Np₂O₅.² This difference arises in part because of the propensity of chalcogens to form Q–Q bonds. In these Np₃Q₅ compounds formal oxidation states of +3 and +4 are found for Np; in contrast aqueous species exhibit stable oxidation states for Np of +4, +5, +6, and, under very alkaline conditions, +7.⁵

The An₃Q₈ (An = U, Np; Q = S, Se) compounds are of particular interest because they are borderline between the metal-like actinide-rich compounds and the semiconducting chalcogen-rich phases. Both charge balance and crystal structures suggest that these compounds contain An³⁺ and An⁴⁺ in a ratio of 2:1, consistent with the interpretation of X-ray photoelectron spectroscopic measurements on comparable U compounds and with²³⁷Np Mössbauer spectroscopic measurements.⁶ ,⁷ ,¹² The chemical formula can thus be written as (An³⁺)₂(An⁴⁺)(Q²⁻)₅. U₃S₅ and U₃Se₅ have been extensively studied,⁶ ,⁷ ,¹¹ ,¹–¹⁶ They crystallize in the space group Pnma with U³⁺ and U⁴⁺ cations occupying the

Wyckoff positions 8d (site symmetry 1) and 4c (site symmetry .m.), respectively. $U_{S_5}$ is a semiconductor and ferromagnet ($T_N = 29 \text{ K}$) that displays a large negative magnetoresistance effect. $U_{S_5}$ is also a semiconductor; it orders ferromagnetically below 24 K. $U_{Te_5}$ adopts a different structure type. In contrast, Np$_3$Q$_5$ (Q = S, Se) have been identified only from powder X-ray diffraction data from which it was deduced that they are isostructural with $U_{S_5}$. Electrical resistivity measurements on a cold-pressed powder pellet have shown that Np$_3$S$_5$ is a semiconductor, whereas Np$_3$Se$_5$ exhibits semimetallic behavior.

There are no reliable magnetic data for Np$_3$Q$_5$, although $^{237}\text{Np}$ Mössbauer measurements at 4.2 K have suggested that the magnetic moment of Np should order at low temperatures.

**Experimental Section**

**Syntheses.** S (Alfa–Aesar, 99.99%), Se (Cerac 99.999%), and CsCl (Strem Chemicals, 99.999%) were used as received. Brittle pieces of high-purity arc-melted $^{237}\text{Np}$ metal (ORNL) were crushed and used in these syntheses.

**Caution!** $^{237}\text{Np}$ and any ingrown daughter products are $\alpha$- and $\beta$-emitting radioisotopes and as such are considered a health risk. Its use requires appropriate infrastructure and personnel trained in its use and safety.

**Additional data** for Np$_3$S$_5$ and Np$_3$Se$_5$ were collected with the use of a Quantum Design SQUID magnetometer on 2.3 mg of Np$_3$S$_5$ and 3.4 mg of Np$_3$Se$_5$, encapsulated to comply with safety regulations. To optimize purity, the samples used for susceptibility measurements were obtained by grinding enough small (~5 $\mu$g) single crystals to provide adequate signal statistics. The signal from the empty sample-holder, which accounted for as much as 90% of the signal at room temperature, was measured separately and subtracted directly from the total magnetic response. Susceptibility data were subsequently corrected for Langevin diamagnetism.

**Magnetic Susceptibility Measurements.** The magnetic susceptibility data were collected with the use of a Quantum Design MPPS 7 SQUID magnetometer on 2.3 mg of Np$_3$S$_5$ and 3.4 mg of Np$_3$Se$_5$, encapsulated to comply with safety regulations. To optimize purity, the samples used for susceptibility measurements were obtained by grinding enough small (~5 $\mu$g) single crystals to provide adequate signal statistics. The signal from the empty sample-holder, which accounted for as much as 90% of the signal at room temperature, was measured separately and subtracted directly from the total magnetic response. Susceptibility data were subsequently corrected for Langevin diamagnetism.

**Field-cooled and zero-field-cooled data showed no significant evidence for simple ferromagnetic ordering down to 5 K.** Variable temperature experiments were carried out between 5 and 320 K, at applied fields of 0.0025, 0.01, 0.05, 0.2, 0.5, and 1 T. These data provided the same results within experimental error, notably after field cycling, thus confirming the sample stability to orientation effects that can possibly arise with powdered samples.

**Results and Discussion**

**Syntheses.** Stoichiometric reactions of Np and Q resulted in 90% yields of Np$_3$Q$_5$ (Q = S, Se) and several NpQ$_x$.
Np$_3$S$_5$ crystals were first obtained from the reaction of Np, Fe, and S with a CsCl flux at 1173 K. They were also found as significant byproducts in other neptunium sulfide reactions, for example, the reactions of Np with P$_2$S$_5$ and S at 973, 1173, and 1248 K, respectively. 27

This indicates that Np$_3$S$_5$ has a high stability. In contrast, similar reactions of U, Fe, S, and CsCl at 1173 K 28 resulted in $\beta$-US$_2$ 29 and US$_3$ 30 as byproducts, both of which contain U$^{4+}$. In fact, they are the most common binary U$_x$S$_y$ compounds found in solid-state reactions that involve uranium and sulfur. Clearly, the sulfide chemistries of Np and U differ significantly.

**Structures.** Our single-crystal structures for Np$_3$S$_5$ and Np$_3$Se$_5$ agree with those deduced from powder studies but are much more precise (Tables 1 and 2). These compounds are isostructural with U$_3$Q$_5$, crystallizing in the space group $Pnma$ (Figure 1). The structure includes two crystallographic unique metal positions, Np(1) at the Wyckoff position 8d (site symmetry $I$) and Np(2) at the Wyckoff position 4c (site symmetry $m$). Each Np(1) cation is connected to eight Q anions in a distorted bicapped trigonal prism whereas the Np(2) cation is surrounded by seven Q anions in a highly distorted 7-octahedron (Figure 2). Np(1)Q$_8$ polyhedra share faces with each other along the $b$ and $c$ axes to form two-dimensional layers (circled in red in Figure 1) and further share Q(2) edges (circled in purple in Figure 1) to form a three-dimensional channel structure. The space inside each channel is filled by one single edge-sharing Np(2)Q$_7$ chain running down the $b$ axis (circled in black in Figure 1). The connectivities within each layer of Np(1)Q$_8$ and single chain of Np(2)Q$_7$ are shown in Figure 2a and Figure 2b, respectively. The condensed packing pattern of these Np(1)Q$_8$ bicapped trigonal prisms is not common. Similar layers of Gd(1)S$_8$ bicapped trigonal prisms occur in the structure of Gd$_3$S$_5$; however, there are no further connect-

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**Table 2.** Selected Interatomic Distances (Å) for Np$_3$S$_5$ and Np$_3$Se$_5$

<table>
<thead>
<tr>
<th>Distance</th>
<th>Np$_3$S$_5$</th>
<th>Np$_3$Se$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(1)–Q(1)</td>
<td>2.8652(9)</td>
<td>2.9922(5)</td>
</tr>
<tr>
<td>Np(1)–Q(1)</td>
<td>2.9000(9)</td>
<td>3.0214(5)</td>
</tr>
<tr>
<td>Np(1)–Q(2)</td>
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<td>3.0295(5)</td>
</tr>
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<td>Np(1)–Q(3)</td>
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<td>3.0617(5)</td>
</tr>
<tr>
<td>Np(1)–Q(3)</td>
<td>2.9489(9)</td>
<td>3.0761(5)</td>
</tr>
<tr>
<td>Np(1)–Q(4)</td>
<td>3.024(1)</td>
<td>3.1322(5)</td>
</tr>
<tr>
<td>Np(2)–Q(1)</td>
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<td>3.0626(5)</td>
</tr>
<tr>
<td>Np(2)–Q(2)</td>
<td>2.926(1)</td>
<td>3.0395(5)</td>
</tr>
<tr>
<td>Np(2)–Q(1) × 2</td>
<td>2.6527(9)</td>
<td>2.7738(5)</td>
</tr>
<tr>
<td>Np(2)–Q(1) × 2</td>
<td>2.7213(9)</td>
<td>2.8415(5)</td>
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<td>2.9770(7)</td>
</tr>
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<td>Np(2)–Q(3)</td>
<td>2.756(1)</td>
<td>2.8895(7)</td>
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<tr>
<td>Np(2)–Q(4)</td>
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<td>2.8964(7)</td>
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<tr>
<td>Np(1)–Np(1)</td>
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<td>4.1660(4)</td>
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<td>Np(1)–Np(2)</td>
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<td>4.3674(3)</td>
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<tr>
<td>Np(2)–Np(2)</td>
<td>4.1681(2)</td>
<td>4.3331(2)</td>
</tr>
</tbody>
</table>

---

**Figure 1.** Structure of Np$_3$S$_5$ and Np$_3$Se$_5$.

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**Figure 2.** Depictions of an individual Np(1)Q$_8$ layer (a) and Np(2)Q$_7$ chain (b) viewed down the $b$ axis.

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The seven-coordinate Np$^{4+}$ cations have Np(2)$-$S distances that range from 2.6527(9) to 2.852(1) Å; these are generally longer than those of 2.681(2) to 2.754(1) Å for the six-coordinate Np$^{4+}$ cations in AMNpS$_3$ ($A = K$, Rb, Cs; $M = Cu$, Ag)$^{19}$ and shorter than those of 2.889(2) and 2.9067(8) Å in the nine-coordinate Np$^{4+}$ cations in NpOS. $^{20}$ Similarly the Np(2)$-$Se distances range from 2.7738(5) to 2.9770(7) Å; these are shorter than those of 3.0055(5) and 3.077(1) Å found for the nine-coordinate Np$^{4+}$ cations in NpOSe.$^{20}$ The eight-coordinate Np$^{3+}$ cations have Np(1)$-$Se distances that range from 2.9922(5) to 3.1522(5) Å; these are longer than those of 2.9330(6) to 3.1419(6) Å for the seven-coordinate Np$^{3+}$ cations in NpCuSe$_2$.$^{34}$

The empirical bond-valence analysis has been widely employed to estimate the formal oxidation states of metal atoms in a given compound. Such analyses depend on the availability of a large number of results for a given bond type. However, there are only a few Np$-$S and even fewer Np$-$Se distances available from single-crystal studies. A value of the necessary bond-valence parameter $R_0$ of 2.57 was obtained from the Np$-$S distances in KCuNpS$_3$, RbCuNpS$_3$, CsCuNpS$_3$, KAgNpS$_3$, and CsAgNpS$_3$; these compounds contain Np$^{4+}$. $^{18}$ If we take into consideration the present Np(1)$^{3+}$-$S$ and Np(2)$^{4+}$-$S$ distances, the new average value of $R_0$ is 2.56 for the six compounds KCuNpS$_3$, RbCuNpS$_3$, CsCuNpS$_3$, KAgNpS$_3$, CsAgNpS$_3$, and Np$_3$S$_5$. With this value of $R_0$ the bond valences of Np(1) and Np(2) are calculated to be 3.03 and 4.45, respectively, in Np$_3$S$_5$. Because there are only three Np$-$Se distances known from single-crystal studies (NpCuSe$_2$ $^{34}$ and the present Np$_3$Se$_5$) it is not possible to perform similar calculations for Np$-$Se distances. Np$-$Q distances from NpOQ$^{20}$ compounds are not included in the current discussion, as they are affected by the Np$-$O interactions. Obviously, more Np$-$Q distances would be needed to optimize the bond-valence parameters for Np$-$Q compounds.

**Magnetism.** As noted above, the structure of the Np$_3$Q$_5$ compounds contains a Np$^{3+}$ cation at Wyckoff position 8d (site symmetry 1) and a Np$^{4+}$ cation at Wyckoff position 4c (site symmetry $m1$). If we assume Russell–Saunders coupling, then Np$^{3+}$, with a 5$f^3$ configuration, is a non-Kramers ion that, under the reduced site symmetry, may have a singlet ground state. In contrast, Np$^{4+}$, with a 5$f^4$ configuration, is a Kramers ion and as such will have a magnetic ground state irrespective of site symmetry.

Representative susceptibilities of Np$_3$S$_5$ and Np$_3$Se$_5$, compared as $\chi$ versus $T$ in Figure 3, exhibit cusps in their susceptibilities at 35(1) and 36(1) K, respectively, evidence suggesting long-range magnetic ordering below those temperatures. With Np$\cdots$Np distances in both structures longer than 4.0 Å, well in excess of the Hill limit, $^{35}$ the observed ordering temperatures are consistent with the presence of localized moments. Previous studies on the magnetic susceptibility of Np$_3$Se$_5$ found no evidence for magnetic ordering down to temperatures as low as 4.2 K.$^{18,36}$ However, note that the published figure in the previous study $^{18}$ does not include data for the temperature range 5 to 30 K, the range over which the cusp is observed in our data. In addition, a previous $^{237}$Np Mössbauer study of Np$_3$S$_5$ included spectra obtained at 77 and 4.2 K. $^{12}$ Both spectra indicated the presence of two distinct Np sites, with the isomer shifts identifying one as Np$^{3+}$ and the other as Np$^{4+}$. The low-temperature spectrum is more complex, showing contributions from both internal electric and magnetic fields, a result consistent with but not proof of long-range magnetic order. Similar magnetic hyperfine fields were found at the two Np sites, indicating that both Np$^{3+}$ and Np$^{4+}$ may be participating in the magnetic ordering in Np$_3$S$_5$. In our magnetic susceptibility data the cusp for Np$_3$S$_5$ is much more pronounced than that for Np$_3$Se$_5$, which may indicate only one sublattice is ordering in the latter material. For comparative interest, Np$_3$Se$_5$, which contains only Np$^{4+}$, orders ferromagnetically at 51 K with a second ordering at 18 K. $^{18}$ In contrast, Np$_3$S$_5$, which contains exclusively Np$^{3+}$, shows no evidence of magnetic splitting in the Mössbauer data obtained at 4.2 K. $^{4}$ We assume the Np$\cdots$Np distances in these compounds are comparable to those in their isostructural uranium analogues.$^{7,37,38}$ The results from the Np compounds are expected because the low symmetries of the Np sites should yield singlet ground states for the Np$^{3+}$ ions and magnetic doublets for the Np$^{4+}$ Kramers ions. On the basis of these expectations, ordering in the Np$_3$Q$_5$ compounds should be largely driven by the Np$^{4+}$ sublattices.

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The magnetic ordering at about 35 K, both Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5} behave as classic paramagnets. With the assumption of non-interacting spins, the data may be fit to a modified Curie–Weiss law:

\[ \chi = C/(T - \theta) + \chi_0 \]

over the temperature range 70 to 300 K, where \( C \) is the Curie constant from which the effective moment is related by \( \mu_{\text{eff}} = (8C)^{1/2} \), \( \theta \) is the Weiss constant, representing either magnetic correlations or low-lying crystal-field states, and \( \chi_0 \) is the temperature-independent paramagnetic term (TIP), a term meant to account for itineracy (Pauli paramagnetism) or the influence of low-lying crystal-field states (van Vleck paramagnetism). The best fits yield the results shown in Table 3.

The effective moment is defined as \( \mu_{\text{eff}} = g(J(J+1))^{1/2} \), where \( J \) is the Russell–Saunders full angular momentum. Np\textsuperscript{3+}, with \( J = 4 \) ground level, has a free-ion moment of 2.68 \( \mu_B \), whereas Np\textsuperscript{4+}, with \( J = 9/2 \) ground level, has a free-ion moment of 3.62 \( \mu_B \). The effective moments measured experimentally are slightly smaller than, or of the same magnitude as the full free-ion moment predicted from Hund’s rules for a 2:1 ratio of Np\textsuperscript{3+}/Np\textsuperscript{4+}. This result confirms the presence of at least some Np\textsuperscript{4+}, because the free-ion moment from Np\textsuperscript{3+} would not be sufficient to explain the observed effective moments. The observation of a full moment in the paramagnetic regime is somewhat surprising for a lower-valent, light actinide 5f ion, given the expected large crystal-field contribution to the term splittings relative to the spin–orbit interaction. Consistent with the form of the Curie–Weiss law expressed in eq 1, the negative Weiss temperatures are consistent with the antiferromagnetic interactions suggested by the cusps in the susceptibilities. The general magnitudes of the TIP contributions to the susceptibilities are also within the range expected for nonmetallic systems. The smaller value of the contribution measured for Np\textsubscript{3}S\textsubscript{5} compared to Np\textsubscript{3}Se\textsubscript{5} results in the offset of the two susceptibility curves (Figure 3). An understanding of the large difference in the \( \chi_0 \) terms is not the result of differences in crystal-field state energies. The larger (softer) selenide ion would be expected to have a larger overlap integral with the Np ions than would the sulfide ion. The implication of this result is the formation of enhanced Np-ligand bonding interactions in the selenide compound.

### Conclusions

The compounds Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5} are unique examples of mixed-valent binary neptunium chalcogenides containing both Np\textsuperscript{3+} and Np\textsuperscript{4+} cations. We have successfully prepared large single crystals of Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5} utilizing a CsCl flux. The structures of these isostructural compounds were redetermined by single-crystal X-ray diffraction methods. The results confirm those from earlier studies on powders but provide more accurate Np–S and Np–Se distances. Magnetic susceptibility measurements for Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5}, conducted on crushed single crystals, indicate that both compounds exhibit evidence for long-range antiferromagnetic orderings at low temperatures. Above the transition temperatures, Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5} behave as typical paramagnets. Their magnetic susceptibilities have been fit to a modified Curie–Weiss law with a larger temperature-independent paramagnetic contribution for the selenide over the sulfide. These results, which indicate that the Np–Se bonding interactions are stronger than are the Np–S interactions, are consistent with previous 23\(^{\text{NP}}\) Mössbauer studies and resistivity measurements on Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5}. Furthermore, the magnetic results for Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5} clarify their magnetic properties and provide some understanding of the interactions between magnetic cations in these compounds.

### Acknowledgment

The 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 and at Argonne National Laboratory by the U.S. Department of Energy, OSES, Chemical Sciences and Engineering Division, under contract DEAC02-06CH11357.

### Supporting Information Available

Crystallographic files in cif format for Np\textsubscript{3}S\textsubscript{5} and Np\textsubscript{3}Se\textsubscript{5}. This material is available free of charge via the Internet at http://pubs.acs.org.