Reinvestigation of the Uranium(3.5+) Rare-Earth Oxysulfides “(UO)2LnS3”  
(Ln = Yb, Y)

Geng Bang Jin, † Eun Sang Choi,‡ and James A. Ibers*†

† Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, and  
‡ Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee,  
Florida 32310

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Dark-red square plates of the previously reported compounds “(UO)2LnS3” (Ln = Yb, Y) have been synthesized by solid-state reactions of UOS and YbS or Y2S3 with Sb2S3 as a flux at 1273 K. The structure of these isotypic compounds was reinvestigated by single-crystal X-ray diffraction methods and an inductively coupled plasma experiment. The actual formula of “(UO)2LnS3” (Ln = Yb, Y) is (U0.5Ln0.5O)2LnS3, that is, ULn2O2S3, which can be charge-balanced with U4+ and Ln3+. The layered structure comprises (ULn)O2S2 square antiprisms alternating with LnS octahedra. U and Ln atoms disorder on the eight-coordinate metal position, but Ln2 atoms occupy the six-coordinate metal position exclusively. UYb2O2S3 is a modified Curie—Weiss paramagnet between 293 and 32 K. Below which part of the paramagnetic moments go through a possible ferromagnetic transition. The band gaps of ULn2O2S3 (Ln = Yb, Y) are around 2 eV.

Introduction

Layered ternary metal oxychalcogenides have been extensively studied because of their electronic and magnetic properties.1 Because of the differences in the oxophilicity and chalcophilicity of the metals, oxides and chalcogenides often form individual layers with distinct electronic properties. A combination of these layers results in interesting physical properties. For example, the LnCuQ compounds (Ln = rare-earth metal; Q = S, Se, Te), consisting of alternating charge-carrying Cu/Q layers and insulating Ln/O layers, are promising transparent p-type conductors.2–5

Compared to other layered metal oxychalcogenides, those containing U have been much less explored. The diffuse nature of 5f electrons of U can lead to diverse electronic and magnetic properties. For example, the UOQ compounds (Q = S, Se) are semiconductors and antiferromagnets that display considerable magnetic anisotropy.6–9 However, uranium oxychalcogenides are very difficult to synthesize because of the high stability of uranium oxides. The compounds denoted as (UO)2LnS3 (Ln = Gd—Lu, Y)10,11 and (UOS)LuS12 are the only reported layered uranium oxychalcogenides besides UOQ (Q = S, Se, Te)8,13–15 because of the high stability of uranium oxides. The structures described as (UO)2ErS311 and (UOS)4LuS12 have been synthesized by a combination of eight or nine S and O atoms, and the Ln atoms are surrounded by six S atoms to form distinct UO and LnS layers. In the crystal structure of (UO)2ErS3, there is only one independent U position and there are no S—S bonds. Charge balance then leads to the formal oxidation state of 3.5+ for U. Similarly, the formal oxidation states

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References

Crystal-Structure Determinations. Single-crystal X-ray diffraction data for \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) and \( \text{U}_4\text{O}_4\text{S}_8 \) were collected with the use of graphite-monochromated Mo Kα radiation (\( \lambda = 0.71073 \, \text{Å} \)) at 100 K on a Bruker Smart-1000 CCD diffractometer.\(^{(10)} \) The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by collecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in \( \omega \) in groups of 606 frames at \( \varphi \) settings of 0°, 90°, 180°, and 270°. The exposure times for \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) and \( \text{U}_4\text{O}_4\text{S}_8 \) were 40 and 50 s frame\(^{-1} \), respectively. The collection of the intensity data was carried out with the program \( \text{SMART} \).\(^{(19)} \) Cell refinement and data reduction were carried out with the use of the program \( \text{APEX2} \).\(^{(20)} \) A Leitz microscope equipped with a calibrated traveling micrometre eyepiece was employed to measure accurately the dimensions of each data crystal. Face-indexed absorption corrections were performed numerically with the use of the program \( \text{XPREP} \).\(^{(21)} \) Then the program \( \text{SADABS} \)\(^{(19)} \) was employed to make incident beam and decay corrections.

The \( \text{SHELX} \) suite of programs was used for all calculations.\(^{(21)} \) Beginning with the model for \( \text{UOS}_2\text{ErS}_3 \), the isotropic refinement of \( \text{UOS}_2\text{YbS}_3 \) proceeded smoothly to an \( R_1 \) index of 0.030. An unusual feature was that the isotropic displacement sphere for U was larger than that for Yb. (This is also true for the earlier structure determination of \( \text{UOS}_2\text{ErS}_3 \).) However, this same model did not refine for \( \text{UOS}_2\text{YS}_3 \). The structure was solved again with the program \( \text{SHELXS} \). It became clear that a successful model could only be found if the scattering density at the U position was reduced significantly. An unrestricted anisotropic model in which U and Y atoms were disordered at the U site refined successfully and led to \( U:Y = 0.5:0.1 \) (Table 1). The restricted refinement \( (U:Y = 0.5:1) \) gave the same result. The unrestricted and restricted refinements for the Yb compound are also shown in Table 1. Whereas the unrestricted refinement is slightly better, we do not consider it to be significantly so.

In all of these refinements, the displacement ellipsoids of atom S2, which is at the origin of the cell, remained positive-definite but were highly prolate. This is also true in the original structure determination of \( \text{UOS}_2\text{ErS}_3 \).\(^{(11)} \) It may be that there is some disorder in the position of atom S2; there is no evidence in any of these structure determinations to support a lower-symmetry space group.

The program \( \text{STRUCTURE TIDY} \)\(^{(22)} \) was used to standardize the positional parameters. Additional experimental details are given in Table 2 and the Supporting Information.

Magnetic Susceptibility Measurements. As noted above, \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) crystals grew together with \( \text{UOS}_2\text{YbS}_3 \) and UOS. Large clusters of \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) crystals were crushed, and small clusters comprising 7.8 mg of \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) crystals were carefully collected and then ground. The X-ray diffraction pattern of the resultant powder confirmed that it was \( \text{U}_2\text{Yb}_2\text{O}_4\text{S}_3 \) contaminated by a small amount of \( \text{UOS}_2\text{YbS}_3 \). Neither UOS nor SbS\(_3\) was detected.

The powder sample was loaded into a polycarbonate capsule holder, which was then placed in a Quantum Design MPMS instrument. Direct-current susceptibility measurements were made from 2 to 300 K under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The contribution of the diamagnetic background of the sample holder was removed using the experimental values from a separate run on an empty capsule. The temperature-independent background term

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Results

Syntheses. UYb$_2$O$_2$S$_3$ and UY$_2$O$_2$S$_3$ were originally prepared at high temperatures ($\geq 1773$ K) through solid-state reactions between UOS and LnS or Ln$_2$S$_3$. In the present study, efforts were made to lower the reaction temperature through the use of various fluxes, including alkali-metal halides, alkali-metal chalcogenides, and Sb$_2$S$_3$. No reactions were detected below 1123 K. Between 1123 and 1273 K, alkali-metal halides and chalcogenides were observed to etch the carbon-coated fused-silica tubes and react with the rare-earth sulfides to form ternary compounds. For example, the reaction of UOS and YbS with Sb$_2$S$_3$ at 1273 K produced K$_3$Yb$_7$S$_{12}$, which was obtained in about 5% yield.

Two different products were formed from the reaction of UOS and Y$_2$S$_3$ with Sb$_2$S$_3$ as a flux. One was the desired product UYb$_2$O$_2$S$_3$, which was obtained in about 5% yield. The other, which was obtained in about 10% yield, was the new compound UY$_4$O$_2$S$_5$. Most of the UY$_2$O$_2$S$_3$ crystals were mixed with UOS or Y$_2$S$_3$. Attempts to collect enough clean crystals for ICP and magnetic measurements failed.

Numerous variations in the starting materials and stoichiometries did not improve the yields of UYb$_2$O$_2$S$_3$ or UY$_2$O$_2$S$_3$ crystals.

Structures. The structure of the isostructural compounds UYb$_2$O$_2$S$_3$ and UY$_2$O$_2$S$_3$ is shown in Figure 1. It is constructed from alternating layers of double (U/Ln)-O$_2$S$_4$ layers and single edge-sharing LnS$_6$ octahedral layers. The U and Ln(1) atoms, which disorder on a site of symmetry 4mm, are connected to four O and four S atoms in a square antiprism. The Ln(2) atoms, located on a site of symmetry 4/mmm, are connected to six S atoms. Within the double (U/Ln)O$_2$S$_4$ layers, each U/LnO$_2$S$_4$ square antiprism shares one O and two S 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.

The structure of ULn$_2$O$_2$S$_3$ (Ln = Yb, Y) and that characterized as “(UOS)$_4$LuS$_6$” are related to that of UOS$_4$LuS$_6$ as shown in Figure 2. The U atoms in UOS are surrounded by four O and five S atoms in a monocapped square antiprism structure. The structure of ULn$_2$O$_2$S$_3$ (Ln = Yb, Y) can be obtained by removing all of the capping U–S bonds in the UOS structure and inserting LnS$_6$ octahedral layers. The structure of (UOS)$_4$LuS$_6$ can be obtained by removing half of the capping U–S bonds in the UOS structure and inserting LnS$_6$ octahedral layers. Therefore, half of the U atoms in the (UOS)$_4$LuS$_6$ structure are still bonded to four O and five S atoms and half of them are bonded to four O and four S atoms.

Selected interatomic distances for UYb$_2$O$_2$S$_3$ and UY$_2$O$_2$S$_3$ are listed in Table 3. The U/Ln(1) disorder does not allow detailed comparisons to be made. However, the Ln(2)–S distances clearly show the effect of the lanthanide contraction. The Yb(2)–S distances of 2.631(5) and 2.670(2) Å are consistent with those of 2.660–2.788 Å in Yb$_2$S$_3$.24 and the Y–S distances of 2.676(2) and 2.631(5) Å are consistent with those of 2.670–2.686 Å in Yb$_2$S$_3$.


Table 1. Least-Squares Refinements for ULn$_2$O$_2$S$_3$

<table>
<thead>
<tr>
<th>compound</th>
<th>$R(F)$</th>
<th>$R_w(F^2)$</th>
<th>U–Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>UYb$_2$O$_2$S$_3$</td>
<td>0.0256</td>
<td>0.076</td>
<td>0.51 (restricted)</td>
</tr>
<tr>
<td>UY$_2$O$_2$S$_3$</td>
<td>0.0238</td>
<td>0.0662</td>
<td>0.83(4):1 (unrestricted)</td>
</tr>
</tbody>
</table>

$\chi$ and $w$ subtracted as a background.

FT spectrophotometer. The absorbances of oil and glass were measured on the UYb$_2$O$_2$S$_3$ sample.

Several red square plates of UYb$_2$O$_2$S$_3$ and UY$_2$O$_2$S$_3$ were selected and placed on a glass slide. Optical absorption data were collected for each compound from 380 nm (3.27 eV) to 900 nm (1.38 eV) at 293 K with a Hitachi U6000 microscope.

The absorbances of oil and glass were measured on the UYb$_2$O$_2$S$_3$ sample.

Table 2. Crystal Data and Structure Refinements for ULn$_2$O$_2$S$_3$

<table>
<thead>
<tr>
<th>compound</th>
<th>UYb$_2$O$_2$S$_3$</th>
<th>UY$_2$O$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fw</td>
<td>712.29</td>
<td>544.03</td>
</tr>
<tr>
<td>$\alpha$ (Å)</td>
<td>3.7762(9)</td>
<td>3.8077(9)</td>
</tr>
<tr>
<td>$\epsilon$ (Å)</td>
<td>20.691(5)</td>
<td>20.889(5)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>295.0(1)</td>
<td>302.9(1)</td>
</tr>
<tr>
<td>$\rho$ (g cm$^{-3}$)</td>
<td>8.018</td>
<td>5.966</td>
</tr>
<tr>
<td>$\mu$ (cm$^{-1}$)</td>
<td>597.61</td>
<td>465.95</td>
</tr>
</tbody>
</table>

$\chi$ and $w$ subtracted as a background.

Figure 1. Two-dimensional-layered structure of ULn$_2$O$_2$S$_3$ (Ln = Yb, Y).
Figure 2. Views of the structures of (a) UOS, (b) ULn$_2$O$_2$S$_3$ (Ln = Yb, Y), and (c) (UOS)$_4$LuS down the $b$ axis.

Figure 3. ZFC magnetic susceptibility $\chi$ vs $T$ for UYb$_2$O$_2$S$_3$ under $H_{app} = 0.1$ T. The line indicates a modified Curie–Weiss fitting for $\chi^{-1}$ for $100 < T < 300$ K. The inset shows the inverse susceptibility at low temperatures with a linear fitting below 8 K. The line in the $\chi$ plot represents a hypothetical susceptibility of UYb$_2$S$_3$O$_3$ without $\epsilon$-Yb$_2$S$_3$ and UOS impurities.

from the original data of contributions of 10 wt % $\epsilon$-Yb$_2$S$_3$\textsuperscript{29} and 5 wt % UOS.\textsuperscript{28} Even though these quantities of impurities are overestimated, the two $\chi(T)$ curves are practically identical. This suggests that the $1/T$ dependence is an inherent property of UYb$_2$O$_2$S$_3$.

Nevertheless, the presence of two different magnetic ions (U$^{4+}$ and Yb$^{3+}$) in UYb$_2$O$_2$S$_3$ makes it difficult to separate their contributions to the magnetic moment. For instance, a full contribution of each of the free ions (3.6 $\mu_B$ from U$^{4+}$ and 4.9 $\mu_B$ from Yb$^{3+}$)\textsuperscript{30} gives $\langle \mu \rangle = [\mu(U^{4+}) + 2\mu(Yb^{3+})]^{1/2} = 7.3 \mu_B/\text{fu}$, which is much larger than the observed value [5.6(2) $\mu_B/\text{fu}$]. In fact, the values of the effective moments in rare-earth and actinide compounds are often smaller than those for the free ion because of the crystalline electric field (CEF) effect. Usually 5f electrons

Table 3. Selected Interatomic Distances (Å) for ULn$_2$O$_2$S$_3$\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th>ULn$_2$O$_2$S$_3$</th>
<th>UY$_2$O$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(1)/Ln(1)–O(1)</td>
<td>2.28(2)</td>
<td>2.29(1)</td>
</tr>
<tr>
<td>U(1)/Ln(1)–S(1)</td>
<td>2.96(2)</td>
<td>2.98(1)</td>
</tr>
<tr>
<td>Ln(2)–S(1)</td>
<td>2.63(5)</td>
<td>2.67(6)</td>
</tr>
<tr>
<td>Ln(2)–S(2)</td>
<td>2.6925(6)</td>
<td>2.6925(6)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}U(1)/Ln(1)–O and U(1)/Ln(1)–S interatomic distances are truncated to two decimal places because of the U/Ln(1) disorder. The difference between the effective ionic radii of U$^{4+}$ and Yb$^{3+}$ is 0.02 Å and that between U$^{4+}$ and Y$^{3+}$ is 0.01 Å.\textsuperscript{39} \textsuperscript{b}Restricted refinement.

2.6925(6) Å are in the range of those of 2.626(3) Å for $\delta$-Y$_2$S$_3$.\textsuperscript{25}

Although bond-valence sums\textsuperscript{26} are strictly empirical, they are often thought to provide an indication of formal oxidation states for various cations in solid-state compounds. In the present instance, the sums are as follows: for UYb$_2$O$_2$S$_3$, U(1) = 3.90, Yb(1) = 2.76, and Yb(2) = 3.25; for UY$_2$O$_2$S$_3$, U(1) = 3.76, Y(1) = 2.93, and Y(2) = 3.44.

Magnetic Susceptibility of UYb$_2$O$_2$S$_3$. Figure 3 shows the temperature dependence of the ZFC susceptibility $\chi$ and $1/\chi$ for UYb$_2$O$_2$S$_3$ at 0.1 T applied field. At both high temperatures ($100 < T < 300$ K) and low temperatures ($1.8 < T < 8$ K), the susceptibility of UYb$_2$O$_2$S$_3$ shows a modified Curie–Weiss temperature dependence ($\propto 1/T$). In the intermediate temperature range, the $1/T$ dependence starts to show deviation from the high-temperature side and a sudden increase of $\chi$ is observed below 32 K.

Before doing further analysis, we examined contributions from the possible magnetic impurities $\epsilon$-Yb$_2$S$_3$ (detected from powder X-ray diffraction measurements) and UOS (not so detected). Both $\epsilon$-Yb$_2$S$_3$\textsuperscript{27} and UOS\textsuperscript{28} are known to show a paramagnetic-to-antiferromagnetic phase transition at 7 and 55 K respectively. The dotted line of Figure 3 is $\chi(T)$ of UYb$_2$O$_2$S$_3$ after subtraction

\textsuperscript{(29)} $\chi$ vs $T$ of $\epsilon$-Yb$_2$S$_3$ measured here shows a paramagnetic-to-antiferromagnetic transition at 5 K.
in actinides are more subject to the CEF because they tend to be less localized than the 4f electrons in rare earths. When the CEF lifts the degeneracy of the ground state of a Hund multiplet, the spin population at higher CEF levels will be decreased at finite temperatures, resulting in a reduced effective moment. The Curie-type susceptibility ($\chi \sim 1/T$) can be observed even under the CEF effect. When the temperature is much smaller than the CEF splitting, the effective moment will be reduced. When it is much larger, the free-ion value will apply.

In $\text{UYb}_2\text{O}_2\text{S}_3$, the CEF will play different roles for U$^{4+}$ and Yb$^{3+}$ because U$^{4+}$ ($5f^5, {}^4\text{H}_3$) is a non-Kramers ion with a less symmetric CEF environment and Yb$^{3+}$ ($4f^{13}, {}^2\text{F}_{7/2}$) is a Kramers ion under a rather symmetric (octahedral Yb$\text{S}_6$) CEF field. The observed $1/T$ dependence of $\chi$ at low temperatures should be mostly from the Kramers doublet of Yb$^{3+}$, with the excited CEF level larger than the thermal energy. If we exploit the $1/T$ dependence by assuming a weak temperature dependence of $\chi$ of U$^{4+}$ at low temperatures, then the effective moment of Yb$^{3+}$ is about $3.0 \mu_B$. If we use this value for the $\chi \sim 1/T$ dependence at high temperatures, we obtain $3.7 \mu_B$ for the effective moment of U$^{4+}$, which is very close to the free-ion value. However, we note that this is valid only with several conditions being satisfied: (1) $\chi$ of U$^{4+}$ is weakly temperature-dependent from nonmagnetic CEF singlets at low temperatures; (2) the Yb$^{3+}$ ground-state doublet is the only accessible energy level up to $300 \text{ K}$; (3) U$^{4+}$ CEF splitting is smaller than $\sim 100 \text{ K}$. Experiments involving other physical measurements would be needed to clarify the issues.

Now we turn our attention to the intermediate temperature range. The anomaly around $32 \text{ K}$ likely arises from a ferromagnetic transition, as suggested by differences between ZFC and FC susceptibilities (Figure 4). The broad maximum of ZFC susceptibility between 13 and $20 \text{ K}$ can be attributed to randomly oriented ferromagnetic domains. The magnetization data measured at $20 \text{ K}$ (Figure 4 inset), which show the hysteresis and saturation of magnetization after subtraction of the paramagnetic background as estimated from the high-field region, are also typical of ferromagnetism. However, the saturation moment of $0.01 \mu_B/\text{U}$ (or equivalently $0.005 \mu_B/\text{Yb}$) is much lower by 2 orders of magnitude than those of typical ferromagnetic U compounds. Very low saturation moments in actinide compounds are not unprecedented, but they have been mostly found in U–d metal intermetallics. The models proposed for those compounds are not applicable to the present rare-earth compounds. Another possible cause for the anomaly around $32 \text{ K}$ is the presence of ferromagnetic impurities that were below the level that could be detected by x-ray diffraction measurements. Impurity phases that could conceivably be present include ferromagnetic US ($T_c = 180 \text{ K}$),$^{32}$ ferromagnetic U$_3$S$_5$($T_c = 29 \text{ K}$),$^{33}$ and the antiferromagnetic phases UOS ($T_N = 55 \text{ K}$),$^{35}$ U$_2$S$_5$ ($T_N = 50 \text{ K}$),$^{34}$ UO$_2$ ($T_I = 50 \text{ K}$),$^{35}$ Yb$_2$O$_3$ ($T_N = 2.4 \text{ K}$),$^{36}$ and Yb$_2$S$_5$O ($T_N = 2.65 \text{ K}$).$^{37}$ Among these, the only possible impurity responsible for the anomaly would be U$_3$S$_5$. From the synthetic conditions, we consider U$_3$S$_5$ to be extremely unlikely.

Even with this uncertainty, it is useful to note the difference of the magnetic structure of UYb$_2$O$_2$S$_3$ from that of UOS, which is an antiferromagnet, with the U moment being aligned along the c axis in a type 1A stacking order (+ + – –). In UOS, U atoms within each UO$_4$S$_4$ layer couple antiferromagnetically with other U atoms from adjacent layers through U–O–U interactions. These antiferromagnetic double UOS layers stack along the c axis, and this leads to long-range antiferromagnetic ordering. To obtain the structure of UYb$_2$O$_2$S$_3$, a YbS$_6$ octahedral layer is inserted between two double UOS layers and half of the U atoms in the UOS layers are replaced by Yb atoms. The U–U interactions between the double layers will thereby be weakened by the increased interlayer distance. Both U–U direct exchange and U–O–U superexchange within the double layer will be weakened by dilution. U–U couplings will become less important compared to possible Yb–U or Yb–Yb interactions that we speculate may give rise to this different magnetic behavior. A further understanding of the magnetic properties of this material requires measurements on a compound with the same structure but with nonmagnetic rare-earth atoms, namely, UY$_2$O$_3$S$_3$. Unfortunately, we were unable to synthesize the necessary quantity of this material.

**Optical Properties.** Single-crystal absorption data, collected on several samples of UYb$_2$O$_2$S$_3$ and UY$_2$O$_3$S$_3$, are reproducible. Typical spectra of ULn$_2$O$_3$S$_3$ are plotted together with that of UY$_4$O$_5$S$_8$ in Figure 5. The fine structures near the absorption edge that arise from U f–f transitions are very similar in all three compounds. This is not surprising because the coordination environments of the U atoms are similar. Because of these f–f transitions, we can only estimate the band gaps to be around 2 eV, consistent with the dark-red colors of these compounds.

The decrease of the intensity for the transition around 1.75 eV in the order UY$_2$O$_2$S$_3$ to UYb$_2$O$_2$S$_3$ to UY$_4$O$_3$S$_5$ most probably results from the decrease of the U mass concentration.

**Formal Oxidation States.** One goal of the present work was to clarify the apparent oxidation state of U$^{3.5+}$ in compounds that had been characterized previously as \((\text{UO})_2\text{-LnS}_3\) (Ln = Gd−Lu, Y),\textsuperscript{10} on the basis of a crystal structure determination of \((\text{UO})_2\text{ErS}_3\).\textsuperscript{11} We were unable to solve the crystal structure of \((\text{UO})_2\text{YS}_3\) starting with the Er model. Rather we discovered that there was U/Y disorder and that the compound is actually UY$_2$O$_2$S$_3$. Because there are no S$^-$S interactions in the structure, charge balance leads to the formal oxidation states U$^4+$ and Y$^3+$. The ionic radii of these two ions differ by only 0.01 Å, so disorder is not surprising.

A similar analysis of the crystal structure of \((\text{UO})_2\text{YbS}_3\) again reveals disorder and leads to an X-ray-derived ratio U:Yb = 0.83(3):1 (Table 1). This refinement is marginally better than one in which U:Yb is restricted to be 0.5:1, but given that the scattering powers of U (atomic number 92) and Yb (atomic number 70) are relatively close, we do not believe the two refinements differ significantly. Moreover, the U:Yb ratio of 0.59(1):1 derived from ICP measurements adds further credence to a formula of UYb$_2$O$_2$S$_3$, in which charge balance is achieved with U$^{4+}$ and Yb$^{3+}$.

Crystals used for the present structure determinations were prepared from UOS and Ln$_2$S$_3$ with Sb$_2$S$_3$ as a flux at 1273 K followed by slow cooling, whereas those used in the structure determination of \((\text{UO})_2\text{ErS}_3\)\textsuperscript{11} were prepared from UOS and ErS at 1770 K and rapid fusion at 2070 K followed by quenching. Are these the same materials structurally, or is it possible that the Er compound did not exhibit U/Er disorder but was indeed the U$^{3.5+}$ compound \((\text{UO})_2\text{ErS}_3\)? For the following reasons, we believe that there was U/Er disorder and that the compound was actually UEr$_2$O$_2$S$_3$: (1) The structure determinations show the same trends in displacement parameters; (2) the higher reaction conditions that generated the Er compound, both the higher temperatures and the quenching, should favor a disordered rather than an ordered structure; (3) reducing some of the U$^{4+}$ to U$^{3+}$ in the original preparation requires the oxidation of S$^-$ or Er$^{2+}$ (if that is the actual oxidation state in the monosulfide). Given the great oxophilicity of U, its reduction in the presence of O$^-$ seems exceedingly unlikely.

The question then arises as to the nature of the U atoms in the compound previously described as \((\text{UOS})_4\text{LuS}\).\textsuperscript{12} From the structure, charge balance is achieved with equal numbers of U atoms in the formal oxidation states of U$^{3.5+}$ and U$^{4+}$. Given the results on the present compounds, it is reasonable to expect that undetected U/Lu disorder is the source of “U$^{3.5+}$”. The effective ionic radius of U$^{4+}$ is 0.03 Å larger than that of Lu$^{3+}$.\textsuperscript{39} U and Lu atoms could disorder on the eight-coordinate metal position with an occupancy of 0.5:0.5. Alternatively, U and Lu atoms could also disorder on both eight- and nine-coordinate metal positions with an average occupancy of 0.75:0.25. In either instance, a new formula, U$_3$Lu$_2$O$_4$S$_5$, may be assigned in which charge balance is achieved with U$^{4+}$ and Lu$^{3+}$. Specifics of the possible disorder in \((\text{UOS})_4\text{LuS}\) must await a redetermination of its structure as well as an ICP analysis.

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**Supporting Information Available:** Crystallographic files in CIF format for UYb$_2$O$_2$S$_3$ and UY$_2$O$_2$S$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 5.** Single-crystal absorption spectra of ULn$_2$O$_2$S$_3$ (Ln = Yb, Y) and UY$_2$O$_2$S$_3$. 