UTa$\textsubscript{2}$O(S$\textsubscript{2}$)$_{3}$Cl$_{6}$: A ribbon structure containing a heterobimetallic 5$d$–5$f$ M$_{3}$ cluster

Daniel M. Wells$^{a}$, George H. Chan$^{a}$, Donald E. Ellis$^{a,b}$, James A. Ibers$^{a,*}$

$^{a}$Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA
$^{b}$Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

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A new solid-state compound containing a heterobimetallic cluster of U and Ta, UTa$\textsubscript{2}$O(S$\textsubscript{2}$)$_{3}$Cl$_{6}$, has been synthesized and its structure has been characterized by single-crystal X-ray diffraction methods. UTa$\textsubscript{2}$O(S$\textsubscript{2}$)$_{3}$Cl$_{6}$ was synthesized from UCl$_{4}$ and Ta$_{1.2}$S$_{2}$ at 883 K. The O is believed to have originated in the Ta$_{1.2}$S$_{2}$ reactant. The compound crystallizes in the space group P1 of the triclinic system. The structure comprises a UTa$_{2}$ unit bridged by μ$_{2}$-S$_{2}$ and μ$_{4}$-O groups. Each Ta atom bonds to two μ$_{2}$-S$_{2}$, the μ$_{3}$-O, and two terminal Cl atoms. Each U atom bonds to two μ$_{2}$-S$_{2}$, the μ$_{3}$-O, and four Cl atoms. The Cl atoms bridge in pairs to neighboring U atoms to form a ribbon structure. The bond distances are normal and are consistent with formal oxidation states of +IV/+V/–II/–I/–I for U/Ta/O/S/Cl, respectively. The optical absorbance spectrum displays characteristic transition peaks near the absorption edge. Density functional theory was used to assign these peaks to transitions between 5$f^{1}$–5d–6f hybrid bands. Density-of-states analysis shows overlap between Ta 5$d$ and U bands, consistent with metal–metal interactions.

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1. Introduction

Trimetallic cluster compounds that contain bridging μ$_{3}$-oxo and dichalcogenido ligands are well established in organometallic chemistry [1–3]. However, none of these compounds contains U. The few trimetallic clusters that contain U involve OCMe$_{3}$ [4], hexadentate Schiff base [5], or multiple μ$_{3}$-I ligands [6]. Several other multimetallic molecular compounds involving U are known where large ligands allow for binding to multiple metals or the U atoms are bridged by multidentate ligands [7–9]. Examples of trinuclear Ta complexes are also rare compared to those involving neighboring Mo or W atoms. Those known Ta complexes contain bridging μ$_{2}$-O [10–12] rather than μ$_{2}$-S$_{2}$ ligands found here and are common for Mo and W. Most of the three-center-heterometallic complexes that have been synthesized contain multiple μ$_{3}$-S ligands [13,14]. Compounds containing both 5$d$-transition metals and 5$f$-actinides and a chalcogen (S, Se, or Te) are also rare [15]. In the U/Ta system there appear to be no examples.

Several years ago we began to investigate the use of UCl$_{4}$ in the high-temperature syntheses of new solid-state uranium transition-metal chalcogenides. Although we have subsequently successfully used UCl$_{4}$ in metathesis reactions [16], initially we explored the types of products that we could obtain with UCl$_{4}$ in the presence of various transition-metal chalcogenides where no metathesis was expected. One such reaction involved TaS$_{2}$: the results of that reaction are described here where we present the crystal structure, optical absorption spectrum, and density functional theory analysis of the compound UTa$_{2}$O(S$_{2}$)$_{3}$Cl$_{6}$ whose crystal structure contains a heterobimetallic cluster.

2. Experimental

2.1. Synthesis

UCl$_{4}$ was prepared by a modification [16] of a literature procedure [17]. TaS$_{2}$ (Johnson Matthey, 99.8%), denoted herein as the old lot, had resided in this laboratory for an unknown number of years. TaS$_{2}$ (Alfa, 99.8%), denoted herein as the new lot, was used as supplied.

A mixture of UCl$_{4}$ (0.105 mmol) and TaS$_{2}$ (old lot, 0.168 mmol) was loaded into a fused-silica tube that was then evacuated and sealed. The tube was heated in a computer-controlled furnace to 373 K in 2 h, heated to 883 K in 99 h, held at 883 K for 24 h, slow cooled at 4.1 K/h to 473 K, and then slow cooled at 4.9 K/h to 293 K. The product consisted of small orange needles of what turned out to be UTa$_{2}$O(S$_{2}$)$_{3}$Cl$_{6}$ in approximately 40% yield. Even though the yield was relatively high, almost all of these air-sensitive crystals were imbedded in a dark brown residual powder. Analysis by powder X-ray diffraction and EDS methods indicated that the byproducts were unreacted UCl$_{4}$ and TaS$_{2}$.
2.2. Structure determination

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda=0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [18]. The crystal-to-detector distance was 5,023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. 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 15 s/frame. The collection of the intensity data was carried out with the program SMART [18]. Cell refinement and data reduction were carried out with the use of the program APEX2 [19]. A Leitz microscope equipped with a calibrated traveling micrometer eyepiece was employed to measure accurately the crystal dimensions. Face-indexed absorption, incident beam, and decay corrections were performed numerically 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 [20]. After the U, Ta, S, and Cl atoms had been located and their positions refined, there remained a residual peak in the difference electron density synthesis that was located about 0.6 Å below the $U\overline{T}a_2$ plane. When this peak was assigned to O and then the O atom was included in the refinements, reasonable displacement parameters for $O$ and $T$ were assigned. The reaction tube was not etched. Therefore, the density synthesis that was located about 0.6 Å below the $U\overline{T}a_2$ plane. After the U, Ta, S, and Cl atoms had been located and their positions refined, there remained a residual peak in the difference electron density synthesis that was located about 0.6 Å below the $U\overline{T}a_2$ plane. When this peak was assigned to O and then the O atom was included in the refinements, reasonable displacement parameters for $O$ and $T$ were assigned.

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lowest energy positions before SOC and an onsite Coulomb correction were applied. Because the magnetic properties of UTa$_2$O(S$_2$)$_3$Cl$_6$ are unknown and the unit cell contains two U atoms, both the antiferromagnetic and ferromagnetic structures were relaxed and the final energies were compared. An onsite Coulomb correction was not used at this point because $U_{\text{eff}}$ would change depending upon magnetic polarization. Hence, comparisons between calculations with different values of $U_{\text{eff}}$ would be meaningless. Charge balance in the structure suggested tetra-valent U ($5f^6$) and nonmagnetic pentavalent Ta ($5d^6$); however, magnetic moments on the Ta centers, though initially set to 0, were not constrained.

For analysis purposes charge density within the cell was divided into atomic spheres of Wigner–Seitz radii, $R_{\text{WS}}$. These were initially set to the standard radii [32] and then increased to fill the unit-cell volume. Final values of $R_{\text{WS}}$ were 1.35, 0.90, 1.50, 1.80, and 2.00 Å for U, Ta, O, S, and Cl, respectively. Even though the Bader topological method [33] has been used with success in some systems, we have found that it does not predict oxidation states in others [34]. Often there is some covalent bonding around U(IV) centers; as a result the Bader method finds electron-density-zero-flux surfaces between the bonded atoms and very little charge transfer. Therefore, only the $R_{\text{WS}}$ method was applied here. Calculated oxidation states here are defined as the PAW valence minus the final relaxed $R_{\text{WS}}$ charge.

3. Results and discussion

3.1. Synthesis

Air-sensitive orange crystals of UTa$_2$O(S$_2$)$_3$Cl$_6$ were synthesized in approximately 40% yield from the reaction of UCl$_4$ with TaS$_2$ (old lot) in a 1:1.6 molar ratio. Almost all of these crystals were imbedded in a brown residual mass. Only a few that were large enough for a single-crystal X-ray diffraction study could be dislodged.

3.2. The source of oxygen in UTa$_2$O(S$_2$)$_3$Cl$_6$?

The reaction of UCl$_4$ with TaS$_2$ cannot lead to the oxygen-containing compound shown in Fig. 1. The assignment of a $\mu_2$–O atom to the electron density at that site is based on the high oxophilicity of U, the reasonable U–O and Ta–O bond distances that ensued, the known $M_2$($\mu_2$–O)($S_2$)$_3$$^-_2$ type clusters, and the reasonable displacement parameters.

The synthesis of UTa$_2$O(S$_2$)$_3$Cl$_6$, as described above, is repeatable with the old lot of TaS$_2$. Syntheses with TaS$_2$ (new lot) and other oxygen sources, including UOS, UO$_2$, UO$_3$, and Ta$_2$O$_5$, proved to be unsuccessful. TaS$_2$ (old lot) we characterized by powder diffraction methods as Ta$_{1+y}$S$_2$, although it is possible that there are some other 6s-Ta$_{1+y}$S$_2$ compounds present. The many polymorphs of layered TaS$_2$ differ in Ta:S ratio and Ta coordination environments [35]. Three low-angle peaks were found reasonably close to those corresponding to the 00$^\alpha$ peaks from monoclinic Ta$_2$O$_5$ [30] and orthorhombic Ta$_{7.30}$O$_{11.36}$ [36]; however, the amounts of these O-containing compounds could not be quantified. The new lot of TaS$_2$ was found by powder diffraction methods to contain Ta$_{0.70}$O$_{1.65}$ [37] and 1s-TaS$_2$ [35,38] in an approximately 1:9 ratio. Even though this new lot contains an oxide, its use in the synthesis did not result in UTa$_2$O(S$_2$)$_3$Cl$_6$ as a product. Thus, it seems likely that there is some other oxygen contamination in the old lot of TaS$_2$, or the form of the TaS$_2$ or oxide is critical. Purchase of pure “Ta$_{1.2}$S$_2$” is unlikely because there are many binary Ta/S polymorphs and the synthesis of a single polymorph is reported to be extremely difficult, especially because annealing increases the amount of 6s-TaS$_2$ [35]. All vendors contacted stated their TaS$_2$ products contained a mixture of phases.

A rough calculation suggests a composition Ta$_{1.2}$S$_{1.8}$O$_{0.2}$ would account for the yield of UTa$_2$O(S$_2$)$_3$Cl$_6$. However, there are no known Ta$_{1+y}$S$_2$–O$_x$ structures and so the calculation of theoretical powder patterns is not possible.

3.3. Structure

The structure (Fig. 1) comprises UTa$_2$O(S$_2$)$_3$Cl$_6$ clusters. Each cluster is connected to two other clusters through four $\mu_2$–Cl atoms to generate a ribbon that propagates along the $a$-axis. Each cluster (Fig. 2) consists of one U and two Ta atoms bridged by $\mu_2$–S$_2$$^-_2$ disulfide units. In addition the heavy atoms share a central $\mu_3$–O atom to form a triangular cluster. The O atom is located 0.57 Å below the UTa$_2$ plane whereas the S$_2$$^-_2$ units are situated so one S atom is about 0.23 Å below the plane and the other about 1.63 Å above the plane. The S–S single bonds are 2.077(4), 2.081(4), and 2.081(4) Å, reasonably close to the range of S–S bonds found in S$_8$ (2.035(2)–2.060(2) Å) [39]. In addition to four S bonds and one O bond, each Ta atom bonds to two terminal Cl atoms. The terminal Cl atoms are oriented so one is about 0.99 Å above the UTa$_2$ plane whereas the other is about 2.20 Å below the plane. The structure is similar to that of Mo$_2$S$_2$Cl$_6$, but in that structure two Mo atoms of the triangular unit bridge to neighboring moieties and only one of the Mo atoms has terminal Cl atoms [40].

Fig. 1. View down [010] of the structure of UTa$_2$O(S$_2$)$_3$Cl$_6$.

Fig. 2. The UTa$_2$O(S$_2$)$_3$Cl$_6$ cluster with completed coordination sphere around U.
Charge balance may be achieved with the formal oxidation states of +IV for U and +V for Ta.

It is interesting that unintended O contamination is not uncommon and continues to aid in the syntheses of novel solid-state compounds [3,7,41–43].

Selected bond distances and angles may be found in Table 2. The U–Ta interactions of 3.5887(7) and 3.5989(7) Å are reasonable compared to those in U/Ta oxide compounds where they range from 3.468(1) to 3.709(1) Å [44–47]. The Ta–Ta interaction at 3.2977(7) Å is also normal when compared to other Ta₃(μ₃-O) clusters where the distances range from 3.1185(3) to 3.3378(3) Å [11]. The U–U distances are 4.424 and 4.502 Å, well beyond the Hill limit for f-f overlap (about 3.4 Å) [48].

The other bond distances are also normal. For the U atoms the following comparisons can be made to other six- and eight-coordinate tetravalent U compounds: U–O, 2.298(7) Å vs. 2.27(3) Å in the μ₃-O in the U₃(O)(OCMe₃)₁₀ structure [4]; U–S, 2.819(3)–2.929(3) Å vs. 2.846(2) Å in K₀.₉₁U₁.₇₉S₆ [49]; U–Cl, 2.759(3) to 2.805(3) Å vs. 2.644(2) to 2.889(1) Å in the UCl₄ structure [50]. For Ta the following comparisons can be made to other five-, six-, and eight-coordinate pentavalent Ta compounds: Ta–O, 1.979(7) and 2.013(7) Å vs. 2.058(3)–2.148(3) Å in Ta₃(μ₃-O) clusters [11,12]; Ta–S, 2.439(3)–2.570(3) Å vs. 2.540(2) and 2.578(3) in Ta(PS₄)(S₂) [51]; Ta–Cl, 2.291(3)–2.368(3) Å vs. 2.320(1)–2.344(1) for terminal Cl in Ta₂Cl₈(C₆H₁₃Cl₂N₂PSi₂)₂ [52].

3.4. Single-crystal optical measurements

The optical absorbance of UTa₂O(S₂)₃Cl₆ from unpolarized light between 3.10 eV (400 nm) and 1.38 eV (900 nm) is displayed in Fig. 3. Absorbance data obtained with polarized light are similar. Two absorbance peaks at 2.04 and 1.76 eV were observed. The presence of these peaks make accurate determination of the optical band gap difficult, but an optical transition at approximately 2.08 eV was determined from a linear regression analysis. This result is consistent with the orange color of UTa₂O(S₂)₃Cl₆.

3.5. Theoretical geometric, electronic, and magnetic structure

It did not prove to be possible to obtain enough single crystals of UTa₂O(S₂)₃Cl₆ for magnetic measurements. However, an energy
comparison was made within the LSDA+GGA+SOC method between the two possible magnetic structures. The ferromagnetic alignment of U magnetic moments was found to be 65 meV lower in energy than the antiferromagnetic alignment. For this lowest energy structure, the relaxed positions of the bridging Cl atoms moved the largest amount (0.06 Å) with all other atoms moving less than 0.04 Å. The calculated oxidation state can be written as U⁴⁺/Ta⁵⁺/O²⁻/S¹.⁴⁻/Cl⁻. The extra 0.4e⁻ on S is likely the result of slight overlap of the K₂S sphere with spheres around neighboring U and Ta sites. The total magnetic moment M₀ on the U atoms was 1.71μₜ with parallel to the axis of magnetization, [001], predominately from the 5f²⁻ with a small 0.03μₜ contribution from the 6d⁶⁵ electrons. All other atoms had magnetic moments less than 0.02μₜ.

The onsite Coulomb correction U_eff was varied between −0.5 and 1.8 eV and fit to the experimentally determined optical absorption transitions and band gap. A value of 0.40 eV was found. This value had little effect on the U 5f occupancy and only increased the value of M₀ on U to 1.74μₜ with a ratio of orbital and spin components, Mₖ/Mₜ = −0.64. The negative value here is indicative of the antiparallel nature of Mₖ and Mₜ. The U magnetization also had small spin and orbital components of magnetization of approximately 0.2μₜ perpendicular to the magnetic field direction. As the onsite Coulomb potential was only applied to the U 5f-shell the largest effect was the shifting of the 5f band energies described above.

### 3.6. Density of states analysis

The total DOS and partial DOS of each ion calculated with the optimized value of U_eff are plotted in Fig. 4. As occurs in many U compounds [53–56], the states surrounding the Fermi energy E_F are dominated by the U 5f-states with small contributions from the 6d states. The determined 5f²⁻⁴⁶⁵ electrons on U are located in hybridized 5f–6d–6s bands at the top of the valence band from approximately −1.5 to −2.0 eV. These states overlap mainly with S 3p states but there are also small contributions from all the other states, including those of Ta. In this region the U and Ta states form broad bands that have similar features; this suggests some U/Ta overlap and hence U/Ta interaction in the UTa₂O₆S₆Cl₆ cluster. The higher energy region between −2.75 and −6.5 eV comprises predominately O, S, and Cl states.

Although many studies have been conducted on the optical transitions of tetravalent U because of its 5f² configuration [57], none has been carried out on such complex a system as the present one. The two peaks in the band gap are identified as major 5f states, but there are small contributions again from U 6d, S 3p, and Cl 3p states. These f-peaks contain contributions from all Mₖ component f-orbitals; this suggests considerable exchange, spin-orbit, and crystal-field splitting of the states in this asymmetric heteronuclear coordination environment. It may be too simplistic to describe the observed optical transitions as f→f transitions because there is considerable evidence of 6d- and 5f-orbital hybridization and covalent overlap with S and Cl orbitals in both the valence and conduction bands.

### 4. Supporting material

The crystallographic data for UTa₂O₆S₆Cl₆ have been deposited with FIZ Karlsruhe as CSD number 420806. These data maybe 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 10.1016/j.jssc.2009.10.012.