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Formation of a Uranium Trithiocarbonate Complex via the Nucleophilic Addition of a Sulfide-Bridged Uranium Complex to CS_2

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Supporting Information

ABSTRACT: The uranium(IV)/uranium(IV) μ-sulfide complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}S)]$ reacts with CS_2 to form the trithiocarbonate-bridged complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}CS_3)]$. The trithiocarbonate complex can alternatively be formed in low yields from low-valent $[((^{Ad}ArO)_3N)U(DME)]$ through the reductive cleavage of CS_2.

Reductive cleavage of CO_2 and CS_2 to form carbonates and trithiocarbonates has been well-documented for transition-metal complexes.[1−7] With respect to *f*-element coordination chemistry, however, there are only three reports of carbonate formation from reductive splitting of CO_2[8−10] and, to the best of our knowledge, no records of trithiocarbonate formation from reductive splitting of CS_2. For the most part, the mechanisms and intermediates of carbonate formation remain unclear. A couple of pathways have been proposed in the transformation of CO_2 to CO_3^{2-}. One involves the reductive cleavage of CO_2 to form oxo complexes with concomitant evolution of CO, followed by the addition of 1 equiv of CO_2.[10] Another route involves transformation of the initially formed reductive coupling product, oxalate, with subsequent elimination of CO.[10] As for trithiocarbonate formation from disproportionation of CS_2, a mechanism has not been proposed.

Recently, we reported the formation of a carbonate-bridged uranium complex through the reductive cleavage of CO_2 by the highly reactive uranium(III) complex $[((^{Ad}ArO)_3N)U(DME)]$ (**1**) and verified that the reaction proceeds via the oxo-bridged intermediate $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}O)]$ (**5**).[8] Oxo-bridged complexes of the lanthanide and actinide metals are often very stable compounds and do not exhibit further reactivity. Compared to such an inert complex, $[\{((^{t\text{-}Bu}ArO)_3tacn)U\}_2(\mu\text{-}O)]$,[11] the surprisingly high reactivity of **5** is attributed to the chelating ligand's less encumbering and flexible nature, which allows substrate access to the highly nucleophilic oxygen. From these observations, one would surmise that **1** would react similarly with CS_2. However, the reaction of **1** with CS_2 yields predominantly the tetrathiooxalate reductive coupling product $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**4**),[12] with the trithiocarbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}CS_3)]$ (**3-DME**) forming as a byproduct in only 20% yield. Alternatively, the trithiocarbonate complex **3-DME** can be synthesized analytically pure from the reaction of $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}S)]$ (**2**) with CS_2. The possible formation pathways of this complex from **1** and CS_2 will be rationalized via density functional theory (DFT) studies.

Herein, we report the synthesis and characterization of the only example of a trithiocarbonate complex containing an *f* element.

The trivalent complex **1** engages in one- and two-electron reduction of CS_2, giving rise to two different products (Scheme 1). The purple precipitate was characterized as the tetrathiooxalate complex **4**[12] and forms in approximately 80% yield. The mother liquor of this reaction contains the orange trithiocarbonate complex **3-DME** in 20% yield and was identified through ^1H NMR spectroscopy. Alternatively, the deep-red-orange trithiocarbonate complex **3-DME** can be synthesized in excellent yields directly from the nucleophilic addition of CS_2 to the sulfide-bridged complex **2**.[13] From this reaction, a red-orange solid was isolated in 89% yield and characterized as the uranium trithiocarbonate complex **3-DME** (Scheme 2).

Single crystals of **3-DME** suitable for X-ray diffraction (XRD) studies were obtained by allowing a concentrated solution of 1,2-dimethoxyethane (DME) to stand at room temperature. The molecular structure reveals the dianionic trithiocarbonate ligand bound in a $\mu\text{-}\kappa^2(S,S')\text{:}\kappa^2(S,S'')$ fashion to the two U(IV) centers (Figure 1). This binding mode is in contrast to the uranium carbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1{:}\kappa^2\text{-}CO_3)]$, which features the CO_3^{2-} ligand bound in a $\mu\text{-}\eta^1(O)\text{:}\kappa^2(O',O'')$ fashion (Figure 2). The U1−O_{avg} and U2−O_{avg} bond distances of 2.147 and 2.133 Å remain unaltered from those of the bridging sulfide complex **2**. Likewise, the U1−N1 and U2−N2 distances of 2.587(3) and 2.625(3) Å are as expected. The U1−S1 and U2−S1 distances [3.096(2) and 3.130(2) Å] are significantly longer than the U1−S2 and U2−S3 distances [2.872(2) and 2.868(2) Å]. The C−S bond lengths of 1.724(4), 1.707(4), and 1.710(4) Å are nearly equivalent, suggesting that there is complete delocalization of electrons over the $\mu\text{-}CS_3^{2-}$ unit.

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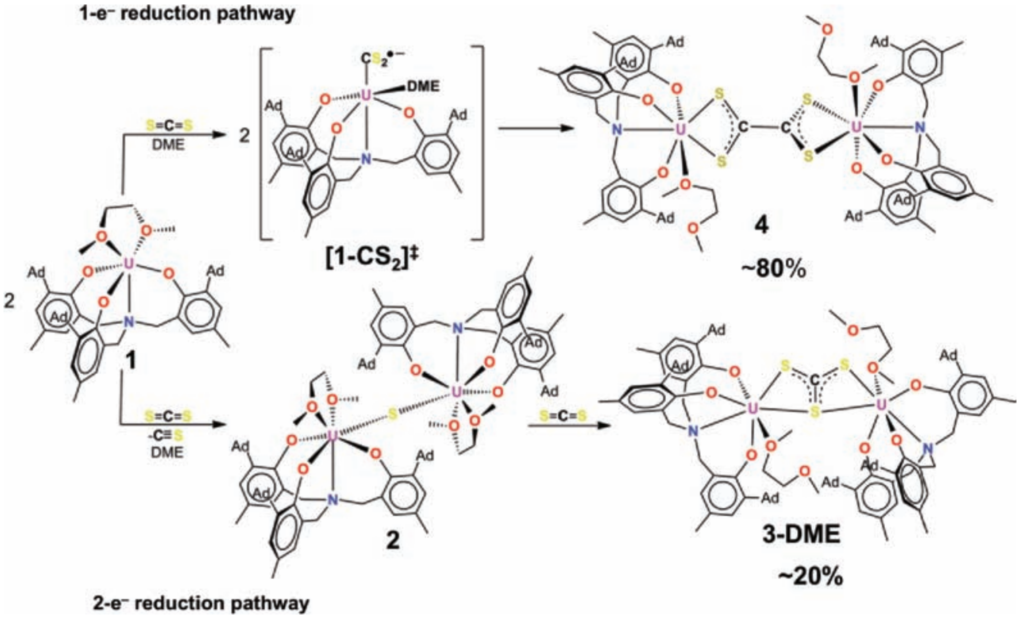
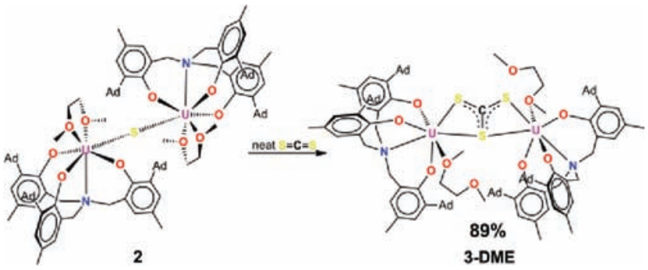
Scheme 1. Formation of the Uranium Trithiocarbonate Complex 3-DME from the Reductive Cleavage of CS_2 in Low Yields (20% Yield, Bottom) and the Major Product, the Tetrathiooxalate Complex 4[12] (80% Yield, Top), Presumably Formed through a U(IV) radical anionic $CS_2^{\bullet -}$ Intermediate Complex $[1\text{-}CS_2]^{\ddagger}$



Scheme 2. Formation of the Uranium Trithiocarbonate Complex 3-DME through the Nucleophilic Addition of the Uranium Bridging Sulfide Complex 2 to CS_2



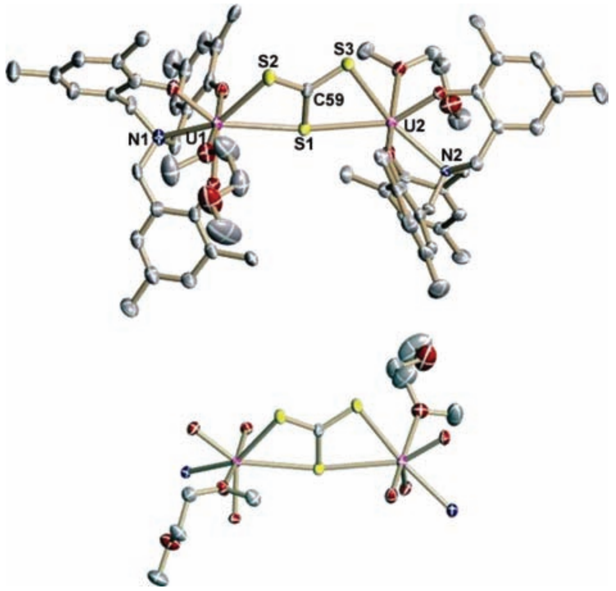


Figure 1. Molecular structure of the uranium trithiocarbonate complex **3-DME** (top) and core (bottom). Hydrogen and adamantyl groups have been omitted for clarity. Thermal ellipsoids are at 50% probability level.

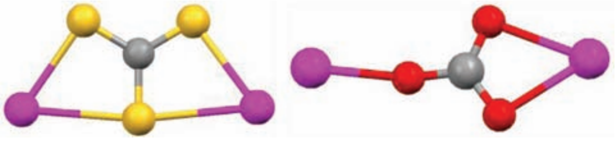


Figure 2. $\mu\text{-}\kappa^2(S,S')\text{:}\kappa^2(S,S'')$ coordination mode of the trithiocarbonate complex **3-DME** (left) and the $\mu\text{-}\eta^1(O)\text{:}\kappa^2(O',O'')$ coordination mode of the carbonate complex $[\{((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}\}_2(\mu\text{-}\eta^1\text{:}\kappa^2\text{-}\mathrm{CO}_3)]$[8] (right).

The variable-temperature SQUID magnetization data are characteristic of U(IV) centers and also very similar to those of the uranium carbonate complex $[\{((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}\}_2(\mu\text{-}\eta^1\text{:}\kappa^2\text{-}\mathrm{CO}_3)]$,[8] where magnetic moments of 3.49 μ_B at 300 K and 0.40 μ_B at 2 K are observed (see the Supporting Information). Overall, the magnetization data support tetravalent uranium centers for complex **3-DME**.

The preference of **1** to undergo disproportionation of CO_2 over CS_2 may be explained by examining the relative proclivity at which the uranium oxo-bridged complex versus the uranium sulfide-bridged complex (**2**) is formed. Hence, DFT studies were performed on the uranium oxo-bridged complex and **2**. The reaction profiles leading to the oxo-bridged uranium complex and **2** are shown in Figure 3. The formation of intermediate species **A**, a uranium(IV)/uranium(IV) complex bridged by a CS_2^{2-} ligand, $[\{U\}_2(\mu\text{-}CS_2^{2-})]$, is exergonic by 17.3 kcal/mol, while formation of the analogous intermediate **C**, $[\{U\}_2(\mu\text{-}CO_2^{2-})]$, is exergonic by 22.8 kcal/mol. The transition state species **B** and **D** represent the C−S and C−O bond-breaking processes, with optimized structures of $[(CS)U(\mu\text{-}S^{2-})U]^{\ddagger}$ and $[(CO)U(\mu\text{-}O^{2-})U]^{\ddagger}$, respectively. Transition states **B** and **D** have activation barriers of 24.4 and 22.3 kcal/mol, respectively. While the formation of oxo-bridged species **5** is exergonic (31.6 kcal/mol), the generation of sulfide-bridged species **2** is slightly endergonic (2.6 kcal/mol). The DFT studies clearly reveal that the formation of CS is not as favorable as that of CO. Carbon

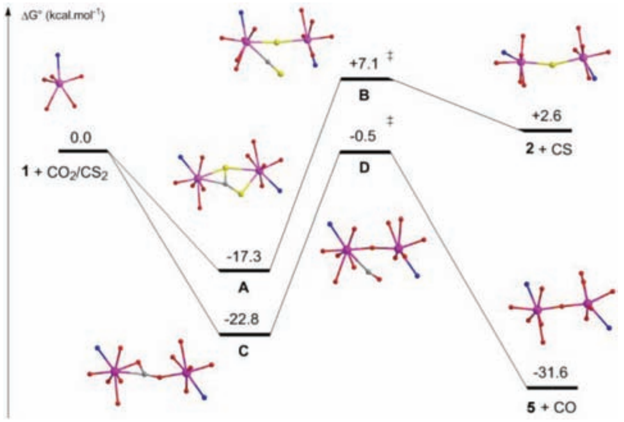


Figure 3. Reaction profiles for the formation of **2** and **5**.

monosulfide is known to be very unstable;[14] however, there have been instances where CS was trapped in situ during reductive disproportionation processes of CS_2.[3,5] The driving force for formation of the bridged complex is clearly the large energy gain from the formation of a very stable CO molecule. This driving force is not as strong in disproportionation reactions with CS_2, and hence only 20% of the uranium trithiocarbonate product **3-DME** is observed. An additional contribution to the preference of carbonate generation may also be the formation of two U–O bonds over two U–S bonds. Although, Andersen's report of a uranium sulfide-bridged complex from the reaction of $[(CH_3C_5H_4)_3U{\cdot}THF]$ with COS suggests that the formation of CO versus CS is the main competing driving force rather than the formation of the U–O versus U–S bond.[15]

Finally, the possibility of the involvement of a mononuclear U=S species, and its subsequent reaction with CS_2, has also been investigated theoretically. The formation of the mononuclear complex is endergonic (by 20 kcal/mol) with respect to the U–S–U dinuclear species. Moreover, the transition state of CS_2 insertion has also been located and is 16.5 kcal/mol higher in energy than the one found for the U–S–U dimer. Accordingly, this pathway is energetically too demanding and, thus, is unlikely (for the full profile, see the Supporting Information).

However, the independent synthesis and isolation of the sulfide-bridged complex, followed by the reaction with CS_2, generates the uranium trithiocarbonate complex **3-DME** in high yields.

In conclusion, we have shown that the reaction of **1** with CS_2 resulted in the formation of a major product, the uranium tetrathiooxalate complex **4**,[12] and a minor product, the uranium trithiocarbonate complex **3-DME**. This parallel one- and two-electron reduction of CS_2 is remarkable in itself, showcasing the versatility of trivalent uranium as a reducing agent. The uranium trithiocarbonate complex can be synthesized in excellent yields by the addition of CS_2 to the sulfide-bridged **2**. This process to trithiocarbonate synthesis is unique; no such reaction pathway has been described in the literature. The reactivity of **5** and **2** have now been established. Future studies will focus on mapping the reactivity of related uranium μ-chalcogenides complexes such as $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-Se})]$ and $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-Te})]$ and their reactivity toward heteroallenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, SQUID data, electronic absorption spectra, and XRD and DFT details. This material is available free of charge via the Internet at http://pubs.acs.org.

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