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CS$_2$ Activation

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C–C Bond Formation through Reductive Coupling of CS_2 to Yield Uranium Tetrathiooxalate and Ethylenetetrathiolate Complexes**

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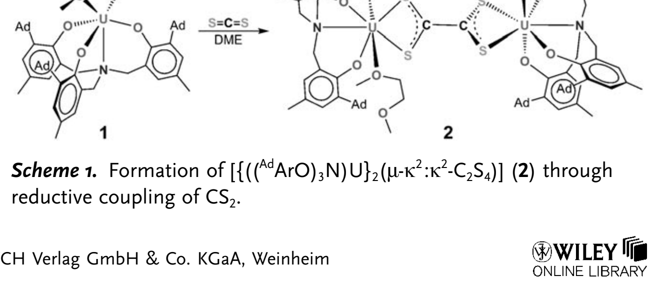
Activation and functionalization of CO_2[1–4] and its thio analogue, CS_2,[5–7] are of interest to researchers in the context of creating new C–C bonds. Employing the appropriate metal and ligand is key to overcoming the challenging task of activating the relatively stable C=O and C=S bonds. Generation of trithiocarbonate complexes from CS_2 has been well-documented.[8–10] However, the formation of $C_2S_4^{n-}$ units from the reductive coupling of CS_2 is uncommon[11–17] despite C_2S_4 ligands being implicated as the conducting units in multimetallic complexes.[18–20] Unlike dianionic $C_2O_4^{2-}$, the $C_2S_4^{n-}$ moiety can exist in various oxidation states, ranging from tetraanionic ethylenetetrathiolate ($C_2S_4^{4-}$) to dianionic tetrathiooxalate ($C_2S_4^{2-}$). Hence, the conducting properties of the $C_2S_4^{n-}$ ligand are partly derived from its ability to act as an electron source/sink.

The C–C bond length is often used in determining the oxidation state of the C_2S_4 ligands. C–C distances of approximately 1.35 Å for $C_2S_4^{4-}$ ligands and approximately 1.46 Å for $C_2S_4^{2-}$ ligands have been observed.[21] The longest C–C bond reported to date for a C_2S_4 ligand produced from reductive coupling of CS_2 is 1.41 Å, corresponding to an intermediate oxidation state between $C_2S_4^{2-}$ and $C_2S_4^{4-}$.[15] However, all examples of purely dianionic tetrathiooxalate compounds have been synthesized from their respective thiooxalate salts and not from reductive coupling of CS_2.[18–20] The first cases of CS_2 reduction were reported in 1980, where head-to-tail reductive coupling of CS_2 resulted in complexes of the types {RhC=S(S)C=S(S)} and {RhSC=S(S)CSRh}.[11,12] Recently, a Sm^{II} complex was reported to undergo C–S reductive coupling of CS_2 to yield $[(Giso)_2Sm(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2CSCS)Sm(Giso)_2]$ (Giso = $[(ArN)_2CNCy_2]$, Ar = 2,6-diisopropylphenyl, Cy = cyclohexyl).[22] To date, reductive head-to-head coupling of CS_2 has resulted only in formation of ethylenetetrathiolate ($C_2S_4^{4-}$)[13,14,16,17] or $C_2S_4^{4-}$-like thiooxalate complexes.[15] Compared to the C–C σ-bond in oxalate dianion $C_2O_4^{2-}$, the C–C σ-bond in C_2S_4 is relatively weak. The prevalence of ethylenetetrathiolate complexes is thus due to the additional stabilization by a C–C π-bond in the $C_2S_4^{4-}$ ligand.[13]

Herein we report the first example of a dinuclear U^{IV} tetrathiooxalate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**2**; Ad = adamantyl) formed through head-to-head reductive coupling of CS_2. The reaction is mediated by trivalent uranium $[((^{Ad}ArO)_3N)U]$ (**1**), generating a tetrathiooxalate complex that features a nonplanar $C_2S_4^{2-}$ unit in a previously unobserved binding mode. Tetrathiooxalate ($C_2S_4^{2-}$) complex **2** can further be reduced by two electrons to yield the ethylenetetrathiolate ($C_2S_4^{4-}$) complex, $[Na(dme)_3]_2$-$[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}C_2S_4)]$ (**3**). In a recent report, trivalent uranium complexes **1** and $[((^{tBu}ArO)_3mes)U]$ undergo reductive cleavage of CO_2 to form the dinuclear U^{IV} bridging carbonate complexes $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1{:}\kappa^2\text{-}CO_3)]$ and $[\{((^{tBu}ArO)_3mes)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}CO_3)]$, respectively.[23] Both, the formation of $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1{:}\kappa^2\text{-}CO_3)]$ and $[\{((^{tBu}ArO)_3mes)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}CO_3)]$, have been found to occur through bridging oxo intermediates, $[\{U\}_2(\mu\text{-}O)]$ that could be isolated.[23] In case of the $[\{((^{tBu}ArO)_3mes)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}CO_3)]$ complex, the intermediate oxo species has also been verified through DFT calculations.[24] Herein, the reductive pathway leading to the thiooxalate derivative **2** (instead of the thiocarbonate) from reaction of trivalent **1** and CS_2 is reported. Additionally, X-ray diffraction and spectroscopic studies are presented for the tetrathiooxalate complex **2** and ethylenetetrathiolate complex **3**.

Treating a brown suspension of the U^{III} complex **1** in DME with 3 equivalents of CS_2 for 3 h results in a purple precipitate from a dark-green solution. The purple precipitate was isolated and identified as the dinuclear uranium bridging tetrathiooxalate complex **2** (Scheme 1). Dark-green single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **2** in DME at room temperature. The molecular structure reveals a dinuclear complex, in which the two uranium centers are in distorted pentagonal bipyramidal environments (Figure 1). The pentagonal plane surrounding each uranium center comprises two sulfide ligands of the tetrathiooxalate unit, two aryloxide oxygen donors, and



1 **2**

Scheme 1. Formation of $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**2**) through reductive coupling of CS_2.

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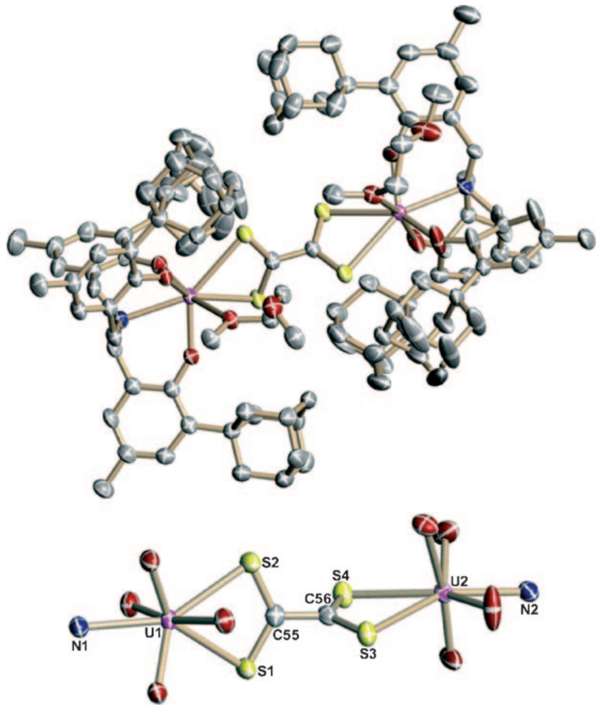
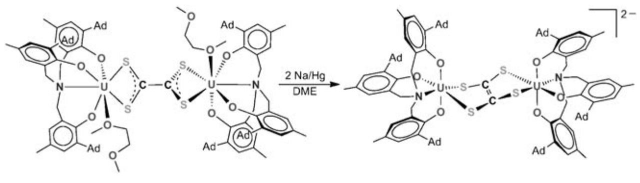


Figure 1. Molecular structure $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**2**) and core. Co-crystallized solvents and hydrogen atoms are removed for clarity. Thermal ellipsoids are at 50% probability.

the N-anchor of the tetradentate ligand. The third aryloxide arm and one DME molecule, coordinated in an η^1-fashion, complete the coordination sphere around the two U^{IV} atoms. The bridging dianionic thiooxalate fragment is bound in an unusual $\mu\text{-}\kappa^2(S,S'){:}\kappa^2(S'',S''')$-fashion; to our knowledge, this binding mode has not been observed before for the $C_2S_4^{2-}$ ligand. In all reported cases, where the complexes have a metal:ligand ratio of $n+1{:}n$ ($n=1, 2\ldots$), the C_2S_4 ligand fragment is bound to the metal (M) such that metal-containing five-membered rings MSCCS, are formed rather than the four-membered rings, MSCS, as seen in **2**.[18–21,25] The non-planar nature of the $C_2S_4^{2-}$ unit in **2** is equally unusual and can be explained by examining the bonding mode of the $C_2S_4^{2-}$ unit. Rotation about the C–C bond can occur in **2** when the $C_2S_4^{2-}$ fragment is bound in a $\mu\text{-}\kappa^2(S,S'){:}\kappa^2(S'',S''')$ fashion, whereas for all tetrathiooxalate complexes reported, the five membered MSCCS ring enforces a planar C_2S_4 unit. The four U–S bonds at 2.914(1), 2.946(1), 2.959(1), and 2.984(1) Å are longer than other related U^{IV}–S dithiolene bonds.[26,27] In fact, the central C–C bond (C55–C56) of 1.498(5) Å in **2** is the second longest bond of this type reported[18–21,25,28] and slightly longer than in $[PPh_4]_2[C_2S_4]$ (1.461 Å).[29] Consequently, the four C–S bond lengths, 1.679(4), 1.671(4), 1.690(4), 1.687(4) Å, are much shorter than those that have been reported.[18,19,21,25]

Treating complex **2** with 2 equivalents of Na/Hg in DME results in an orange precipitate, which was isolated by filtration and characterized as the ethylenetetrathiolate complex **3** (Scheme 2). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated solution of **3** in DME. Complex **3** crystallizes in the triclinic space group $P\bar{1}$



Scheme 2. Two-electron reduction of $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**2**) yielding $[Na(dme)_3]_2[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}C_2S_4)]$ (**3**).

with two independent molecules of **3** in the asymmetric unit. Each molecule lies on an inversion center in the unit cell; thus, only half of the bond distances are experimentally determined and the other half is symmetry-generated. The two independent molecules have very similar structural parameters, and therefore, the average of the metric parameters in the two complexes is discussed. The molecular structure of dianionic **3** is charge-balanced by two Na^+ ions, each solvated by three DME molecules, and reveals that a significant structural rearrangement has occurred upon reduction of **2** (Figure 2). The two U^{IV} centers in **3** are now

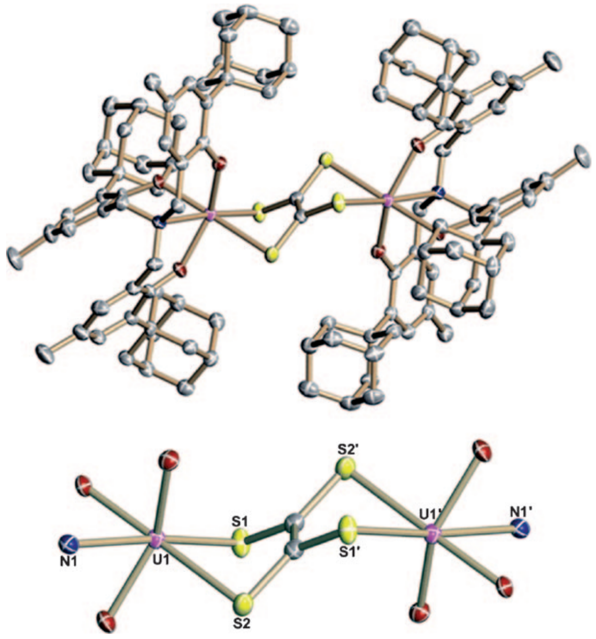


Figure 2. Molecular structure of $[Na(dme)_3]_2[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}C_2S_4)]$ (**3**) and core atoms shown for clarity. Co-crystallized solvents and hydrogen atoms are removed for clarity. Thermal ellipsoids are at 50% probability.

in distorted octahedral ligand environments. The tetraanionic $C_2S_4^{4-}$ ligand is planar and has rearranged from a $\mu\text{-}\kappa^2(S,S'){:}\kappa^2(S'',S''')$ coordination mode in **2** to a MSCCS binding mode. Unlike most complexes with the MSCCS binding mode, the five-membered ring in **3** is not planar and is reminiscent of the tetrathiolene complex $[\{(\eta^5\text{-}C_5H_5)_2Ti\}_2(\mu\text{-}C_2S_4)]$.[15] The folding angle of the uranium centers with respect to the C_2S_4 plane of 62.1° is significantly larger than the 46° found in $[\{(\eta^5\text{-}C_5H_5)_2Ti\}_2(\mu\text{-}C_2S_4)]$.[15] This large folding angle is similar to the uranium dithiolene complex $[U(cot)(dddt)_2]^-$ (65.7° and

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76.2°)[26] and indicates significant molecular stabilization derived from overlap of the metal orbitals with the π-acceptor orbitals on the $C_2S_4^{4-}$ ligand.[15,26] The U1–S1 and U1–S2 bonds in **3** of 2.700(1) and 2.682(1) Å, are much shorter than in **2** (Table 1) and comparable to the U–S bonds of the uranium dithiolene complex $[U(cot)(dddt)_2]^-$ (averaging 2.69 Å)[26]. In accordance with a two-electron reduction process, the bond order increases to a C=C double bond as indicated in the C55–C55′ bond of 1.383(8) Å that is comparable to reported ethylenetetrathiolate complexes.[13,16,17] The C55–S1 and C55–S2 bond lengths (1.789(4) and 1.766(4) Å) in **3** and longer than in **2** and in other ethylenetetrathiolate complexes (ca. 1.70–1.76 Å).[13,16,17]

Table 1: Selected bond lengths for complexes **2** and **3** [Å].

Structural parameters	2	3
U1,2–N1,2	2.577(3), 2.595(3)	2.641(3)
U1,2–OAr1,2 (av.)	2.145, 2.123	2.187
U–S (av.)	2.951	2.691
C55–C56,55′	1.498(5)	1.383(8)
C–S (av.)	1.682	1.779

The variable-temperature SQUID magnetization data of complexes **2** and **3** are similar. Complex **2** exhibits magnetic moments of 0.52 B.M. at 2 K and 3.61 B.M. at 300 K, while **3** has magnetic moments of 0.55 B.M. at 2 K and 3.40 B.M. at 300 K (Figure 3). These values describe the temperature-dependent magnetic behavior typically observed for U^{IV} uranium complexes and confirm that the oxidation state of the uranium centers is preserved upon reduction of **2** to **3**. Additionally, the molar magnetic susceptibility (χ_M) versus temperature (T) plots show that **2** and **3** behave as "normal" Curie paramagnets; no antiferromagnetic exchange is observed (see Supporting Information).

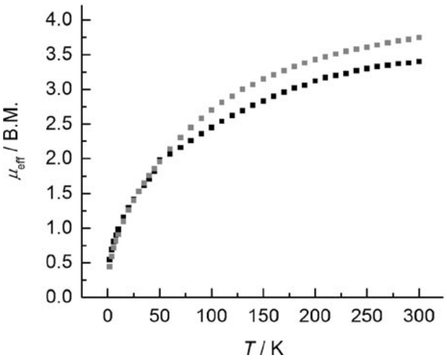

Figure 3. Variable temperature SQUID magnetization data (top) for complexes **2** (gray) and **3** (black).

Dark-green complex **2** and orange complex **3** have distinctly different electronic absorption spectra, particularly in the visible region. The spectrum of **2** features two distinct charge-transfer transitions centered at $\lambda_{max} = 375$ nm ($\varepsilon = 9000$ L mol^{-1} cm^{-1}) and $\lambda_{max} = 500$ nm ($\varepsilon = 1715$ L mol^{-1} cm^{-1}), while the spectrum of **3** shows one transition at $\lambda_{max} = 508$ nm ($\varepsilon = 1600$ L mol^{-1} cm^{-1}; see the Supporting Information). Additionally, broad low-intensity absorption bands at $\lambda \approx 700$–1600 nm, $\varepsilon \approx 50$–500 L mol^{-1} cm^{-1}, are also observed for **2** and **3**; these bands can be assigned to metal centered f–f transitions. The f–f features of **2** and **3** are similar with only slight variations in intensity, which further supports the magnetization data that the U^{IV} centers are unaltered upon reduction of **2**.

Considering that CS_2 can be regarded as a model molecule for CO_2, the formation of the tetrathiooxalate complex **2** from **1** and CS_2, rather than formation of the bridging trithiocarbonate complex, seems surprising. This is especially noteworthy in light of our recent report on formation of the carbonate bridged uranium complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1{:}\kappa^2\text{-}CO_3)]$ from **1** and CO_2.[23]

However, $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1{:}\kappa^2\text{-}CO_3)]$ forms through CO_2 addition to the μ-O^{2-} intermediate, with the formation of a thermodynamically stable μ-O^{2-} complex[24] and concomitant liberation of the very stable CO molecule as the driving force. Formation of CS is not as favorable—its heat of formation is 64.6 kcal mol^{-1} [30] compared to −26.4 kcal mol^{-1} for CO.[31] Hence, this difference in stability between CS and CO accounts for the retardation in formation of the trithiocarbonate congener.

In summary, C–C coupling by low-valent uranium complexes is rare,[32] and we have observed C–C coupling in formation of the first tetrathiooxalate ($C_2S_4^{2-}$) complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}C_2S_4)]$ (**2**) through reductive coupling of CS_2. Complex **2** features a new $\kappa^2{:}\kappa^2$ binding mode for the tetrathiooxalate ligand. The tetrathiooxalate complex **2** is also the only f-element example of its kind. Additionally, tetrathiolene complexes of uranium are not known. Upon reduction of **2**, a C=C double bond is formed and through a significant structural rearrangement of the C_2S_4 ligand, the ethylenetetrathiolate complex $[Na(dme)_3]_2[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}C_2S_4)]$ (**3**) is generated. The isolated tetrathiooxalate and ethylenetetrathiolate pair offers direct structural comparison, because the chelating ligand environment and the uranium oxidation state are identical. Future studies will focus on the exploration of the reactivity of tris(aryloxide) U^{III} complex **1** with other chalcogenide reagents, such as COS and CSe_2, as well as the determination of factors that dictate oxalate versus carbonate formation.

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