JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Reactivity of U−E−U (E = S, Se) Toward CO_2, CS_2, and COS: New Mixed-Carbonate Complexes of the Types U−CO_2E−U (E = S, Se), U−CS_2E−U (E = O, Se), and U−COSSe−U

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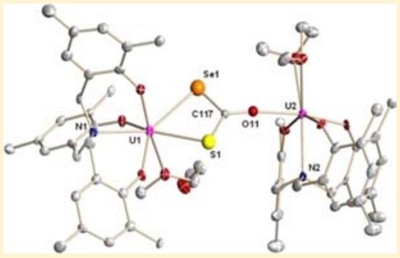
Supporting Information

ABSTRACT: We recently reported the formation of a bridging carbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_3)]$ via reductive cleavage of CO_2, yielding a μ-oxo bridged complex, followed by the insertion of another molecule of CO_2. In a similar strategy, we were able to isolate and characterize a series of mixed carbonate complexes U−CO_2E−U, U−CS_2E−U, and even U−OC(S)Se−U, by reacting bridged chalcogenide complexes $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}E)]$ (E = S, Se) with CO_2, CS_2, and COS. These chalcogenido mixed-carbonate complexes represent the first of their kind.



INTRODUCTION

Chalcogenocarbonate compounds [$-CO_2E-$ (E ≠ O) and $-CS_2E-$ (E ≠ S)] have been found to possess a wide range of applications in chemical, biological, and industrial processes.[1] For instance, alkyl selenocarbonates and tellurocarbonates are effective precursors to alkyl and oxyacyl radicals, the latter of which are used in intramolecular alkene addition reactions to furnish δ- and γ-lactones.[2,3] In the context of coordination complexes, chalcogenocarbonato ligands are not well-known, particularly those of the heavier chalcogenides, CO_2ER^- (E = Se, Te),[4,5] CS_2ER^- (E = Se, Te),[6,7] and $COSSeR^-$.[8] In contrast to numerous carbonate and trithiocarbonate (CO_3^{2-} and CS_3^{2-}) complexes,[9−15] there are no coordination complexes reported that contain thiocarbonato (CO_2S^{2-}), selenocarbonato (CO_2Se^{2-}), selenodithiocarbonato (CS_2Se^{2-}), or selenothiocarbonato ($COSSe^{2-}$) ligands. These unusual dianionic chalcogenocarbonate moieties are known to be unstable and have eluded isolation and characterization aside from NMR spectroscopy and theoretical studies.[16−18] For instance, potassium salts of mono- and dithiocarbonate are highly unstable, precluding their isolation as pure materials.[17] Synthetic routes to making CO_2ER^- (E = S, Se) complexes mainly involve the insertion of a $-CO_2-$ fragment into metal−chalcogen bonds, M−ER, M−E−M, or M−ER−M (E = S or Se). The samarium complexes $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$ (E = S, Se) were synthesized in such a manner.[5] Routes to complexes containing the COS_2^{2-} ligand predominantly involve CO insertion into S−S bonds.[19,20] There is no example of an entirely mixed chalcogenocarbonate compound, $COSSe^{2-}$, although an Fe complex containing the monoanionic $COSSePhCl^-$ ligand has been isolated.[8]

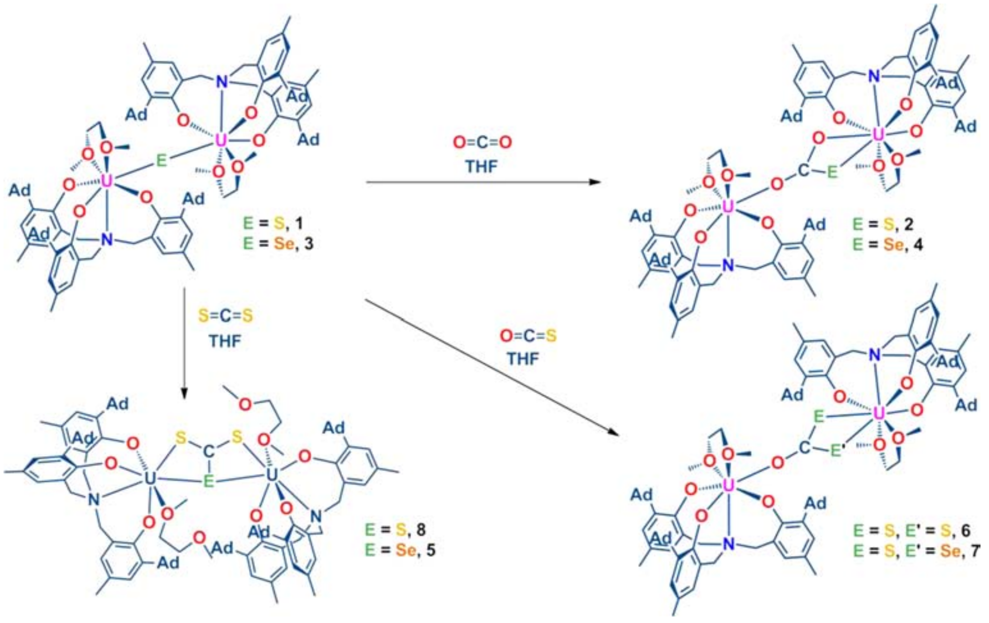
Recently, we have reported the formation of uranium carbonate $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_3)]$[21] and trithiocarbonate $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\kappa^2{:}\kappa^2\text{-}CS_3)]$[22] complexes from CO_2 insertion into oxo-bridged complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}O)]$[21] and CS_2 insertion into sulfide-bridged complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}S)]$,[23] respectively. Employing this strategy, we have been able to isolate and fully characterize a series of chalcogenocarbonate complexes generated from CO_2 insertion into U−E−U (E = S, Se) bonds, CS_2 insertion into a U−Se−U bond, and COS insertion into U−E−U (E = S, Se) bonds. To the best of our knowledge, the resulting chalcogenocarbonate complexes reported here, namely, $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_2S)]$, $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_2Se)]$, $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\kappa^2{:}\kappa^2\text{-}CS_2Se)]$, and $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}COSSe)]$, are the first complexes containing these dianionic chalcogenocarbonate units. Herein, we report the synthesis, XRD studies, and SQUID magnetization data of these unique species.

RESULTS AND DISCUSSION

Treatment of yellow-green uranium sulfide-bridged $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}S)]$ (**1**)[23] and yellow-orange selenide-bridged $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}Se)]$ (**3**)[23] complexes with CO_2 resulted in green reaction mixtures. The volatiles were removed to yield fine green powders, which were identified as uranium thiocarbonate $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_2S)]$ (**2**) and uranium selenocarbonate $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\eta^1{:}\kappa^2\text{-}CO_2Se)]$ (**4**) complexes, respectively (Scheme 1, right). Similarly, treating μ-Se complex **3** with 1 equiv of CS_2 leads to an intensely orange solution. Upon removal of volatiles, an intensely orange powder was isolated and characterized as the uranium selenodithiocarbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu{-}\kappa^2{:}\kappa^2\text{-}CS_2Se)]$ (**5**) (Scheme 1, bottom left).

Received: August 10, 2012
Published: September 12, 2012

Scheme 1. Formation of Uranium Thiocarbonate (2) and Selenocarbonate (4) Complexes from Addition of CO_2 to μ-S (1) and μ-Se (3) Complexes, Respectively[a]



[a] Addition of CS_2 to the μ-S complex (**1**) generates the previously reported trithiocarbonate complex (**8**) and addition of CS_2 to the μ-Se complex (**3**) yields the uranium selenodithiocarbonate complex (**5**). Uranium dithiocarbonate (**6**) and uranium selenothiocarbonate (**7**) can be obtained by addition of COS to μ-S (**1**) and μ-Se (**3**) complexes, respectively.

In the same manner, uranium dithiocarbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}COS_2)]$ (**6**) and uranium selenothiocarbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2COSSe)]$ (**7**) can be obtained via treatment of uranium sulfide-bridged complex (**1**) and selenide-bridged complex (**3**) with COS, respectively, (Scheme 1, bottom right) leading to green reaction mixtures and yielding green powders upon removal of the volatiles.

Green XRD-quality single crystals of complexes **2**, **4**, **6**, and **7** and orange single crystals of **5** were all obtained from saturated solutions of DME at room temperature.

The molecular structures of **2** and **4** reveal two tetravalent uranium centers bridged by CO_2S^{2-} and CO_2Se^{2-} ligands in $\mu-\eta^1(O):\kappa^2(O',S)$ and $\mu-\eta^1(O):\kappa^2(O',Se)$ fashions, respectively (Figure 1). Each uranium center contains a DME molecule coordinated in a bidentate fashion. Compounds **2** and **4** are isostructural to each other and to the reported uranium carbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}CO_3)]$.[21] The U–N distances are unremarkable for **2** [2.554(4), 2.572(4) Å] and **4** [2.573(5), 2.580(5) Å] (Table 1). The average U–O distances are slightly longer in **4** (2.167 and 2.194 Å) than in **2** (2.159 and 2.187 Å). The $U-O_{carbonate}$ distances are nearly equivalent for **2** [2.225(3) and 2.422(3) Å] and **4** [2.241(4) and 2.438(4) Å]. The C113–O distances are also statistically equivalent for **2** [1.283(5), 1.262(5) Å] and **4** [1.285(8), 1.252(8) Å]. The distinction between **2** and **4** is observed in the U–S, U–Se, C–S, and C–Se bonds. The U–Se and C–Se distances in **4** of 3.0122(10) and 1.925(7) Å are significantly longer than the U–S and C–S distances in **2** of 2.892(1) and 1.742(5) Å, in accordance with a larger and softer selenium atom compared to sulfur. The C–S distance [1.742(5) Å] in **2** is comparable to monoanionic alkyl thiocarbonate complexes $[CpFe(CO)_2SCO_2Et]$[24] [1.748(3) Å] and $[fac\text{-}(CO)_3(dppe)\text{-}MnSC(O)OCH_3]$[25] [1.729(10) Å]. The distinguishing feature is in the C–O distances, where for $[CpFe(CO)_2SCO_2Et]$[24] and $[fac\text{-}(CO)_3(dppe)Mn(SC(O)OCH_3)]$[25] the C–O distance is closer to a double bond [1.197(3) and 1.200(11) Å, respectively] and the C–OR bonds are long, 1.346(4) and 1.354(10) Å, respectively. The two C–O distances in **2**, measuring 1.283(5) and 1.262(5) Å, are suggestive of electron delocalization and further confirm the coordination of a dianionic CO_2S^{2-} ligand. Similarly, the C–Se distance in **4** of

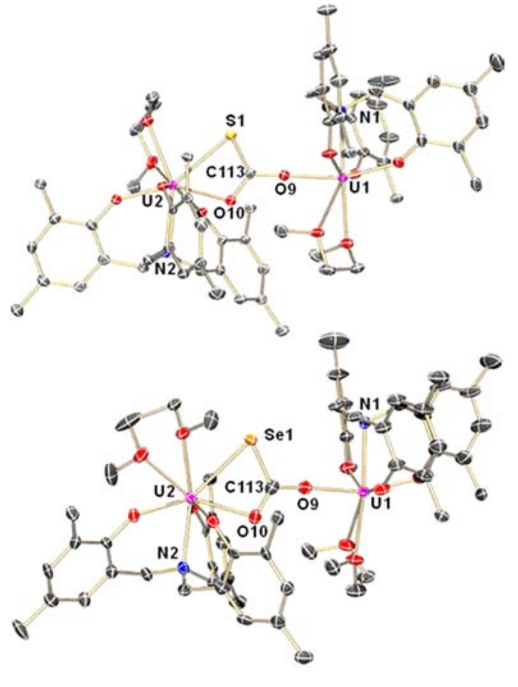


Figure 1. Molecular structures of uranium thiocarbonate complex **2** (top) and uranium selenocarbonate complex **4** (bottom). Adamantyl groups and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability.

Table 1. Selected Bond Distances for Complexes 2 and 4 (in Å)

structural parameters	2	4
$U_{1,2}-N_{1,2}$	2.554(4), 2.572(4)	2.573(5), 2.580(5)
$U_{1,2}-O_{Ar}$ (avg)	2.159, 2.187	2.167, 2.194
U_1-O_9/U_2-O_{10}	2.225(3), 2.422(3)	2.241(4), 2.438(4)
U_2-E_1	3.0122(10)	3.012(1)
$C_{113}-O_{9,10}$	1.283(5),1.262(5)	1.285(8), 1.252(8)
$C_{113}-E_1$	1.742(5)	1.925(7)

1.925(7) Å is comparable to that of monoanionic alkyl selenocarbonate complex $[CpFe(CO)_2SeCO_2Et]$[24] [1.914(4) Å], and the nearly equivalent C−O distances in **4** are also attributed to electron delocalization of a coordinating dianionic CO_2Se^{2-} ligand.

The molecular structure of selenodithiocarbonate complex **5** features two U(IV) centers bridged by a CS_2Se^{2-} ligand coordinated in a $\mu-\kappa^2(S,Se):\kappa^2(S',Se)$ fashion (Figure 2, top).

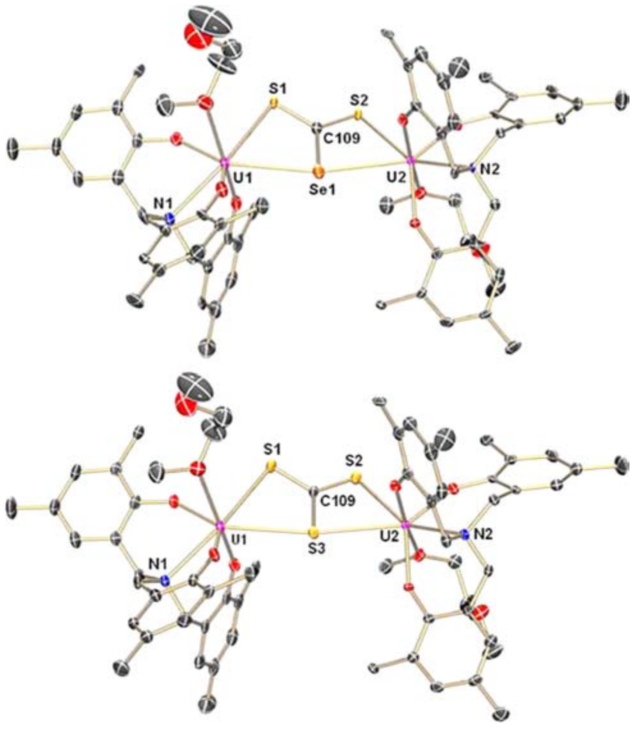


Figure 2. Molecular structures of uranium dithioselenocarbonate complex **5** (top) and recently reported uranium trithiocarbonate complex **8** (bottom).[22] Adamantyl groups and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability.

Table 2. Selected Bond Distances for Complexes 5 and 8[22] (in Å)

structural parameters	5	8
$U_{1,2}-N_{1,2}$	2.588(5), 2.627(5)	2.587(3), 2.625(3)
$U_{1,2}-O_{Ar}$ (avg)	2.150, 2.135	2.147, 2.134
$U_{1,2}-S_{1,2}$	2.913(2), 2.910(2)	2.868(2), 2.872(2)
$U_{1,2}-Se_1/\ U_{1,2}\text{-}S_3$	3.1509(7), 3.1702(7)	3.096(2), 3.130(2)
$C-S_{1,2}$	1.715(6), 1.715(6)	1.707(4), 1.710(4)
$C-Se_1/\ C-S_3$	1.880(6)	1.724(4)

Each of the U(IV) centers in **5** also contains one coordinated DME molecule; however, unlike **2** and **4**, the DME molecules in **5** bind as monodentate ligands. Complex **5** is isostructural to the uranium trithiocarbonate complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\kappa^2:\kappa^2\text{-}CS_3)]$ (**8**).[22] As a comparison, the structural parameters of **5** and **8** are given in Table 2. The U_1-N_1, U_2-N_2, average U_1-O_{Ar}, and average U_2-O_{Ar} of 2.588(5), 2.627(5), 2.150, and 2.135 Å, respectively, are unexceptional and very similar to those of complex **8**. The U_1-S_1 and U_2-S_2 bond lengths [2.913(2) and 2.910(2) Å] and the $C_{109}-S_1$ and $C_{109}-S_2$ distances [1.715(6) and 1.715(6) Å] of **5** are also similar to those of **8**. The U_1-Se_1 and U_2-Se_1 bond distances of 3.1509(7) and 3.1702(7) Å in **5** are longer than the U_1-S_1 and U_2-S_1 bonds of **8** [3.096(2) and 3.130(2) Å]. In accordance with a larger and softer Se atom in **5** compared to the S atom in **8**, the $C_{109}-Se_1$ bond length in **5** of 1.880(6) Å is significantly longer than the $C_{109}-S_3$ bond in **8** [1.724(4) Å].

The molecular structure of **6** shows two tetravalent uranium centers bridged by a COS_2^{2-} ligand in a $\mu-\eta^1(O):\kappa^2(S,\ S')$ fashion (Figure 3, left) that is structurally and electronically similar to the structures of **2** and **4**. The two uranium centers possess different coordination geometries than those of **2** and **4**. Attributing to the two larger S atoms, the DME molecules behave as monodentate ligands. This is reflected in the bond distances that are slightly longer overall for U_1-O_{Ar} = 2.159(3) Å and U_1-N_1 = 2.601(3) Å compared to U_2-O_{Ar} = 2.143 Å and U_2-N_2 = 2.526(3) Å. The U_1-S bond distances [2.9107(11) and 2.8917(11) Å] and the $C_{117}-S$ distances [1.720(5) and 1.708(4) Å] are similar to those of **5** and are consistent, with a coordinated dianionic COS_2^{2-} ligand. The U_2-O_{11} bond length of 2.260(3) Å compares well with those observed in **2** and **4**.

For compound **7**, only a preliminary X-ray crystal structure could be obtained due to weakly diffracting crystals further suffering from a disorder between sulfur and selenium (For details, see Supporting Information). We will therefore discuss molecular features on a merely qualitative basis. The molecular structure of **7** (Figure 3, right) shows two U(IV) centers bridged by an all-mixed $COSSe^{2-}$ ligand. Elemental analyses results on pure crystalline samples also reproducibly support the identity of **7** as the all-mixed carbonate. The bridging $COSSe^{2-}$ ligand is coordinated in a $\mu-\eta^1(O):\kappa^2(S,\ Se)$ fashion and is isostructural to complexes **2**, **4**, and **6**. Each uranium center features one molecule of DME, which binds at U_1 in a monodentate fashion and at U_2 in a bidentate fashion. The tetradentate ligand environment at the uranium centers is similar to **6** and shows comparable distances for the respective $U-O_{Ar}$ (U_1-O_{Ar} = 2.167 Å, U_2-O_{Ar} = 2.160 Å) and U−N (U_1-N_1 = 2.569 Å, U_2-N_2 = 2.536 Å) bonds. The bond lengths for U_2-O_{11} = 2.319 Å and $C_{117}-O_{11}$ = 1.26 Å compare well with the respective distances in **6** and are unremarkable (Table 3). The U_1-S bond distance of 2.99 Å in **7** is longer than expected compared to the U_1-S_1 bond distance in **2** of 2.892(1) Å, while the U1−Se bond distance of 3.009 Å in **7** compares well to the one observed in **4** (3.008 Å). The bond distances for $C_{117}-S_1$ of 1.75 Å and $C_{117}-Se_1$ of 1.86 Å correspond to prospective values but suffer from the disorder observed for the central $COSSe^{2-}$ unit and will not be discussed. Unfortunately, attempts to isolate the free $COSSe^{2-}$ ligand for further investigations were unsuccessful due to its high instability.

The variable temperature SQUID magnetization data of complexes **2** and **4**−**7** are very similar, all exhibiting magnetic moments of ∼0.40 μ_B at 2 K and ∼3.70 μ_B at 300 K (see

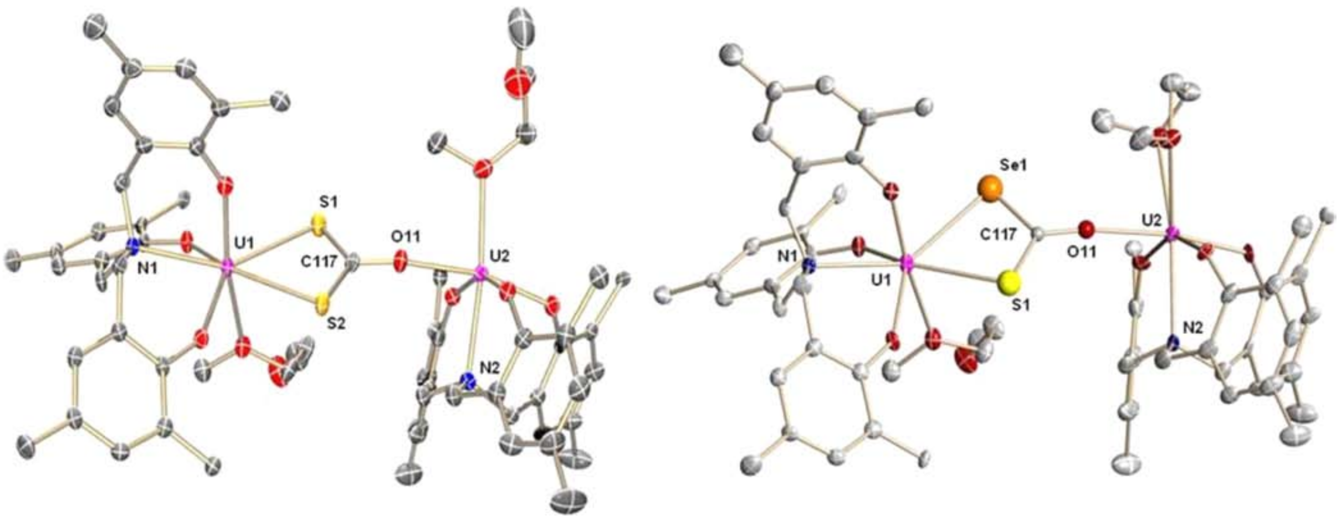


Figure 3. Molecular structures of uranium dithiocarbonate complex **6** (left) and uranium selenothiocarbonate complex **7** (right). Adamantyl groups and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at 50% probability, the atoms of the central COSSe unit in **7** are drawn as spheres of arbitrary size.

Table 3. Selected Bond Distances for Complexes 6 and 7 (in Å)

structural parameters	**6**	**7**
$U_{1,2}-N_{1,2}$	2.601(3), 2.526(3)	2.569, 2.536
$U_{1,2}-O_{Ar(avg)}$	2.159, 2.143	2.167, 2.160
$U_{1,2}-S_{1,2}$	2.892(1), 2.9107(1)	2.99
$U_{1,2}-Se_1$	–	3.009
U_2-O_{11}	2.260(3)	2.319
$C_{117}-O_{11}$	1.282(5)	1.26
$C-S_{1,2}$	1.720(5), 1.708(4)	1.75
$C-Se_1$	–	1.86

Supporting Information). These values describe the temperature-dependent magnetic behavior typically observed for tetravalent uranium complexes and confirm that the oxidation state of the uranium centers is +4 for complexes **2** and **4**–**7**.

■ CONCLUSION

In summary, we have successfully synthesized and isolated the first complexes containing dianionic chalcogenocarbonate ligands, namely, $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2S)]$, $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2Se)]$, $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\kappa^2:\kappa^2-CS_2Se)]$, through CO_2 addition to $[\{((^{Ad}ArO)_3N)U\}_2(\mu-O)]$ and $[\{((^{Ad}ArO)_3N)U\}_2(\mu-S)]$ complexes and CS_2 addition to a $[\{((^{Ad}ArO)_3N)U\}_2(\mu-Se)]$ complex. Similarly, COS insertion into $[\{((^{Ad}ArO)_3N)U\}_2(\mu-S)]$ and $[\{((^{Ad}ArO)_3N)U\}_2(\mu-Se)]$ afforded $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-COS_2)]$ and $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-COSSe)]$, respectively. The entirely mixed $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-COSSe)]$ is highly unusual and has eluded characterization in the past. The isolation of these chalcogenocarbonate complexes along with carbonate and trithiocarbonate complexes $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_3)]$[21] and $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\kappa^2:\kappa^2-CS_3)]$[22] has provided a unique series for structural and spectroscopic comparison studies. Compared to potassium salts of thiocarbonates, the uranium thiocarbonate complexes are remarkably stable in solid state and in solution. The selenocarbonates and even more so the all-mixed selenothiocarbonate complex, $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-COSSe)]$, are considerably less stable but isolable. All attempts to liberate and isolate the free carbonate ligands via hydrolysis of the complexes or silylation of the carbonates failed, thus clearly demonstrating the stabilizing effect of uranium coordination. Similarly, reduction of the bridged carbonate U(IV/IV) complex did not liberate the inorganic carbonate with concomitant regeneration of the U(III) precursor.

■ EXPERIMENTAL SECTION

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2S)]$ (2). A solution of **1** (100 mg, 0.045 mmol) in THF (8 mL) was fitted with a balloon containing CO_2. After 3–4 min, the reaction mixture turned light green and was stirred for another 30 min. The volatiles were removed, and the light green precipitate was dried in vacuo. Light green crystals of **2** can be obtained from a concentrated solution of DME. Yield: 83.0 mg (0.036 mmol, 82%). Anal. Calcd for $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2S)]\cdot 5DME$: C, 60.12; H, 7.44; N, 1.02; S, 1.17. Found: C, 59.41; H, 7.24; N, 0.99; S, 0.85. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 25.05, 22.15, 12.40, 7.75, 7.71, 7.31, 6.97, 6.90, 6.27, 6.08, 5.18, 4.47, 4.36, 3.78, 3.23, 3.02, 2.84, 2.55, 1.86, 1.65, 1.41, 1.23, 1.16, 0.81, 0.22, −0.68, −1.13.

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2Se)]$ (4). A solution of **3** (100 mg, 0.044 mmol) in THF (8 mL) was fitted with a balloon containing CO_2. After 3–4 min, the reaction mixture turned light green and was stirred for another 30 min. The volatiles were removed, and the light green precipitate was dried in vacuo. Light green crystals of **4** can be obtained from a concentrated solution of DME. Yield: 78.0 mg (0.033 mmol, 75%). Anal. Calcd for $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2-CO_2Se)]\cdot 3DME$: C, 59.50; H, 7.05; N, 1.08. Found: C, 59.78; H, 7.21; N, 1.07. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 24.33, 18.30, 17.54, 12.41, 11.02, 8.69, 7.75, 7.37, 6.87, 6.79, 5.69, 3.56, 2.80, 0.23, −0.89, −12.94.

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\kappa^2:\kappa^2-CS_2Se)]$ (5). CS_2 (3 μL, 0.05 mmol) was added to a solution of **3** (100 mg, 0.044 mmol) in THF (8 mL). The reaction mixture quickly turned orange, an orange precipitate formed after 20 min, and the reaction mixture was stirred for another 30 min. The orange solids were collected by filtration, washed with THF three times (3 mL), and dried in vacuo. Orange crystals of **5** can be obtained from a concentrated solution of DME. Yield: 87.3 mg (0.038 mmol, 85%). Anal. Calcd for $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\kappa^2:\kappa^2-CS_2Se)]\cdot DME$: C, 59.18; H, 6.65; N, 1.14; S, 2.61. Found: C, 58.88; H, 6.78; N, 1.10; S, 2.01. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 64.19, 60.04, 35.00, 19.01, 18.32, 17.58, 13.56, 12.42, 11.03, 4.91, 3.77, 3.11, 1.99, 1.24, 0.92, 0.57, −0.89, −1.93, −3.76, −11.34, −12.93, −16.69, −18.99, −34.12.

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}COS_2)]$ (6). A solution of **1** (100 mg, 0.045 mmol) in THF (8 mL) was fitted with a balloon containing COS. The reaction mixture quickly turned green, a green precipitate formed after 20 min, and the reaction mixture was stirred for another 30 min. The green solids were collected by filtration, washed with THF three times (3 mL), and dried in vacuo. Green crystals of **6** can be obtained from a concentrated solution of DME. Yield: 84.7 mg (0.037 mmol, 82%). Anal. Calcd for $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}COS_2)]\cdot 2DME$: C, 61.03; H, 6.65; N, 1.22; S, 2.79. Found: C, 61.34; H, 6.51; N, 1.29; S, 2.43. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 18.60, 17.37, 16.58, 15.21, 14.61, 13.76, 13.03, 11.80, 11.47, 10.50, 10.39, 7.27, 6.88, 6.04, 4.31, 4.17, 3.80, 3.23, 2.03, 1.56, 1.19, 1.16, 0.82, 0.80, 0.61, 0.41, −0.72, −1.16, −3.18, −4.39, −5.76, −9.59.

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}COSSe)]$ (7). A solution of **3** (100 mg, 0.044 mmol) in THF (8 mL) was fitted with a balloon containing COS. The reaction mixture quickly turned green, a green precipitate formed after 20 min, and the reaction mixture was stirred for another 30 min. The green solids were collected by filtration, washed with THF three times (3 mL), and dried in vacuo. Green crystals of **7** can be obtained from a concentrated solution of DME. Yield: 84.3 mg (0.036 mmol, 81%). Anal. Calcd for $[\{((^{Ad}ArO)_3N)U\}_2(\mu-\eta^1:\kappa^2\text{-}COSSe)]\cdot 2DME$: C, 59.81; H, 6.52; N, 1.19; S, 1.36. Found: C, 59.80; H, 6.45; N, 1.17; S, 0.98. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 64.67, 60.78, 47.31, 35.27, 32.94, 25.76, 19.54, 18.54, 15.30, 15.29, 13.80, 11.53, 11.18, 10.58, 9.70, 8.43, 7.63, 7.35, 6.95, 6.82, 6.67, 5.22, 4.95, 4.34, 4.25, 3.99, 3.34, 3.28, 3.15, 3.04, 2.96, 2.79, 2.69, 1.51, 1.36, 1.28, 1.23, 1.00, 0.96, 0.29, −0.26, −0.84, −1.17, −1.37, −2.00, −2.26, −3.14, −4.31, −4.48, −4.60, −4.98, −5.28, −5.55, −5.66, −9.29, −9.45, −9.57, −11.34, −11.42, −12.03, −13.03, −14.74, −15.91, −16.81, −17.44, −18.56, −19.12, −20.99.

■ ASSOCIATED CONTENT

Supporting Information

General considerations, crystallographic techniques and tables, SQUID magnetization data, and synthetic details for compounds **2** and **4**−**7** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by grants from the German Bundesministerium für Bildung und Forschung (BMBF project 02NUK012C) and Deutsche Forschungsgemeinschaft (DFG) through SFB 583. The FAU Erlangen-Nuremberg is gratefully acknowledged for financial support as is COST Action CM1006.

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