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Authors

Godinho, Gabriella S

Ordoñez, Osvaldo

Feng, Qien

et al.

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Homoleptic 1,2-Benzenedithiolate Complexes of Thorium and Uranium

*Gabriella S. Godinho, Osvaldo Ordoñez, Qien Feng, Guang Wu, and Trevor W. Hayton**

Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106, United States

E-mail: hayton@chem.ucsb.edu.

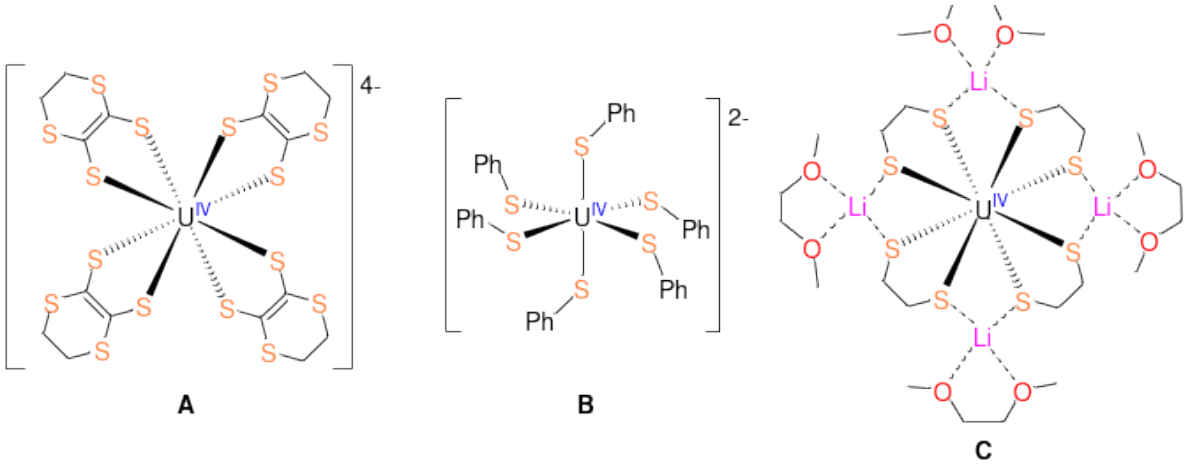
Abstract

Reaction of 4 equiv of $[Li(TMEDA)]_2[1,2\text{-}S_2C_6H_4]$ with $[ThCl_4(DME)_2]$ or $[UCl_4(THF)_3]$ in THF results in formation of $[Li(THF)_2]_4[An(1,2\text{-}S_2C_6H_4)_4]$ (An = Th, **1**; An = U, **2**), whereas reaction of 4 equiv of $[Li(TMEDA)]_2[1,2\text{-}S_2C_6H_4]$ with UCl_4 in Et_2O results in formation of $[Li(TMEDA)]_4[U(1,2\text{-}S_2C_6H_4)_4]$ (**3**). Complexes **1**-**3** represent the first reported benzenedithiolate complexes of the actinides. They were characterized by NMR spectroscopy and X-ray crystallography. In the solid state, complexes **1**-**3** exhibit triangular dodecahedral geometries about their actinide centers. Additionally, their Li^+ cations are bound by two sulfur atoms of adjacent $[1,2\text{-}S_2C_6H_4]^{2-}$ ligands, in addition to two solvent donor atoms. In solution, complexes **2** and **3** exhibit spectral data consistent with S_4 symmetry (and non-exchanging Li^+ sites), whereas complex **1** exhibits spectral properties consistent labile Li^+ cations.

Introduction

A number of U(IV) and U(III) thiolate complexes have been reported over the past three decades,[1-6] including a number of homoleptic examples, such as $[U(dddt)_4]^{4-}$ (**A**), $[U(dddt)_3]^{3-}$ (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate),[7] $[U(SPh)_6]^{2-}$ (**B**),[4, 8] and $[Li(DME)]_4[U(SCH_2CH_2S)_4]$ (**C**) (Scheme 1).[9] Their syntheses were motivated, in part, by the observation that sulfur donors can discriminate between the minor actinides and the lanthanides in liquid-liquid extractions.[10-22] Study of these soft donor complexes have generated important insights into actinide-ligand bonding, especially in regards to covalency in these elements.[13, 23-26]

Scheme 1. Previously reported homoleptic uranium thiolate complexes.

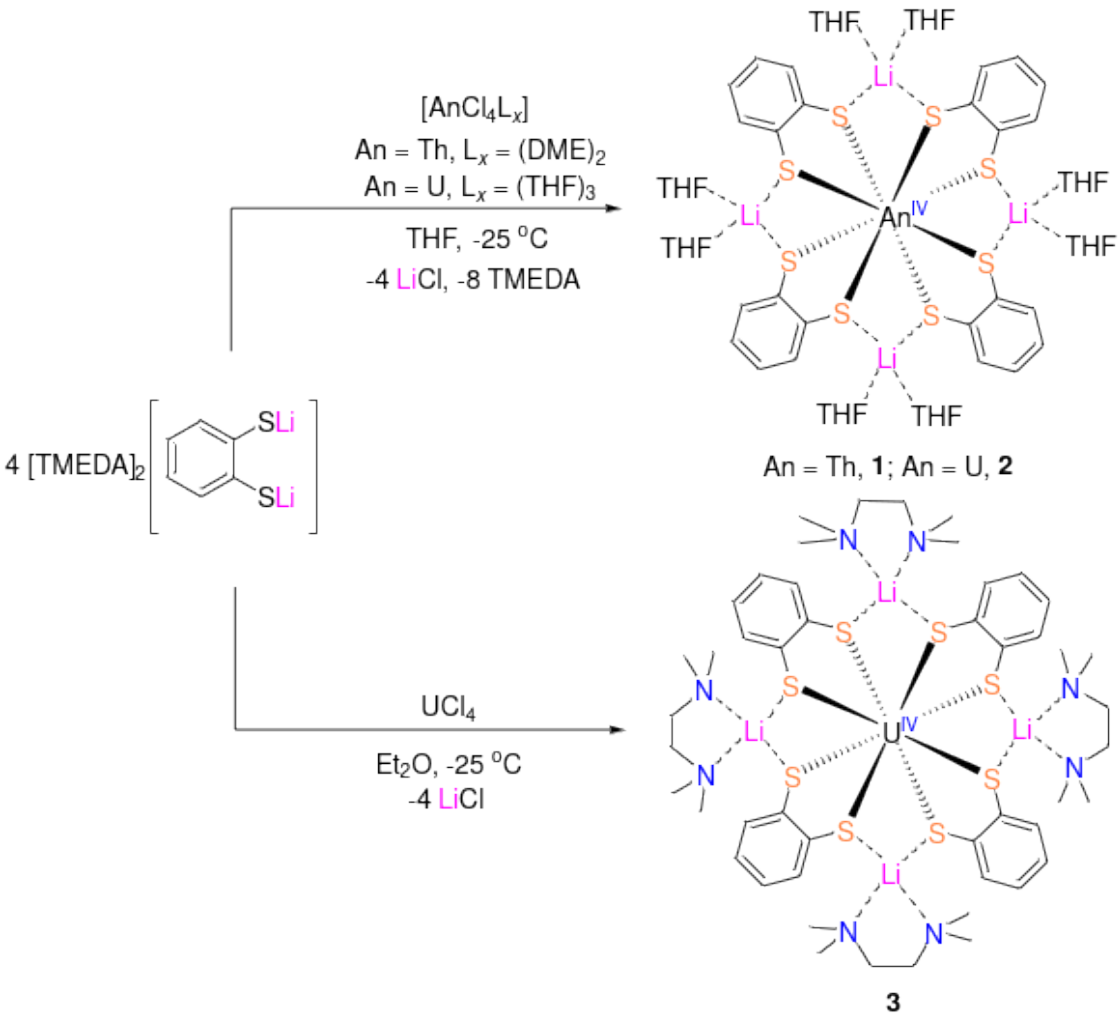


Over the past 15 years, our research group has synthesized a series of homoleptic alkyl, alkoxide, amide, and ketimide complexes of An(IV) (An = Th, U), including $[U(O^tBu)_6]^{2-}$, $[An(CH_2SiMe_3)_5]^-$ (An = Th, U), $[An(CH_2Ph)_6]^{2-}$ (An = Th, U), $[U(NH^tBu)_6]^{2-}$, $[U(NC_5H_{10})_5]^-$, $[An(N{=}C^tBuPh)_6]^{2-}$ (An = Th, U), and $[ThPh_6]^{2-}$.[27-33] While these ligands offer a range of σ- and π-donor abilities,[34] they consist exclusively of "hard" donor atoms, i.e., C, N, and O. In an effort to extend our homoleptic actinide chemistry beyond hard donors, we endeavoured to synthesize an An(IV) complex featuring a soft donor ligand (e.g., S, Se). In particular, we chose to focus on the synthesis of actinide 1,2-benzenedithiolate complexes, in part, because, surprisingly, no 1,2-benzenedithiolate complexes have yet been reported for the actinides. In contrast, a large number of homoleptic transition metal 1,2-benzenedithiolate complexes have been reported.[35-49] Herein, we describe the synthesis of three homoleptic An(IV) 1,2-benzenedithiolate complexes, namely, $[Li(THF)_2]_4[An(1,2\text{-}S_2C_6H_4)_4]$ (An = Th, **1**; An = U, **2**) and $[Li(TMEDA)]_4[U(1,2\text{-}S_2C_6H_4)_4]$ (**3**), along with an investigation of their solution and solid-state structures.

Results and Discussion

Addition of a cold (-25 °C) THF solution of 4 equiv of $[Li(TMEDA)]_2[1,2\text{-}S_2C_6H_4]$ to a cold (-25 °C) THF solution of $[ThCl_4(DME)_2]$ or $[UCl_4(THF)_3]$ results in an immediate color change. Work-up of the reaction mixtures, followed by crystallization from THF/hexanes (for **1**) or concentrated Et_2O (for **2**) affords $[Li(THF)_2]_4[An(1,2\text{-}S_2C_6H_4)_4]$ (An = Th, **1**; An = U, **2**) in 35% (for **1**) and 49% (for **2**) yields (Scheme 2). Complexes **1** and **2** were isolated as colorless plates and orange blocks, respectively. In contrast, slow addition of a cold (-25 °C) Et_2O solution of 4 equiv of $[Li(TMEDA)]_2[1,2\text{-}S_2C_6H_4]$ to a cold (-25 °C) Et_2O suspension of UCl_4 results in immediate formation of dark yellow solution. Work-up of the reaction mixture, followed by crystallization from Et_2O/hexanes, affords $[Li(TMEDA)]_4[U(1,2\text{-}S_2C_6H_4)_4]$ (**3**), which can be isolated as yellow plates in 62% yield. Presumably, the weakly-donating Et_2O cannot outcompete with TMEDA binding to Li^+, in contrast to the THF reactions (Scheme 2), permitting the isolation of the TMEDA-containing complex. Attempts to make the thorium analogue of **3** were unsuccessful. Complexes **1**, **2**, and **3** are also formed upon addition of only 3 equiv of $[Li(TMEDA)]_2[1,2\text{-}S_2C_6H_4]$ to the actinide salt. They are soluble in Et_2O, THF, and benzene, but insoluble in hexanes. Complexes **1** and **2** are thermally stable. C_6D_6 solutions of either complex show no evidence of decomposition upon standing at room temperature for 1 week. They are also moderately air stable; however, they are highly moisture sensitive. For example, exposure of complex **1** to H_2O in C_6D_6 results in complete consumption of **1** and formation of $1,2\text{-}C_6H_4(SH)_2$ as the major product,[50] concomitant with the deposition of copious amounts of white solid.

Scheme 2. Syntheses of Complexes **1**-**3**.



The ^{1}H NMR spectrum of **1** in benzene-d_6 reveals two distinct resonances at 7.63 ppm and 6.84 ppm, assignable to *ortho* and *meta* positions of the $[1,2\text{-}S_2C_6H_4]^{2-}$ fragment. These resonances are present in a 1:1 ratio (Figure S2). Additionally, its ^{7}Li{^{1}H} NMR spectrum displays a single resonance at 1.57 ppm (Figure S4). These results contrast with the S_4 symmetry observed in solid state (see below), which would result in four unique ^{1}H environments for the $[1,2\text{-}S_2C_6H_4]^{2-}$ ligand. To explain these results, we suggest that the Li^{+} cations in **1** can rapidly exchange between the benzenedithiolate binding sites at room

temperature. Interestingly, the ^{1}H NMR spectrum of **2** in benzene-d_6 reveals four distinct, paramagnetically-shifted resonances at 17.68 ppm, 11.88 ppm, 7.95 ppm, and 2.11 ppm, which are assignable to the $[1,2\text{-}S_2C_6H_4]^{2-}$ fragment (Figure S5). These resonances are present in a 1:1:1:1 ratio, and indicate that the S_4 symmetry observed in the solid-state is maintained in solution (see below). Similar behavior is observed in the ^{1}H NMR spectrum of complex **3**, as well as the previously reported dithiolate complex, $[Li(DME)]_4[U(SCH_2CH_2S)_4]$.[9] Finally, the ^{7}Li{^{1}H} NMR spectrum of **2** displays a single resonance at 7.31 ppm (Figure S6). The relatively large downfield shift observed for the ^{7}Li resonance is indicative of a paramagnetic pseudo-contact shift and provides further evidence that the Li^+ cations remain bound to the benzenedithiolate ligands in solution, as suggested by the ^{1}H NMR spectral data.

Complexes **1** and **2** crystallize in the tetragonal space group $P\bar{4}2_1c$ as the THF solvates, **1** · 2THF and **2** · 2THF (Figures 1 and S1), whereas complex **3** crystallizes in the orthorhombic space group $P2_12_12$ (Figure 1). The metal centers in all three complexes lie on special positions. According to the continuous shape measure,[51] their coordination geometries are best described as distorted triangular dodecahedra (CSM = 1.015 for **1**, 1.161 for **2**, and 1.928 for **3**). Each actinide center features eight An-S σ-bonds to four $[1,2\text{-}S_2C_6H_4]^{2-}$ ligands. For all three complexes, the chelating C_6H_4 rings occupy the "m" edges of the dodecahedron, which results in approximate D_{2d} point group symmetry.[52] A similar arrangement of the chelating groups is observed for $[U(SCH_2CH_2S)_4]^{4-}$.[9] Additionally, the Li^+ cations in **1** and **2** are coordinated by two sulfur atoms of adjacent $[1,2\text{-}S_2C_6H_4]^{2-}$ ligands and two oxygen atoms of the THF ligands. Similarly, **3** features Li^+ cations coordinated by two sulfur atoms of adjacent $[1,2\text{-}S_2C_6H_4]^{2-}$ ligands and two nitrogen atoms of TMEDA. For all three structures, the Li

cations occupy "g" edges of the dodecahedron,[52] and their arrangement among the eight "g" edges gives each complex S_4 symmetry.

The average Th-S distance in **1** (2.89 Å) is notably longer than other reported Th-S single bonds, likely due to the high charge on the Th center.[53, 54] For example, the Th-S distances in $[Cp^*_2Th(SPh)_2]$ are 2.7488(11) and 2.7451(10) Å,[55] whereas the Th-S distance in $[Th(SCPh_3)(NR_2)_3]$ (R = $SiMe_3$) is 2.718(3) Å.[56] The average U-S distances in **2** (2.82 Å) and **3** (2.81 Å) are shorter than that found in **1**, consistent with the smaller ionic radius of the U(IV) ion,[57] but similar to those found in previously reported U(IV) dithiolate complexes.[58] For instance, the average U-S distance in $[U(dddt)_4]^{4-}$ is 2.83 Å,[7] whereas the average U-S distance in $[U(SCH_2CH_2S)_4]^{4-}$ is 2.85 Å.[9] However, the average U-S distances in **2** and **3** are longer than that found in $[U(SPh)_4(Py)_3]$ (2.74 Å).[59] Finally, the average Li-S distances found in **1** (2.50 Å), **2** (2.46 Å), and **3** (2.46 Å) are consistent with previously reported Li-S dative interactions.[9, 60, 61] The S-Li-S angles are also similar for **1** (102.2(8)°), **2** (101.3(4)°), and **3** (103.7(4) and 103.2(5)°). The similarity of the Li^+ environments across all three complexes is surprising, given the differing solution-state behavior for complex **1** versus complexes **2** and **3**. The reason for this differing solution behavior is presently unknown.

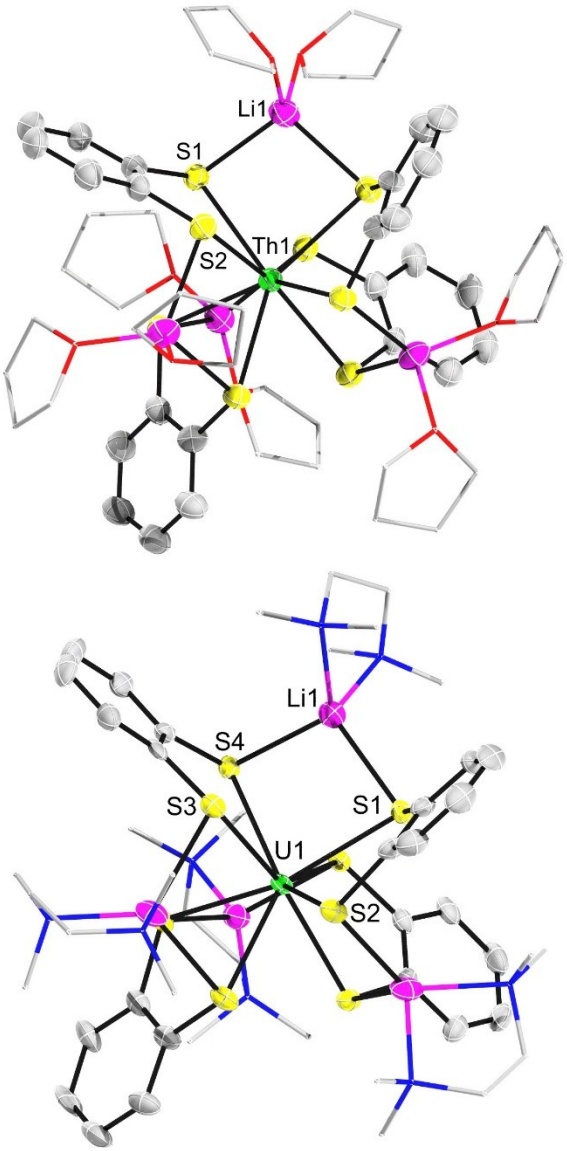


Figure 1. Solid-state molecular structure of **1** · 2THF shown with 50% probability ellipsoids (top). Solid-state molecular structure of **3** shown with 50% probability ellipsoids (bottom). The THF and TMEDA ligands are shown in wireframe style and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **1** · 2THF: Th1-S1 = 2.885(3), Th1-S2 = 2.892(3), Li1-S1 = 2.50(2), Li1-S2 = 2.48(2), Li1-O1 = 1.94(3), Li1-O2 = 1.91(2), S1-Th1-S2 = 69.75(9), S2-Li1-S1 = 102.2(8). **2** · 2THF: U1-S1 = 2.8169(12), U1-S2 = 2.8275(11), Li1-S1

= 2.467(10), Li1-S2 = 2.460(10), Li1-O1 = 1.935(11), Li1-O2 = 1.946(11), S1-U1-S2 = 70.52(3), S1-Li1-S2 = 101.3(4). **3**: U1-S1 = 2.8011(16), U1-S2 = 2.8184(16), U1-S3 = 2.7827(17), U1-S4 = 2.8224(16), Li1-S1 = 2.487(12), Li1-S4 = 2.460(12), Li2-S2 = 2.447(13), Li2-S3 = 2.482(12), Li1-N1 = 2.103(12), Li1-N2 = 2.084(13), Li2-S3 = 2.056(14), Li2-N4 = 2.068(13), S1-U1-S2 =70.56(5), S3-U1-S4 = 70.48(5), S4-Li1-S1 = 103.7(4), S2-Li2-S3 = 103.2(5).

Conclusion

In summary, we have prepared and characterized three homoleptic actinide benzenedithiolato complexes, namely, $[Li(THF)_2]_4[An(S_2C_6H_4)_4]$ (An = Th, U) and $[Li(TMEDA)]_4[U(S_2C_6H_4)_4]$, and we confirmed their formulations using X-ray crystallography and multi-nuclear NMR spectroscopy. These complexes represent the first reported 1,2-benzenedithiolate complexes of the actinides, which is surprising considering the widespread application of benzenedithiolate ligands in transition metal chemistry. Their solid-state and solution phase characterization will assist in the development of highly-selective soft-donor chelators for actinide binding and separation. Their isolation also sets the stage for synthesis of the Np and Pu analogues, which we plan to pursue in a future study.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic details, and spectral data for complexes **1**, **2**, and **3** (PDF).

AUTHOR INFORMATION

Corresponding Author

*hayton@chem.ucsb.edu,

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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