

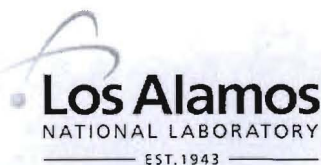
LA-UR- 09-00904

Approved for public release;
distribution is unlimited.

Title: Uranium (VI)Bis(imido) Chalcogenate Complexes: Synthesis
and Density Functional Theory Analysis

Author(s): Liam P. Spencer, Ping Yang, Brian L. Scott, Enrique R.
Batista, James M. Boncella

Intended for: Inorganic Chemistry



Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Uranium(VI) Bis(imido) Chalcogenate Complexes: Synthesis and Density Functional Theory Analysis

Liam P. Spencer,[†] Ping Yang,[‡] Brian L. Scott,[†] Enrique R. Batista,[‡] and James M. Boncella^{*†}

Materials, Physics and Applications Division, Los Alamos National Laboratory, MS J514, Los Alamos, New Mexico 87545, and Theoretical Division, Los Alamos National Laboratory, MS B268, Los Alamos, New Mexico 87545

Received November 18, 2008

Bis(imido) uranium(VI) *trans*- and *cis*-dichalcogenate complexes with the general formula $U(N^iBu)_2(EAr)_2(OPPh_3)_2$ ($EAr = O-2\text{-}^iBuC_6H_4$, SPh, SePh, TePh) and $U(N^iBu)_2(EAr)_2(R_2bpy)$ ($EAr = SPh, SePh, TePh$) ($R_2bpy = 4,4'$ -disubstituted-2,2'-bipyridyl, $R = Me, ^iBu$) have been prepared. This family of complexes includes the first reported monodentate selenolate and tellurolate complexes of uranium(VI). Density functional theory calculations show that covalent interactions in the U–E bond increase in the *trans*-dichalcogenate series $U(N^iBu)_2(EAr)_2(OPPh_3)_2$ as the size of the chalcogenate donor increases and that both 5f and 6d orbital participation is important in the M–E bonds of U–S, U–Se, and U–Te complexes.

Introduction

The significance of covalent interactions and the role of f-orbitals in metal ligand bonds in f-element complexes is an intensely studied and greatly debated area in actinide chemistry. Studies of uranyl (UO_2^{2+}) complexes have been crucial in developing an understanding of the importance of these issues in f-element complexes, in particular their function in the formation of U=O multiple bonds.¹ The interactions of ligands in the equatorial plane perpendicular to the dioxo ligands are also important because of the relevance of the UO_2^{2+} ion in lanthanide/actinide separation schemes and speciation of the UO_2^{2+} ion in the environment. Coordination chemistry studies of this ion have shown that the majority of complexes involve hard donor ligands (i.e., O, N, and halide)² which suggests that the equatorial U–L bonds possess significant ionic character.³ The coordination of soft donor ligands to the UO_2^{2+} ion holds promise for

further understanding covalency and f-orbital participation in U–L bonding; however, few of these complexes have been reported.⁴

We have recently reported the isolation of the imido analogue of the uranyl ion ($U(NR)_2^{2+}$) and found that there are some striking differences between this ion and the uranyl ion.⁵ Density functional theory (DFT) calculations and X-ray absorption near edge structure (XANES) experiments have shown that there is less positive charge present on the uranium center in the $U(NR)_2^{2+}$ ion, which suggests a greater degree of covalency in the U=N bond in comparison to the U=O bond in the UO_2^{2+} ion.^{5a} We have also found that soft phosphine donor ligands can coordinate to the $U(NR)_2^{2+}$ ion in contrast to the UO_2^{2+} fragment.^{5b,d} This finding suggests that the metal center in the $U(NR)_2^{2+}$ ion is a softer Lewis acid than its UO_2^{2+} counterpart which presents the op-

* To whom correspondence should be addressed. E-mail: boncella@lanl.gov.

[†] Materials, Physics and Applications Division.

[‡] Theoretical Division.

- (1) (a) Grenthe, I. et al. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer-Verlag: New York, 2006; Vol. 1, pp 253–698.
- (2) (a) Bagnall, K. W. I. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, 1987; Vol. 3, p 1187. (b) King, R. B. *J. Coord. Chem.* **2005**, *58*, 47. (c) Szabo, Z.; Toraiishi, T.; Vallet, V.; Grenthe, I. *Coord. Chem. Rev.* **2006**, *250*, 784.
- (3) Pierloot, K.; van Besien, E. *J. Chem. Phys.* **2005**, *123*, 204309.

- (4) (a) Kannan, S.; Barnes, C. L.; Duval, P. B. *Inorg. Chem.* **2005**, *44*, 9137. (b) Crawford, M. J.; Ellern, A.; Noth, H.; Suter, M. *J. Am. Chem. Soc.* **2003**, *125*, 11778. (c) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Chem. Commun.* **2004**, 870. (d) Crawford, M. J.; Ellern, A.; Karaghiosoff, K.; Mayer, P.; Noth, H.; Suter, M. *Inorg. Chem.* **2004**, *43*, 7120. (e) Rose, D.; Chang, Y. D.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 5167. (f) Rose, D. J.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1998**, *268*, 163. (g) Crawford, M. J.; Mayer, P. *Inorg. Chem.* **2005**, *44*, 5547.
- (5) (a) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. *J. Science* **2005**, *310*, 1941. (b) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 10549. (c) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2930. (d) Spencer, L. P.; Gdula, R. L.; Hayton, T. W.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Chem. Commun.* **2008**, 4986.

portunity to investigate the coordination of other soft donor ligands and evaluate how covalent interactions and orbital participation in U(VI)–L bonds change as the softness of the L donor is varied.

In this paper, we report the synthesis of a family of bis(imido) uranium(VI) dichalcogenate complexes U(NⁱBu)₂-(EAR)₂(OPPh₃)₂ (EAR = O-2-ⁱBuC₆H₄, SPh, SePh, TePh) and U(NⁱBu)₂(EAR)₂(R₂bpy) (EAR = SPh, SePh, TePh) (R₂bpy = 4,4'-disubstituted-2,2'-bipyridyl, R = Me, ⁱBu). DFT calculations have been performed on the *trans*-dichalcogenate complexes U(NⁱBu)₂(EAR)₂(OPPh₃)₂ to investigate the trends in covalent interactions as the size of the chalcogenate donor changes and to evaluate the participation of d- and f-orbitals in the U–E bonds.

Experimental Section

Methods and Materials. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under either a high vacuum or an atmosphere of helium or argon. Hexanes and tetrahydrofuran (THF) were dried by passage over activated alumina, and CH₂Cl₂ was purchased anhydrous and stored over activated 4 Å molecular sieves for 24 h before use. CD₂Cl₂ and C₃D₅N were dried over activated 4 Å molecular sieves for 24 h before use. U(NⁱBu)₂I₂(OPPh₃)₂,^{5b} NaSPh-1/4 dme (dme = CH₃OCH₂CH₂OCH₃),⁶ KO(2-ⁱBuC₆H₄)₂⁷ were synthesized by published procedures or derivations based on published procedures. All other reagents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a Bruker AVA300 spectrometer. ¹H and ¹³C(¹H) NMR spectra are referenced to external SiMe₄ using the residual protio solvent peaks as internal standards (¹H NMR experiments) or the characteristic resonances of the solvent nuclei (¹³C NMR experiments). The ³¹P(¹H) NMR spectra were referenced to external 85% H₃PO₄. The ⁷⁷Se(¹H) NMR spectrum was referenced to external Ph₂Se₂ which has a chemical shift of 460 ppm relative to Me₂Se. The ¹²⁵Te(¹H) NMR spectrum was referenced to external Ph₂Te₂ which has a chemical shift of 420 ppm relative to Me₂Te. Elemental analyses were performed at the UC Berkeley Microanalytical Facility on a Perkin-Elmer Series II 2400 CHNS analyzer.

Synthesis of NaEPh-S (E = Se, S = 1/2 DME; E = Te, S = 1/2 THF). The following procedure is representative of the synthesis of NaEPh-S. To a stirring DME (3 mL) suspension of Na metal (31.3 mg, 1.4 mmol) at room temperature was added a DME solution (2 mL) of Ph₂Se₂ (250 mg, 0.8 mmol). The pale yellow suspension was stirred overnight at which time a yellow solution had formed. The solution was filtered through Celite, and the solvent removed until a white precipitate began to form. Hexanes were added, and the solution was left at –30 °C overnight to complete precipitation of a powdery white solid (95% yield based on Na metal used). The solid was filtered, dried in vacuo, and identified by ¹H NMR spectroscopy. In the case of NaTePh, the residue was recrystallized from THF/hexanes and recovered as a white powder. **NaSePh-1/2 DME:** ¹H NMR (C₅D₅N): 3.28 (s, 3H, -OCH₃), 3.50 (s, 2H, -OCH₂), 6.94–6.97 (m, 3H, -*p*-ArH and -*m*-ArH), 8.32 (d, ³J(H,H) = 4 Hz, 2H, -*o*-ArH). **NaTePh-1/2 THF:** ¹H NMR (C₂D₅N): 1.62 (m, 2H, THF), 3.66 (m, 2H, THF), 6.86

(m, 2H, -*m*-ArH), 7.05 (m, 1H, -*p*-ArH), 8.65 (d, ³J(H,H) = 6 Hz, 2H, -*o*-ArH).

Synthesis of U(NⁱBu)₂(EAR)₂(OPPh₃)₂ (EAR = O-2-ⁱBuC₆H₄ (1), SPh (2), SePh (3), TePh (4)). The following procedure is representative of the synthesis of 1–4. To a cooled (–30 °C) THF (5 mL) solution of U(NⁱBu)₂(I)₂(OPPh₃)₂ (175 mg, 0.15 mmol) in a 20 mL scintillation vial was added a chilled (–30 °C) THF solution (2 mL) of KO(2-ⁱBuC₆H₄)₂ (55.4 mg, 0.30 mmol). The mixture slowly darkens upon warming to room temperature. After being stirred overnight, the brown suspension was filtered through Celite, and the solvent removed until several milliliters remained. Hexanes (10 mL) were added to precipitate a dark red-brown powder (138 mg, 76%), which was recrystallized from CH₂Cl₂/hexanes. **1:** (Yield = 76%) ¹H NMR (C₆D₆): δ 0.33 (s, 18H, -NC(CH₃)₃), 2.15 (s, 18H, -C(CH₃)₃), 6.89–7.08 (m, 22H, -OPPh₃ and -ArH), 7.85 (d, ³J(H,H) = 9 Hz, 2H, -ArH), 8.03 (d, 2H, ³J(H,H) = 9 Hz, -ArH), 8.25–8.29 (m, 12H, -OPPh₃). ¹³C(¹H) NMR (C₆D₆): δ 18.6 (-C(CH₃)₃), 35.9 (-NC(CH₃)₃), 40.9 (C(CH₃)₃), 67.0 (-NC(CH₃)₃), 123.7 (-ArC), 128.6 (-ArC), 129.9 (-ArC), 130.5 (-ArC), 133.4 (-ArC), 135.6 (-ArC), 137.8 (¹J(C,P) = 14 Hz, -ArC), 146.8 (-ArC). ³¹P(¹H) NMR (C₆D₆): δ 42.7. **Anal. Calcd. for C₆₄H₇₄UN₂O₄P₂:** %C, 62.23; %H, 5.94; %N, 2.27. **Found:** %C, 62.09; %H, 5.56; %N, 2.16. **2:** (Yield = 86%) ¹H NMR (C₆D₆): δ 0.25 (s, 18H, -NC(CH₃)₃), 6.88 (t, ³J(H,H) = 8 Hz, 4H, -*m*-ArH), 7.11–7.24 (m, 20H, -OPPh₃ and -*p*-ArH), 8.31 (d, 4H, ³J(H,H) = 8 Hz, -*o*-ArH), 8.53–8.62 (m, 12H, -ArH, -OPPh₃). ¹³C(¹H) NMR (C₆D₆): δ 35.4 (-C(CH₃)₃), 65.3 (-C(CH₃)₃), 124.8 (-ArC), 128.2 (-ArC), 129.2 (-ArC), 131.4 (-ArC), 134.1 (-ArC), 134.8 (-ArC), 136.8 (¹J(C,P) = 14 Hz, -ArC), 143.5 (-ArC). ³¹P(¹H) NMR (C₆D₆): δ 43.6. **Anal. Calcd. for C₅₆H₅₈UN₂O₂P₂Se₂:** %C, 58.22; %H, 5.06; %N, 2.43. **Found:** %C, 58.74; %H, 4.54; %N, 2.30. **3:** (Yield = 81%) ¹H NMR (CD₂Cl₂): δ –0.17 (s, 18H, -NC(CH₃)₃), 6.91 (t, ³J(H,H) = 8 Hz, 4H, -*m*-ArH), 7.04 (t, ³J(H,H) = 8 Hz, 2H, -*p*-ArH), 7.42–7.72 (m, 18H, -OPPh₃), 8.12 (d, 4H, ³J(H,H) = 8 Hz, -*o*-ArH), 8.41–8.56 (m, 12H, -OPPh₃). ¹³C(¹H) NMR (CD₂Cl₂): δ 36.8 (-C(CH₃)₃), 66.1 (-C(CH₃)₃), 122.9 (-ArC), 127.6 (-ArC), 128.6 (-ArC), 130.2 (-ArC), 133.3 (-ArC), 135.8 (-ArC), 137.0 (¹J(C,P) = 14 Hz, -ArC), 145.2 (-ArC). ³¹P(¹H) NMR (CD₂Cl₂): δ 43.7. ⁷⁷Se(¹H) NMR (CD₂Cl₂): δ 134.3. **Anal. Calcd. for C₅₆H₅₈UN₂O₂P₂Se₂:** %C, 53.32; %H, 4.55; %N, 2.39. **4:** (Yield = 73%) ¹H NMR (CD₂Cl₂): δ –0.11 (s, 18H, -NC(CH₃)₃), 6.94 (t, ³J(H,H) = 8 Hz, 4H, -*m*-ArH), 7.52–7.68 (m, 18H, -OPPh₃), 7.18 (t, ³J(H,H) = 8 Hz, -*p*-ArH), 8.06 (d, 4H, ³J(H,H) = 8 Hz, -*o*-ArH), 8.37–8.51 (m, 12H, -ArH, -OPPh₃). ¹³C(¹H) NMR (CD₂Cl₂): δ 34.9 (-C(CH₃)₃), 64.9 (-C(CH₃)₃), 121.6 (-ArC), 127.1 (-ArC), 127.9 (-ArC), 129.8 (-ArC), 134.7 (-ArC), 135.1 (-ArC), 136.3 (¹J(C,P) = 14 Hz, -ArC), 142.5 (-ArC). ³¹P(¹H) NMR (CD₂Cl₂): δ 44.3. ¹²⁵Te(¹H) NMR (CD₂Cl₂): δ 216.8. **Anal. Calcd. for C₅₆H₅₈UN₂O₂Te₂:** %C, 49.96; %H, 4.34; %N, 2.08. **Found:** %C, 49.78; %H, 4.07; %N, 2.38.

Synthesis of U(NⁱBu)₂(I)₂(R₂bpy) (R = Me (5), ⁱBu (6)). The following procedure is representative of the synthesis of 5 and 6. A toluene (5 mL) solution of U(NⁱBu)₂(I)₂(THF)₂ (500 mg, 0.64 mmol) was treated with a toluene (2 mL) solution of Me₂bpy (118 mg, 0.64 mmol) and stirred for 2 h. The red-orange precipitate was collected by filtration and washed with toluene (2 × 5 mL) and dried in vacuo. (526 mg, Yield = 97%), **5:** ¹H NMR (CD₂Cl₂): δ 0.12 (s, 18H, -C(CH₃)₃), 2.77 (s, 6H, -CH₃), 7.90 (d, ³J(H,H) = 5 Hz, 2H, -bpyH), 8.60 (s, 2H, -bpyH), 10.74 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H) NMR (CD₂Cl₂): δ 29.3 (-C(CH₃)₃), 34.2 (-CH₃), 72.3 (-C(CH₃)₃), 122.6 (-bpyC), 124.6 (-bpyC), 148.2 (-bpyC), 155.7 (-bpyC), 165.0 (-bpyC). **Anal. Calcd. For**

(6) Bartucz, T. Y.; Golombek, A.; Lough, A. J.; Maltby, P. A.; Morris, R. H.; Ramachandran, R.; Schlaf, M. *Inorg. Chem.* **1998**, *37*, 1555.
(7) Buzzeo, M. C.; Zakharov, L. N.; Rheingold, A. L.; Doerrer, L. H. *J. Mol. Struct.* **2003**, *657*, 19.

Uranium(VI) Bis(imido) Chalcogenate Complexes

167 **C₂₀H₃₀N₄I₂U**: %C 29.36; %H, 3.70; %N, 6.85. Found: %C, 29.44;
168 %H, 3.62; %N, 6.66. **6**: ¹H NMR (CD₂Cl₂): δ 0.12 (s, 18H,
169 -C(CH₃)₃), 1.59 (s, 6H, -C(CH₃)₃), 8.08 (d, ³J(H,H) = 5 Hz, 2H,
170 -bpyH), 8.66 (s, 2H, -bpyH), 10.80 (d, ³J(H,H) = 5 Hz, 2H,
171 -bpyH). ¹³C(¹H) NMR (CD₂Cl₂): δ 30.5 (-C(CH₃)₃), 30.7
172 (-C(CH₃)₃), 55.4 (-C(CH₃)₃), 76.5 (-C(CH₃)₃), 121.2 (-bpyC), 123.5
173 (-bpyC), 149.1 (-bpyC), 157.2 (-bpyC), 166.0 (-bpyC). **Anal. Calcd.**
174 **For C₂₆H₄₂N₄I₂U**: %C, 34.60; %H, 4.69; %N, 6.21. Found: %C,
175 34.52; %H, 4.52; %N, 6.15.

176 **Synthesis of U(NⁱBu)₂(EPh)₂(R₂bpy) (E = S, R = Me (7);**
177 **E = S, R = ⁱBu (8); E = Se, R = Me (9); E = Se, R = ⁱBu**
178 **(10); E = Te, R = Me (11); E = Te, R = ⁱBu (12)).** The following
179 procedure is representative of the synthesis of **7–12**. To a cooled
180 (–30 °C) THF (5 mL) solution of **5** (175 mg, 0.21 mmol) in a 20
181 mL scintillation vial was added a chilled (–30 °C) THF solution
182 (2 mL) of NaSPh-1/4 dme (95 mg, 0.42 mmol). The mixture slowly
183 turns a deep red color upon warming to room temperature. After
184 being stirred overnight, the red suspension was filtered through
185 Celite, and the solvent removed until several milliliters remained.
186 Hexanes (10 mL) were added to precipitate a bright red powder
187 (138 mg, 76%), which was recrystallized from CH₂Cl₂/hexanes.
188 (mg, Yield = %) **7**: ¹H NMR (CD₂Cl₂): δ –0.29 (s, 18H,
189 -C(CH₃)₃), 2.74 (s, 6H, -CH₃), 6.86 (t, *J* = 7 Hz, 2H, -*p*-SArH),
190 7.21 (t, ³J(H,H) = 7 Hz, 4H, -*m*-SArH), 7.89 (d, ³J(H,H) = 5 Hz,
191 2H, -*H*), 8.09 (d, ³J(H,H) = 7 Hz, 4H, -*o*-SArH), 8.50 (s, 2H,
192 -bpyH), 10.85 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H) NMR (CD₂
193 Cl₂): δ 29.9 (-C(CH₃)₃), 35.0 (-CH₃), 71.3 (-C(CH₃)₃), 122.9
194 (-bpyC), 123.8 (-ArC), 125.9 (-bpyC), 128.6 (-ArC), 147.1 (-bpyC),
195 152.2 (-ArC), 153.5 (-bpyC), 164.2 (-bpyC). **Anal. Calcd. For**
196 **C₃₂H₄₀N₄S₂U**: %C, 49.09; %H, 5.15; %N, 7.19. Found: %C, 48.98;
197 %H, 5.07; %N, 7.11. **8**: Three molecules of THF were present in
198 the solid state lattice. Under vacuum, the crystalline material
199 obtained readily loses this solvent. ¹H NMR (CD₂Cl₂): δ –0.29
200 (s, 18H, -C(CH₃)₃), 1.58 (s, 18H, -C(CH₃)₃), 6.87 (t, *J* = 7 Hz,
201 2H, -*p*-SArH), 7.22 (t, ³J(H,H) = 7 Hz, 4H, -*m*-SArH), 8.10 (br s,
202 6H, -bpyH and -*o*-SArH), 8.60 (s, 2H, -bpyH), 10.89 (d, ³J(H,H)
203 = 5 Hz, 2H, -bpyH). ¹³C(¹H) NMR (CD₂Cl₂): δ 32.3 (-C(CH₃)₃),
204 33.0 (-C(CH₃)₃), 53.2 (-C(CH₃)₃), 75.8 (-C(CH₃)₃), 123.4 (-bpyC),
205 125.3 (-ArC), 125.9 (-bpyC), 129.1 (-ArC), 133.7 (-ArC), 149.0
206 (-bpyC), 150.6 (-ArC), 152.9 (-bpyC), 163.3 (-bpyC). **Anal. Calcd.**
207 **For C₃₈H₅₂N₄S₂U**: %C, 52.64; %H, 6.05; %N, 6.46. Found: %C,
208 52.59; %H, 6.13; %N, 6.37. **9**: ¹H NMR (CD₂Cl₂): δ –0.21 (s,
209 18H, -C(CH₃)₃), 2.75 (s, 6H, -CH₃), 6.95 (t, *J* = 7 Hz, 2H, -*p*-
210 SeArH), 7.19 (t, ³J(H,H) = 7 Hz, 4H, -*m*-SeArH), 7.90 (d, ³J(H,H)
211 = 5 Hz, 2H, -bpyH), 8.23 (d, ³J(H,H) = 7 Hz, 4H, -*o*-SeArH), 8.53
212 (s, 2H, -bpyH), 10.87 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H)
213 NMR (CD₂Cl₂): δ 29.3 (-C(CH₃)₃), 35.7 (-CH₃), 72.5 (-C(CH₃)₃),
214 123.6 (-bpyC), 124.8 (-ArC), 127.4 (-bpyC), 129.1 (-ArC), 148.0
215 (-bpyC), 151.6 (-ArC), 153.0 (-bpyC), 165.3 (-bpyC). ⁷⁷Se(¹H)
216 NMR (CD₂Cl₂): δ 142.8 **Anal. Calcd. For C₃₂H₄₀N₄Se₂U**: %C,
217 43.84; %H, 4.71; %N, 6.39. Found: %C, 43.80; %H, 4.71; %N,
218 6.29. **10**: ¹H NMR (CD₂Cl₂): δ –0.23 (s, 18H, -C(CH₃)₃), 1.58 (s,
219 18H, -C(CH₃)₃), 6.95 (t, ³J(H,H) = 8 Hz, 2H, -*p*-SeArH), 7.18 (t,
220 ³J(H,H) = 7 Hz, 4H, -*m*-SeArH), 8.08 (d, ³J(H,H) = 5 Hz, 2H,
221 -bpyH), 8.26 (d, ³J(H,H) = 7 Hz, 4H, -*o*-SeArH), 8.60 (s, 2H,
222 -bpyH), 10.90 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H) NMR
223 (CD₂Cl₂): δ 30.2 (-C(CH₃)₃), 30.6 (-C(CH₃)₃), 55.5 (-C(CH₃)₃), 77.2
224 (-C(CH₃)₃), 124.9 (-bpyC), 125.6 (-ArC), 125.3 (-bpyC), 129.9
225 (-ArC), 134.1 (-ArC), 149.5 (-bpyC), 150.0 (-ArC), 153.1 (-bpyC),
226 165.8 (-bpyC). ⁷⁷Se(¹H) NMR (CD₂Cl₂): δ 145.0. **Anal. Calcd.**
227 **For C₃₈H₅₂N₄Se₂U**: %C, 47.50; %H, 5.46; %N, 5.83. Found: %C,
228 47.61; %H, 5.60; %N, 5.72. **11**: ¹H NMR (CD₂Cl₂): δ –0.10 (s, 18H,
229 -C(CH₃)₃), 1.89 (s, 18H, -C(CH₃)₃), 6.79 (t, ³J(H,H) = 8 Hz, 2H,

-*p*-TeArH), 7.01 (t, ³J(H,H) = 7 Hz, 4H, -*m*-TeArH), 7.50 ³J(H,H) 230
= 5 Hz, 2H, -bpyH), 8.19 (d, ³J(H,H) = 7 Hz, 4H, -*o*-TeArH), 231
8.97 (s, 2H, -bpyH), 11.06 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H) 232
NMR (CD₂Cl₂): δ 30.5 (-C(CH₃)₃), 34.2 (-CH₃), 73.9 (-C(CH₃)₃), 233
121.7 (-bpyC), 124.0 (-ArC), 126.3 (-bpyC), 129.4 (-ArC), 146.2 234
(-bpyC), 153.1 (-ArC), 155.0 (-bpyC), 163.9 (-bpyC). ¹²⁵Te(¹H) 235
NMR (CD₂Cl₂): δ 226.3 **Anal. Calcd. For C₃₂H₄₀N₄Te₂U**: %C, 236
39.46; %H, 4.14; %N, 5.75. Found: %C, 39.40; %H, 4.21; %N, 237
5.71. **12**: ¹H NMR (CD₂Cl₂): δ –0.092 (s, 18H, -C(CH₃)₃), 1.56 (s, 238
18H, -C(CH₃)₃), 6.91 (t, ³J(H,H) = 8 Hz, 2H, -*p*-TeArH), 7.07 (t, 239
³J(H,H) = 7 Hz, 4H, -*m*-TeArH), 7.51 (d, ³J(H,H) = 5 Hz, 2H, 240
-bpyH), 8.24 (d, ³J(H,H) = 7 Hz, 4H, -*o*-TeArH), 8.83 (s, 2H, 241
-bpyH), 10.93 (d, ³J(H,H) = 5 Hz, 2H, -bpyH). ¹³C(¹H) NMR 242
(CD₂Cl₂): δ 31.0 (-C(CH₃)₃), 31.2 (-C(CH₃)₃), 53.6 (-C(CH₃)₃), 75.3 243
(-C(CH₃)₃), 123.8 (-bpyC), 124.2 (-ArC), 124.9 (-bpyC), 128.6 244
(-ArC), 133.0 (-ArC), 148.6 (-bpyC), 151.4 (-ArC), 152.6 (-bpyC), 245
164.6 (-bpyC). ¹²⁵Te(¹H) NMR (CD₂Cl₂): δ 224.0 **Anal. Calcd.** 246
For C₃₈H₅₂N₄Te₂U: %C, 43.13; %H, 4.95; %N, 5.30. Found: %C, 247
42.98; %H, 4.88; %N, 5.23. 248

X-ray Crystallographic Details. The crystal structures of 249
compounds **1–4**, **5**, **8**, **9**, and **12** were determined as follows: The 250
crystal was mounted in a nylon cryoloop from Paratone-N oil under 251
argon gas flow. The data were collected on a Bruker SMART APEX 252
II charge-coupled-device (CCD) diffractometer, with KRYO-FLEX 253
liquid nitrogen vapor cooling device. The instrument was equipped 254
with graphite monochromatized Mo K α X-ray source (λ = 0.71073 255
Å), with MonoCap X-ray source optics. A hemisphere of data was 256
collected using ω scans, with 5 s frame exposures and 0.3° frame 257
widths. Data collection and initial indexing and cell refinement were 258
handled using APEX II software.⁸ Frame integration, including 259
Lorentz-polarization corrections, and final cell parameter calcula- 260
tions were carried out using the SAINT+ software.⁹ The data were 261
corrected for absorption using the SADABS program.¹⁰ Decay of 262
reflection intensity was monitored via analysis of redundant frames. 263
The structure was solved using Direct methods and difference 264
Fourier techniques. All hydrogen atom positions were idealized, 265
and rode on the atom they were attached to. The final refinement 266
included anisotropic temperature factors on all non-hydrogen atoms. 267
Structure solution, refinement, graphics, and creation of publication 268
materials were performed using SHELXTL.¹¹ 269

Computational Details. The B3LYP hybrid density functional 270
was employed to optimize the equilibrium molecular structures of 271
all the complexes studied.¹² The small-core Stuttgart RSC 1997 272
relativistic effective core potential (RECP) was used to model the 273
uranium center,¹³ with the associate basis set [6s/6p/5d/3f]. For 274
light chalcogenate atoms, that is, oxygen, sulfur, and selenium, the 275
6-31+G* basis sets were used. While for the heavy chalcogenate 276
atoms, selenium, tellurium, and polonium, the calculations use the 277
Stuttgart relativistic large core ECP.¹⁴ To compare systematically 278
and avoid spurious effects while comparing all-electron calculations 279
with pseudopotential ones, we also applied the same Stuttgart ECP 280
on oxygen and sulfur complexes. The geometries of all the 281
molecules were optimized without symmetry constraints. The 282
geometries from the all electron and RECP calculation were 283

(8) APEX II, 1.08; Bruker AXS, Inc.: Madison, WI, 2004; S15.

(9) SAINT+, 7.06; Bruker AXS, Inc.: Madison, WI, 2003.

(10) Sheldrick, G. M. SADABS, 2.03; University of Göttingen: Göttingen, Germany, 2001.

(11) SHELXTL, 5.10; Bruker AXS, Inc.: Madison, WI, 1997.

(12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.(13) Kühle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.(14) (a) Fuentealba, P.; Preuss, H.; Stoll, H.; Szenpaly, L. v. *Chem. Phys. Lett.* **1982**, *89*, 418–422. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245–1263.

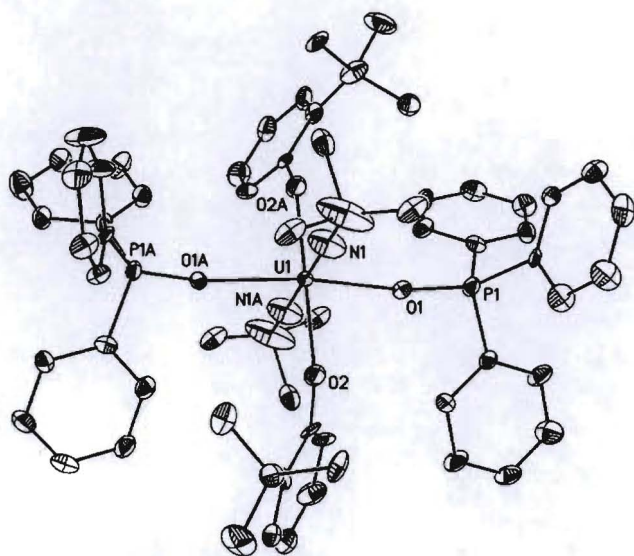


Figure 1. Solid state molecular structure of $[U(N^tBu)_2(O-2-BuC_6H_4)_2(OPPh_3)_2]$ (**1**) with thermal ellipsoids drawn at the 50% probability level (Symmetry codes: (A) $-x, 1-y, z$). Selected bond lengths (Å) and angles (deg): U1–N1 = 1.870(6), U1–O1 = 2.341(7), U1–O2 = 2.267(6), O1–P1 = 1.539(7), N1–U1–N1A = 180.0, U1–O2–C5 = 145.1(4).

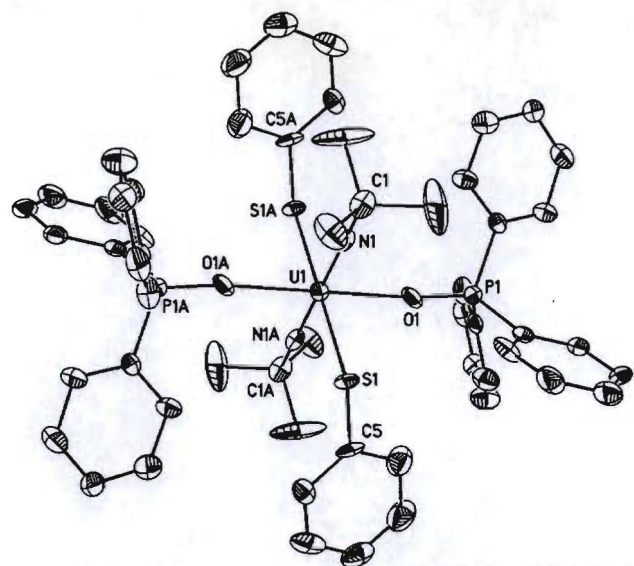
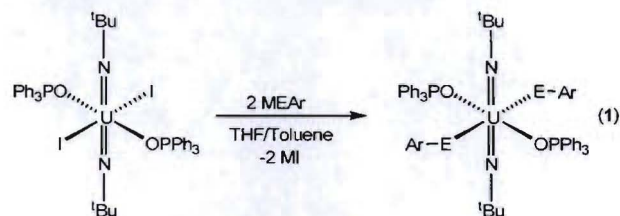
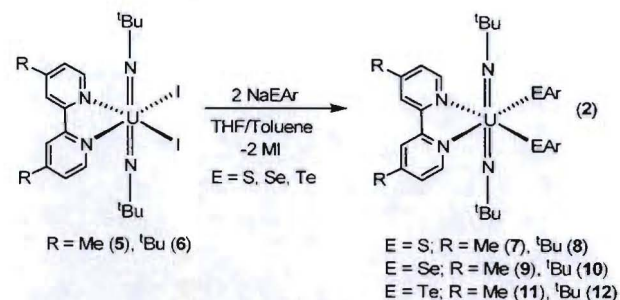


Figure 2. Solid state molecular structure of $[U(N^tBu)_2(SPh)_2(OPPh_3)_2]$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 1.840(7), U1–S1 = 2.757(10), U1–O1 = 2.322(5), O1–P1 = 1.533(6), U1–S1–C5 = 110.6(2), N1–U1–N1A = 180.0.

enylphosphine oxide analogue, $U(N^tBu)_2(I)_2(OPPh_3)_2$, which has enabled us to follow reactions by ^{31}P NMR spectroscopy. The reactions between 2 equiv of aryl chalcogenate reagents MEAr (M = K, EAr = O-2- tBuC_6H_4 ; M = Na, EAr = SPh, SePh, TePh) and $U(N^tBu)_2(I)_2(OPPh_3)_2$ provide the uranium(VI) *trans*-dichalcogenate complexes $U(N^tBu)_2(EAr)_2(OPPh_3)_2$ (**1–4**, eq 1). The *cis*-dichalcogenate complexes $U(N^tBu)_2(EAr)_2(R_2bpy)$ (EAr = SPh, SePh, TePh) (**7–12**, eq 2) were prepared in a similar fashion from the bis(imido) uranium(VI) diiodide complexes $U(N^tBu)_2(I)_2(R_2bpy)$ (**5, 6**). To our knowledge, the selenolate and telluroate complexes in this family of complexes represent the first monodentate uranium(VI)-selenolate and -telluroate complexes reported. The 1H NMR spectrum of **1** is representative and features two equivalent tBu -phenoxide donors with a singlet at 2.15 ppm and multiplets at 7.85, 8.03, and 8.27 ppm. In addition, there are multiplets at 6.90 and 8.27 ppm indicative of the $OPPh_3$ ligands and a singlet at 0.33 ppm attributable to the *tert*-butyl imido group. The ^{31}P NMR of **1** shows a singlet at 42.7 ppm that is shifted downfield from the starting material $U(N^tBu)_2(I)_2(OPPh_3)_2$. An interesting aspect of compounds **3** and **4** is the $^{77}Se(^1H)$ and $^{125}Te(^1H)$ NMR spectra that feature singlets at 134.3 and 216.8 ppm, respectively. Similar ^{77}Se and ^{125}Te chemical shifts were also observed in the *cis*-dichalcogenate complexes **9–12**.



- 1; M = K, E = O, Ar = 2- tBuC_6H_4
- 2; M = Na, E = S, E = Ph
- 3; M = Na, E = Se, E = Ph
- 4; M = Na, E = Te, E = Ph



R = Me (**5**), tBu (**6**)

E = S; R = Me (**7**), tBu (**8**)
E = Se; R = Me (**9**), tBu (**10**)
E = Te; R = Me (**11**), tBu (**12**)

284 essentially identical and in good agreement with the experimental
285 structures (see below). The molecular orbital energies from the two
286 methodologies are equivalent and the components of the orbitals
287 are the same. All the calculations reported in this paper were carried
288 out with the Gaussian 03 code.¹⁵

289 Results and Discussion

290 We have previously shown that the iodide ligands in the bis(imido) uranium(VI) complex $U(NR)_2(I)_2(THF)_x$ (R = tBu ,
291 $x = 2$; Ph, $x = 3$) can undergo metathesis reactions to
292 generate new uranium(VI) complexes.^{5b} Rather than use
293 these uranium(VI) synthons as an entry to chalcogenate
294 complexes, we focused on the reactivity of the triph-
295

296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331

Reactions between the *cis*-disposed diiodide complexes **5** and **6** and 2 equiv of NaOR (R = C_6H_5 , 4-Me C_6H_4 , 2- tBuC_6H_4) give unexpected products. Instead of the anticipated bis(imido) uranium(VI) bis(phenolate) complexes, a family of mixed valent uranium(V)–uranium(VI) complexes was recovered that have been identified by NMR spectroscopy and X-ray diffraction experiments. A full description of these complexes will be published in due course.

We have also explored the reactions between 2 equiv of NaEPh (E = Se, Te) and $UO_2I_2(OPPh_3)_2$ in an attempt to form analogous selenolate and telluroate complexes of the

Uranium(VI) Bis(imido) Chalcogenate Complexes

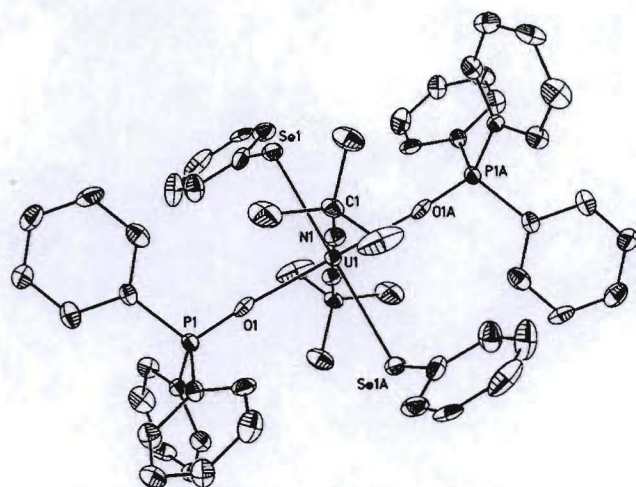


Figure 3. Solid state molecular structure of $[U(N^tBu)_2(SePh)_2(OPPh_3)_2]$ (**3**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 1.861(6), U1–Se1 = 2.8868(8), U1–O1 = 2.360(5), O1–P1 = 1.483(6), N1–U1–N1A = 180.0, U1–Se1–C5 = 106.4(2).

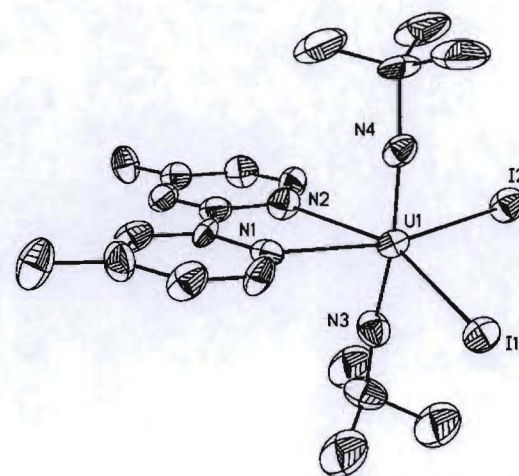


Figure 4. Solid state molecular structure of $[U(N^tBu)_2(I)_2(Me_2bpy)]$ (**5**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 2.530(11), U1–N2 = 2.480(10), U1–N3 = 1.822(11), U1–N4 = 1.810(11), U1–I1 = 3.0526(15), U1–I2 = 3.0115(18), N1–U1–N2 = 64.2(3), N3–U1–N4 = 171.3(5), I1–U1–I2 = 105.11(4).

332 UO_2^{2+} ion. Given the simple nature of these compounds and
 333 the extensive coordination studies performed with the uranyl
 334 ion, it is surprising that these complexes have yet to be
 335 reported. Our attempts to prepare these complexes did not
 336 provide unidentate selenolate or telluroate complexes but
 337 rather unidentifiable materials as evidenced by 1H NMR
 338 spectroscopy. Similar findings were observed in a previous
 339 study that examined the coordination of unidentate thiolate
 340 ligands to the UO_2^{2+} ion. In this report, stable mononuclear
 341 uranyl-thiolate complexes were only isolated with mono-
 342 dentate thiolate ligands that possessed significant electron-
 343 withdrawing properties and provided steric protection at the
 344 uranium(VI) center.^{4a} In light of these findings and our failed
 345 attempts to prepare simple Se- and Te-analogues of the
 346 UO_2^{2+} ion, it appears that the nature of the uranium center
 347 in the $U(NR)_2^{2+}$ and UO_2^{2+} ions has a significant effect on
 348 the isolation of stable uranium(VI) chalcogenate complexes.
 349 This striking difference has facilitated the isolation of novel
 350 uranium(VI) complexes with unique U(VI)–E bonds (E =
 351 S, Se, Te, P).

352 The solid state molecular structures of **1–5**, **8**, **9**, and **12**
 353 were determined by X-ray crystallography. Their respective
 354 thermal ellipsoid plots are shown in Figures 1–7. In the case
 355 of **4**, there is considerable disorder among the phos-

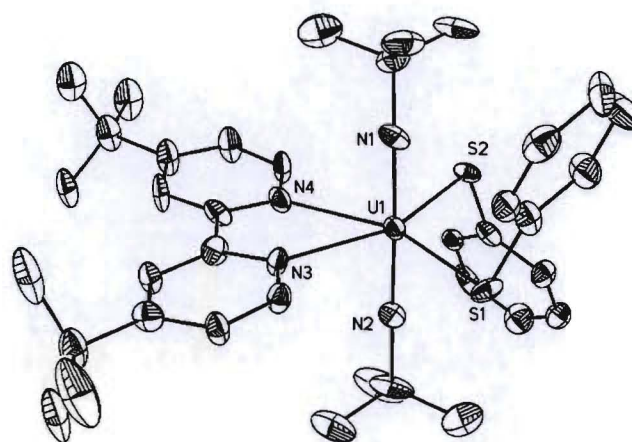


Figure 5. Solid state molecular structure of $[U(N^tBu)_2(SPh)_2(tBu_2bpy)]$ (**8**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 1.835(11), U1–N2 = 1.846(11), U1–N3 = 2.565(11), U1–N4 = 2.533(12), U1–S1 = 2.690(3), U1–S2 = 2.682(3), N1–U1–N2 = 178.4(5), N3–U1–N4 = 62.2(4), U1–S1–C27 = 108.0(5), U1–S2–C33 = 110.1(4).

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

356 phine oxide and imido ligands. Despite this disorder, the
 357 structure confirms the substitution at the uranium center (see
 358 Supporting Information, Figure 1S) and possesses a small
 359 estimated standard deviation for U–Te bond distances and
 360 angles. Selected average bond lengths and angles of both
 361 *trans*- and *cis*-dichalcogenate complexes are shown in Table
 362 1. Complexes with the general formula $U(N^tBu)_2(EAR)_2-$
 363 $(OPPh_3)_2$ (**1–4**) are isostructural and feature a uranium center
 364 in a *pseudo*-octahedral geometry with imido, aryl chalcoge-
 365 nate, and phosphine oxide ligands in an all *trans*-disposition.
 366 The U–N(imido), U–I, and U–O(phosphine oxide) bond
 367 lengths are all comparable to analogous bond lengths in other
 368 structurally characterized uranium bis(imido) complexes.⁵
 369 The U1–O2 phenolate bond length in **1** is 2.267(6) Å and
 370 is longer than the U–O phenolate bond distances in the

(16) Wilkerson, M. P.; Burns, C. J.; Morris, D. E.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **2002**, *41*, 3110.

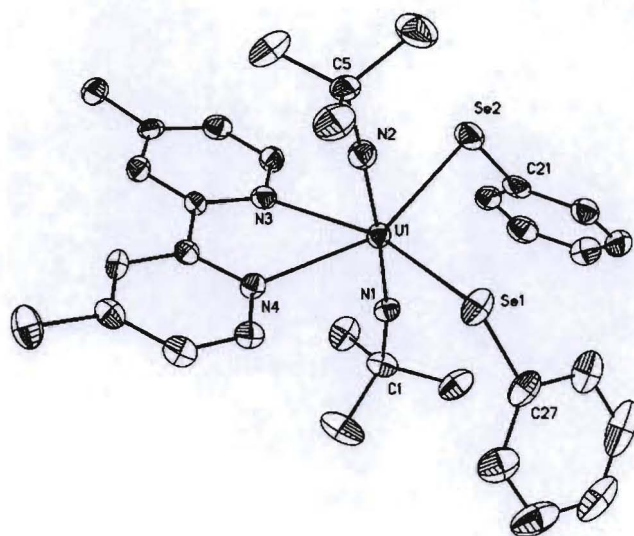


Figure 6. Solid state molecular structure of $[U(N^iBu)_2(SePh)_2(Me_2bpy)]$ (**9**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 1.843(4), U1–N2 = 1.846(4), U1–N3 = 2.526(4), U1–N4 = 2.532(4), U1–Se1 = 2.8375(5), U1–Se2 = 2.8073(5), N1–U1–N2 = 175.94(17), N3–U1–N4 = 62.93(12), U1–Se1–C21 = 108.54(14), U1–Se2–C27 = 104.83(14).

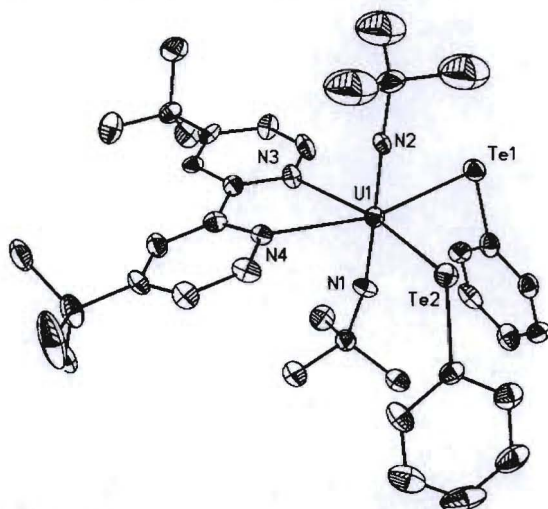


Figure 7. Solid state molecular structure of $[U(N^iBu)_2(TePh)_2(Bu_2bpy)]$ (**12**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1–N1 = 1.824(8), U1–N2 = 1.832(8), U1–N3 = 2.544(8), U1–N4 = 2.521(8), U1–Te1 = 3.0405(8), U1–Te2 = 3.0335(8), N1–U1–N2 = 177.4(3), N3–U1–N4 = 63.4(3), U1–Te1–C27 = 100.2(3), U1–Te2–C33 = 103.0(3).

of 2.8868(8) Å in **3** is significantly shorter than the only other structurally characterized uranium(VI) compound that has a U–Se bond, $[UO_2[Et_2NCSe_2]_2(Ph_3AsO)]$ (average U–Se bond length = 2.981(5) Å)¹⁸ but is longer than the terminal U–Se bond distances found in the uranium(IV) selenolate complex $[U(SePh)_2(\mu-SePh)_2(CH_3CN)_2]_2$ (U–Se_{terminal} = 2.8491(12) Å).¹⁹ In the case of complex **4**, the U(1)–Te(1) bond lengths (3.0920(13) Å) possesses a small estimated standard deviation and are shorter than the average U–Te bond reported lengths in the uranium (III) species $U(N(TeP^iPr)_2)_3$ (U–Te = 3.1639(7) Å)²⁰ but longer than average U–Te bond lengths in the uranium(IV) complex $(C_5Me_5)_2U(TePh)_2$ (U–Te = 3.0444(6) Å).²¹ *cis*-Disposed dichalcogenate complexes **5**, **8**, **9**, and **12** possess structural features that are similar to their *trans*-oriented congeners. The diiodo complex **5** possesses U–N(imido) and U–I bond lengths typical of many bis(imido) uranium(VI) complexes. The U–N(bpy) bond lengths are also similar to bipyridyl complexes of the uranyl(VI) ion.²² The U–E chalcogenate bond lengths in **8**, **9**, and **12** have values are similar to those in the *trans*-series.

These structural studies reveal a trend in the U–E–C_{ipso} angles of the *trans*-series **1–4** and the *cis*-series **8**, **9**, and **12**. In **1**, a U(1)–O(2)–C(5) bond angle of 145.1(4)° is observed that gradually decreases in going to the heavier chalcogenate donor complexes **2** (U(1)–S(1)–C(5) = 110.0(6)°), **3** (U(1)–Se(1)–C(5) = 106.4(2)°), and **4** (U(1)–Te(1)–C(5) = 103.9(3)°). The family of *cis*-dichalcogenate complexes shows a similar decrease from the thiolate complex **8** (109.1(5)°) to the heavier selenolate complex **9** (106.69(14)°) and telluroate complex **12** (101.6(3)°). This trend of a decreasing U–E–C_{ipso} bond angle has also been observed in $(C_5Me_5)_2U(EPh)_2$ (E = S, Se, Te)²¹ and $(C_5Me_5)_2Sm(EPh)THF$ (E = S, Se, Te)²³ complexes and is consistent with a decrease in the degree of s hybridization of the E atoms in the U–E bond as the atomic number of E increases.

Theoretical Calculations

The series of $U(N^iBu)_2(EAr)_2(OPPh_3)_2$ compounds was studied using hybrid density functional theory (DFT) to investigate trends in the covalency and the participation of f-orbitals in the U–E bonds. The polonium analogue, $U(N^iBu)_2(PoPh)_2(OPPh_3)_2$ (**5**), was also studied to complete the chalcogenate series. The optimized structures of $U(N^iBu)_2(EAr)_2(OPPh_3)_2$ as predicted by DFT calculations are shown in Table 2 and agree well with U–E bond lengths and U–E–C_{ipso} bond angles determined from crystal-

(18) Zarli, B.; Graziani, R.; Forselli, E.; Croatto, U.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1501.

(19) Gaunt, A. J.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2006**, *45*, 7401.

(20) Gaunt, A. J.; Scott, B. L.; Neu, M. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 1638.

(21) Evans, W. J.; Miller, K. A.; Ziller, J. W.; Dipasquale, A. G.; Heroux, K. J.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4287.

(22) (a) Alcock, N. W.; Flanders, D. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1985**, 1001. (b) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Chem. Commun.* **2003**, 1660.

(23) Evans, W. J.; Miller, K. A.; Lee, D. S.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 4326.

371 neutral monomeric uranium(VI) phenolate complexes $[UO_2(O-$
372 $2,6-^iBu_2C_6H_3)(THF)_2]$ (avg. U–O(phenolate) = 2.200(8)
373 Å),¹⁶ $[UO_2(O-2,6-Ph_2C_6H_3)_2(THF)_2]$ (avg. U–O(phenolate)
374 = 2.199(11) Å),¹⁶ and $[UO_2(O-2,6-^iPr_2C_6H_3)_2(py)_3]$ (avg.
375 U–O(phenolate) = 2.197(5) Å).¹⁷ The U(1)–S(1) bond
376 distance of 2.757(10) Å in **2** is slightly longer than the bond
377 lengths reported for the unidentate thiolate uranium(VI)
378 complex $[UO_2(S-2,6-Cl_2C_6H_3)L_2]$ (avg. = 2.7234(8) Å)^{4a} but
379 shorter than the bond lengths reported for $[UO_2(o-$
380 $C_5H_4NS)(NO_3)_2]^-$ (2.805(6) Å) and $[UO_2(o-C_5H_4NS-3-$
381 $SiMe_3)(NO_3)_2]$ (2.813(8) Å).^{4f} The U(1)–Se(1) bond length

(17) Barnhart, D. M.; Burns, C. J.; Sauer, N. N.; Watkin, J. G. *Inorg. Chem.* **1995**, *34*, 4079.

Uranium(VI) Bis(imido) Chalcogenate Complexes

Table 1. Selected Average Bond Lengths (Å) and Angles (deg) of *trans*-Dichalcogenates (1–4) and *cis*-Dichalcogenates (8, 9, and 12)

	1 (E = O)	2 (E = S)	3 (E = Se)	4 (E = Te)	8 (E = S)	9 (E = Se)	12 (E = Te)
U–N _{imido}	1.870(6)	1.840(7)	1.861(6)	1.829(19)	1.841(11)	1.845(4)	1.828(8)
U–E	2.267(6)	2.757(10)	2.886(8)	3.0920(13)	2.686(3)	2.8224(5)	3.0370(8)
U–O _{ippo}	2.341(7)	2.322(5)	2.360(5)	2.39(2)			
U–N _{bpy}					2.549(12)	2.529(4)	2.532(8)
U–E–C _{ippo}	145.1(4)	110.6(2)	106.4(2)	103.9(3)	109.1(5)	106.69(14)	101.6(3)

Table 2. Comparison of Selected Experimental and Theoretical Metrical Parameters in Complexes 1–5

E	experimental geometry				at optimized geometry			
	U–E–C _{ippo} (deg)	U–E (Å)	U–OPPh ₃ (Å)	U=N (Å)	U–E–C _{ippo} (deg)	U–E (Å)	U–OPPh ₃ (Å)	U=N (Å)
O	145.06	2.267	2.341	1.870	149.9	2.261	2.451	1.875
S	109.98	2.757	2.322	1.840	119.2	2.791	2.433	1.862
Se	106.43	2.887	2.360	1.861	115.2	2.933	2.431	1.860
Te	103.90	3.092	2.366	1.863	111.8	3.184	2.428	1.857
Po	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	111.1	3.252	2.427	1.856

^a Complex was not synthesized.**Table 3.** Mulliken Charges for the Uranium Center, the N=U=N unit, and the Chalcogenate Atom in U(N^tBu)₂(EAR)₂(OPPh₃)₂

E	all electron			RECP		
	U	UN ₂	E	U	UN ₂	E
O	1.65	0.41	−0.72	1.64	0.39	−0.71
S	1.36	0.11	−0.21	1.35	0.09	−0.19
Se	1.33	0.07	−0.16	1.34	0.07	−0.15
Te	<i>a</i>	<i>a</i>	<i>a</i>	1.31	0.03	−0.06
Po	<i>a</i>	<i>a</i>	<i>a</i>	1.33	0.04	−0.04

^a Were not calculated.**Table 4.** Molecular Orbitals Involved in the Bonding between the Uranium Center and Chalcogen Donor^a

E	MOs	energy (eV)	U-6d	U-5f	E- <i>np</i> (each)
O	H-2	−5.37	11.3		9.8
	H-8	−6.22		10.1	28.3
	H-9	−6.73	10.1		23.2
S	H-0	−4.54		5.2	26.0
	H-1	−4.75	4.8		27.5
	H-2	−5.12		6.0	42.3
	H-3	−5.41	6.1		35.8
Se	H-30	−8.30	4.8		9.7
	H-0	−4.44		6.1	31.2
	H-1	−4.65	5.4		36.8
	H-2	−4.79		5.9	43.8
	H-3	−5.16	6.9		31.1
Te	H-11	−6.79	7.5		12.8
	H-26	−7.89	5.8		13.7
	H-0	−4.35		6.6	35.9
	H-1	−4.45	5.0		41.9
	H-2	−4.54		5.8	44.1
Po	H-3	−5.05	8.9		30.5
	H-11	−6.62	10.4		7.8
	H-26	−7.52	8.4		12.9
	H-0	−4.19		6.3	38.6
	H-2	−4.34		6.5	43.2
	H-3	−4.94	10.7		31.2
H-11	−6.54	12.6		5.3	
	H-14	−7.02		3.5	12.5
	H-23	−7.32	7.8		11.2

^a Values of the uranium 6d and 5f-orbitals are expressed as the percentage contribution in the specified molecular orbital in the U–E bonds of complexes 1–5. The participating orbitals are referenced to the highest occupied molecular orbital (HOMO, H-0 means HOMO and H-2 corresponds to HOMO-2 orbital). The values given are the percent contributions from the uranium 6d and 5f orbitals and the *np* orbitals of the chalcogenide atom to each MO.

findings. Similar discrepancies between experimental and theoretical values have also been observed for other uranium(VI) imido complexes at a similar level of computational theory.⁵

The amount of electronic charge in (1) the uranium and E centers and (2) the N=U=N core were examined to assess the nature of covalent interactions in the U–E bonds in complexes 1–5. Table 2 shows a consistent trend where the E center becomes less negative and the U center less positive as the size of the chalcogenate donor increases. For example, a significant decrease in charge in both U and E centers and the N=U=N unit is observed between the O-complex 1 and the S-complex 2, which suggests that the U–O bond possesses a more ionic character compared to U–S bonds. This finding suggests a monotonic shift in the covalent nature in the U–E bond as the size of the chalcogenate donor increases which is also consistent with previous reports on a series of uranium(III) chalcogenate complexes.¹⁴

The relative bonding strength of the U–E bond was evaluated by comparing the interaction energies of the two charged fragments, that is, one [U(N^tBu)₂(OPPh₃)₂]²⁺ unit and two EAR[−] ions, at the geometry of the molecular complex, with the delocalized molecular complexes. The calculations show interaction energies of −160.8, −140.7, −135.7, −129.6, and −127.7 kcal/mol, per EAR[−] unit, for E corresponding to O, S, Se, Te, and Po, respectively. Although these energies are not true values for U–E bond energies because they are in the totally ionic limit, the differences between these numbers show that the relative strength of the U–E bond decreases as the size of chalcogen atom becomes larger.

These results suggest that a correlation exists between covalency and relative U–E bond strength in U(N^tBu)₂(EAR)₂(OPPh₃)₂ complexes. As the size of the E donor is increased, the covalency in the U–E bond increases and the relative U–E bond strength decreases. Recent studies of uranium(IV)–L multiple bonds in Cp₂U=L (L = O, NMe) have also shown this correlation between covalency and U–L bond strength.¹⁵ In the case of Cp₂U=O, the U=O bond contains less covalent character compared to the U=N analogue but possesses a stronger U–L multiple bond.

429 lographic measurements. In the case of complex 2, the U–E
430 and U–E–C_{ippo} (E = O, S, Se, Te) values determined by
431 DFT calculations are within 3% and 9° of experimental

473 The molecular orbitals involved in the U–E bond are
 474 decomposed in uranium 6d and 5f, and chalcogenate *np*
 475 component in Table 3. The values are given as percentage
 476 of the total MO using a Mulliken population decomposition.
 477 For this type of analysis, where one looks at trends in charge
 478 migration from one center to another, the Mulliken decom-
 479 position gives a reasonable description as the overlap between
 480 uranium and chalcogenate basis functions is not large and
 481 each center is described by a complete enough basis set. The
 482 MOs of complexes **1–5** show significant mixing of uranium
 483 6d and 5f orbitals with the *np* orbitals of the chalcogenate
 484 atom (Table 4). This finding suggests covalent interactions
 485 are important in the formation of U–E bonds in the family
 486 of U(N^tBu)₂(EAr)₂(OPPh₃)₂ complexes.

487 Conclusion

488 We have shown that a series of bis(imido) uranium(VI)
 489 *trans*- and *cis*-dichalcogenate complexes can be synthesized
 490 and report the first examples of monodentate selenolate and
 491 telluroate-uranium(VI) complexes. These results further
 492 exemplify the differences between UO₂²⁺ and U(NR)₂²⁺ ions,
 493 as Se- and Te-donor ligands are not known to coordinate to
 494 the UO₂²⁺ ion. DFT calculations show that covalent interac-
 495 tions in the U–E bond increase as the size of the chalco-
 496 genate donor increases and that there is both 5f and 6d orbital

(24) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272.

497 participation in the M–E bond of U–S, U–Se, and U–Te
 498 complexes. While it is not possible to obtain a quantitative
 499 view of covalency in these complexes, it is clear that covalent
 500 interactions and f-orbitals are important U(VI)–E bonds in
 501 this series of uranium(VI) chalcogenate complexes. We are
 502 currently investigating the use X-ray absorption spectroscopy
 503 to further evaluate the electronic structure of this family of
 504 uranium(VI) complexes.

Acknowledgment. P.Y. and L.S. thank the Seaborg
 505 Institute for their postdoctoral fellowships. E.R.B. and J.M.B.
 506 were partially supported by the Division of Chemical
 507 Sciences, Office of Basic Energy Sciences, U.S. Department
 508 of Energy under the Heavy Element Chemistry program at
 509 LANL. We thank the Center for Integrated Nanotechnology
 510 at LANL for computing support. LANL is operated by Los
 511 Alamos National Security, LLC, for the National Nuclear
 512 Security Administration of the US DOE under contract DE-
 513 AC52-06NA25396. 514

Supporting Information Available: Complete X-ray crystal-
 515 lographic details (as CIF files) of **1–4**, **5**, **8**, **9**, and **12**. Geometries
 516 of the calculated structures of **1–5**. This material is available free
 517 of charge via the Internet at <http://pubs.acs.org>. 518

IC802212M 519

- (25) (a) Gaunt, A. J.; Reilly, S. D.; Enriquez, A. E.; Scott, B. L.; Ibers, J. A.; Sekar, P.; Ingram, K. I. M.; Kaltsoyannis, N.; Neu, M. P. *Inorg. Chem.* **2008**, *47*, 29. (b) Ingram, K. I. M.; Kaltsoyannis, N.; Gaunt, A. J.; Neu, M. P. *J. Alloys Compd.* **2007**, *444–445*, 369.
 (26) Barros, N.; Maynau, D.; Maron, L.; Eisenstein, O.; Zi, G. F.; Andersen, R. A. *Organometallics* **2007**, *26*, 5059.