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| Journal: | <i>ChemComm</i> |
| Manuscript ID | CC-COM-09-2022-005066.R1 |
| Article Type: | Communication |
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Elemental Chalcogen Reactions of a Tetravalent Uranium Imidophosphorane Complex: Cleavage of Dioxygen

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

Herein we report the first example of a mononuclear uranium complex, [U⁴⁺(NP(pip)₃)₄] (1-U), that selectively reduces dioxygen to produce a terminal oxo complex, [U⁶⁺O(NP(pip)₃)₄] (2-U; [NP(pip)₃]₃¹⁻ is tris(piperidinyl)imidophosphorane). Reactions between 1-U and the heavier elemental chalcogens, S₈ or Se⁰, result in six-coordinate U(VI) complexes, [U⁶⁺(κ²-E₃)(NP(pip)₃)₄] (E = S (3-U) or Se (4-U)).

Molecular uranium compounds have rich redox chemistry and have been demonstrated to activate a wide range of biologically and industrially important small molecules including CO, CO₂, H₂, N₂, and N₂O.¹⁻⁸ However, there are few examples of dioxygen reactivity.⁹⁻¹² To date, there are no examples of mononuclear molecular uranium(IV) compounds that undergo 2-electron atom-transfer reactivity at the metal center to cleave O₂.¹³⁻¹⁶ This lack of selectivity holds true for both reactions of O₂ involving the the U^{III/IV} and U^{IV/VI} redox pairs. The lack of O₂ reactivity with uranium complexes likely reflects two points: (1) many coordination chemists avoid exposure to O₂, and (2) the significant oxidation potential of the small molecule which can lead to outer-sphere reactions and ligand scrambling.⁴

Synthetically, the coordination sphere must control both binding and subsequent redox events to yield selective reactions with O₂. Recently, a homoleptic U(IV) complex supported by a dialkylamidoimidophosphorane ligand was shown to be sufficiently reducing to undergo 2-electron oxidative atom/group transfer chemistry with mesityl azide and N₂O.^{7, 17} In this example, the homoleptic coordination of the tris(piperidinyl)-imidophosphorane ligand, [NP(pip)₃]₃¹⁻ (where, pip = piperidinyl), displayed the ability to rearrange in order to accommodate a new ligand in the coordination sphere of

uranium, despite its steric bulk. A key feature of these dialkylamidoimidophosphorane ligands is their relative (e.g. in comparison to cyclopentadienyl ligands) oxidative stability. As a result, these monodentate, weak field ligands have afforded access to unique redox chemistry across the transition metals, lanthanides, and actinides.¹⁸⁻²² Altogether, these results make the homoleptic U(IV) complex supported by the [NP(pip)₃]₃¹⁻ ligand, [U(NP(pip)₃)₄] (1-U), a promising candidate to undergo metal-centered 2-electron oxidative atom transfer with O₂. Herein we report the reactivity between 1-U and O₂, and the heavier chalcogens in their elemental forms.

The reactivity of 1-U was directly probed by exposure of a THF solution of 1-U to an excess of d O₂ at room temperature. Immediately upon exposure to O₂, the pink solution adopted a dark red, brown color. After workup, the exclusive reaction product observed by ¹H and ³¹P{¹H} NMR was the previously reported U(VI) mono-oxo complex, [UO(NP(pip)₃)₄] (2-U, Scheme 1). The reaction proceeds rapidly at room temperature and attempts to identify intermediates at -78 °C revealed only unreacted starting material and the mono-oxo product, 2-U.

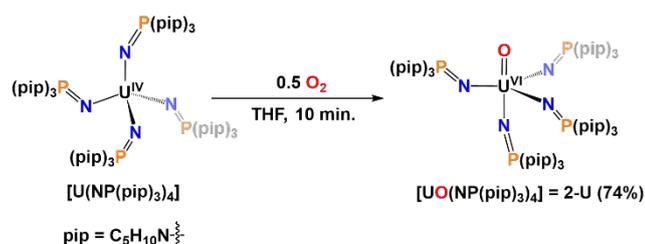
The formation of 2-U was investigated computationally (DFT, B3PW91). Previous studies demonstrated that in uranium chemistry, small molecule activation often involves the formation of bimetallic species since the two uranium centres are each acting as a 1e⁻ reductant, and usually when starting from a U(III) center.^{1, 23} However, recently, our group, Liddle, and others showed that uranium can act as a 2e⁻ reductant while in the +IV oxidation state.^{7, 24-30} Two possibilities were investigated (Figure 1, For computational details, see ESI). The formation of the bimetallic species bridged by O₂ is endothermic by 29.1 kcal.mol⁻¹, therefore the formation of such an intermediate is very unlikely. The coordination/reduction to O₂ to 1-U was thus investigated in more detail. Two very stable intermediates were located on the potential energy surface on the triplet and singlet spin states. The triplet state complex corresponds to a uranium superoxo complex and it lies 27.6 kcal.mol⁻¹ below the separated reactants. In this system the O–O bond distance is 1.31 Å which corresponds to a O₂ radical

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† Electronic supplementary information (ESI) available: Experimental procedures and crystallographic data (PDF and CIF). CCDC 2129557 and 2205631. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXXXXXXXXXXXXXX

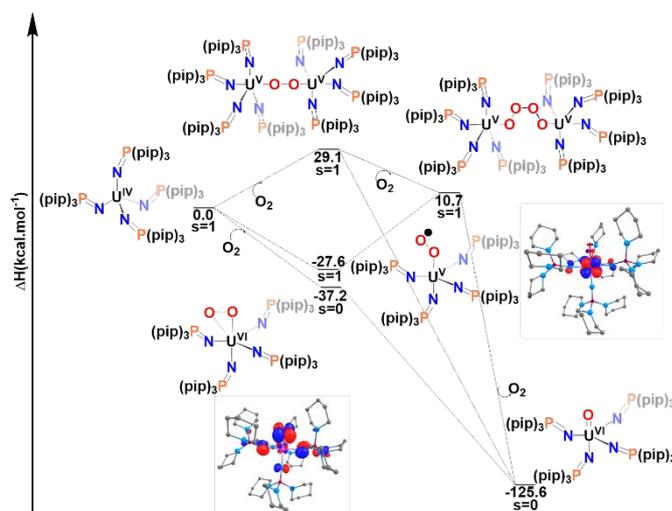


Scheme 1. Synthesis of 2-U.

anion bonded to a uranium center. In this system the O_2 radical anion is η^2 -bonded to the uranium (U–O distances of 2.38 and 2.41 Å) and the two SOMOs (see Figure S11 in ESI) clearly show one unpaired electron on U and one on the $\text{O}_2 \pi^*$, in line with $1e^-$ oxidation of U(IV) to U(V). The associated O–O Wiberg Index (WBI) is 1.22 in line with the presence of residual covalent π interaction in the oxygen radical anion. The singlet complex is better described as a peroxy complex and is the most stable intermediate ($-37.2 \text{ kcal}\cdot\text{mol}^{-1}$). The O–O distance is 1.43 Å, in line with O_2 dianion. O_2 is also η^2 -bonded to the uranium (U–O distances of 2.11 and 2.13 Å). The system is a closed-shell and the HOMO (Figure S12 in ESI) is a pure $\text{O}_2 \pi^*$, in line with a $2e^-$ oxidation of the uranium center to U(VI) and the formation of a peroxy anion. The O–O WBI is 0.96 in line with a full disruption of the O–O π bond. Therefore, the uranium is acting as a $2e^-$ reductant. The peroxy complex then loses an O atom to form complex 2-U (88 $\text{kcal}\cdot\text{mol}^{-1}$ more stable).

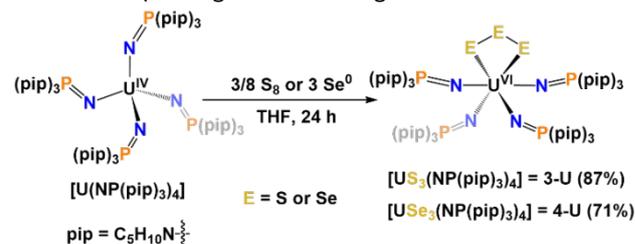
To assess the reactivity with the heavier chalcogens, and to potentially draw structural comparisons with the mono-oxo product (2-U), the reactivity of compound 1-U with elemental sulphur (S_8), selenium powder (Se^0), and tellurium powder (Te^0) was explored. The dark brown products obtained from the reactions with S_8 (3-U) and Se^0 (4-U) were isolated (Scheme 2). Unlike in the cases of S_8 and Se^0 , no reaction between 1-U and Te^0 was observed. Single-crystal X-Ray diffraction (SC-XRD) revealed the molecular structures of 3-U and 4-U, which are isostructural and crystallize in the $\text{P2}_1/\text{n}$ space group, to be a 6-coordinate U(VI) complexes with 4 terminal $[\text{NP}(\text{pip})_3]^{1-}$ ligands and either a $[\text{S}_3]^{2-}$ (3-U) or $[\text{Se}_3]^{2-}$ (4-U) ligand that coordinates to the metal center in a κ^2 -mode along the equatorial plane, as shown in Figure 2. These complexes co-crystallize with a minor component of $[\text{S}_2]^{2-}$ or $[\text{Se}_2]^{2-}$, respectively, on the same lattice site. This minor component is not discernible by ^1H , $^{13}\text{C}\{^1\text{H}\}$, or $^{31}\text{P}\{^1\text{H}\}$ NMR nor by elemental analysis. See SI for crystallographic details of this minor component.

These reactions do not afford the terminal chalcogen metal-ligand multiple bonds.³⁰ While reaction products between molecular U(III) and U(IV) compounds with elemental selenium and sulfur are known, they remain uncommon.^{31–35} Some of these examples lead to the formation of a terminal uranium chalcogenide bond. There are reports of U-S_2 complexes produced from reactions with S_8 , but only one example that goes from U(IV) to U(VI).^{31, 36} While US_3 complexes are known, they are known at a U(IV) center where the trisulfide ligand is the mono-anionic radical, $[\text{S}_3]^-$.³⁷ There are no reports of a USe_3 complex. The 6-coordinate compounds, 3-U and 4-U, are

Figure 1. Computed enthalpy profile for the reaction between 1-U and O_2 .

produced regardless of whether a 1:1 or 1:3 ratio of 1-U to E (where E = S or Se) is used.

The SC-XRD structures of both 3-U and 4-U show that the the 6-coordinate uranium complex contains two $[\text{NP}(\text{pip})_3]^{1-}$ ligands that are mutually *trans*- to one another and two that are mutually *cis*- with respect to each other and *trans*- to either a S- or Se- atom belonging to the $[\text{S}_3]^{2-}$ or $[\text{Se}_3]^{2-}$ ligand. The average U–N distances corresponding to the set of *trans*- $[\text{NP}(\text{pip})_3]^{1-}$ ligands is 2.078(6) Å for 3-U and 2.073(5) Å for 4-U, while the average U–N distance for the set of *cis*- ligands is 2.139(6) Å for 3-U and 2.104(5) Å for 4-U. The slight contraction the U–N bonds of the mutually *trans*- $[\text{NP}(\text{pip})_3]^{1-}$ ligands in 3-U (~ 0.06 Å) and 4-U (~ 0.03 Å) are indicative of the inverse *trans*-influence.^{7, 38, 39} The average U–S and U–Se distances in 3-U (2.763(4) Å) and 4-U (2.930(2) Å). In both 3-U and 4-U, the pseudo-octahedral coordination about the metal center is slightly distorted. The N–U–N angle for the *trans*- $[\text{NP}(\text{pip})_3]^{1-}$ set is 165.4(3)° for 3-U and 161.5(3)° for 4-U, and the N–U–N angle for the *cis*- $[\text{NP}(\text{pip})_3]^{1-}$ set is 93.6(3)° for 3-U and 94.3(2)° for 4-U. The average N–P distance of the *trans*- $[\text{NP}(\text{pip})_3]^{1-}$ ligands is 1.560(4) Å for 3-U and 1.561(4) Å for 4-U, while the average N–P distance of the *cis*- $[\text{NP}(\text{pip})_3]^{1-}$ ligands is 1.557(4) Å for 3-U and 1.558(4) Å for 4-U. The distinct electronic environment between the sets of *cis*- and *trans*- $[\text{NP}(\text{pip})_3]^{1-}$ ligands in the solid state is preserved in solution, as evidenced by the presence of two signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 3-U (δ 4.54, -7.98 ppm) and 4-U (δ 7.99, -11.77 ppm) at room temperature that integrate to a 1:1 relative ratio (see Figure S3 and Figure S5 in the ESI for full



Scheme 2. Synthesis of 3-U and 4-U.

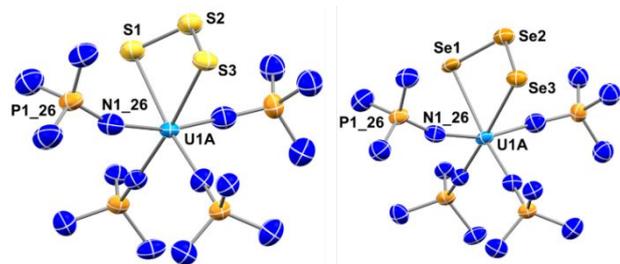


Figure 2. Molecular structures of **3-U** (left) and **4-U** (right) shown with thermal ellipsoids at 50% probability. Piperidinyl carbon and hydrogen atoms are omitted for clarity. See ESI for full structures.

spectra). This solution behavior differs from that of **2-U**, which displays a single signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature (at low temperature it decoalesces to two peaks with the expected 3:1 ratio).⁷

The UV-Vis-NIR spectrum of **3-U** displays two intense and broad bands at 331 nm ($\epsilon = 9021 \text{ cm}^{-1}\text{M}^{-1}$) and 702 nm ($\epsilon = 700 \text{ cm}^{-1}\text{M}^{-1}$). The UV-Vis-NIR spectrum of **4-U** also displays two broad and intense bands at 295 nm ($\epsilon = 16821 \text{ cm}^{-1}\text{M}^{-1}$) and 510 nm ($\epsilon = 2965 \text{ cm}^{-1}\text{M}^{-1}$). The energies and extinction coefficients of all of the observed absorption features correspond to ligand-to-metal charge transfer (LMCT) transitions, which are commonly observed in U(VI) spectra. The UV-Vis-NIR spectra of **3-U** and **4-U** are consistent with the previously reported spectrum of **2-U** and $[\text{U}(\text{NMe}_2)(\text{NP}(\text{pip})_3)_4]$ (where Mes = mesityl).⁷ This validates the oxidation state assignment of **3-U** and **4-U** as U(VI) for both compounds. The spectroscopic data for **3-U** also serves as confirmation of our structural assessment of the trisulfide ligand as a $[\text{S}_3]^{2-}$ dianion as opposed to the more ubiquitous $[\text{S}_3]^{1-}$ radical mono-anion.⁴⁰⁻⁴³

In conclusion, we have shown that the homoleptic imidophosphorane U(IV) compound, **1-U**, reacts readily with O_2 in THF to produce the mono-oxo U(VI) complex, **2-U**, under mild conditions. This marks the first example of a mono-metallic uranium complex that undergoes a metal-centered cleavage of O_2 in the absence of a redox-active ligand. Complex **1-U** also reacts with the heavier chalcogens, S_8 , Se^0 to produce the U(VI) $[\text{S}_3]^{2-}$ (**3-U**) and $[\text{Se}_3]^{2-}$ (**4-U**) coordination compounds respectively. Compounds **3-U** and **4-U** display structurally and spectroscopically divergent behavior to **2-U**, which highlights new ways in which the tris(piperidinyl)imidophosphorane ligand can afford access to unique $2e^-$ oxidative atom transfer chemistry at a U(IV) and accommodate chalcogen ligands of varying sizes and nuclearities. The divergent oxidative atom transfer redox chemistry shown herein lays the synthetic blueprint for future studies that examine the electronic structure of the oxidation products of heavier actinides with elemental chalcogen reagents.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support was provided by the Georgia Institute of Technology, the Department of Energy, Heavy Element Chemistry Program (DE-SC0019385), and CONACYT Graduate Fellowship to LMAQ. LM is a senior member of the Institut Universitaire de France. CalMip is acknowledged for a generous grant of computing time.

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