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Synthesis, structure, spectroscopy and redox energetics of a series of uranium(IV) mixed-ligand metallocene complexes

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ABSTRACT

A series of uranium(IV) mixed-ligand amide–halide/pseudohalide complexes $(C_5Me_5)_2U[N(SiMe_3)_2](X)$ (X = F (**1**), Cl (**2**), Br (**3**), I (**4**), N_3 (**5**), NCO (**6**)), $(C_5Me_5)_2U(NPh_2)(X)$ (X = Cl (**7**), N_3 (**8**)), and $(C_5Me_5)_2U[N(Ph)(SiMe_3)](X)$ (X = Cl (**9**), N_3 (**10**)) have been prepared by one electron oxidation of the corresponding uranium(III) amide precursors using either copper halides, silver isocyanate, or triphenylphosphine gold(I)azide. Agostic U···H–C interactions and η^3-(*N,C,C′*) coordination are observed for these complexes in both the solid-state and solution. There is a linear correlation between the chemical shift values of the C_5Me_5 ligand protons in the ^1H NMR spectra and the U^{IV}/U^{III} reduction potentials of the $(C_5Me_5)_2U[N(SiMe_3)_2](X)$ complexes, suggesting that there is a common origin, that is overall σ-/π-donation from the ancillary (X) ligand to the metal, contributing to both observables. Optical spectroscopy of the series of complexes **1**–**6** is dominated by the $(C_5Me_5)_2U[N(SiMe_3)_2]$ core, with small variations derived from the identity of the halide/pseudohalide. The considerable π-donating ability of the fluoride ligand is reflected in both the electrochemistry and UV-visible-NIR spectroscopic behavior of the fluoride complex $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (**1**). The syntheses of the new trivalent uranium amide complex, $(C_5Me_5)_2U[N(Ph)(SiMe_3)](THF)$, and the two new weakly-coordinating electrolytes, $[Pr_4N][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ and $[Pr_4N][B(C_6F_5)_4]$, are also reported.

1. Introduction

Mixed-ligand metallocene complexes of the type $(C_5Me_5)_2U(X)(Y)$ serve as important starting materials for organometallic actinide chemistry, but access to this set of molecules has historically been limited to very specific reaction chemistries [1–7]; consequently, very little is known about the electronic structure and redox energetics for this rare class of compounds. We have been developing oxidative functionalization chemistry of trivalent uranium with copper(I) [8,9] and gold(I) [10] compounds to provide simple and mild methods for synthesizing U^{IV} mixed-ligand metallocene complexes of the type $(C_5Me_5)_2U(X)(Y)$ (where X = halogen, azide, acetylide, etc.; Y = amide). Since uncontrolled oxidation and ligand redistribution are not observed with the Au- or Cu-based $U^{III} \rightarrow U^{IV}$ oxidation procedures, they provide attractive synthetic routes for the preparation of a variety of mixed-ligand metallocene complexes. For example, reaction of the trivalent uranium complex $(C_5Me_5)_2U(NPh_2)(THF)$ with copper(I) iodide or $(Ph_3P)Au\text{-}N_3$ affords the corresponding tetravalent uranium amide-iodide and -azide complexes $(C_5Me_5)_2U(NPh_2)(I)$ [9] and $(C_5Me_5)_2U(NPh_2)(N_3)$ [11], respectively (Eq. (1)).

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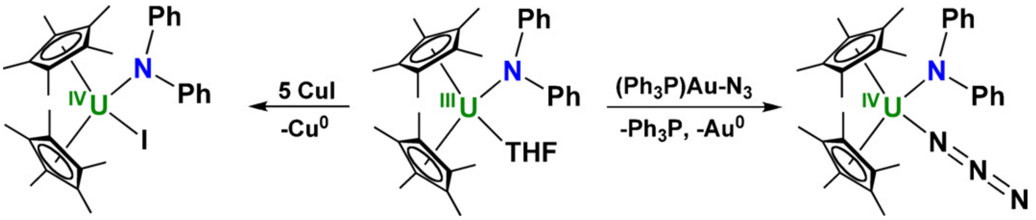

(1)

During the course of these studies, it became evident that the amide mixed-ligand framework provided the opportunity to examine a new homologous structural series from which we can draw new inferences regarding uranium metal–ligand bonding. This falls within the broader context of our continuing efforts to map out trends in the redox energetics and electronic structure of metallocene complexes of the early actinides and correlate these trends with structural chemistry [12–16]. In particular, the amide complexes represent an important end-member along the nitrogenous ligand series: imide (A) [17–20], ketimide (B) [21–24], hydrazonato (C) [2,25–27], amide (D) [8,9,28], as illustrated in Fig. 1.

The uranium–amide bonding interaction should have the lowest degree of π-donation from the nitrogen lone-pair among this series, and this should be reflected in both spectral and electrochemical data. In this contribution, we report the synthesis and structural characterization of a series of mixed-ligand tetravalent uranium complexes of the type $(C_5Me_5)_2U(X)(Y)$ ($Y = N(SiMe_3)_2$, NPh_2, $N(Ph)(SiMe_3)$; X = halide/pseudohalide) from the reaction of Cu, Ag, and Au reagents with the corresponding U^{III} amide precursors. Further, we describe the electrochemical and spectroscopic characterization of a series of related U^{IV} complexes, $(C_5Me_5)_2U[N(SiMe_3)_2](X)$, from this rare class of uranium complexes. We also report the synthesis of the new trivalent uranium amide complex, $(C_5Me_5)_2U[N(Ph)(SiMe_3)](THF)$, and the two new weakly-coordinating electrolytes, $[Pr_4N][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ and $[Pr_4N][B(C_6F_5)_4]$.

2. Results and discussion

2.1. Synthesis and structural characterization

2.1.1. $(C_5Me_5)_2U[N(SiMe_3)_2](X)$ complexes

Oxidative functionalization provides convenient access to mixed-ligand metallocene complexes of the type $(C_5Me_5)_2U(X)(Y)$ (where Y is an amide ligand). As summarized in Scheme 1, reaction of the trivalent uranium amide complex $(C_5Me_5)_2U[N(SiMe_3)_2]$ [29] with various Cu, Ag, and Au reagents afforded the series of related complexes $(C_5Me_5)_2U[N(SiMe_3)_2](X)$ (X = F (**1**), Cl (**2**), Br (**3**), I (**4**), N_3 (**5**), and NCO (**6**)). Specifically, the U^{IV} amide–halide complexes $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (**1**), $(C_5Me_5)_2U[N(SiMe_3)_2](Cl)$ (**2**), $(C_5Me_5)_2U[N(SiMe_3)_2](Br)$ (**3**), and $(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**4**) were obtained by oxidation of $(C_5Me_5)_2U[N(SiMe_3)_2]$ using an excess (5 equiv.) of the appropriate Cu halide salt. Separation of the insoluble Cu salts from the reaction products was accomplished by filtration through Celite. Following crystallization, the U^{IV} amide–halide complexes were isolated in moderate to high yields (up to 93%) as crystalline red solids. The amide–azide complex $(C_5Me_5)_2U[N(SiMe_3)_2](N_3)$ (**5**) was prepared in a similar manner using $(Ph_3P)Au\text{-}N_3$ as the oxidant [11]. The complexes were characterized by a combination of ^1H NMR spectroscopy, elemental analyses and X-ray crystallography.

The amide–isocyanate derivative $(C_5Me_5)_2U[N(SiMe_3)_2](NCO)$ (**6**) was synthesized in 71% isolated yield by oxidation of $(C_5Me_5)_2U[N(SiMe_3)_2]$ with AgNCO. Oxidations using copper halides occur over 12 h with an excess of the oxidant (5 equiv.), however use of excess AgNCO or reaction times longer than 2–3 h lead to decomposition of the uranium isocyanate product. This is most likely attributable to the much stronger oxidizing power of Ag^I over Cu^I [30].

The molecular structures of the amide–chloride $(C_5Me_5)_2U[N(SiMe_3)_2](Cl)$ (**2**) (left) and amide–isocyanate $(C_5Me_5)_2U[N(SiMe_3)_2](NCO)$ (**6**) (right) complexes are shown in Fig. 2. Compound **6** represents a rare example of a structurally characterized actinide isocyanate complex, of which there are only two other known complexes [31,32]. Both complexes **2** and **6** feature a bent-metallocene framework with the amide and chloride (for **2**) or isocyanate (for **6**) ligands contained within the metallocene wedge. For $(C_5Me_5)_2U[N(SiMe_3)_2](Cl)$ (**2**), the U(1)–Cl(1) (2.606(3) Å) and U(1)–N(1) (2.268(4) Å) bond lengths are typical of U^{IV}–Cl [3,5,33,34] and U^{IV}–N_{amide} [5,8,9,34–37] bond lengths.

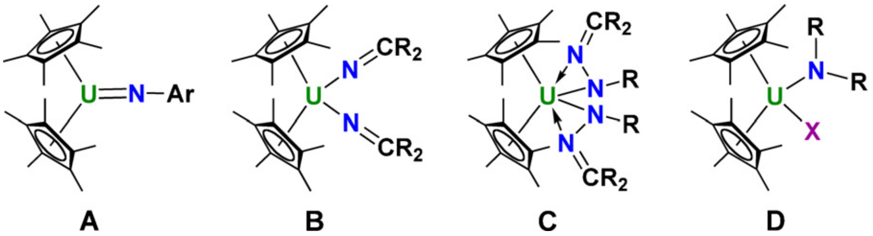

Fig. 1. Uranium metallocene complexes with electronically different nitrogen-based-donor ligands: imide (A), ketimide (B), hydrazonato (C), mixed-amide halide/pseudohalide (D).