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THEIR REACTIVITY

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Early actinide organonitrile compounds and their reactivity

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Introduction

The actinide trihalides are an important class of materials. Anhydrous AnX_3 compounds have been prepared via high temperature synthetic techniques, but they exist as polymeric solids, which are insoluble in organic solvents.¹⁻³ Transuranic complexes $AnI_3(THF)_x$ have been prepared by the reaction of metals with $C_2H_4I_2$ in THF solutions ($An = Pu, x = 5$; $An = Np, x = 4$)⁴ and can be viewed as a net oxidation of An metal with 1.5 equivalents molecular iodine. A convenient preparation of organic solvent soluble trivalent actinide compounds has been described where 1.5 equivalents of I_2 are added to actinide (An) metal turnings ($An = Pu, U, Np$) suspended in aprotic organic coordinating solvent.^{5,6} Since virtually all nonaqueous $An(III)$ complexes have been prepared through the triiodide-tetrahydrofuran complex, we are interested in preparing complexes with solvents other than tetrahydrofuran. And, since uranium is often used as a surrogate for studying the chemistry of transuranic actinides, we are seeking to elucidate the chemical differences between the transuranic elements and uranium. In this presentation we describe new $Pu(III)$ complexes prepared by plutonium metal oxidation with either iodine

or metal hexafluorophosphate salts in acetonitrile. We also revisit the oxidation of uranium metal by iodine in acetonitrile.⁷⁻⁹ Finally, we also describe a new, versatile, mononuclear U(IV) product, $\text{UI}_4(\text{NCPH})_4$, obtained from the oxidation of uranium metal by iodine in benzonitrile.

Results

Treatment of plutonium metal suspended in acetonitrile by iodine generated a blue solution. We attribute the blue color to *in-situ* generation of $\text{PuI}_3(\text{NCMe})_x$ (**1**). Although we have been unable to characterize **1**, addition of a single equivalent of the f-element extractant *tpza* (*tpza* = tris[2-pyrazinyl)methyl]amine = $\text{N}(\text{CH}_2(\text{C}_4\text{H}_3\text{N}_2))_3$) to the blue solution resulted in isolation of the Pu(III) derivative, $(\text{tpza})\text{PuI}_3(\text{NCMe})$ (**2**). Green crystals of **2** were characterized by x-ray crystallography.

Oxidation of excess uranium metal with 1.5 equivalents of iodine in acetonitrile has been reported to provide $\text{UI}_3(\text{NCMe})_4$ (**3**)⁷. We were able to isolate a single crystal from this reaction after the solution was cooled to -38°C . X-ray crystallography identified this product as the mixed valence U(IV)/U(III) compound $[\text{UI}_6][\text{U}(\text{NCMe})_9][\text{I}]$ (**4**). The cationic portion of the molecule is a homoleptic U(III) ion surrounded by nine acetonitrile molecules. This nine-coordinate cation is flanked by a non-coordinating iodide and the U(IV) dianion UI_6^{2-} . When the oxidation of uranium metal was carried out in benzonitrile, the mononuclear U(IV) product $\text{UI}_4(\text{NCPH})_4$ (**5**) is obtained in ~80% yield.

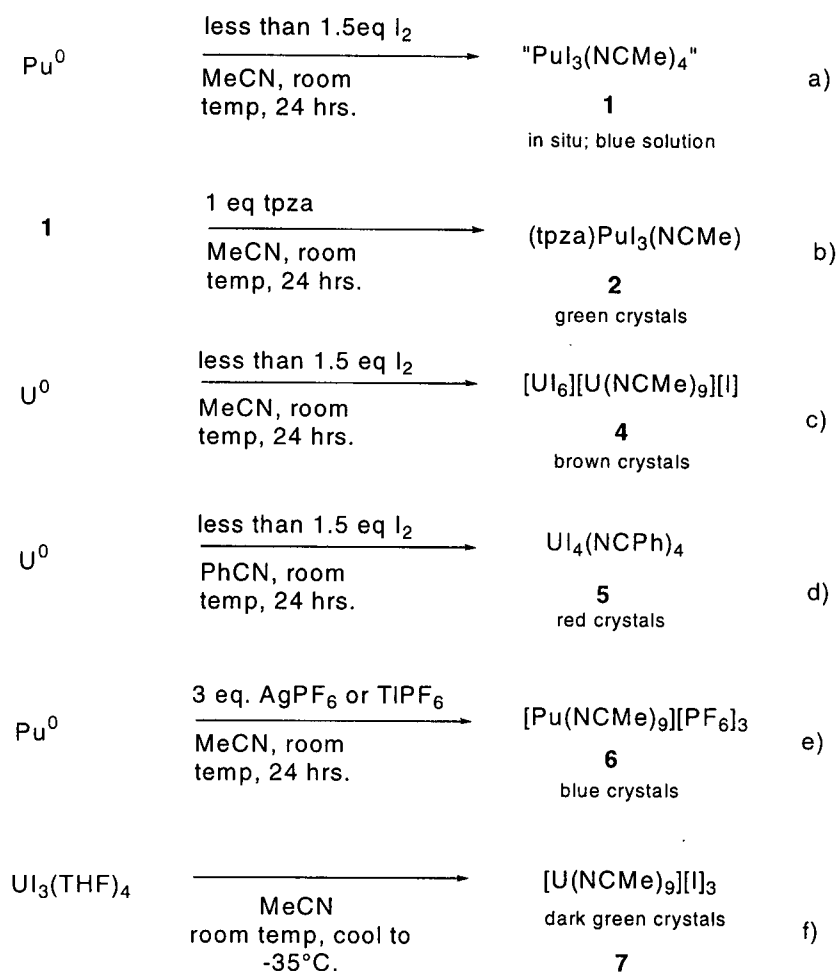


Figure 1. Preparation of Pu (III), U (III) and U(IV) nitrile complexes.

Addition of three equivalents of either AgPF_6 or TlPF_6 to an acetonitrile suspension of ^{239}Pu metal gradually provided a blue solution as plutonium metal dissolved and either silver or thallium metal precipitated. Filtration of the solution followed by slow evaporation of acetonitrile formed blue crystalline $[\text{Pu}(\text{NCMe})_9][\text{PF}_6]_3 \cdot \text{MeCN}$ (**6**) in ~80% yield. Attempts to prepare the nine-coordinate homoleptic acetonitrile uranium analogue of **6** by treatment of uranium turnings suspended in acetonitrile with either AgPF_6 or TlPF_6 were unsuccessful. No reaction was

observed even after days of stirring. However, dissolution of blue $\text{UI}_3(\text{thf})_4$ in acetonitrile resulted in a dark green solution which, upon cooling to -38°C , provided dark-green crystals of the nine-coordinate U(III) acetonitrile salt $[\text{U}(\text{NCMe})_9][\text{I}]_3$ (**6**). Crystals of **6**, unlike the plutonium analogue **5**, are thermally unstable and rapidly decompose at room temperature to an undetermined black residue.

Discussion

The uranium and plutonium nitrile compounds isolated from An^0 oxidation reactions in polar aprotic solvents are consistent with known differences between the reactivities of uranium and plutonium metal. For example, plutonium oxidation by iodine in either thf or pyridine solutions gives well characterized $\text{PuI}_3(\text{sol})_4$ products (these Pu(III) have been characterized by TGA, ^1H NMR, IR and UV/vis/near-IR spectroscopies). Our efforts to isolate and structurally characterize **1**, the intermediate prepared by oxidation of Pu^0 with iodine in MeCN, have been unsuccessful. However, **1** is clearly Pu(III) because it can be trapped by tpza to form the Pu(III) compound **2**. Plutonium metal also undergoes a unique reaction in acetonitrile when it is treated with silver and thallium hexafluorophosphate salts to provide the homoleptic Pu(III) acetonitrile salt **6**. We have not yet prepared a Pu(IV) compound by direct oxidation of Pu^0 in polar aprotic solvents.

Unlike plutonium, uranium metal can be oxidized by iodine in polar aprotic solvents to provide both U(III) and U(IV) products. When excess metal is present, U^0 oxidation by 1.5 equivalents of iodine in thf, pyridine, or dme solvents gives the well characterized U(III) products $\text{UI}_3(\text{sol})_x$ (thf and py, $x = 4$; dme, $x = 2$) (although $\text{UI}_3(\text{thf})_4$ is the only one to be structurally characterized). Preparation of $\text{UI}_3(\text{NCMe})_4$ in an

analogous fashion has been reported. Our attempts to prepare this complex by direct oxidation of U^0 with iodine in acetonitrile gave the dark brown crystalline mixed valence U(IV)/U(III) salt **4**. Curiously, oxidation of excess uranium metal in benzonitrile with iodine cleanly provides crystalline **5** in high yield. No evidence for a U(III) product is observed. Complex **5** is soluble and stable in toluene, benzene, and methylene chloride for days. However, when **5** is dissolved in acetonitrile a reaction occurs. The crystalline material isolated from the reaction is a brown product characterized by x-ray crystallography as $[UI_6][U(NCMe)_7I_2]$. We are currently examining the reactivity of **5** towards neutral and anionic chelating ligands.

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