Nanostructured Materials

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Synthesis of Air-Stable, Volatile Uranium(IV) and (VI) Compounds and Their Gas-Phase Conversion To Uranium Oxide Films**

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Abstract: *Four air-stable, volatile uranium heteroarylalkenolates have been synthesized and characterized by three synthetic approaches and their gas phase deposition to uranium oxide films has been examined.*

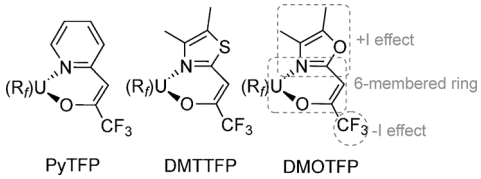
The synthesis of volatile uranium compounds was first explored in the Manhattan Project in search of efficient ways to separate uranium isotopes. During this period, uranium fluorides, alkoxides, amides, dithiocarbamates, mercaptides, borohydrides, and β-diketonates containing uranium in different oxidation states were reported by the groups of Gilman and Brown.[1] Subsequent investigations of homo- and heteroleptic uranium alkoxides by Bradley et al. introduced new U^{V} and U^{VI} derivatives including several uranyl alkoxides as well as siloxides,[2] which were mainly characterized by elemental analyses and molecular weight studies. As a result, the information on their solid-state structures was rather limited.[3]

The chemistry of volatile uranium compounds was revisited for laser-induced isotope separation.[4] These studies primarily focused on the hexamethoxide of U^{VI} and its fluorine-substituted derivatives, $U(OMe)_xF_{6-x}$, because volatility was found to rise with increasing oxidation state (IV→VI).[5]

The resurgence of interest in understanding the versatile and often unprecedented chemistry of uranium is demonstrated by recent publications reporting on unusual oxidation states[6] and exciting structural chemistry with single and multiple metal–ligand bonds.[7] Several of these molecules show potential for application in organocatalysis.[8] In terms of the application of uranium compounds in material synthesis, so far only one example of a gas phase deposition of UO_3 has been reported.[9] This is possibly due to the fact that U^{IV} compounds tend to promptly react with atmospheric oxygen and moisture. In addition, some of them are pyrophoric, which limits their potential as suitable precursors.[10]

We have recently demonstrated the application of substituted heteroarylalkenolates to obtain air-stable and volatile precursors of both transition and noble metals.[11] Herein we report that the versatile heteroaryl-substituted alkenol ligand system can produce a highly stable and volatile class of uranium compounds.

The bidentate chelating ligands 3,3,3-trifluoro-1-(pyridine-2-yl)propen-2-ol (PyTFP), 3,3,3-trifluoro-1-(4,5-dimethyloxazole-2-yl)propen-2-ol (DMOTFP), and 3,3,3-trifluoro-1-(4,5-dimethylthiazole-2-yl)propen-2-ol (DMTTFP; Scheme 1) offer a customizable conjugated system to significantly improve the physicochemical properties of a large number of homoleptic metal alkoxides as shown for Nb, Ta, Fe, Zn, Pt, Pd, Cu, Co, and Al derivatives.[11,12]



Scheme 1. Structure and stabilizing factors of β-heteroarylalkenolates.

Compared with β-diketonates these ligands form a stable six-membered metallacycle reinforced by a positive inductive effect of the heterocyclic moiety and a negative inductive effect of the CF_3 groups (pseudo push–pull effect). Further, the volatility of the molecules was found to depend on the fluorine content. Sievers et al. have examined this phenomenon by measuring the vapor pressure of several metal β-diketonates, in which the CH_3 group had been exchanged by CF_3 and C_3F_7 groups. The measured vapor pressure along with the thermogravimetric data confirmed a direct dependency of volatility on the extent of fluorination of the examined metal β-diketonates.[13] This observation is also valid for the class of β-heteroarylalkenols and has been verified in recent reports.[11,12]

Uranium dioxide is most commonly used as a nuclear fuel, but because only 0.7% of the natural occurring uranium isotopes can be used in reactors, efforts have been undertaken to use depleted uranium compounds.[14] Since discarded fuel rod storage is a critical safety and environmental issue, there

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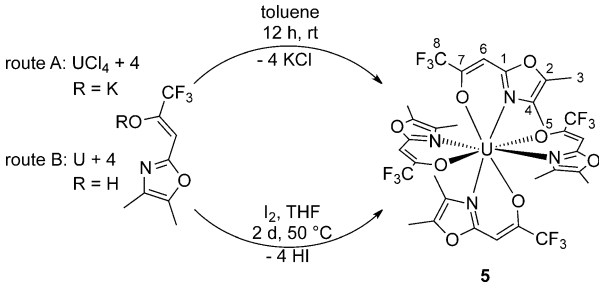
is a growing interest in mitigating the migration of radionuclides in the environment.[15] Other potential uses of uranium oxides are radiation shields, catalysts in thermopower applications, and recently as potential semiconductor material for solar cells.[16,17] The semiconducting properties of UO_2 are tunable to either n- or p-type behavior depending on the content of the adsorbed oxygen and offer vast opportunities to optimize electronic properties of useful materials.[18]

We report here the synthesis and structural characterization of four volatile nonpyrophoric uranium(IV) species with remarkable stability toward air and moisture as solids. Their conversion to uranium oxide films is also described.

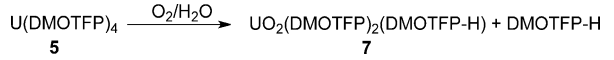
The homoleptic uranium(IV) heteroarylalkenolates were obtained by three synthetic pathways. The salt metathesis reaction of uranium(IV) chloride with the potassium salts K-PyTFP **1**, K-DMOTFP **2**, and K-DMTTFP **3** (route A) afforded compounds **4**–**6**, respectively, in >85% yield (Scheme 2).[19]



Scheme 2. Reaction conditions and chemicals to prepare $U(PyTFP)_4$ **4**, $U(DMOTFP)_4$ **5**, and $U(DMTTFP)_4$ **6** exemplified with **5** including arbitrary atomic numbering.

The direct oxidation of uranium by iodine (route B) led to the same complexes in a slightly reduced yield (75%) and required longer reaction times at elevated temperatures. Purification steps required the prior sublimation of residual iodine at 110°C under reduced pressure.[20] Attempts to synthesize the equivalent U^{III} species by the reaction of $UI_3(THF)_4$ with K-ligand resulted in the oxidation to U^{IV} compounds. Since the complexes are sublimable, method B appeared to be more feasible due to single-step preparation.

Paramagnetic **4** exhibited a set of broad signals for the aromatic protons that could not be unambiguously assigned. Compounds **5** and **6** were characterized by multinuclear 1D and 2D NMR spectroscopy despite their paramagnetic nature. The ^1H NMR spectrum of **5** showed only one set of resonances at $\delta = 11.8$, -3.1, and -13.8 ppm for the vinylic protons and methyl groups in a ratio of 1:3:3, which is consistent with uranium in a symmetric eight coordinate environment such as the square antiprism found in the solid states structure (see below). The signal shifted to higher field was assigned to the methyl group oriented toward the uranium center. Additional ^{19}F NMR experiments showed one singlet at -67.0 ppm for coordinated CF_3 groups, which seem to be less influenced by the paramagnetic uranium (compared to the free ligand -74.2 ppm).[12c] Although the broadening of NMR signals as a result of paramagnetism can inhibit the detection of carbon signals, resonances could be detected through $^1H,^{13}C$ and $^{19}F,^{13}C$ HSQC and HMBC experiments. The ^{13}C resonances depended on the distance to uranium. These experiments showed that **5** is slowly oxidized to diamagnetic $UO_2(DMOTFP)_2$ in solution depending on the water and oxygen content in the deuterated solvent. The direct synthetic approach to the hexavalent compound **7** was established by bubbling O_2 into a solution of **5** (Scheme 3.)



Scheme 3. Postulated reaction to form **7**.

The monomeric nature and volatility of the uranium heteroarylalkenolates were confirmed by electron impact mass spectrometry (EI-MS). Each complex exhibited the distinctive molecular ion peak as well as signals derived from a loss of ligand (e.g., $[U(DMOTFP)_3]^+$). This three-fold coordinated radical cation represented the ion with the highest intensity giving further proof of stability, because no other uranium-containing radical cations could be detected. Other signals representing lower masses were assigned to the typical fragmentation patterns of the substituted alkenol ligands.[11,12] The NMR and EI-MS data can be found in the Supporting Information (SI).

Single crystals of $U(PyTFP)_4$ **4** and $U(DMOTFP)_4$ **5** were grown from THF solutions.[21] $U(PyTFP)_4$ crystallized in the orthorhombic space group *Pbca*, whereas $U(DMOTFP)_4$ crystallized in the monoclinic centrosymmetric space group *C*2/*c* with four molecules per unit cell. The uranium atoms exhibit a distorted square antiprismatic coordination sphere in both **4** and **5**.

The opposing basal planes of **5** ($O2^i$-N2-$O1^i$-$N1^i$ and O1-N1-O2-$N2^i$) are misaligned by ca. 20.5°, whereas the ones of **4** (O2-N3-O1-N4 and O3-N2-O4-N1) are twisted by ca. 50.4°, which makes **4** a more severely distorted species. The two ligands of the smallest asymmetric unit of **5** or the four ligands of **4**, respectively, are *trans* to each other, so that the difference in bond lengths of U–N and U–O causes a deviation from the ideal symmetry (SI and Figure 1).

The mean U–O distances of both **4** and **5** (ca. 2.24 Å) are shorter than those reported for uranium beta-diketonates (2.32 Å).[22] Crystals of compound **7**, grown directly after the oxidation procedure from toluene, crystallized in the triclinic space group $P\bar{1}$ with two chelating ligands, one neutral ligand as ketoenamine tautomer and two oxygen atoms coordinated to the uranium center. The uranium atom exhibits a pentagonal bipyramidal coordination sphere. As expected, the bond lengths of uranyl oxygen atoms U1–O1 = 1.721(13) Å and U1–O2 = 1.714(13) Å to uranium are much shorter than the bonds between uranium and the ligand oxygen atoms. The O1-U1-O2 = 178.6(6)° uranyl bond angle is near linear as expected (Figure 1).

TG/DTA measurements on **4**–**7**, performed in air, display their remarkable stability, because no mass losses were observed until the onset of decomposition between 200°C

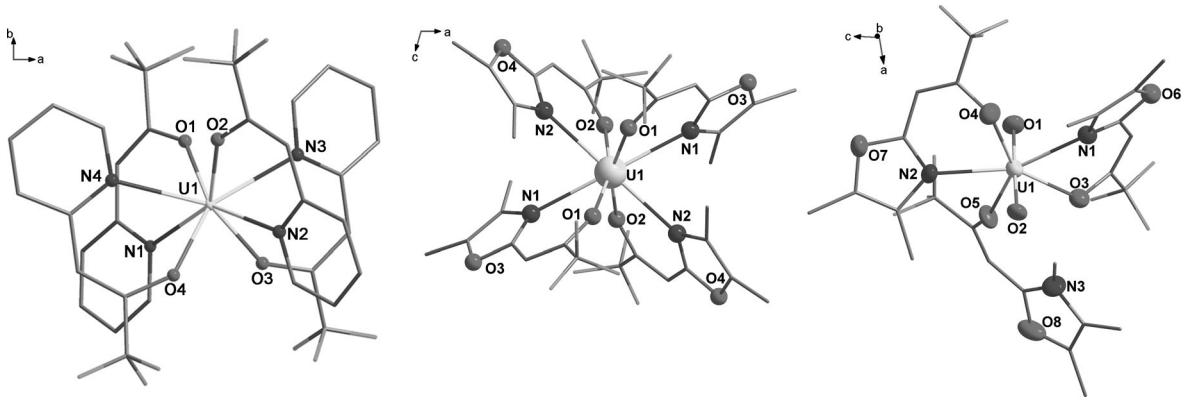


Figure 1. Molecular structure and unit cell of U(PyTFP)$_4$ **4**,[21] U(DMOTFP)$_4$ **5**,[22] and UO$_2$(DMOTFP)$_2$(DMOTFP-H) **7**.[23] Thermal ellipsoids are shown at 30% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths for: **4** [Å]: U1–O1 2.211(1), U1–O2 2.219(1), U1–O3 2.235(1), U1–O4 2.226(1), U1–N1 2.664(1), U1–N2 2.696(1), U1–N3 2.684(1), U1–N4 2.639(2); **5** [Å]: U1–O1 2.246(4), U1–O2 2.240(4), U1–N1 2.650(5), U1–N2 2.672(5); **7** [Å]: U1–O1 1.721(13), U1–O2 1.714(13), U1–O3 2.374(12), U1–O4 2.296(13), U1–O5 2.337(12), U1–N1 2.562(16), U1–N2 2.537(14).

and 260 °C, which occurs in single steps (Figure 2). These decompositions are accompanied by exo- and endothermic processes, respectively. Complete combustion was detected at 530 °C (**4**) > 450 °C (**7**) > 330 °C (**5**) > 290 °C (**6**) with measured mass losses of 77% (**4**), 61% (**5**), 53% (**6**), and 61% (**7**). The mass loss for compounds **4**–**7** to uranium oxide should be higher, but since no additional oxygen was added during the measurement, carbon contamination may explain the mismatch.

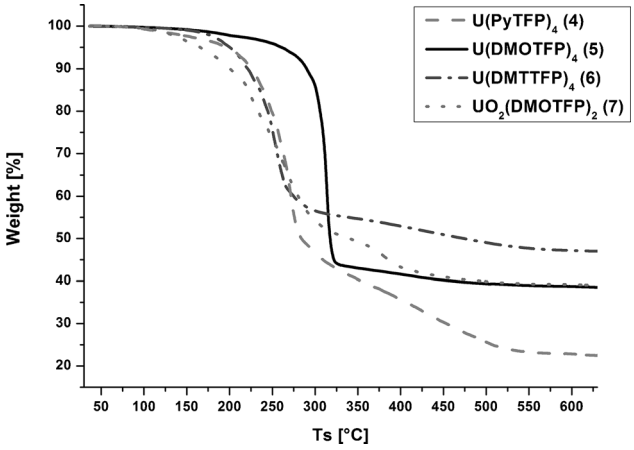


Figure 2. TG/DTA measurement of compounds **4**–**6**.

Preliminary chemical vapor deposition experiments showed the potential of these compounds as precursors to UO_x materials. Exemplarily, **5** was used in a thermal CVD process to obtain a thin film consisting of uranium oxide phases. The coexistence of hexavalent UO_3 and mixed penta- and hexavalent U_3O_8 compositions in the films indicates the high reactivity of the uranium oxide phases and a pronounced tendency to switch oxidation states.

Figure 3 shows the scanning electron micrograph of a CVD deposit. Figure 4 displays the corresponding X-ray diffractogram, which exhibits signals corresponding to crystalline UO_3 and U_3O_8 phases, which is supported by the high resolution XPS scan (Figure 5 and SI).[23] Future efforts will concentrate on the phase-selective CVD of UO_x films and

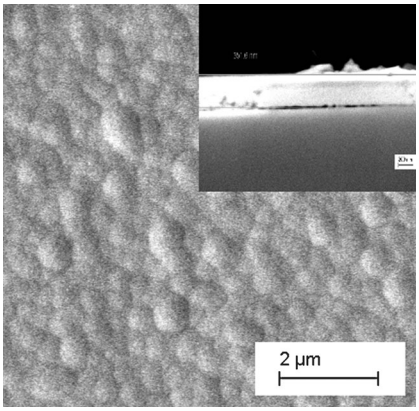


Figure 3. SEM and cross section of as-deposited uranium oxide thin films. Scale bar in the inset: 3 µm.

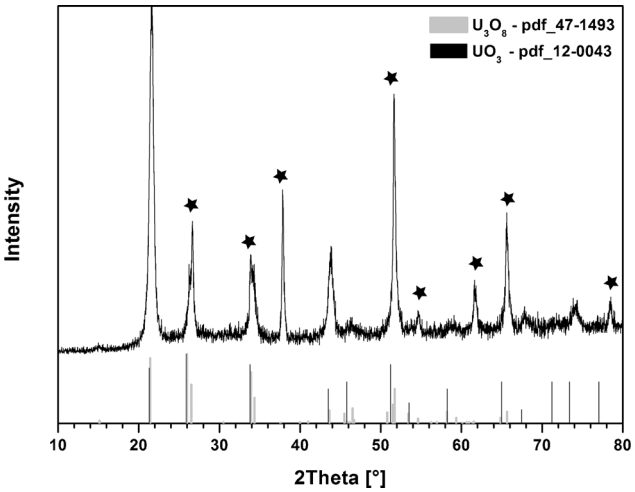


Figure 4. XRD of as-deposited uranium oxide thin films.

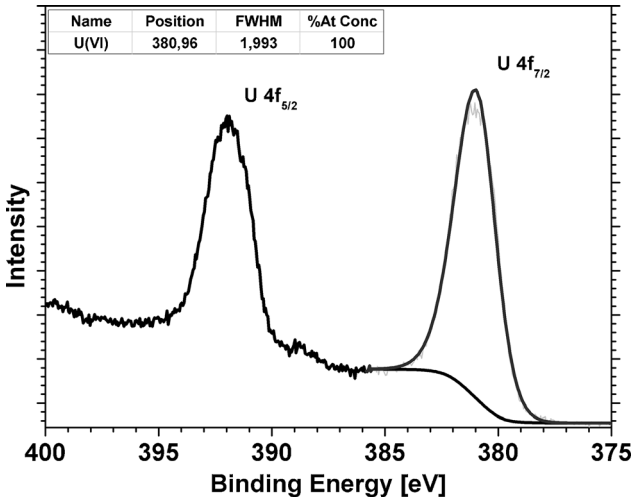


Figure 5. High-resolution XPS of as-deposited uranium oxide thin films.

their possible use in (photo)catalytic applications. Also, the potential of compounds **4**, **5**, and **7** as precursors will be evaluated.

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[19] The potassium salts of heteroalkylalkenoles were synthesized by the reaction of potassiumhexamethyldisilazide (KHMDS) as a base with the ligand in THF. Subsequent multinuclear NMR analysis revealed that the signals had been shifted toward lower field with loss of the acidic proton. To saturate the coordination sphere of potassium the compounds were crystallized in the presence of one equivalent of 18-crown-6 ether (experimental and crystallographic data as well as a molecular structure of compound **2** can be found in SI).

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