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New air-stable uranium(IV) complexes with enhanced volatility†

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Jennifer Leduc, Rajitha Ravithas, Lisa Rathgeber and Sanjay Mathur*

Herein we report the synthesis and characterization of new air-stable uranium(IV) complexes based on three different heteroarylalkenolate ligands namely DMOPFB (1) (1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluoro-but-1-en-2-ol) with an elongated fluorinated alkyl chain compared to DMOTFP (2) (3,3,3-trifluoro-1-(4,5-dimethyloxazol-2-yl) propen-2-ol) and the tetradentate enaminone TFB-en (3) (*N*,*N*′-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylenediamine). These new complexes exhibit sufficiently high volatilities, with respect to previously reported uranium compounds, and are thus promising precursors for chemical vapor deposition (CVD) of uranium oxide materials.

Investigations on uranium complexes have recently attracted substantial attention in fields ranging from subvalent (U(II)) compounds, isotope separation to materials science.[1–6] Uranium complexes with fluoride-,[7] borohydride-,[8] amide-,[9] silazane-,[9] alkoxide-[10,11] and acetylacetonate[12] ligands are known to be volatile and have been studied especially for isotope separation applications. However, these complexes are mostly not suitable for the gas phase synthesis of uranium oxide materials by chemical vapor deposition (CVD) due to their low vapor pressure,[7] uncontrolled thermal decomposition,[8] reactivity towards moisture[9,10] and visible and UV light sensitivity[11] or unsuitability for safe long-term storage.[7,8] Recently, we have demonstrated the synthesis of air-stable, volatile uranium(IV) heteroarylalkenolates as well as their gas phase conversion to uranium oxide films.[5] However, when applied in a thermal CVD process relatively high precursor temperatures (~150 °C) were required for the heteroarylalkenolates. In our quest for new uranium complexes with enhanced volatility, we report here on two alternative synthetic approaches based on the modification (elongation) of the perfluoroalkyl chain of β-donor alkenolates, which are known to enhance the volatility of metal complexes due to electrostatic repulsions between the C_xF_y-groups that suppress intermolecular interaction in the solid-state[13,14] and the reduction of the overall molecular weight using a smaller tetradentate ligand. The heteroarylalkenolate ligand DMOPFB **1** was synthesized using 2,4,5-trimethyloxazole, pentafluoropropionic anhydride and pyridine as base. The reaction proceeded at room temperature for 12 hours to produce the target ligand that was purified *via* sublimation (45 °C, 10^{-3} mbar) in 52% yield. It was characterized using 1D and 2D NMR spectroscopy. The ^{1}H NMR spectrum of **1** showed signals corresponding to the enol and enaminone tautomers: the signals at 11.55 and 11.48 ppm could be assigned to the –OH and –NH protons, respectively, whereas the singlet at 5.89 ppm could be attributed to a vinylic proton indicating the existence of the enolic form of **1**. Comparison of the sublimation temperatures with DMOTFP **2** (s.p. 55 °C, 10^{-3} mbar)[15] showed that **1** was more volatile (s.p. 45 °C, 10^{-3} mbar). Tetradentate enaminone ligand **3** was prepared in a straightforward two-step synthesis. In the first step, 1-ethoxy-4,4,4-trifluorobut-1-en-3-one (TFAE) was synthesized according to the procedure of S. Matsuo *et al.*[16,20] The resulting product was reacted with ethylenediamine[17] resulting in TFB-en (*N*,*N*′-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylendiamine **3**) with an isolated yield of 75%.

The reaction of uranium turnings with **2** equiv. of iodine and **4** equiv. of **1** at 50 °C for 2 days resulted in the formation of $U(DMOPFB)_4$ **4** as a green solid in 50% yield (Scheme 1A).[5,18] Compound **4** was characterized using 1D and 2D NMR spectroscopy, elemental analysis and single crystal X-ray diffraction analysis. Compared to the free DMOPFB ligand, the signal of the vinylic proton was strongly shifted downfield to 13.1 ppm, and the signals of the methyl groups were shifted upfield to −2.4 and −18.0 ppm, respectively, plausibly due to the paramagnetic character of the complex. The strong upfield signal of −18.0 ppm was assigned to the methyl group oriented toward the uranium center. Since ^{1}H NMR data showed only a signal set for the ligand, it can be deduced that the uranium center maintains the symmetric eight-coordinate environment such as the square antiprism found in the solid-state structure. In comparison to the

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Chair of Materials and Inorganic Chemistry, University of Cologne, Greinstr. 6, 50939 Cologne, Germany. E-mail: sanjay.mathur@uni-koeln.de

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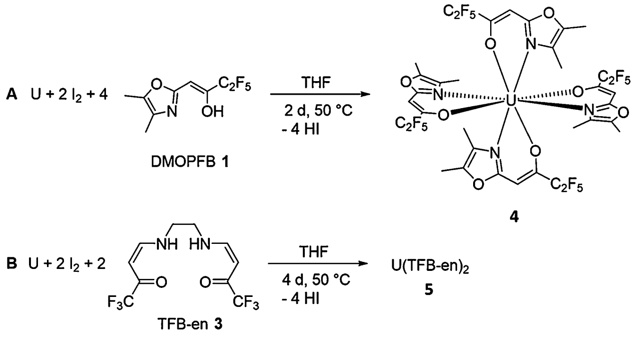

Scheme 1 Synthesis of $U(DMOPFB)_4$ **4** (A) and $U(TFB\text{-}en)_2$ **5** (B).

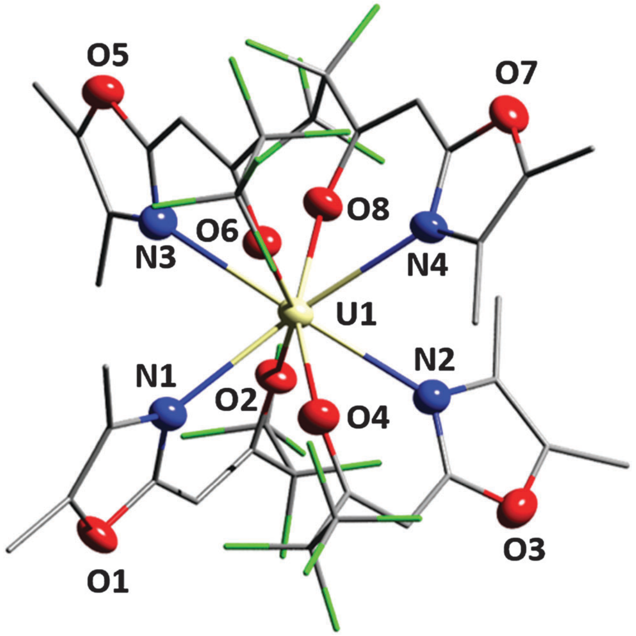

Fig. 2 Molecular structure of $U(DMOPFB)_4$ **4**. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): U1–O2 2.231(5), U1–O4 2.266(5), U1–O6 2.236(5), U1–O8 2.253(5), U1–N1 2.586(6), U1–N2 2.619(7), U1–N3 2.649(6), U1–N4 2.646(6).

$U(DMOTFP)_4$ complex **6**,[5] the chemical shifts were more pronounced. The fluorine signals appeared at −76.1 ($-CF_3$) and −107.3 ppm ($-CF_2$) (Fig. 1).

Time-dependent NMR analysis showed that **4** is slowly oxidized to the diamagnetic species $UO_2(DMOPFB)_2(H\text{-}DMOPFB)$ **8** in THF-d_8 probably due to its reaction with water and oxygen inadvertently present in the solvent (further information in the ESI†). Single crystals of $U(DMOPFB)_4$ **4** were obtained by recrystallization from heptane solution.

Compound **4** crystallized in the orthorhombic space group *Pbca*, with eight molecules per unit cell, whereas **6** was reported to crystallize 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 (Fig. 2). The two ligands generating one distorted square plane are aligned *trans* to each other. The difference in bond lengths of U–N and U–O is responsible for the distortion of the square antiprismatic coordination sphere resulting in angles deviating from ideal 90° by ±15° for N3–N4–O6–O8 and by ±10° for N1–N2–O2–O4. The mean U–O distances of **4** (*ca.* 2.25 Å) were similar to those observed in $U(DMOTFP)_4$ **6** (2.24 Å).[5]

The higher volatility of **4** was confirmed using electron impact mass spectrometry (EI-MS). Due to the technical limit of the mass spectrometer at m/z = 1200, the M^+ signal (m/z = 1262) could not be detected. Instead, the radical cation derived from the loss of one DMOPFB ligand was found to possess the highest intensity ($[U(DMOPFB)_3]^+$; m/z = 1006). Other signals representing lower masses probably result from the fragmentation of the DMOPFB ligand. This proved the stability of **4** in the gas phase at elevated temperatures.

Thermogravimetric analysis of **4** performed under nitrogen showed a lower decomposition temperature, when compared with the DMOTFP complex **6**. No mass losses were observed until the onset of decomposition at 240 °C (Fig. 3). Decomposition occurs in one step and complete combustion was achieved at >290 °C. The experimental weight loss (74%) due to the formation of UO_2 is in good agreement with the theoretical value (79%).

Complex **5** was synthesized following an analogous pathway as described for **4** by reacting uranium turnings with 2 equiv. of

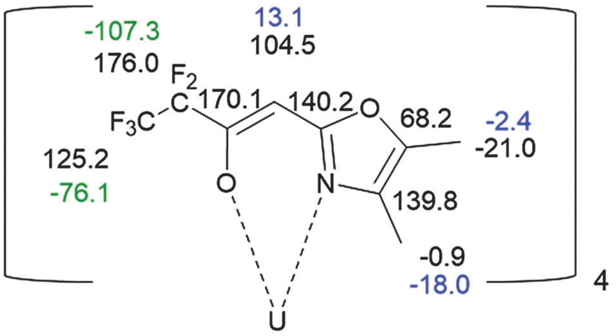

Fig. 1 Assignment of ^1H (blue), ^{13}C (black) and ^{19}F (green) NMR shifts of $U(DMOPFB)_4$ **4** in THF-d_8 exemplarily shown for one of the four DMOPFB ligands in [ppm].

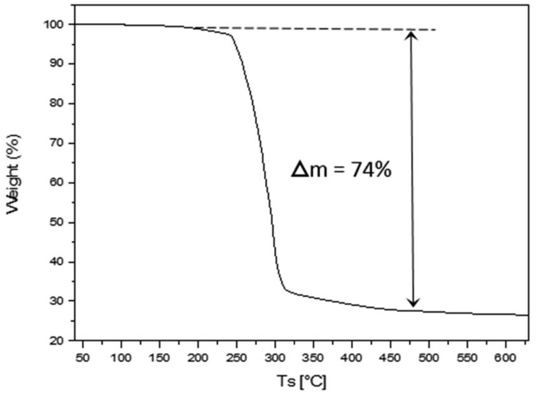

Fig. 3 Thermogravimetric analysis of $U(DMOPFB)_4$ **4** under a nitrogen atmosphere.

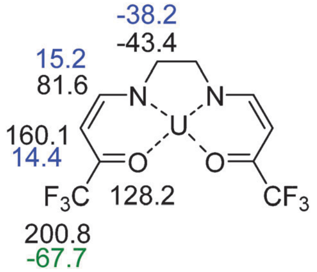

Fig. 4 Assignment of ^{1}H (blue), ^{13}C (black) and ^{19}F (green) NMR shifts of U(TFB-en)$_2$ **5** in THF-d$_8$ exemplarily shown for one ligand in [ppm].

iodine and 2 equiv. of TFB-en **3** at 50 °C. The reaction was sluggish and 4 days were needed for full conversion of the educts into products showing a less pronounced tendency of TFB-en towards the complexation of uranium. U(TFB-en)$_2$ **5** was isolated after sublimation at 130 °C (10^{-3} mbar) in 20% yield. Compound **5** was characterized using ^{1}H, ^{13}C as well as ^{19}F NMR spectroscopy (Fig. 4) and mass spectrometric analysis.

The proton and carbon signals of the ethylene bridge were strongly upfield shifted (−38.2 ppm, ^{1}H and −43.4 ppm, ^{13}C). The vinylic protons displayed a downfield shift to 15.2 ppm and 14.4 ppm. As observed for **4**, EI-MS showed that **5** also exhibited enhanced volatility compared to our previously published uranium(IV) complexes.[5] The M$^+$ signal (m/z = 842) with the highest intensity was detected at 110 °C. Elemental analysis as well as EI-MS data showed that the compound still contained slight impurities of iodine, which was removed by additional washing with heptane and crystallization of **5** from toluene at −30 °C. However, the resulting green/brownish solid was found by ^{1}H NMR analysis to be a mixture of **5** and **3**. Further attempts to purify the compound like solvent extraction or recrystallization were unsuccessful and only resulted in decomposition of **5**. Similar to the derivative **4**, **5** decomposed in undried THF-d$_8$ to give TFB-en **3** and a diamagnetic, bright yellow compound from NMR signals, which could be best assigned to UO$_2$(TFB-en)(THF) **9**.[19]

In summary, we could show that the length of the fluorinated alkyl chain in the oxazole-ligand and the decrease in the molecular weight of the complexes by using a tetradentate enaminone ligand represent viable approaches for increasing the volatility of uranium(IV) compounds. Both complexes are stable as solids in air; however only **4** may prove as the useful precursor for CVD processes since **5** could not be completely purified due to its instability. Further efforts are currently underway.

Experimental

Tetrakis[η^2-*N*,*O*-1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluorobut-1-en-2-olato] uranium(IV) (4)

Oxide-coated uranium turnings (0.40 g, 1.70 mmol) were stirred for 5 min in 5 ml of concentrated nitric acid and rinsed with deionized water and acetone to remove the native oxide. A 100 ml Schlenk flask was charged with freshly obtained oxide-free uranium metal turnings, iodine (0.90 g, 3.50 mmol), 1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluorobut-1-en-2-ol (DMOPFB) 1 (1.80 g, 7.00 mmol) and 20 ml THF. The reaction mixture was vigorously stirred for 2 d at 50 °C yielding a brown suspension. The reaction mixture was cooled to rt and decanted to collect a mixture of green and black crystals. The mixture was washed with hexane and dried under reduced pressure. The remaining iodine was removed *via* sublimation at 110 °C under reduced pressure and the product was obtained as a green solid (1.1 g, 50%).

^{1}H-NMR (300 MHz, rt, THF-d$_8$): δ [ppm] = 13.1 (s, 4H); −2.4 (s, 12H); −18.0 (s, 12H).

^{19}F-NMR (282 MHz, rt, THF-d$_8$): δ [ppm] = −76.1 (s, 12F); −107.3 (s, 8F).

^{13}C-NMR (75 MHz, rt, THF-d$_8$): δ [ppm] = 176.0, 170.1, 140.2, 139.8, 125.2, 104.5, 68.2, −0.9, −21.0.

CHNS (found/calculated) [%]: C (34.09/34.24); N (4.21/4.44); H (2.25/2.24).

EI-MS (20 eV, 115 °C): m/z = 1005 [M]$^+$ (100%), 257 [M-(CF$_2$CF$_3$)]$^+$ (8%), 138 [C$_6$H$_7$NO]$^+$ (20%).

Bis[η^2-*N*,*O*-*N*,*N*′-bis-(4,4,4-trifluorobut-1-en-3-on) ethylenediamine] uranium(IV) (5)

Oxide-coated uranium turnings (0.62 g, 2.61 mmol) were stirred for 5 min in 5 ml of concentrated nitric acid and rinsed with deionized water and acetone to remove the native oxide. A 100 ml Schlenk flask was charged with freshly obtained oxide-free uranium metal turnings, iodine (1.33 g, 5.22 mmol), *N*,*N*′-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylendiamine (TFB-en) 3 (1.59 g, 5.22 mmol) and 25 ml THF. The reaction mixture was vigorously stirred for 4 d at 50 °C yielding a brown suspension. The solvent was directly removed under reduced pressure. The remaining iodine was removed *via* sublimation at 110 °C under reduced pressure. The crude product was purified *via* sublimation at 130 °C (10^{-3} mbar) and the product was obtained as brownish crystals (0.42 g, 20%).

^{1}H-NMR (300 MHz, rt, THF-d$_8$): δ [ppm] = 15.2 (d, 4H); 14.4 (d, 4H); −38.2 (s, 8H).

^{19}F-NMR (282 MHz, rt, THF-d$_8$): δ [ppm] = −67.7 (s, 12F).

^{13}C-NMR (75 MHz, rt, THF-d$_8$): δ [ppm] = 200.8, 160.1, 128.2, 81.6, −43.4.

CHNS (found/calculated) [%]: C (27.51/28.52); N (6.36/6.65); H (2.32/1.91).

EI-MS (70 eV, 110 °C): m/z = 842 [M]$^+$ (100%), 152 [C$_5$H$_5$F$_3$NO]$^+$ (62%), 82 [C$_4$H$_5$NO]$^+$ (25%).

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