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Controlled Chemical Reduction of Uranyl Salts into $UX_4(MeCN)_4$ (X = Cl, Br, I) with Me_3SiX Reagents

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$UO_2I_2(thf)_3$ or $UO_2(OTf)_2$ are easily reduced by Me_3SiX (X = Cl, Br, I) in acetonitrile into the tetravalent $UX_4(MeCN)_4$ complexes, which are useful precursors in uranium chemistry.

Introduction

A variety of methods have been designed for the preparation of the uranium tetrahalides UX_4 (X = Cl, Br, I) and their Lewis base adducts, which are ordinary and convenient precursors for the synthesis of a large range of uranium derivatives.[1] Most of the usual procedures are based on the treatment of solid UO_2 or UO_3 with gaseous X_2 or HX at high temperature, or with halogenated liquid reagents under reflux conditions, which releases very toxic side-on gases.[1] In an attempt to avoid the thermal decomposition of UI_4, the synthesis of $UI_4(PhCN)_4$ was performed by the oxidation of uranium turnings with iodine in benzonitrile,[2] but a similar reaction in acetonitrile failed to produce pure $UI_4(MeCN)_4$,[2,3] which was conveniently obtained by metathesis of UCl_4 in acetonitrile by using excess Me_3SiI.[4] The Me_3SiX molecules are versatile reagents that have found numerous applications in organic and inorganic syntheses.[5] In addition to being very efficient in metathesis reactions of d- and f-transition-metal halides,[4–6] they are also capable of inducing redox transformations.[5] Thus, UF_6 was reduced into UF_5 or UF_4 with Me_3SiCl;[7] $RuCl_3$ reacted with Me_3SiI to give the Ru^{II} compound $[Ru(MeCN)_6][I_4]$,[5] and $CrCl_2$ was oxidized with Me_3SiI into the Cr^{III} iodide $[CrI_2(MeCN)_4][CrI_4(MeCN)_2]$.[5] However, it seems surprising, in view of the strength of the Si–O bond, that the Me_3SiX reagents have seldom been considered for the deoxygenation of metal oxides and their conversion into the corresponding halides.[8]

Activation of the reputedly inert U=O bond of the uranyl ion $[UO_2]^{2+}$ and the controlled reduction of this species represent a particularly active field of research that attracts much attention for both its fundamental aspects and applications.[9] Although the photosensitivity of the $[UO_2]^{2+}$ ion to UV light is a well-documented feature, leading generally to insoluble UO_2 or rare U^{IV} coordination complexes,[10] chemical reduction of uranyl salts into interesting derivatives remains a challenging goal. Such transformations have mostly been observed serendipitously,[11,12] and it is only recently that some smooth and controlled reactions of the $[UO_2]^{2+}$ ion proved successful, revealing new aspects of uranyl chemistry.[13] These advances were made possible by the use of strictly anhydrous experimental conditions. Here we report the reduction of $UO_2I_2(thf)_3$[14] or $UO_2(OTf)_2$[15] with Me_3SiX (X = Cl, Br, I) in acetonitrile, which provides a novel and convenient synthetic route to tetrahalides $UX_4(MeCN)_4$. These reactions, which involve deoxygenation, halide exchange and reduction processes, are much influenced by the nature of the solvent, the Me_3SiX reagent and the uranyl salt.

Results and Discussion

We previously reported that treatment of $UO_2(OTf)_2$ with pure Me_3SiI led to the formation of UO_2I_2 in almost quantitative yield.[14] This compound, which likely has a polymeric structure, is quite insoluble and stable in Me_3SiI. However, after dissolution of UO_2I_2 in coordinating solvents, the molecular Lewis base adducts $UO_2I_2L_n$ (L = thf, py, MeCN) were found to react with the iodosilane. Reactions of $UO_2I_2(thf)_3$ with a large excess of Me_3SiX (X = Cl, Br, I) were first examined in thf at 25° or 100 °C. Metathetical exchange with Me_3SiCl afforded the uranyl chloride, which was inert in the presence of the chlorosilane, as previously observed in the dehydration of $UO_2Cl_2(H_2O)_n$.[16] However, $UO_2I_2(thf)_3$ was found to react with Me_3SiBr, as shown by the colour change of the solution, from red to green, characteristic of uranium(IV) compounds. Similar treatment of $UO_2I_2(thf)_3$ with Me_3SiI gave a mixture of

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complexes among which red crystals of $[U(O\{CH_2\}_4I)_2(thf)_5][I_3]_2[I_2]$ were characterized by X-ray diffraction analysis;[17] this alkoxide derivative obviously resulted from thf ring-opening reaction, which is currently initiated by Me_3SiI and iodo uranium complexes.[18,19] The uranyl iodide $UO_2I_2(thf)_3$ was more reactive towards Me_3SiX in pyridine, but the reduction led to a mixture of the two uranium(IV) complexes $UX_4(py)_4$ and $[UX_6]^{2-}$ (X = Cl, Br).[17]

Eventually, the uranium(IV) tetrahalides $UX_4(MeCN)_4$ [X = Cl (**1**), Br (**2**), I (**3**)] were simply obtained by the addition of an excess of Me_3SiX to a solution of UO_2I_2 or $UO_2I_2(thf)_3$ in acetonitrile at room temperature [Equation (1)]; **1** and **2** were deposited as light green crystals and **3** as an orange powder in good yields (68– 93%).

$$UO_2I_2(thf)_3 \xrightarrow[MeCN]{\text{Excess } Me_3SiX} UX_4(MeCN)_4 \quad \begin{matrix}\mathbf{1}\text{: X = Cl}\\ \mathbf{2}\text{: X = Br}\\ \mathbf{3}\text{: X = I}\end{matrix} \qquad (1)$$

The rate of the reaction was found to depend markedly on X and followed the unusual order Br >> I > Cl. Thus, $UO_2I_2(thf)_3$ was immediately transformed into **2**, whereas its complete conversion into **1** and **3** required 24 h at 25 °C. The reasons for this trend, which could be related to opposite electronic and steric effects,[20] are not obvious.

While $MoO_2X'_2$ or CrO_3 reacted with Me_3SiX to give the partially deoxygenated derivatives $MoOX_2X'_2$ or CrO_2Cl_2, respectively,[8a,8c] complete deoxygenation of the uranyl ion was achieved, as shown by the absence in the IR spectra of the reaction products of any band that could be assigned to the $\nu_{asym}(UO)$ frequency.

Compounds **1**–**3** were characterized by their elemental analyses (C, H, N) and their IR spectra. These spectra, which are identical to those of $UX_4(MeCN)_4$ that was prepared from the uranium tetrahalides, show two bands in the CN region; the strong stretching frequencies (2275–2277 cm^{-1}) correspond to those previously reported for $UX_4(MeCN)_4$ (X = Cl, Br, I),[3,21] and they show a ca. 25 cm^{-1} increase in the coordinated nitrile CN stretching frequency relative to ν(CN) = 2249 cm^{-1} for free acetonitrile.[21]

Crystals of **2** were characterized by X-ray diffraction analysis; a view of the complex is shown in Figure 1 together with selected bond lengths. The structure is identical to that of $UCl_4(MeCN)_4$,[22] and the uranium atom is in a dodecahedral configuration defined by the two orthogonal trapezia Br1–N1–N1′–Br1′ and Br2–N2–N2′–Br2′, with the nitrogen atoms in the A sites.[23] The average U–N and U–Br distances of 2.56(3) and 2.80(2) Å, respectively, are comparable to those measured in $UCl_4(MeCN)_4$ [2.531(17) Å][22] and $UBr_4(OPPh_3)_2$ [2.771(2) Å].[24]

$UO_2(OTf)_2$ is a more accessible precursor than the iodide counterpart and access to the $UX_4(MeCN)_4$ compounds directly from $UO_2(OTf)_2$ would be a much more convenient route.[14] In agreement with previous observations on the distinct reactivities of analogous halide and triflate metal

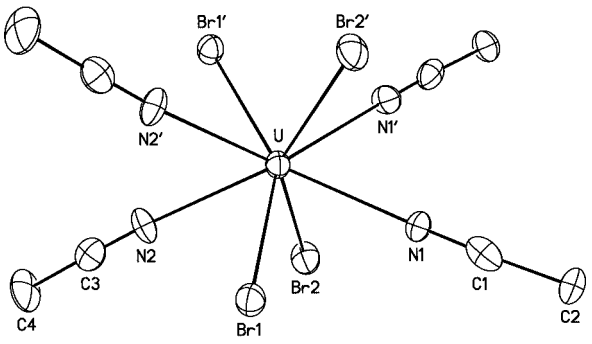

Figure 1. View of $UBr_4(MeCN)_4$ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: ′ = *y*, *x*, 2 – *z*. Selected bond lengths [Å]: U–Br1 2.7751(6), U–Br2 2.8157(5), U–N1 2.527(4), U–N2 2.583(4), N1–C1 1.150(7), N2–C3 1.143(6).

compounds,[14–16,18,19] reactions of $UO_2(OTf)_2$ with Me_3SiX in acetonitrile at 20 °C were slower than those of UO_2I_2 and required heating to go to completion. Whereas $UO_2(OTf)_2$ was inert towards an excess of Me_3SiCl in acetonitrile at 100 °C, its treatment under the same conditions with Me_3SiX led to the formation of $UX_4(MeCN)_4$ (X = Br, I) and the successful preparation of tetrabromide **2**, which was isolated in 72% yield. These results demonstrate that the nature of the uranyl precursor has a major influence on the course of its reactions with the halogenosilanes. The lower reactivity of $UO_2(OTf)_2$ likely reflects the weaker lability of OTf^- versus I^-; however, the facile access to **2** constitutes the most convenient synthesis of this U^{IV} compound.

Conclusions

Reactions of $UO_2I_2(thf)_3$ or $UO_2(OTf)_2$ with Me_3SiX provide rare examples of the controlled activation and reduction of the $[UO_2]^{2+}$ ion and new convenient and safe routes to the tetrahalides $UX_4(MeCN)_4$. In particular, the facile synthesis of **2** is attractive for extending the poorly developed chemistry of uranium bromides, which are susceptible to display solubility, structural and reactivity patterns different from those of the other halides and triflate species.[4,14,25]

Experimental Section

General: All experiments were carried out under an atmosphere of argon (<5 ppm oxygen or water) by using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were dried by standard methods and distilled immediately before use. IR samples were prepared as Nujol mulls between KBr round cell windows, and the spectra were recorded with a Perkin-Elmer FTIR 1725X spectrometer. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The Me_3SiX reagents (Aldrich) were distilled and stored over 4-Å molecular sieves; $UO_2I_2(thf)_3$[13] and $UO_2(OTf)_2$[14] were prepared by published methods.

$UCl_4(MeCN)_4$ (1): A flask was charged with $UO_2I_2(thf)_3$ (200 mg, 0.27 mmol), MeCN (6 mL) and Me_3SiCl (6 mL, 49 mmol). After 24 h at 25 °C, light green crystals of **1** were deposited from the dark brown solution. After filtration, the crystals were washed with

MeCN/Et_2O (1:4, 25 mL) and dried under vacuum (99 mg, 68%). IR: $\tilde{\nu}$ = 2277 (s) (NC), 2307(m) (NC) cm^{-1}. $C_8H_{12}Cl_4N_4U$ (544.05): calcd. C 17.66, H 2.22, N 10.29; found C 17.41, H 2.22, N 10.12.

Synthesis of $UBr_4(MeCN)_4$ (2)

(a) From $UO_2I_2(thf)_3$: A flask was charged with $UO_2I_2(thf)_3$ (200 mg, 0.27 mmol) and MeCN (6 mL). The dark red solution immediately turned colourless upon the addition of Me_3SiBr (6 mL, 46 mmol) at 25 °C, and light green crystals of **2** were deposited. The crystals were filtered off, washed with pentane and dried under vacuum (181 mg, 93%). IR: $\tilde{\nu}$ = 2275 (s) (NC), 2307(m) (NC) cm^{-1}. $C_8H_{12}Br_4N_4U$ (721.85): calcd. C 13.31, H 1.67, N 7.76; found C 13.41, H 1.87, N 7.90.

(b) From $UO_2(OTf)_2$: A flask was charged with $UO_2(OTf)_2$ (40 mg, 0.07 mmol) and MeCN (0.4 mL). The initially yellow solution immediately turned orange upon the addition of Me_3SiBr (0.4 mL, 3 mmol) at 25 °C, and an orange powder was deposited. After 24 h at 100 °C, light green crystals of **2** were deposited from the dark brown solution, and another crop of crystals was collected after the addition of Et_2O (1.5 mL) onto the concentrated MeCN solution (0.2 mL). The crystals were washed with MeCN/Et_2O (1:4, 5 mL) and dried under vacuum (36.7 mg, 72%). IR: $\tilde{\nu}$ = 2275(s) (NC), 2307(m) (NC) cm^{-1}. $C_8H_{12}Br_4N_4U$ (721.85): calcd. C 13.31, H 1.67, N 7.76; found C 13.46, H 1.75, N 7.82.

Synthesis of $UI_4(MeCN)_4$ (3)

(a) From $UO_2I_2(thf)_3$: A flask was charged with $UO_2I_2(thf)_3$ (200 mg, 0.27 mmol) and MeCN (6 mL). The addition of Me_3SiI (6 mL, 42 mmol) to the dark red solution immediately led to an orange precipitate. After 24 h at 25 °C, Et_2O (30 mL) was condensed in, which induced increased precipitation of **3**. Product **3** (212 mg, 87%) was recovered as an orange powder after filtration, washing with pentane and drying under vacuum. IR: $\tilde{\nu}$ = 2275(s) (NC), 2301(m) (NC) cm^{-1}. $C_8H_{12}I_4N_4U$ (909.85): calcd C 10.56, H 1.33, N 6.15; found C 10.35, H 1.54, N 5.99.

(b) From $UO_2(OTf)_2$: An NMR tube was charged with $UO_2(OTf)_2$ (10 mg, 0.018 mmol) and acetonitrile (0.2 mL). The addition of Me_3SiI (0.2 mL, 1.4 mmol) at 25 °C to the yellow solution gave immediately a dark red solution from which red-brown crystals of **3** were deposited in a few minutes. Further precipitation was induced by heating the mixture at 100 °C for 24 h.

X-ray Crystallography: The data were collected at 110(2) K with a Nonius Kappa-CCD area-detector diffractometer with Mo-K_α radiation and processed with HKL2000.[26] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.[27] Absorption effects were corrected with SCALEPACK.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data for **2**: $C_8H_{12}Br_4N_4U$, M = 721.89, trigonal, space group $P3_221$, $a = b$ = 8.7269(3) Å, c = 20.6198(10) Å, V = 1359.99(9) $Å^3$, Z = 3, $D_{calcd.}$ = 2.644 $g\,cm^{-3}$, μ = 17.753 mm^{-1}, $F(000)$ = 960, 31861 measured reflections, 1732 independent (R_{int} = 0.085), 1703 with $I > 2\sigma(I)$, 81 parameters, R_1 = 0.025, wR_2 = 0.049, S = 1.054, $\Delta\rho_{min}$ = –1.47, $\Delta\rho_{max}$ = 1.18 $e\,Å^{-3}$.

CCDC-637174 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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