Thiosemicarbazone Complexes of Uranium(IV)

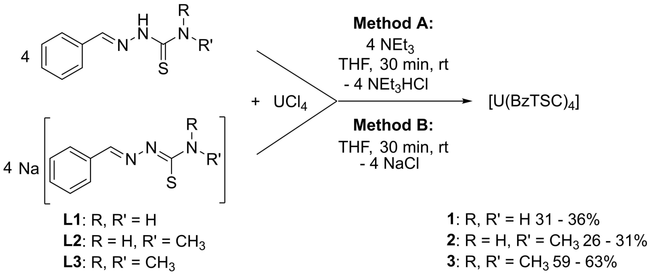
Dennis Grödler,[a] Alexander Haseloer,[a] Christian Tobeck,[a] Yusuf Bulut,[a] Jörg M. Neudörfl,[a] Sanjay Mathur,[a] Uwe Ruschewitz,[a] Axel Klein,[a] Mathias S. Wickleder,[a] and Markus Zegke*[a]

The first homoleptic thiosemicarbazone complexes of uranium were isolated by reacting uranium tetrachloride in a salt metathesis or acid-base reaction with four equivalents of Na(BzTSC) or H(BzTSC) (BzTSC = benzylthiosemicarbazone), carrying a non-methylated (**L1**), monomethylated (**L2**) or dimethylated (**L3**) terminal amino group, in moderate yields. [U(BzTSCNH$_2$)$_4$] (**1**), [U(BzTSCNH(CH$_3$))$_4$] (**2**) and [U(BzTSCN(CH$_3$)$_2$)$_4$] (**3**) show a remarkable stability towards air, with oxidation potentials in THF between +0.43 and +0.53 V and reduction potentials between −2.53 and −2.67 V vs. ferrocene/ferrocenium. The simple methylation of the terminal amino group of the ligand allows for controlled changes in the coordination environments of the complexes. Thermogravimetric analyses indicate that the complexes are stable up to 155 °C.

Introduction

Thiosemicarbazones are versatile chelating ligands towards a considerable range of metal ions. Most compounds are found with divalent late transition metal ions showing chelate N1 S$_{\text{thiolate}}$ or N2 S$_{\text{thiolate}}$ coordination in various coordination polyhedra such as tetrahedral Cu^{2+}, square planar Pt^{2+}, Pd^{2+}, Ni^{2+} or octahedral Ni^{2+} or Zn^{2+} followed by late transition metals in the oxidation state +3.[1–6] For early transition metals, this coordination has been observed for vanadium(IV/V),[7] chromium(III),[8] dioxomolybdenum(VI)[9] as well as tungsten (0)[10] and others.[11–16] Other applications are found in the synthesis of semiconducting materials. Due to the preliminary formed bond between metal and sulfur, thiosemicarbazone complexes are promising single source precursors for chemical vapor deposition (CVD) of metal sulfides. Aerosol assisted CVD was carried out with homoleptic zinc(II) thiosemicarbazones and heteroleptic tribenzyltin(IV)chloride thiosemicarbazones of the type Bz$_3$SnCl(TSC) to deposit ZnS and SnS thin films, respectively.[17,18] Remarkably, among only three heteroleptic Ln complexes[19,20] and four uranyl compounds,[21–23] no research has been carried out on lanthanides and actinides with such ligands. Herein we present the first thiosemicarbazone complexes of uranium(IV). Treatment of one equivalent of UCl$_4$ with either four equivalents of triethylamine and the protonated form of the thiosemicarbazone ligands [**L1** (HBzTSCNH$_2$), **L2** (HBzTSCNH(CH$_3$)), **L3** (HBzTSCN(CH$_3$)$_2$)] (Method A) or their respective sodium salts (Method B) in THF at room temperature yield the homoleptic complexes **1**, **2** and **3** in moderate yields (26–63 %) (Scheme 1).

The X-ray crystal structure of **1** (CCDC Nr. 2043819) was determined and shows coordination of four BzTSCNH$_2$ ligands via N2 and S1 which results in the formation of a four membered U–N–C–S ring forming a distorted dodecahedron (Figure 1). Hirshfeld analysis of the complex **1** revealed a strong



Scheme 1. Synthesis of complexes **1**, **2** and **3**.

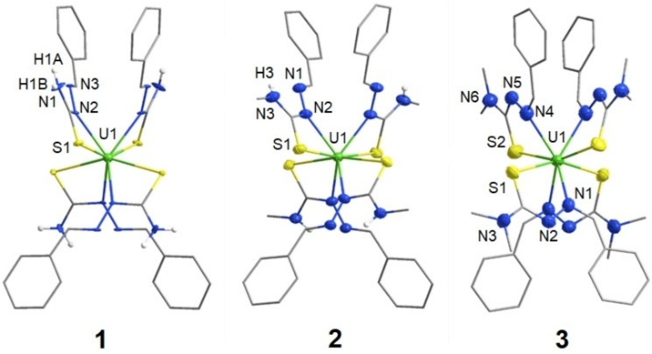


Figure 1. Solid state structures of **1**, **2** and **3**. The THF molecule in **1** and all hydrogen atoms except NH are omitted for clarity (displacement ellipsoids are drawn at 50 % probability). Selected bond lengths (Å) and angles (°): 1: U1–S1 2.828, U1–N1 2.497, S1–U1–N2 57.8. 2: U1–S1 2.832, U1–N1 2.463, S1–U1–N2 57.5. 3: U1–S1 2.739, U1–S2 2.752, U1–N1 2.535, U1–N4 2.569, S1–U1–N1 67.0, S2–U1–N4 67.7.

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[a] D. Grödler, A. Haseloer, C. Tobeck, Y. Bulut, Dr. J. M. Neudörfl, Prof. Dr. Dr. S. Mathur, Prof. Dr. U. Ruschewitz, Prof. Dr. A. Klein, Prof. Dr. M. S. Wickleder, Dr. M. Zegke
Department of Chemistry
University of Cologne
Greinstr. 4–6, 50939 Cologne, Germany
E-mail: m.zegke@uni-koeln.de
https://ac1.uni-koeln.de/en/working-group/dr-markus-zegke

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interaction between the terminal amino moiety with a co-crystallized THF at distance of 2.17 Å. Complexes **2** (CCDC Nr. 2043820) and **3** (CCDC Nr. 2043821) crystallized without further THF (see Figures S4–17).

The U1–S1 and U1–N2 bond lengths of **1** of 2.829 Å and 2.497 Å compare well to other structurally similar complexes (see below). The formation of the four membered ring leads to a bond angle of 57.8° for the S1–U1–N2 coordination. This also applies for the crystal structure of **2** with bond distances of U1–S1, U1–N1 of 2.832 Å and 2.463 Å, respectively. The coordination environment is also a distorted dodecahedron and the bond angle of 57.5° is similar compared to **1**. These complexes compare to only a few literature-known uranium(IV) compounds such as [U(SBT)$_4$(thf)] **I** (SBT = 2-mercapto benzothiazolate),[24] [Cp*U(SBT)$_3$] **II**, and [(Cp*)$_2$U(SBT)$_2$] **III**,[25] [U(Spy)$_4$(thf)] **IV** (Spy = mercapto pyridine)[26] and [(Cp*)$_2$UMe(Spy)] **V**.[27] In those complexes the ligands are coordinated in a similar fashion. However, the ligand environment is much more rigid due to the connection to a benzothiazole ring in **I**–**III** and a mercaptopyridine in **IV** and **V**. The bond distances and angles are of similar values for **I**–**V** as in our complexes (U–S: 2.71–2.87 Å, U–N: 2.45–2.58 Å, S–U–N: 57–61°). There are also uranyl (VI) complexes with this four-membered coordination motif,[28–30] however, due to their different oxidation state these are not directly comparable.

The largest contrast is seen when the terminal NH$_2$ group is fully methylated. In complex **3** the coordination environment changes from a four membered ring to a five membered U–N–N–C-S ring, quite drastically changing the S–U–N bond angles to 67.0° (S1–U1–N1) and 67.7° (S2–U1–N4), respectively. This also results in a change of color of the crystals from yellow (**1** and **2**) to red (**3**). Additionally, the bond distances change with a shortening of the U–S bond to 2.739 Å (U1–S1)/2.752 Å (U1–S2) and an elongation of the U–N bond to 2.535 Å (U1–N1)/2.569 Å (U1–N4). Only five other thiosemicarbazone complexes with uranyl(VI) are known with this five-membered coordination motif.[21,22,31] Thus, this is the first uranium(IV) compound showing this five membered ring and a specific change of the coordination motif by just the methylation of an NH$_2$ group.

While **L1** and **L2** show absorptions at 3412 cm^{-1} and 3373 cm^{-1} for the terminal NH$_2$– or NH(CH$_3$)-group respectively, these absorptions are shifted in complex **1** and **2** towards 3339 cm^{-1} and 3364 cm^{-1}, respectively. **L3** shows no absorption in this region, due to the full methylation in the amino group. But the absorption at 3170 cm^{-1}, which is assigned to the carbazone-NH ν(NH), is no longer observed due to complexation to uranium. The ν(CH)$_{\mathrm{Ph}}$ vibrations of the phenyl ring appear between 3015 cm^{-1} and 3007 cm^{-1} and the ν(=CH) between 2948 cm^{-1} and 2928 cm^{-1}. The corresponding complexes show significant shifts to lower wavenumbers in these regions, indicating a reduced bond strength due to the complexation. Additionally, the methylated derivatives **L2** and **L3** show ν(CH)$_{\mathrm{Me}}$ stretching bands at 2863 cm^{-1} and 2810 cm^{-1}, which are slightly shifted to higher wavenumbers in complex **2** (2860 cm^{-1}) and shifted to lower wavenumbers in complex **3** (2810 cm^{-1}), which can be attributed to the different N-coordination. The fingerprint region shows several stretching bands of ν(C=N), ν(C=S) and deformation vibrations of δ(HNCS) (see Figures S18–21). Despite significant shifts in the IR spectra, no shifts are observed in ^{1}H-NMR spectra (Figures S39–44) and no resonances are observed in the paramagnetic region between +100 and −100 ppm.

Cyclic and square-wave voltammetry allowed to detect one oxidation wave between +0.42 and +0.71 V and two reduction waves for the ligands **L1** to **L3** (Table 1) at around −2.6 V, all of them were irreversible (see SI). A very similar behaviour was observed for the uranium(IV) complexes, but with markedly reduced oxidation potentials for the complexes **1** and **2**, while complex **3** retained the potential compared with **L3**. SEC-UV/Vis (SEC = spectroelectrochemistry)[32] studies showed the decrease of the main absorption at 320 nm while a new band increased at around 360 nm for the ligands, while for the complexes only a subtle decrease in intensity of the 320 nm band was observed (see Figures S26–38). Upon reduction, bands at around 400 nm were observed for both ligands and complexes. The findings indicate a reduction essentially centred at the ligand backbone, probably including the benzylic moiety. The cathodic shift of the oxidation potentials for the complexes **1** and **2** compared with their ligands, suggests a destabilisation of the highest occupied molecular orbital in the complexes. As the differences are not very large, we tentatively assign this shift to the difference between the thione-like structures of the uncoordinated ligands (protonated) and the thiolate character (deprotonated) of the ligands in the complexes. For complex **3** this shift was not observed suggesting that the effect of the double methylation at the N3 atom and the corresponding change from a four- (**1** and **2**) to a five-membered coordination (**3**) compensates for this effect and the different structures for **1** and **2** compared with **3** (Figure 1) are retained in solution.

The thermogravimetric analyses show a very similar behaviour for complexes **1**, **2** and **3** (Figures S22–24). At the first step the complexes lose remaining solvent starting at ca. 50 °C without a DSC signal. The complexes start to decompose at ca. 160 °C and have a large mass loss with three moderately separated steps and three endothermic DSC signals (**1**: 74.0 %; **2**: 72.4 %; **3**: 75.0 %). On a closer look on the first derivative of the TGA it seems that at the beginning of the combustion of **1** and **2** the phenyl group and the two nitrogen atoms split, followed by the release of the amine, while in **3** this order is reversed. In the next step at 350 °C sulfur evaporates. The resulting masses fit very well to uranium and some carbon. For **1** the remaining material was found to be 24.8 % (U calcd.: 24.7 %), for **2** it was 23.7 % (U calcd.: 22.8 %) and for **3** it was 23.1 % (U calcd.: 21.9 %). To get a detailed overview see

Table 1. Redox potentials of **L1**, **L2**, **L3**, **1**, **2**, and **3**.[a]

Redox Process	L1	1	L2	2	L3	3
Oxidation	0.67	0.61	0.71	0.53	0.42	0.43
First Reduction	−2.57	−2.58	−2.74	−2.62	−2.62	−2.67

[a] From cyclic or square-wave voltammetry measured in 0.1 M nBu$_4$NPF$_6$/THF solution at a scan rate of 100 mV/s. All processes are irreversible and given as peak potentials.

Figures S22–24. In PXRD measurements of the residual material after thermal analysis (see Figure S25) all three samples show reflections which can be attributed to $UO_{1.96}$ and an amorphous phase. This is unusual, as the complexes do not contain oxygen, and residual THF solvent has already evaporated. The purity of the compounds has been determined in duplicate by CHN analysis. PXRD measurements of the complexes were attempted. Unfortunately, the complexes lose their crystallinity upon grinding, resulting in poor diffractograms. We could not observe any uranium oxide impurities. Nevertheless, despite all efforts, contamination with oxygen during the TGA measurement, a reaction with the Al_2O_3 of the corundum crucible or contact with air upon removal of the crucible from the device cannot be fully excluded.

Although the thermogravimetric analyses showed the formation of $UO_{1.96}$, MO-CVD (metal-organic chemical vapor deposition) experiments showed no deposition of uranium(IV) oxide phases on Si(001) or Al_2O_3 substrates. All complexes were treated with a precursor temperature of 140 °C and a substrate temperature of 400 °C. In all experiments a decomposition of the complex at 170 °C was observed after 1 h. Considering the molecular structure of the complexes, the π-π interactions between the benzene rings might lead to a reduction of the necessary volatility.

Conclusion

We have isolated the first homoleptic uranium(IV) thiosemicarbazone complexes. Subtle changes in the terminal amino group of the ligand, ranging from non- (**L1**) to mono- (**L2**) to dimethylation (**L3**) change the coordination environment from a four-membered coordination in **1** and **2** to a five-membered coordination in **3**. In contrast, the spectroelectrochemical properties do not change markedly upon coordination of the ligands with U(IV). No evidence for a metal-centred U(IV)/U(V) oxidation or U(IV)/U(III) reduction could be obtained. The complexes were stable in a potential range from $+0.4$ to -2.50 V vs. ferrocene/ferrocenium. In keeping with this, the compounds show a remarkable and unusual stability towards air which is rarely observed in uranium(IV) complexes. Thermal decomposition at temperatures above 155 °C are attributed to the formation of uranium oxide phases.

Deposition Numbers 2043819 (for **1**), 2043820 (for **2**), and 2043821 (for **3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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