Synthesis and X-ray crystal structure of [Na(18-crown-6)][U(Cp*)$_2$(SBu^t)(S)], the first f-element compound containing a metal–sulfur double bond

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The C–S bond cleavage of a thiolate ligand of [U(Cp*)$_2$(SBu^t)$_2$] was induced by treatment with Na(Hg) and the title compound was isolated after addition of 18-crown-6; the crystal structure exhibited the unsupported U–S–Na linkage of the molecular complex, with a U–S bond distance of 2.462(2) Å.

In the course of our studies of uranium complexes with sulfur ligands, we were interested in preparing a molecular compound with a U=S double bond. Such a sulfide of a f-element has not been described so far, whereas transition metal sulfides have received much attention in recent years because of their rich coordination chemistry and their relevance in bioinorganic systems and industrial catalytic processes.[1] A classical route to early transition metal sulfide groups is C–S bond cleavage of coordinated aliphatic thiolate ligands; this reaction is in fact a relatively common decomposition pathway for *tert*-butyl thiolate complexes.[2–5] However, the propensity of sulfides to bridge metal atoms is a serious obstacle in the synthesis of complexes containing M=S multiple bonds,[2,3] and the current formation of clusters has to be avoided by the presence of sterically demanding ligands, as recently demonstrated with pentamethylcyclopentadienyl derivatives of group IV and V metals.[4,5] From these considerations, we decided to examine thiolate C–S bond cleavage in the complexes [U(Cp*)$_2$(SR)$_2$] (R = Pr^i, **1** and Bu^t, **2**). Here we present the synthesis and X-ray crystal structure of [Na(18-crown-6)][U(Cp*)$_2$(SBu^t)(S)] **4**, isolated from the reduction of **2**; the results provide new information about the influence of the metal oxidation state on the cleavage of the thiolate C–S bond.

The uranium(IV) bisthiolate compounds **1** and **2** were simply synthesized by treating [U(Cp*)$_2$Cl$_2$] with a slight excess of NaSR in thf and were isolated as dark red microcrystals in 79 and 85% yield respectively.[6] Compounds **1** and **2** were quite stable in thf or benzene solution and in the solid state. Reduction of **1** (211 mg) with 2% Na(Hg) (369 mg) in the presence of 18-crown-6 (85.5 mg) in thf (100 ml) led to the formation of [Na(18-crown-6)][U(Cp*)$_2$(SPr^i)$_2$] **3** (Scheme 1); the reaction mixture was stirred for 24 h at 20 °C and after filtration and evaporation, the green microcrystals of **3** were washed with pentane and dried under vacuum (243 mg, 80%). The ^{1}H NMR signals of **3** are broader (30–50 Hz) than those of **1** (10–20 Hz) and are characteristic of a U(III) compound. After the triscyclopentadienyl derivative Na[U(Cp)$_3$(SR)],[7] **3** is a new example of a uranium(III) thiolate.

$$\begin{tikzcd} \begin{array}{l} [U(Cp^*)_2(SR)_2] \\ \mathbf{1}\ R = SPr^i \\ \mathbf{2}\ R = Bu^t \end{array} \arrow[r, "i"] \arrow[d, "i"] & \begin{array}{c} [Na(18\text{-crown-}6)][U(Cp^*)_2(SPr^i)_2] \\ \mathbf{3} \end{array} \\ \begin{array}{c} [Na(18\text{-crown-}6)][U(Cp^*)_2(SBu^t)(S)] \\ \mathbf{4} \end{array} & {[Na(thf)_{1.5}][U(Cp^*)_2Cl_2]} \arrow[l, "ii"'] \end{tikzcd}$$

Scheme 1 *Reagents and conditions*: i, Na(Hg), 18-crown-6; ii, NaSBu^t,18-crown-6. All reactions in thf at 20 °C.

Treatment of **2** with sodium amalgam did not afford the corresponding U(III) anionic complex but readily gave a new product which contained, from the NMR spectrum, two Cp* ligands for only one SBu^t group; the narrow resonances indicated that this complex was in the +4 oxidation state. Concomitant formation of isobutylene and isobutane, detected by GLC, suggested that the likely intermediate [U(Cp*)$_2$(SBu^t)$_2$]$^-$ was oxidized into [U(Cp*)$_2$(SBu^t)(S)]$^-$ by facile homolytic C–S bond cleavage of a SBu^t ligand. The same complex was alternatively prepared by reaction of [Na(thf)$_{1.5}$][U(Cp*)$_2$Cl$_2$] (560 mg) and NaSBu^t (313 mg) in thf (50 ml); here again, isobutylene and isobutane evolved. After stirring for 18 h at 20 °C, the red solution was filtered and evaporated and the ochre powder extracted in pentane (482 mg, 95%). In the presence of 18-crown-6, red needles of **4** were obtained from thf-pentane (521 mg, 77%). Complexes **1**–**4** were characterized by elemental analyses (C, H, S) and ^{1}H NMR spectroscopy.†

The crystal structure of **4**, shown in Fig. 1 together with selected data,‡ first revealed the unsupported U–S–Na linkage of the molecular compound. Such heterobimetallics with a single sulfur bridge are very rare, being limited to Ta–M (M = Cr, Mo, W),[8] Re–Ru[9] and Zr–W[10] complexes. However, the most interesting feature of the structure is the U–S distances of the sulfide ligand [2.477(2) and 2.462(2) Å in the two independent molecules] which are shorter than those of the

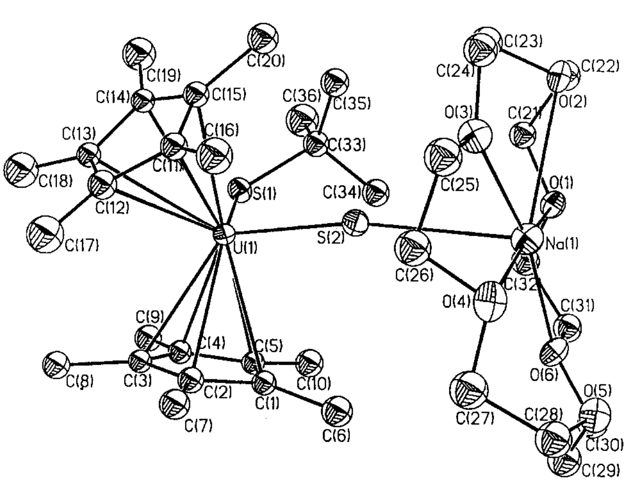

Fig. 1 X-Ray crystal structure of one of the two independent molecules of [Na(18-crown-6)][U(Cp*)$_2$(SBu^t)(S)] with thermal ellipsoids at the 20% probability level. Selected bond distances (Å) and angles (°) : U(1)–S(1) 2.744(2), U(1)–S(2) 2.477(2), Na(1)–S(2) 3.135(4), S(1)–U(1)–S(2) 101.71(7), U(1)–S(2)–Na(1) 168.7(1).

thiolate group [2.744(2) and 2.712(2) Å]. In fact, these are shorter than the shortest U–S distances previously reported, 2.57(2) Å in $[U_3(S)(SBu^t)_{10}]$[2] and 2.60(1) Å in $[\{U(Cp)_3\}_2(\mu\text{-}S)]$,[11] and is consistent with a formal U=S double bond. Thus, **4** ought to be viewed as the adduct of the terminal sulfide $[U(Cp^*)_2(SBu^t)(S)]^-$ to $[Na(18\text{-crown-}6)]^+$. Among the aforementioned compounds which contain an unsupported M–S–M′ linkage, such a dative coordination of a sulfur lone pair of the Ta=S double bond has been encountered in $[Ta(Cp^*)_2(H)(\mu\text{-}S)W(CO)_5]$[8] while the other complexes exhibit single metal–sulfur bonds. In the few adducts of transition metal terminal sulfides with alkali metal ions, such as $[Ti(Cp^*)(OR)(\mu\text{-}S)(\mu\text{-}Cl)Li(thf)_2]$[4] and $[Li_2(thf)_2(Cp^*)TaS_3]$,[5] the metal centres are linked by at least two bridging ligands. The Na–S bond distance and geometrical parameters of the $U(Cp^*)_2$ moiety are unexceptional; steric interactions between the two bulky bridged fragments would explain the large U–S–Na angle [168.7(1) and 174.3(1)°].

Finally, it is worth noting that **2** was stable towards thiolate C–S bond cleavage unless it was reduced by Na(Hg); this fact is in contradiction with previous indications that this reaction would be facilitated by a highly oxidized, electrophilic metal centre.[3] Our results thus give a new insight into the influence of the metal oxidation state on the activation and rupture of thiolate C–S bonds, which is of great importance in catalytic desulfurization processes.

Notes and references

† *Characterising data*. ^{1}H NMR (200 MHz, 30 °C in $[^2H_6]$benzene for **1** and **2** and $[^2H_8]$thf for **3** and **4**). **1**, δ 11.8 (30H, s, Cp*), −18.1 (12H, s, Me), −33.7 (2H, s, CH); **2**, δ 12.2 (30H, s, Cp*), −17.7 (18H, s, Bu^t); **3**, δ 3.8 (24H, s, 18-crown-6), −4.2 (30H, s, Cp*), −6.0 (2H, s, CH), −10.3 (12H, s, Me); **4**, δ 4.5 (24H, s, 18-crown-6), 2.3 (30H, s, Cp*), −17.2 (9H, s, Bu^t). Elemental analyses (calculated values in parentheses). **1**: C, 47.25(47.4); H, 6.85(6.75); S, 9.45(9.75). **2**: C, 48.7(48.95); H, 6.9(7.05); S, 9.15(9.35). **3**: C, 48.0(48.25); H, 7.1(7.25); S, 6.95(6.8). **4**: C, 46.9(47.15); H, 6.8(6.9); S, 6.75(7.0%).

‡ *Crystal data* for $[Na(18\text{-crown-}6)][U(Cp^*)_2(SBu^t)(S)]$: $C_{36}H_{63}NaO_6S_2U$, monoclinic, space group $P2_1/c$, a = 19.174(4), b = 18.548(4), c = 23.132(5) Å, β = 103.31(3)°, V = 8005(3) Å^3, Z = 8, D_c = 1.522 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ = 4.210 mm^{-1}, $F(000)$ = 3696, total reflections = 31073, independent reflections = 8203, data/parameter ratio = 8142/808, R_1 = 0.0334 ,wR_2 = 0.0748, GOF = 1.071, residuals based on $I > 2\sigma(I)$. Diffraction collection was carried out on an Enraf-Nonius diffractometer equipped with a CCD detector at 123 K. Data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by the heavy-atom method and refined by full-matrix least squares on F^2 . There are two independent but similar molecules in the unit cell. A disorder was found on one half of the 18-crown-6 ether of the molecule containing U(2). This disorder is made of two distinct positions that were assigned a 0.5 occupancy factor; they share two carbon atoms which were given an occupancy factor of 1. All non-H atoms were considered anisotropic except those of the disordered half of the crown-ether. H atoms were introduced at calculated positions and constrained to ride on their parent C atoms with displacement parameters of 1.2(CH_2) or 1.5(CH_3) times that of the parent atom. All calculations were performed on an O2 Silicon Graphics Station with the SHELTX package.[13] CCDC 182/1188. See http://www.rsc.org/suppdata/cc/1999/659/ for crystallographic files in .cif format.

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