A mixed-valence uranium(III/IV) bimetallic; structure, magnetism and reactivity

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Reduction of [tris(*tert*-butyldimethylsilylamidoethyl)-amino]chlorouranium(IV) [L^3UCl] with potassium gives the crystallographically characterised mixed-valence (III/IV) dimer [$(L^3U)_2$-μ-Cl] which acts as a source of trivalent uranium giving pentavalent [$L^3U{=}N{-}SiMe_3$] on reaction with trimethylsilylazide.

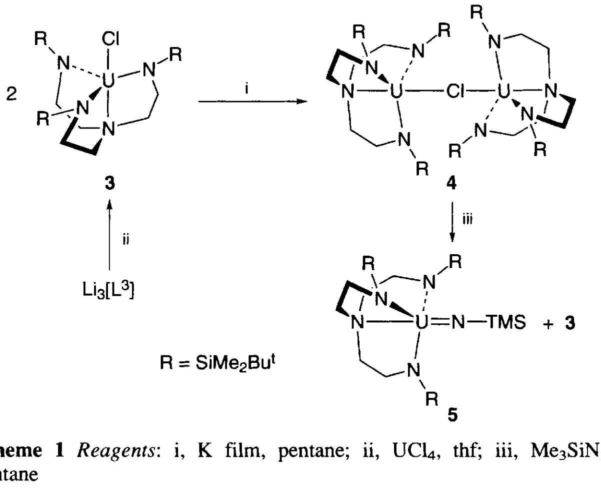
Although the amido ligand (R_2N–) forms complexes with most of the elements, its inherent reactivity limits its use as a spectator ligand.[1] More recently, the use of substituted triamidoamine and tipodal triamido ligands in complexes of the main-group elements[2] and the transition metals[3] has led to an extensive chemistry. Our work on the early actinide elements has shown that the chelate (triamidoamine)uranium fragment is quite robust, tolerating substitution reactions in the auxiliary coordination sphere[4] and allowing the isolation of otherwise unstable complexes.[5] The recent report that three-coordinate alkylarylamido complexes of molybdenum(III) cleave molecular nitrogen under ambient conditions[6] prompted us to investigate the possibility of synthesising related triamidoamine uranium(III) compounds.

Stirring [$(L^1UCl)_2$]† **1**[4] with a potassium film or sodium/potassium alloy led to no detectable reaction. The more sterically encumbered $MePh_2Si$- substituted analogue [L^2UCl] **2**‡ reacted rapidly to give a dark (and thus far) intractable solution. In contrast, reaction of the Bu^tMe_2Si- substituted complex [L^3UCl] **3** in purified pentane with a potassium mirror gave rise to an extremely sensitive deep purple solution (Scheme 1). Filtration of the solution through thoroughly dry glass microfibre and cooling slowly to −30 °C gave long air-sensitive purple needles of mixed valent (III/IV) [$(L^3U)_2$(μ-Cl)] **4** in 93% yield (2 crops). Suitable crystals were mounted under purified helium in Lindemann capillaries and the X-ray structure was determined.§

The molecular structure of **4** is shown in Fig. 1. The principle C_3 axis N(1)–U(1)–Cl–U(1′)–N(1′) and the presence of an inversion centre at Cl determine that **4** has the rather rare D_{3d} symmetry. Threefold symmetric ligation of the triamidoamine ligand is usually observed in complexes of the transition and main-group metals,[2,3] while in complexes of the actinides, distorted structures are more often observed as a consequence of the larger ionic radii.[4] While the amido U(1)–N(2) distances of 2.241(11) Å are only slightly larger than the 2.21–2.22 Å observed in trigonal-bipyramidal tetravalent [$L^1U(O$-*tert*-$C_4F_9)$][7] the distance N(1)–U(1) of 2.78(2) Å is much longer than the 2.624(11) Å in the latter compound, bringing the U atom well out of the chelate ligand cavity.

Bridging U^{IV}–Cl bonds are usually found to be between *ca.* 2.75 and 2.82 Å.[8] In **4** however, the U(1)–Cl distance of 3.020(1) Å (*vide infra*) is longer than the U–Cl bonds in the *trivalent* trimer [$UCl(C_5Me_5)_2]_3$ [2.901(5) Å].[9] We cannot, however, discount the possibility that **4** has an unsymmetric U–Cl–U bridge on the X-ray crystallographic timescale and that the molecule is disordered in the crystal such that an average structure with a symmetric bridge is observed. If this is the case, then since the metal centres in the dimer are otherwise structurally indistinguishable, **4** could be compared to the extensive series of linear-chain class II mixed-valence[10,11] [$Pt^{II/IV}L_4Cl$] polymers in which neighbouring metal sites may be interconverted by axial movement of the bridge.[12]

The UV–VIS spectra of **4** measured in cyclohexane solution from 200 to 1100 nm show broad bands at 331 nm (ε = 2653 $dm^3\ mol^{-1}\ cm^{-1}$), 400 (*ca.* 2200), 538 (1582) and 681 (935). The trigonal-bipyramidal U^{III} compound [$K(thf)_2]_2[U(NHAr')$][13] ($Ar' = C_6H_3Pr^i_2$-2,6) displays a distinct shoulder at 320 nm (11230 $dm^3\ mol^{-1}\ cm^{-1}$) while in contrast



Scheme 1 *Reagents*: i, K film, pentane; ii, UCl_4, thf; iii, Me_3SiN_3, pentane

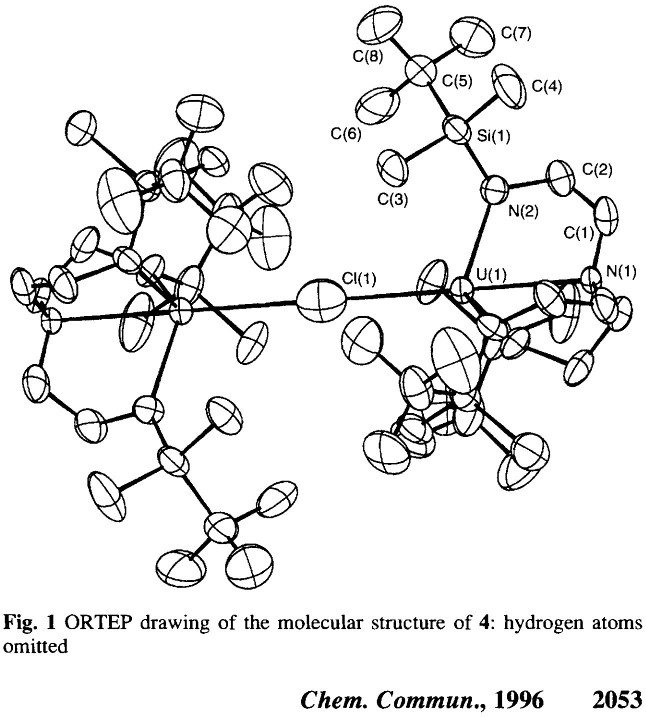


Fig. 1 ORTEP drawing of the molecular structure of **4**: hydrogen atoms omitted

$[UI_3(thf)_4]$[14] has two strong manifolds of absorptions centred at 502 nm (2021 $dm^3\ mol^{-1}\ cm^{-1}$) and 599 nm (1511). We are currently investigating the possibility that one of the bands observed for **4** arises from a $U^{III/IV}$ intervalence charge-transfer process.

Toluene solutions of **4** between 225 and 293 K display Curie–Weiss magnetic behaviour ($\theta = -44.89 \pm 0.01$ K, $C = 1.18$) as determined by the Evans method. This led to a temperature-independent value of $\mu_{eff} = 3.08\ \mu_B$ per uranium atom. Hence, within this temperature range, **4** is behaving as a simple paramagnet. Uranium(IV) amido species exhibit magnetic susceptibilities in the range 2.4–2.8 μ_B, but this is highly dependent on substituent groups and nuclearity.[15] The U^{III} amido compound $[U\{(NSiMe_3)_2\}_3]$ has $\mu_{eff} = 2.51\ \mu_B$.[16]

We have found that **4** is a highly reactive source of trivalent uranium. For example, addition of 1 equiv. of trimethylsilyl azide to a purple pentane solution of **4** at −80 °C causes an immediate colour change to red and the formation of **3** along with a new uranium(V) compound $[L^3U(NSiMe_3)]$ **5** in the ratio 1 : 1 (by ^1H NMR). These compounds were separated by fractional sublimation and crystallisation. Imido derivatives of uranium related to **5** have been described.[17] We hope that the ease of preparation of **5** will allow us to investigate the reactivity of the U–N multiple bond.

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Footnotes

† $L^1 = N(CH_2CH_2NSiMe_3)_3$, $L^2 = N(CH_2CH_2NSiMePh_2)_3$ and $L^3 = N(CH_2CH_2NSiBu^tMe_2)_3$.

‡ The pale green complexes **2** and **3** were prepared in an analogous manner to the trimethylsilyl-substituted analogue **1**.[4] Involatile **2** was purified by recrystallisation from diethyl ether (89% yield), while **3** was purified by sublimation at 180 °C, 10^{-6} mbar followed by recrystallisation from cold pentane (70% yield).

Selected data for **2**: ^1H NMR (298 K, $[^2H_6]$benzene, all peaks $w_{1/2} \approx 50$ Hz): δ 15.8 (s, 6 H, CH_2), 12.8 (s, 12 H, arom. CH), 7.5 (s, 12 H, arom. CH), 6.6 (s, 6 H, arom. CH), −1.8 (s, 9 H, MeSi), −27.3 (s, 6 H, CH_2); MS (EI) *m*/*z* 1005 (24%, M^+), 779 (12%, $M^+ - UCl$). For **3**: ^1H NMR (298 K, $[^2H_6]$benzene, all peaks $w_{1/2} \approx 50$ Hz): δ 7.7 (s, 6 H, CH_2), 6.7 (s, 27 H, Bu^tSi), 6.3 (s, 18 H, Me_2Si), −23.8 (s, 6 H, CH_2); MS (EI) *m*/*z* 759 (42%, M^+), 702 (100%, $M^+ - Bu^t$). For **4**: ^1H NMR (298 K, $[^2H_6]$benzene): δ 26.6 (s, 12 H, CH_2, $w_{1/2} = 150$ Hz), 9.9 (s, 54 H, Bu^tSi, $w_{1/2} = 11$ Hz), −5.6 (s, 36 H, Me_2Si, $w_{1/2} = 300$ Hz), −38.5 (s, 12 H, CH_2, $w_{1/2} = 90$ Hz); MS (EI) *m*/*z* = 759 (44%, $[L^3UCl]^+$), 724 (23%, $[L^3U]^+$), 702 (100%, $[L^3UCl]^+ - Bu^t$). For **5**: ^1H NMR (298 K $[^2H_6]$benzene, all peaks $w_{1/2} \approx 50$ Hz): δ 29.2 (s, 6 H, CH_2), 15.7 (s, 9 H, imido Me_3Si), 6.4 (s, 6 H, CH_2), −4.2 (s, 27 H, Bu^tSi), −12.8 (s, 18 H, Me_2Si); MS (EI) *m*/*z* 811 (14%, M^+), 723 (64%, $M^+ - NSiMe_3$).

§ *Crystal data*: $C_{48}H_{114}ClN_8Si_6U_2$, $M = 1483.52$, trigonal, space group $P\bar{3}1c$, $a = b = 12.635(4)$, $c = 25.55(8)$ Å, $U = 3533(2)$ Å^3, $Z = 2$, $D_c = 1.428$ g cm^{-3}, $F(000) = 1520$. Deep purple air- and dinitrogen-sensitive tablet 0.25 × 0.25 × 0.2 mm in a capillary, $\lambda = 0.71073$ Å, $\mu(Mo\text{-}K\alpha) = 4.790\ mm^{-1}$. Data were collected on an Enraf Nonius CAD4 diffractometer in θ–2θ mode using graphite-monochromated Mo-Kα radiation at 293 K. A total of 4349 reflections were measured ($2° < \theta < 25°$), 2071 unique [$R_{int} = 0.0631$ after absorption correction ($T_{max} = 99.85\%$, $T_{min} = 79.01\%$)], giving 1286 with $I > 2\sigma(I)$. Non-H atoms were located by direct methods (SHELXS-86) and refined by full-matrix least squares on all F^2 with anisotropic thermal parameters (SHELXL-93) and scattering factors from ref. 18. H atoms included in riding mode with $I_{iso}(H) = 1.2\,U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Final $R1$, $wR2$ and S were 0.058, 0.147 and 0.884. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/187.

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