Synthesis, Structure and Electrochemistry of a Paramagnetic (1,4-Diazabutadiene)Thorium Complex

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The first diazabutadiene (DAB) derivative of an actinide metal is characterised by X-ray crystallography and EPR spectroscopy; a comparison of its electrochemistry with that of other DAB complexes suggests a predominantly localised bonding mode.

The structural and electronic properties of 1,4-diazabutadiene derivatives of *s*, *p*, *d* and *f*-block (lanthanide) elements have been investigated by a variety of spectroscopic techniques.[1–3] We have attempted to prepare the hitherto unknown actinide derivatives in order to explore the nature of ligand–metal bonding present. However, a variety of reactions in our laboratory aimed at preparation of homoleptic 1,4-diazabutadiene complexes of uranium and thorium *via* reactions of the metals[2] or metal vapours[3] have thus far been unsuccessful. We have discovered, however, that the sterically demanding aminotris{ethyl(trimethylsilyl)amido} (tren′) ligand, which has previously been used in the synthesis of complexes of main group elements,[4] transition metals,[5] uranium and thorium,[6] provides a suitable environment for the stabilisation of the first diazabutadiene derivative of an actinide.

The reaction of colourless [{(tren′)ThCl}$_2$][6] with green [Li(Bu$^t_2$DAB)$_2$][2] in THF at −80 °C leads to the formation of a bright orange–red solution, [eqn. (1)].

$$[\{(\text{tren}')\text{ThCl}\}_2] + 2\,[\text{Li}(\text{Bu}^t{}_2\text{DAB})_2] \rightarrow 2\,[(\text{tren}')\text{Th}(\text{Bu}^t{}_2\text{DAB})] + 2\,[\text{Li}(\text{Bu}^t{}_2\text{DAB})]\text{Cl} \qquad (1)$$

Evaporation of volatiles and sublimation at 120 °C and 10^{-6} mbar gives analytically pure red crystals of [(tren′)Th(Bu$^t_2$DAB)] **1** in high yield† along with a small amount of pale brown involatile residue. A similar reaction of the analogous uranium compound [{(tren′)UCl}$_2$][6] gave a bright-orange solution at low temperature, but on warming to −50 °C an intractable solid was formed (see below).

Further crystallisation of **1** from hexamethyldisiloxane at −50 °C produces large red crystals. The molecular structure as determined by X-ray diffraction‡ is shown in Fig. 1. The structure of the tren′ fragment is unsurprising in comparison to that in similar uranium compounds,[6] and might be described as occupying four sites of a distorted octahedron. The Th atom lies out of the plane defined by N(1), N(2) and N(3) by *ca.* 0.86 Å; the distance Th–N(4) of 2.671(6) Å, which delimits this distortion is comparable with the shortest of those found in the triamino complex [ThCl$_4$(NMe$_3$)$_3$].[7] The N(5)–Th and N(6)–Th distances of 2.573(6) Å (both) are, as a consequence of the electrostatic contribution to these bonds, somewhat shorter than the amino N(4)–Th distance of 2.671(6) Å. The atoms C(18) and C(22) are distorted away from Si(2) out of the least-squares plane of the DAB fragment by *ca.* 0.21 and 0.20 Å, respectively, presumably to relieve steric compression. Bond lengths within the [Th(Bu$^t_2$DAB)] fragment are consistent with the presence of a singly reduced *i.e.* (Bu$^t_2$DAB)$^{\cdot-}$ ligand, as would be required for a Th^{IV} compound (see below); the C(17)–N(6) and C(16)–N(5) distances of 1.319(10) and 1.317(10) Å and the C–C distance of 1.408(12) are close to those in the anionic ligand of [Li(Bu$^t_2$DAB)$_2$].[2]

The EPR spectrum of **1** in dilute toluene solution is shown in Fig. 2. The value of g_{av} = 1.9902 is slightly lower than that in other complexes containing radical anion DAB ligands.[2] A satisfactory simulation of the spectrum was obtained using hyperfine coupling constants to two N atoms (A_{av} = 4.8 G) and two H atoms (A_{av} = 5.0 G) of the DAB ligand. Although the relatively broad lines obtained limit the certainty of these figures, they compare well with those in similar compounds.[2,8]

We have measured the CV response of **1** [Fig. 3(*a*)] and some other DAB complexes for comparison.§ Complex **1** undergoes a Nernstian but chemically irreversible oxidation at E_p = 0.20 V corresponding to the loss of the electron localised on the π_3 orbital of the DAB fragment, and subsequent further homogeneous reaction (*i.e.* loss of Bu$^t_2$DAB). Electrochemically irreversible reduction occurs at E_p = −1.09 V (v = 100 mV s^{-1}).¶ [Li(Bu$^t_2$DAB)$_2$] undergoes similar electrochemical processes at E_p^{ox} = −0.18 V and E_p^{red} = −1.54 V. In contrast

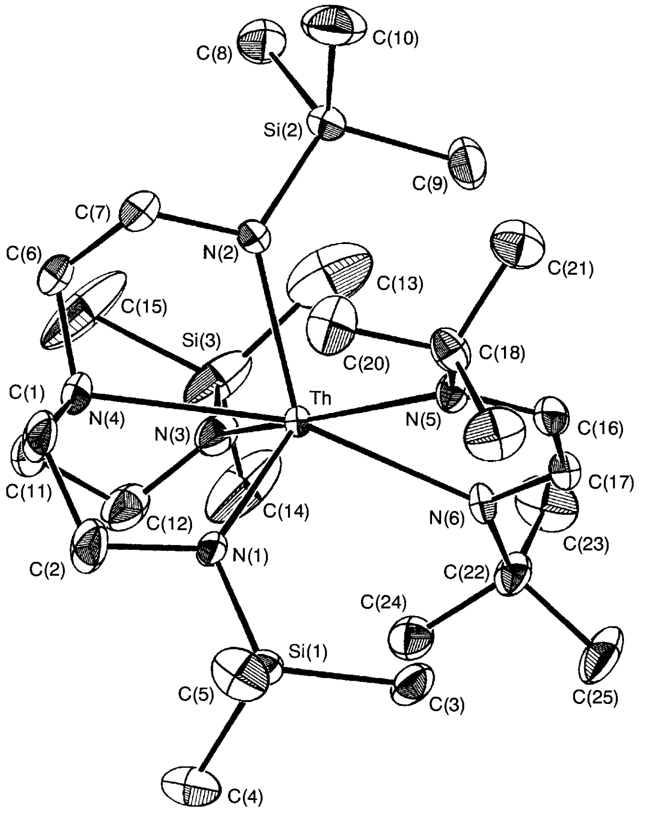

Fig. 1 ORTEP drawing of the molecular structure of **1**; hydrogen atoms omitted

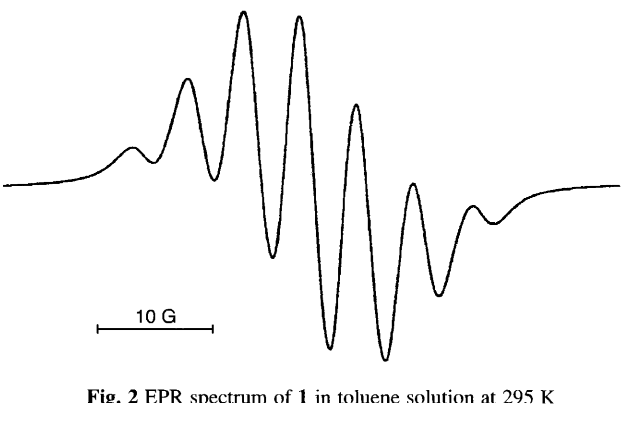

Fig. 2 EPR spectrum of **1** in toluene solution at 295 K

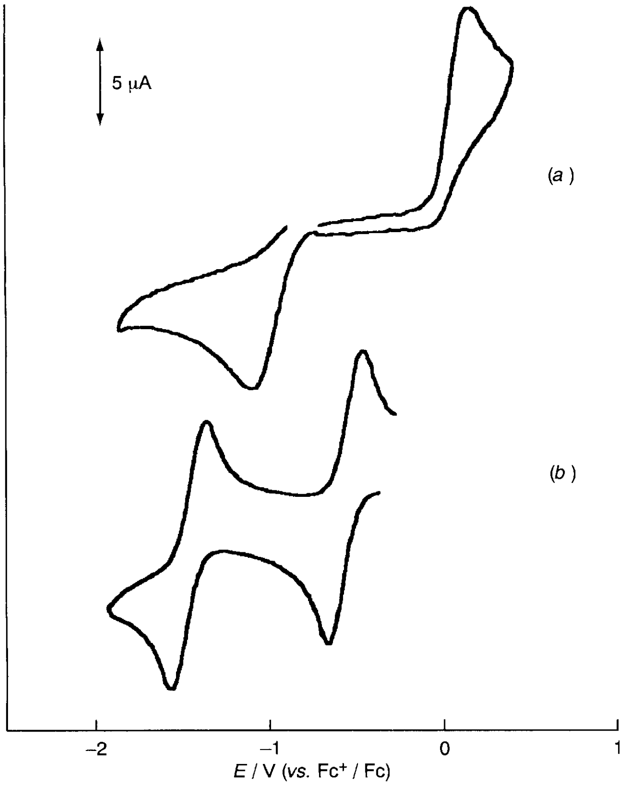

Fig. 3 CV of (*a*) **1** and (*b*) $[\mathrm{Ga(Bu^t{}_2DAB)_2}]$ at scan rate v = 100 mV s^{-1} (Fc = ferrocene)

we have found that $[\mathrm{M(Bu^t{}_2DAB)_2}]$ (M = Al,[3,9] Ga[10]) undergo clean quasi-reversible electrochemistry in this region [Fig. 3(*b*)], and indeed, redox derivatives of these compounds have been isolated.[1,9] Transition metal complexes such as $[\mathrm{Cr(Pr^i{}_2\text{-}DAB)_3}]$ also undergo chemically reversible electron transfer.[11]

The variation in electrochemical behaviour described above has bearing on the discussion[12] regarding electron localisation in complexes of DAB ligands. Addition or removal of electrons occurs, in the case of the *p* and *d*-block compounds, from what are evidently[1] delocalised orbitals with both ligand and metal character. Largely ionic bonding in the *s*-block compounds, and also in **1**, renders them rather more sensitive to the charge on the complex, and thus they undergo chemically irreversible electron transfer.

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Footnotes

† *Characterising data* for **1**: satisfactory elemental analysis for $\mathrm{C_{25}H_{59}N_6Si_3Th}$; MS (EI) *m/z* = 759 (6%, M$^+$), 744 (20%, M − Me), 687 (35%), 591 [100%, M − $(\mathrm{Bu^t{}_2DAB})$].

‡ *Crystallographic data*: $\mathrm{C_{25}H_{61}N_6Si_3Th}$, *M* = 762.1, monoclinic, space group $P2_1/n$ (non-standard No. 14), a = 12.422(4), b = 18.074(3), c = 15.966(4) Å, β = 95.72(2)°, U = 3567(1) Å^3, Z = 4, D_c = 1.42 g cm^{-3}, $F(000)$ = 1540. Orange air-sensitive tablet 0.35 × 0.3 × 0.2 mm in a capillary, λ = 0.71073 Å, μ(Mo-Kα) = 44.5 cm^{-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 9220 reflections were measured (2° $\leqslant \theta \leqslant$ 28°), 8852 unique [R_{int} = 0.02 after absorption correction (T_{max} = 1.00, T_{min} = 0.61)], giving 5164 with $|F^2| > 2\sigma(F^2)$. Decay of 8° in standard reflections was corrected during processing. Non-H atoms were located by heavy-atom methods (SHELXS-86) and refined by full-matrix least-squares analysis with anisotropic thermal parameters using the MOLEN program package[13] and scattering factors from ref. 14. H atoms fixed in calculated positions. Weighting scheme $w = \sigma^2(F)$. Final R, R' and S were 0.049, 0.046 and 1.2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ CV was performed using a Hi-Tec Instruments DT2101 potentiostat and PPR1 waveform generator. Data were acquired on a personal computer using home-made software *via* an ADC. The single-compartment air-tight cell comprised a Pt disk working electrode, Pt wire auxiliary electrode and Ag wire pseudo-reference electrode. Dry THF with 0.2 mol dm^{-3} tetrabutylammonium hexafluorophosphate supporting electrolyte was used throughout. Electrochemical reversibility was judged by comparison of ΔE_{p} with that of ferrocene under the same conditions or by performing variable scan rate experiments (v = 50–1000 mV s^{-1}) as appropriate. Potentials were calibrated by the method of Gagné[15] and are quoted *vs.* the ferrocenium–ferrocene couple.

¶ The decomposition of **1** on oxidation or reduction leads us to speculate that the instability of $[\mathrm{(tren')U(Bu^t{}_2DAB)}]$ is due to reduction of the $\mathrm{U^{IV}}$ centre by the $(\mathrm{Bu^t{}_2DAB})^{\cdot -}$ ion; a pathway that is highly unlikely for $\mathrm{Th^{IV}}$.

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