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Preliminary communication

Synthesis, structure and electrochemistry of the first fulvalene derivative of an actinide ☆

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Abstract

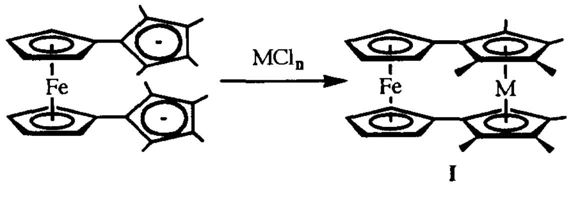
Dilithio[1,1'-bis(tetramethylcyclopentadienyl)ferrocene] and thorium tetrachloride react to give red crystals of [$(Me_4Fv)_2FeThCl_2$] (**1**) (Me_4Fv = 1,2,3,4-tetramethylfulvalene). The molecular structure determined by X-ray diffraction shows that the two metallocene fragments have geometries similar to those observed in analogous mononuclear species. Complex **1** undergoes a quasi-reversible one-electron oxidation at −0.15 V relative to the ferrocenium/ferrocene couple.

Keywords: Iron; Thorium; Electrochemistry; X-ray structure

Several heterobimetallic complexes with a single fulvalene (Fv) ligand bridging the two metal centres have been prepared and their reactivity examined in detail [1]. Also, a few heterobimetallic bis(fulvalene) derivatives have been prepared, either by reaction of the fulvalene dianion with a mixture of transition metal halides [2], or more recently via bis(indenyl)-or bis(tetramethylcyclopentadienyl)-substituted ferrocenes (**1**) [3]. We are interested in extending this class of doubly bridged bimetallocenes in the hope that they will display interesting electrochemical or magnetic properties as a result of strong metal–metal interactions. In the course of this work we have found that, despite the much larger radius of thorium(IV) (1.08 Å) compared with iron(II) (0.77 Å), it can be accommodated in a structure **I** ($M = ThCl_2$) to give the first fulvalene derivative of an actinide metal.

The addition of tetrahydrofuran at −80°C to a mixture of dilithio[1,1'-bis(tetramethylcyclopentadienyl)ferrocene] and thorium tetrachloride leads to dissolution of the solids and formation of a clear orange solution. Evaporation of volatiles, extraction of the residue with diethyl ether and crystallization at low temperature gave a powdery red–orange precipitate. Sublimation of this material at 230°C and 10^{-6} mbar gave a red crystalline solid which was recrystallized from dichloromethane to give analytically pure, clear red crystals of [$(Me_4Fv)_2FeThCl_2$] (**1**) (Me_4Fv = 1,2,3,4-tetramethylfulvalenediyl) in 8% yield [4].

The molecular structure of **1** as determined by X-ray crystallography [5] is shown in Fig. 1. The molecule comprises two tetramethylfulvalene fragments bridging Fe and $ThCl_2$ centres. The Cp_{cent}–Th–Cp'_{cent} angle of ca. 138.5° is well within the usual range, while the C_{Cp}–Th bond lengths (average 2.79 Å) and Th–Cl distances of ca. 2.63 Å are at the lower end of those found in a variety of [$(Me_5Cp)_2ThX_2$] complexes [8]. The distortion from linearity of Cp_{cent}–Fe–Cp'_{cent} (ca. 9.8°) is significantly greater than that observed in [$(Me_4Fv)_2FeZrCl_2$] (0.8°) [3], and as with the latter compound, the MCl_2 fragment points to one side of the ligand framework as a result of its requirement for pseudotetrahedral geometry.



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☆ Dedicated to Professor Dr. Hans-Herbert Brintzinger on the occasion of his 60th birthday.

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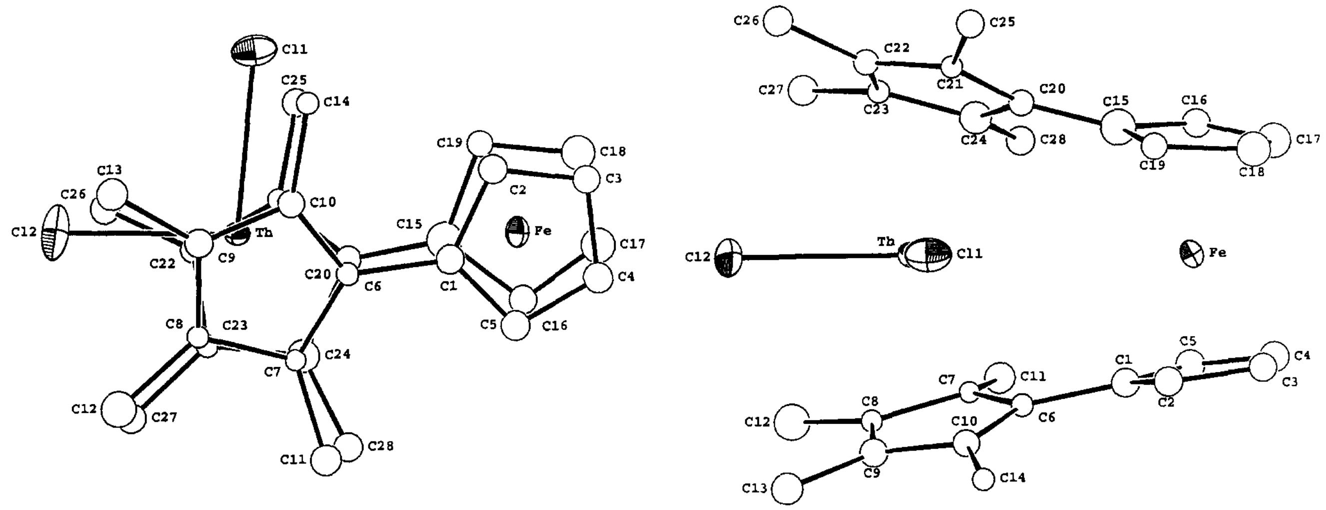

Fig. 1. Two views of the molecular structure of **1**. Selected bond distances (Å): Th–Cp(2) 2.51, Th–Cp(4) 2.51, Th–C_{Cp}(average) 2.79(1), Th–Cl(1) 2.630(11), Th–Cl(2) 2.625(12), Fe–Cp(1) 1.66, Fe–Cp(3) 1.68, Fe–C_{Cp}(average) 2.05(1), C–C [Cp(1) average] 1.39(1), C–C [Cp(2) average] 1.43(1), C–C[Cp(3) average] 1.41(1), C–C [Cp(4) average] 1.44(1), C(15)–C(20) 1.46(5), C(1)–C(6) 1.53(4). Bond angles (deg): Cp(2)–Th–Cp(4) 142.6, Cp(2)–Th–Cl(1) 105.2, Cp(2)–Th–Cl(2) 99.6, Cp(4)–Th–Cl(1) 104.7, Cp(4)–Th–Cl(2) 100.1, Cl(1)–Th–Cl(2) 94.4(4), Cp(1)–Fe–Cp(3) 170.2, Cp(2)–Th–Cp(4) 142.6, Cp(2)–Th–Cp(4) 142.6. The carbocyclic rings and their centroids are labelled thus: Cp(1)[C(1) to C(5)], Cp(2) [C(6) to C(10)], Cp(3) [C(15) to C(19)], Cp(4) [C(20) to C(24)].

The asymmetry of **1** observed in the solid state does not persist in solution. The ^1H NMR spectrum of a d_2-dichloromethane solution of **1** gave only two virtual triplet resonances for the cyclopentadienyl groups on Fe and two singlet resonances for the methyl groups at all accessible temperatures. Hence, the windshield-wiper [3] mechanism which leads to the molecule having a vertical plane of symmetry through the metal atoms is fast on the NMR timescale. ^{13}C NMR spectra also gave only four non-quaternary signals.

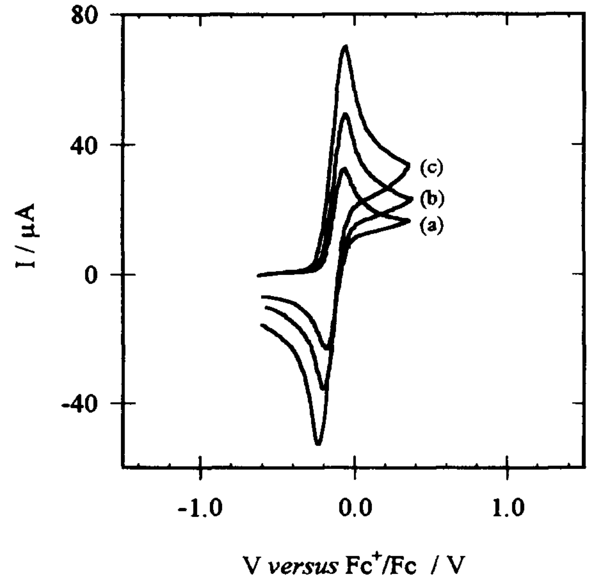

Fig. 2. Cyclic voltammogram of **1** at scan rates of (a) 100, (b) 200 and (c) 500 mV s^{-1}.

The cyclic voltammogram [9] of a solution of **1** in dichloromethane + 0.1 M tetrabutylammonium hexafluorophosphate (Fig. 2) displays a quasi-reversible couple at −0.15 V vs. an internal standard of ferrocene. In comparison, $[(Me_4Fv)_2Fe_2]$ [3] undergoes oxidation at ca. −0.5 V under the same conditions [11], and it is clear that there is a significant interaction between the two Fe centres [12]. For **1**, however, the presence of the $(C_5Me_4)_2ThCl_2$ fragment appears to have little effect on the potential of the Fe^{III}/Fe^{II} couple. On this basis we conclude that **1** is adequately described as a bimetallocene, with electronically distinct metal atoms.

In summary, we have prepared and fully characterized $[(Me_4Fv)_2FeThCl_2]$ **1**, the first fulvalene derivative of an actinide. We hope that the methodology used to prepare this compound will allow us to synthesize similar heterobimetallic complexes involving divalent lanthanides, such as $[(Me_4Fv)_2FeM]$ (M = Yb, Sm, Eu) and to study their electronic structure and magnetism.

Acknowledgements

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References and notes

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[4] Characterizing data for **1**. ^{1}H NMR: δ (CD_2Cl_2, 25°C) 4.75 (4H, vt, $J = 3$ Hz, CH), 4.54 (vt, 4H, $J = 3$ Hz, CH), 2.48 (s, 12H, CH_3), 2.14 (s, 12H, CH_3). $^{13}C\{^1H\}$ DEPT NMR: δ (CD_2Cl_2, 25°C) 69.3 (s, CH), 69.1 (s, CH), 14.0 (s, CH_3), 12.1 (s, CH_3). Anal. Found: C, 46.16; H, 4.54; $C_{28}H_{32}Cl_2FeTh$. Calc. H, 4.43; C, 46.24. MS (EI): 726 (with appropriate isotope pattern, 6%, M^+).

[5] Crystal data for **1** at 293 K, $C_{28}H_{32}Cl_2FeTh$, red block, $0.32 \times 0.2 \times 0.2$ mm^3 in a capillary, $M = 727.4$, monoclinic, $a = 17.495(2)$ Å, $b = 8.530(3)$ Å, $c = 17.715(3)$ Å, $\beta = 108.96(1)°$, $U = 2500(1)$, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.93$ g cm^{-3}, μ(Mo Kα) = 69.6 cm^{-1}. Data were collected on an Enraf Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) in the θ–2θ mode. Lorentz, polarization and absorption ($T_{max} = 1.00$, $T_{min} = 0.58$) corrections were applied. A total of 4875 reflections were collected in the range $4° < 2\theta < 50°$.4729 unique reflections with $|F^2| > 2\sigma(F^2)$ were used. Non-H atoms were located by heavy atom methods and refined by full matrix least squares with anisotropic thermal parameters (for Th, Fe and Cl atoms only) using the MolEN program package [6] and scattering factors from Ref. [7]. Methyl hydrogens were omitted and the Cp H fixed at calculated positions. Final R values were $R = 0.094$ and $R_w = 0.074$ with $S = 1.3$. Structural details have been deposited at the Cambridge Crystallographic Centre.

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[9] Cyclic voltammetry was performed using a Hi-Tec Instruments DT2101 potentiostat and PPR1 waveform generator. Data were acquired on a personal computer with 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. Potentials were calibrated by the method of Gagné [10] and are quoted vs. the potential of the ferrocenium/ferrocene couple. The peak separation ΔE was found to be 105 mV at 100 mV s^{-1}. No compensation for the resistance of the cell was applied. The ratio of peak heights at a given scan rate υ was ca. 1.0.

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