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Supporting Information

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Mixed-Valency in Uranium Multimetallic Complexes

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SUPPORTING INFORMATION

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General Synthetic Procedures. Unless otherwise noted, reactions and manipulations were performed at 20 °C in either a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2) drybox with a MO-40-2 Dri-Train or a recirculating Vacuum Atmospheres NEXUS inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained in either toluene-d_8 or benzene-d_6 using a Bruker Avance 300 MHz spectrometer. Chemical shifts for ^{1}H-NMR spectra were referenced to solvent impurities. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, using either VG ProSpec (EI) or VG70-SE (FAB) mass spectrometers. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Brockman I, Aldrich), and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), diethyl ether (Aldrich), tetrahydrofuran (Aldrich), and hexamethyldisiloxane (Aldrich) were dried over KH for 24 h, passed through a column of activated alumina under nitrogen and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Aldrich), tetrahydrofuran-d_8 (Cambridge Isotopes) and toluene-d_8 (Aldrich) were purified by storage over activated 4 Å molecular sieves under N_2 prior to use. $UI_3(THF)_4$,[1] electrolyte(s),[2] and $(C_5Me_5)_2An[-N=C(-CH_2C_6H_5)(tpy)]$ (An = Th, U)[3] were prepared according to literature procedures.

Caution: Depleted uranium (primarily isotope ^{238}U) and natural thorium (^{232}Th) are weak α-emitters with a half-life 4.47×10^9 years and 1.41×10^{10} years respectively; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of $K(C_5Me_4Et)$.[4] A 125-mL side-arm flask equipped with a stir bar was charged with $KN(SiMe_3)_2$ (15.16 g, 76.0 mmol) and diethyl ether (60 mL). To the resulting slurry was added dropwise C_5Me_4EtH (14.63 g, 97.3 mmol) with stirring. The reaction is exothermic and gas evolves with the addition of C_5Me_4EtH. After the addition of C_5Me_4EtH is complete, the reaction mixture is stirred for 3 h during which time a white solid precipitates from solution. The reaction mixture is filtered through a coarse fritted filter. The solid is collected, washed with diethyl ether (3 × 20 mL) and hexanes (3 × 20 mL), and then dried under reduced pressure to give the product as a white solid (12.33 g, 65.5 mmol, 86%). ^{1}H NMR (tetrahydrofuran-d_8, 298 K): δ 2.37 (quartet, J = 8 Hz, 2H, $-CH_2CH_3$), 1.96 (s, 6H, $-CH_3$), 1.93 (s, 6 H, $-CH_3$), 0.89 (t, J = 8 Hz, 3H, $-CH_2CH_3$).

Synthesis of $(C_5Me_4Et)_2U(I)(THF)$.[5] A 125-mL side-arm flask equipped with a stir bar was charged with purple $UI_3(THF)_4$ (8.52 g, 9.39 mmol) and tetrahydrofuran (100 mL). White $K(C_5Me_4Et)$ (3.79 g, 20.11 mmol) was added to the dark purple solution with stirring. The dark purple solution became blue then green with formation of precipitate. The resulting green suspension was stirred for 16 h at ambient temperature and filtered through a Celite-padded coarse fritted filter to remove an off-white solid, yielding a green solution. The filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_4Et)_2U(I)(THF)$ as a green solid (6.07 g, 8.25 mmol, 88%). X-ray quality crystals of $(C_5Me_4Et)_2U(I)(THF)$ were obtained at −35 ºC from diethyl ether. ^1H NMR (benzene-d_6, 298 K): δ 16.85 (br s, 6H, -$CH_2C\mathit{H}_3$), 0.09 (br s, 4H, -$C\mathit{H}_2$), −0.963 (br s, 4H, -$C\mathit{H}_2$), −3.51 (br s, 12H, -$C\mathit{H}_3$), −4.01 (br s, 12H, -$C\mathit{H}_3$), −18.21 (br s, 12H, -$C\mathit{H}_2CH_3$).

Synthesis of $(C_5Me_4Et)_2U(tpy)$ (4). A potassium mirror (0.029 g, 0.74 mmol, 1 equiv.) was prepared in a 125-mL side-arm flask equipped with a stir bar and containing 30 mL solution of THF. To the potassium mirror was added $(C_5Me_4Et)_2U(I)(THF)$ (0.52 g, 0.70 mmol) and terpyridine (0.16 g, 0.72 mmol, 1 equiv.) to give a green colored solution. This green solution was stirred for 16 h at ambient temperature during which time it turned darker green and a white precipitate formed. The reaction mixture was filtered through a Celite-padded coarse fritted filter remove the precipitate. The filtrate was extracted with a 1:3 v/v mixture of THF and $(Me_3Si)_2O$ and the dark green solution filtered through a Celite-padded coarse fritted filter. Crystalline solid **4** was obtained by chilling the dark green solution at -35 ºC, decanting off the supernatant, washing 3 × 10 mL $(Me_3Si)_2O$ and drying under reduced pressure (0.19 g, 0.25 mmol, 36%). X-ray quality crystals of **5** were obtained by chilling a 1:10 v/v mixture of THF and $(Me_3Si)_2O$ at −35 ºC. ^1H NMR (toluene-d_8, 298 K): δ 25.63 (s, 6H, -$CH_2C\mathit{H}_3$), 15.86 (s, 12H, -$C\mathit{H}_3$), 14.18 (s, 12 H, -$C\mathit{H}_3$), 3.32 (s, 4H, -$C\mathit{H}_2CH_3$), −8.34 (s, 2H, Ar-*H*), −20.05 (s, 2H, Ar-*H*), −28.95 (s, 2H, Ar-*H*), −40.92 (s, 2H, Ar-*H*), −47.73 (s, 2H, Ar-*H*), −126.42 (s, 1H, Ar-*H*). MS (EI, 70 eV): m/z 769.0 (M^+). Anal. Calcd. for $C_{37}H_{45}N_3U$ (769.80 g/mol): C, 57.73; H, 5.89; N, 5.46. Found: C, 57.63; H, 5.99; N, 5.52.

References.

[1] Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248–2256.

[2] (a) LeSuer, R. J.; Geiger, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 248–250. (b) LeSuer, R. J.; Buttolph, C.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395–6401. (c) Barrière, F.; LeSuer, R. J.; Geiger, W. E. In *Trends in Molecular Electrochemistry*; Pombeiro, A. J. L., Amatore, C., Eds.; FontisMedia S. A.; Lausanne (Marcel Dekker Inc.: New York), 2004; pp 413–444. (d) Nafady, A.; Costa, P. J.; Calhorda, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 16587–16599.

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[4] This synthesis is similar to that of K(C_5Me_4H) reported by Evans and co-workers: Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Fagin, A. A.; Bochkarev, M. N. *Inorg. Chem.* **2005**, *44*, 3993–4000.

[5] The synthesis of **4** is essentially identical to that reported for $(C_5Me_5)_2U(I)(THF)$: Avens, L. R.; Burns, C. J.; Butcher, R. J.; Clark, D. L.; Gordon, J. C.; Schake, A. R.;Scott, B. L.; Watkin, J. G.; Zwick, B. D. *Organometallics* **2000,** *19,* 451–457.

Instrumentation and Sample Protocols.

Electronic Absorption Spectrscopy. Electronic absorption spectral data were obtained for THF and/ or toluene solutions of complexes **3a**, **3b** and **4** over the wavelength range 280–2500 nm on a Perkin-Elmer Model Lambda 950 UV-visible-NIR spectrophotometer. All data were collected in 1 mm path length cuvettes loaded in the Vacuum Atmospheres drybox systems described above. Samples were typically run at multiple to optimize absorbance in the UV-visible and near-infrared, respectively. Spectral resolution was typically 2 nm in the visible region and 4–6 nm in the near-infrared.

Electrochemistry. Cyclic wave voltammetric data were obtained in the Vacuum Atmospheres drybox systems described above. All data were collected using a Perkin-Elmer Princeton Applied Research Corporation (PARC) Model 263 potentiostat under computer control with PARC Model 270 software. All sample solutions were ~2-3 mM in complex with 0.1 M $[Bu_4N][B(C_6F_5)]$ or$[Bu_4N][B(3,5\text{-}(CF_3)_2C_6H_3)]$ supporting electrolyte in THF solvent. All data were collected with the positive-feedback IR compensation feature of the software/potentiostat activated to ensure minimal contribution to the voltammetric waves from uncompensated solution resistance (typically ~1 kΩ under the conditions employed). Solutions were contained in PARC Model K0264 microcells consisting of a ~3 mm diameter Pt disk working electrode, a Pt wire counter electrode, and a silver wire quasi-reference electrode. Scan rates from 20–5000 mV/s were employed in the cyclic voltammetry scans to assess the chemical and electrochemical reversibility of the observed redox transformations. Half-wave potentials were determined from the peak values in the square-wave voltammograms or from the average of the cathodic and anodic peak potentials in the reversible cyclic voltammograms. Potential calibrations were performed at the end of each data collection cycle using the ferrocenium/ferrocene couple as an internal standard. Electronic absorption and cyclic voltammetric data were analyzed using Wavemetrics IGOR Pro (Version 4.0) software on a Macintosh platform.

Magnetic Susceptibility. Magnetic susceptibility data were collected using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer at 5 T from 2-350 K. The samples were sealed in a 5mm Wilmad 505-PS NMR tube along with a small amount of quartz wool, which held the sample near the tube center. Contributions to the magnetization from quartz wool and the NMR tube were measured independently and subtracted from the total measured signal. Diamagnetic corrections were made with the use of Pascal's constants.

Crystallographic Experimental Details. Crystals were mounted in a nylon cryoloop using Paratone N oil under argon gas flow. The data were collected on a Bruker D8 APEX II charge-coupled-device (CCD) diffractometer, with KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with graphite monochromatized MoKα X-ray source (λ= 0.71073 Å), with MonoCap X-ray source optics. Hemispheres of data were collected using ω scans. Data collection and initial indexing and cell refinement were handled using APEX II software.[1] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[2] The data were corrected for absorption using the SADABS program.[3] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Unless otherwise noted, non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Residual electron density originating from solvent contributions was removed using SQUEEZE/PLATON.[4] Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[5] Additional details of data collection and structure refinement are listed in the tables below.

References.

[1] *APEX II*, Data Collection Software, Version 1.08; Bruker Analytical X-ray Instruments, Inc.; Madison, WI 53719, 2004.

[2] *SAINT+*, Data Collection Software Version 7.06; Bruker Analytical X-ray Instruments, Inc., Madison, WI 53719, 2003

[3] Sheldrick, G. *SADABS*, Empirical Absorption Corrective Program, Version 2.03; University of Göttingen, Germany, 2001.

[4] Spek, A.L. *Acta Cryst.* **1990**, *A46*, C34.

[5] *SHELXTL*, Version 5.10; Bruker Analytical X-ray Instruments, Inc.; Madison, WI 53719, 1997.

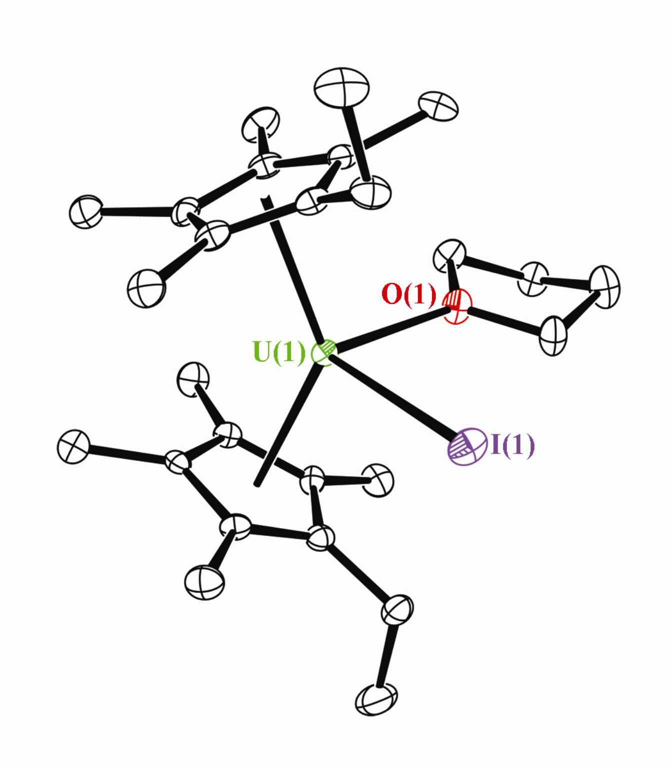


Figure S1. Thermal Ellipsoid Plot of $(C_5Me_4Et)_2U(I)(THF)$ with Ellipsoids Projected at the 50% Probability Level.

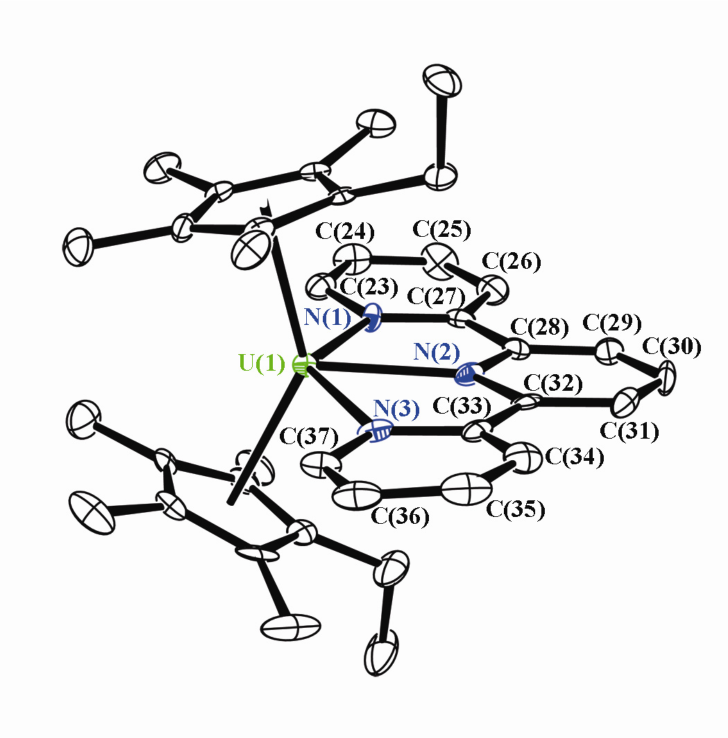


Figure S2. Thermal Ellipsoid Plot of $(C_5Me_4Et)_2U(tpy)$ (4) with Ellipsoids Projected at the 50% Probability Level.

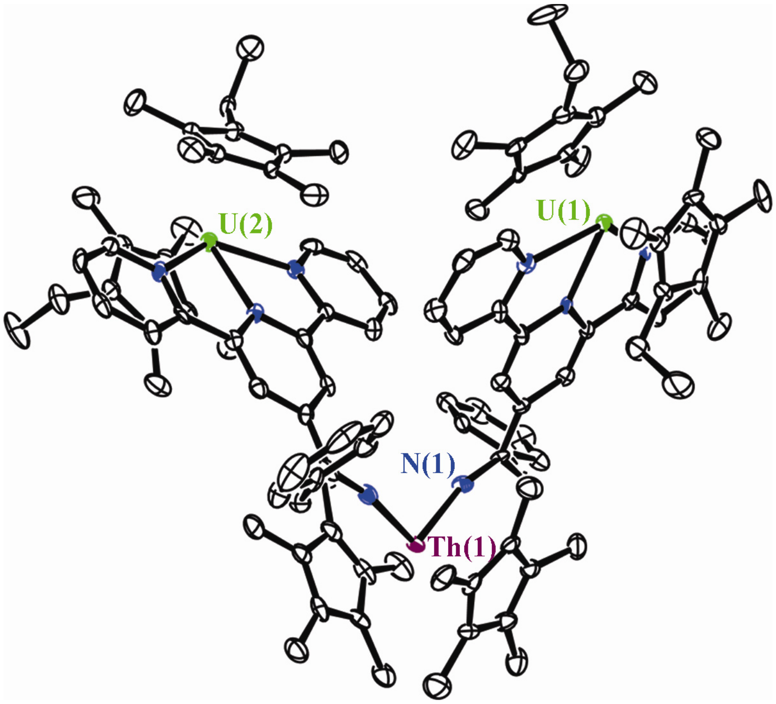
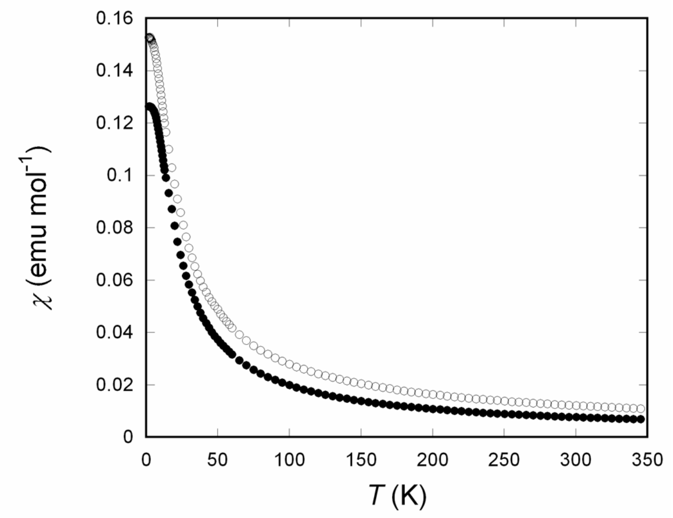


Figure S3. Thermal Ellipsoid Plot of $(C_5Me_5)_2$Th[-N=C(Bz)(tpy-UCp$^{\neq}{}_2$)]$_2$ (3a) with Ellipsoids Drawn at the 30% Probability Level.

Figure S4. Magnetic Susceptibility and Magnetization Data for 3a (●) and 3b (○).



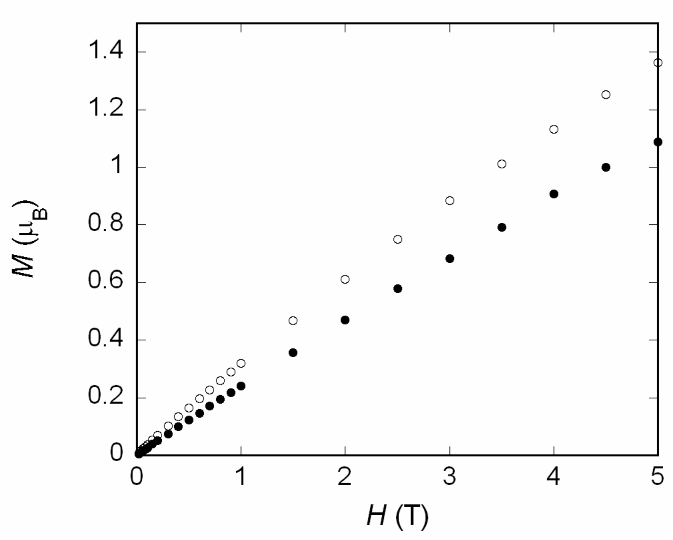


Figure S5. Room temperature electronic absorption spectra for 3a, 3b, 4 and $(C_5Me_5)_2Yb(tpy)$. Noise in the ~6000 cm^{-1} region of the spectrum for 3a is due to incomplete solvent correction.