Pentavalent Uranium Trans-Dihalides and -Pseudohalides

Andrew J. Lewis,[†] Eiko Nakamaru-Ogiso,[‡] James M. Kikkawa,[§] Patrick J. Carroll,[†] Eric J. Schelter*[,†]

[†] *P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104*

[‡] *Department of Biochemistry and Biophysics, Perelman School of Medicine, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

[§] *Department of Physics & Astronomy, University of Pennsylvania, Philadelphia, PA 19104*

E-mail: schelter@sas.upenn.edu

Electronic Supplementary Information

Experimental Procedures

General Methods. All reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H-NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer. EPR spectra were collected with a Bruker Elexsys 500 spectrometer at X-band frequency (9.4 GHz), with the temperature set at 5 K using an Oxford Instrument ESR900 helium flow cryostat. UV-Vis-NIR data were collected on a Cary 5000 spectrometer in toluene in 1 mm path length air-free quartz cuvettes between 275 and 2500 nm, background corrected with pure toluene to eliminate vibrational overtones in the NIR region.

Materials. Tetrahydrofuran, Et_2O, $CHCl_2$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes and pentane), or two columns of neutral alumina (for THF, Et_2O and CH_2Cl_2). Hexamethyldisiloxane [$(Me_3Si)_2O$] was dried over KH for one day, and then filtered through a bed of alumina. All solvents were stored over 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. The complexes used as starting materials for this work: $U[N(SiMe_3)_2]_3$ and $U[N(SiMe_3)_2]_3Cl$ (**4**) were prepared following the published procedures.[1] NaN_3, and NaSCN were dried under vacuum at 150 °C overnight. *Caution!* NaN_3

forms shock sensitive solids when combined with metals and toxic and volatile HN_3 on exposure to strong acids. Care should be taken in the handling and disposal of NaN_3. [TEMPO][BF_4] was prepared according to the literature procedure.[2]

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,[3] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[4] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[5] or SADABS.[6] The structures were solved by direct methods (SHELXS-97).[7] Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[7] All reflections were used during refinements. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Electrochemistry. Voltammetry experiments (CV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an N_2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were ~3 mM in analyte and 100 mM in [^{n}Bu$_4$N][PF_6] in 2 mL of CH_2Cl_2. All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 50–1000 mV/s were performed to determine electrochemical reversibility.

Magnetism. Magnetic data were collected using a Quantum Design Multi-Property Measurement System (MPMS-7) with a Reciprocating Sample Option at 2 T from 2–300 K and at 2 K from 0–7 T. Quartz tubes (3 mm OD, 2 mm ID), quartz rods, and quartz wool were dried at 250 °C prior to use. The sample tubes were loaded with finely ground crystalline sample and packed on both sides with quartz wool in the N_2 atmosphere drybox. Quartz wool ‘slugs’ were packed into separate small lengths of quartz ‘loading tubes’ prior to drying to facilitate direct transfer of the slugs into the quartz tube sample holder before and after loading the sample. The quartz wool slugs were loaded into the sample tube using a quartz ‘tamping’ rod. The sample was loaded through a glass Pasteur pipette that acted as a funnel. The samples and wool were massed to the nearest 0.1 mg with a calibrated and leveled Mettler-Toledo AL-204 analytical balance. Valves with Teflon stopcocks were attached to each end of the tube and the sample was removed from the glovebox. The samples were flame-sealed under dynamic vacuum on a Schlenk line. A short length of heat-shrink tubing was fitted to one end of the quartz tube and affixed to the tube by treatment with a heat gun. The open end of the heat shrink tubing was fitted to the end of the MPMS plastic sample transport, *without* heat shrinking, by fitting a ~1 cm length of drinking straw snugly over the tubing/transport assembly. Corrections for the intrinsic diamagnetism of the samples were made using Pascal’s constants.[8] Data were collected on two independently prepared samples to ensure reproducibility.

Synthetic Details and Characterization.

Synthesis of $U^{V}F_2[N(SiMe_3)_2]_3$ (1).

From $U^{III}[N(SiMe_3)_2]_3$ and $[Ph_3C][PF_6]$. A solution of $U[N(SiMe_3)_2]_3$ (250 mg, 0.35 mmol) in 10 mL of hexanes was added to a vial containing $[Ph_3C][PF_6]$ (270 mg, 0.70 mmol, 2.00 equiv). The resulting slurry turned from dark purple to dark red over about 20 minutes of stirring. After stirring for 5 h, the dark red solution was filtered through Celite packed on a coarse fritted filter and volatiles were removed under reduced pressure. The resulting residue was dissolved in $(Me_3Si)_2O$, filtered through Celite, and volatiles were removed under reduced pressure. Pentane (~10 mL) was added and this solution was stored at –21 °C overnight, which resulted in precipitation of residual Gomberg's dimer [4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene]. Filtration of this solution through Celite and removal of volatiles under reduced pressure produced **1** as a dark red solid. Yield: 187 mg, 0.25 mmol, 71%.

From $U^{III}[N(SiMe_3)_2]_3$ and AgF. A solution of $U[N(SiMe_3)_2]_3$ (100 mg, 0.14 mmol) in 5 mL of hexanes was added to a vial containing AgF (56 mg, 0.44 mmol, 3.14 equiv) in 3 mL of hexane. After stirring 32 h, the resulting dark red solution was filtered through Celite and volatiles were removed under reduced pressure. The resulting residue was dissolved in $(Me_3Si)_2O$, filtered, and concentrated under reduced pressure, yielding **1** as a dark red crystalline solid. Yield: 71 mg, 0.09 mmol, 68%.

From $U^{III}[N(SiMe_3)_2]_3$ and $[TEMPO][BF_4]$. A solution of $U[N(SiMe_3)_2]_3$ (140 mg, 0.19 mmol) in 5 mL of hexanes was added to a vial containing $[TEMPO][BF_4]$ (95 mg 0.39 mmol, 2.05 equiv). The resulting slurry rapidly turned dark red. After stirring 3 h, the mixture was filtered through Celite suspended in a glass pipette, and volatiles were removed under reduced pressure while heating to 50 ^{o}C to ensure removal of TEMPO. The resulting dark red residue was dissolved in $(Me_3Si)_2O$, filtered, and volatiles were removed under reduced pressure, yielding **1** as a dark red crystalline solid. Yield: 96 mg, 0.13 mmol, 65%. ^{1}H NMR (benzene-d_6): δ –1.53 (54H). IR (KBr): 2951 (w), 2899 (w), 1249 (s), 934 (w), 873 (s), 844 (s), 775 (m), 654 (s, $\nu_{U–N}$), 621 (s, $\nu_{U–N}$), 511 (m, $\nu_{U–F}$ asymm. stretch) (cm^{-1}). Elemental analysis found (calculated) for $C_{18}H_{54}F_2N_3Si_6U$: C, 28.97 (28.55); H, 7.52 (7.19); N, 5.22 (5.55).

Synthesis of $U^{V}Cl_2[N(SiMe_3)_2]_3$ (2).

From $U^{III}[N(SiMe_3)_2]_3$ and WCl_6. To a stirring solution of $U[N(SiMe_3)_2]_3$ (30 mg, 0.04 mmol) in 4 mL of hexanes, WCl_6 (16 mg, 0.04 mmol, 1.00 equiv) was added, resulting in rapid color change to dark red-brown with a grey-black solid suspended. After stirring this slurry for 30 minutes, the solution was filtered through a Celite-packed coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The black residue was dissolved in hexanes, filtered again through Celite and the volatiles were removed under reduced pressure. Recrystallization from minimal hexanes at –21 °C produced **2** as a black crystalline solid. Yield: 18 mg, 0.02 mmol, 54%. No $UCl[N(SiMe_3)_2]_3$ was observed in the ^{1}H NMR of an aliquot of this reaction despite the use of 1 equiv WCl_6.

From $U^{III}[N(SiMe_3)_2]_3$ and $CuCl_2$. A solution of $U[N(SiMe_3)_2]_3$ (100 mg, 0.14 mmol) in 5 mL of toluene was added to a vial containing $CuCl_2$ (75 mg, 0.56 mmol, 4.00 equiv), resulting in rapid color change to dark red-brown. After stirring this slurry for 3 h, 2 mL of THF was added and the solution was filtered through a Celite-packed coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The black residue was dissolved in $(SiMe_3)_2O$, filtered again through Celite and volatiles were removed under reduced pressure.

Recrystallization from minimal hexanes at –21 °C produced **2** as a black crystalline solid. Yield: 61 mg, 0.08 mmol, 55%.

From $U^{IV}Cl[N(SiMe_3)_2]_3$ and $CuCl_2$. A solution of $UCl[N(SiMe_3)_2]_3$ (**2**) (1.21 g, 1.59 mmol) in 15 mL of THF was added to a vial containing $CuCl_2$ (225 mg, 1.67 mmol, 1.10 equiv), resulting in a rapid color change to dark red-brown. After stirring this slurry for 5 h, the solution was filtered through Celite on a coarse porosity frit and the volatiles were removed under reduced pressure. The black residue was dissolved in $(SiMe_3)_2O$, again filtered through a Celite-packed coarse porosity fritted filter, and the volatiles were removed under reduced pressure. Recrystallization from minimal hexanes at –21 °C produced **2** as a black crystalline solid. Yield 0.94 g, 1.19 mmol, 74%. ^1H NMR (benzene-d_6, RT): δ 0.84 (18H), –1.59 (18H), –4.01 (18H); (benzene-d_6, 32 °C): δ –1.11 (54H). IR (KBr, cm^{-1}): 2954 (w), 1403 (w), 1251 (s), 843 (s), 774 (m), 648 (s, $\nu_{U–N}$), 624 (s, $\nu_{U–N}$). Elemental analysis found (calculated) for $C_{18}H_{54}Cl_2N_3Si_6U$: C, 27.57 (27.36); H, 6.82 (6.89); N, 5.13 (5.32).

Synthesis of $U^{V}Br_2[N(SiMe_3)_2]_3$ (3). A solution of $U[N(SiMe_3)_2]_3$ (250 mg, 0.35 mmol) in 10 mL of toluene was added to a vial containing $CuBr_2$ (311 mg, 1.39 mmol, 3.97 equiv). The resulting slurry was stirred for 17 h. The dark red solution was filtered through Celite on a coarse frit and volatiles were removed under reduced pressure. The black residue was dissolved in $(Me_3Si)_2O$, filtered through Celite, and concentrated under reduced pressure, yielding **3** as a black crystalline solid. Yield: 251 mg, 0.29 mmol, 82%. ^1H NMR (benzene-d_6): δ 1.70 (18H), –1.01 (18H), –4.14 (18H). IR (KBr): 2956 (w), 1251 (s), 844 (s), 773 (m), 646 (s, ν_{U-N}), 623 (s, ν_{U-N}) (cm^{-1}). Elemental analysis found (calculated) for $C_{18}H_{54}Br_2N_3Si_6U$: C, 24.80 (24.60); H, 6.12 (6.19); N, 4.67 (4.78).

Synthesis of $U^{V}FCl[N(SiMe_3)_2]_3$ (5). To a vial containing CuF_2 (100 mg, 0.98 mmol, 4.90 equiv) stirring in 3 mL THF, **4** (150 mg, 0.20 mmol) dissolved in 5 mL THF was added. The mixture was heated at 50 °C for 3 h with stirring, resulting in a color change to dark red. Removal of volatiles under reduced pressure, dissolution in hexanes, filtration through Celite, and concentration, followed by storage at –21 °C produced **5** as a dark a black crystalline solid. Yield 74 mg, 0.10 mmol, 49%. ^1H NMR (benzene-d_6): δ –1.40 (27H), –1.83 (27H). IR (KBr): 2952 (w), 2900 (w), 1384 (m), 1250 (s), 906 (w), 847 (s), 775 (m), 650 (s, $\nu_{U\text{-}N}$), 623 (s, $\nu_{U\text{-}N}$), 495 (m, $\nu_{U\text{-}F}$ asymm. stretch) (cm^{-1}). Elemental analysis found (calculated) for $C_{18}H_{54}ClFN_3Si_6U$: C, 28.32 (27.95); H, 7.05 (7.04); N, 5.39 (5.43).

Synthesis of $U^{V}(N_3)_2[N(SiMe_3)_2]_3$ (6). To a vial containing NaN_3 (10 mg, 0.154 mmol) stirring in 2 mL THF, **2** (60 mg, 0.08 mmol) dissolved in 5 mL THF was added. This mixture was stirred for 1.5 h, over which time no color change was observed. Filtration through Celite on a coarse porosity fritted filter, removal of the volatiles under reduced pressure, dissolution in pentane, filtration through Celite, and further removal of volatiles under reduced pressure yielded **6** as a dark red solid. Yield 55 mg, 0.07 mmol, 90%. Characterization data matched those previously reported.[9] Additional characterization: IR (KBr, cm^{-1}): 2954 (w), 2079 (s, ν_{N3}-asymm. stretch), 1359 (s, ν_{N3}-symm. stretch), 1251 (s), 844 (s), 773 (s), 650 (s, $\nu_{U\text{–}N(amide)}$), 622 (s, $\nu_{U\text{–}N(amide)}$) (cm^{-1}).

Synthesis of $U^{V}(NCS)_2[N(SiMe_3)_2]_3$ (7). To a vial containing **2** (150 mg, 0.19 mmol) dissolved in 3 mL THF, NaSCN (77 mg, 0.95 mmol, 5.00 equiv) was added as a solid. After stirring for ~30 min, the solution had become completely pale tan. To this mixture, $CuBr_2$ (250 mg, 1.12

mmol) was added as a solid, inducing a color change to dark red-brown and then dark green. After stirring for 3 h, the volatiles were removed under reduced pressure, and the residue was extracted with hexanes. Filtration through Celite packed on a coarse porosity fritted filter produced a dark red filtrate, which was concentrated and stored at –21 °C, producing **7** as opaque red plates collected in two crops. Yield 101 mg, 0.12 mmol, 64%. ^{1}H NMR (benzene-d_6): δ –1.47 (54H). IR (KBr, cm^{-1}): 2955 (w), 1994 (s, $\nu_{N=C}$ stretch), 1403 (w), 1253 (s), 841 (s), 775 (s), 683 (w), 647 (s, $\nu_{U-N(amide)}$), 626 (s, $\nu_{U-N(amide)}$) (cm^{-1}). The $\nu_{C=S}$ stretch was not located, likely due to overlap with silylamide vibrations. Elemental analysis found (calculated) for $C_{20}H_{54}N_5S_2Si_6U$: C, 28.94 (28.76); H, 6.42 (6.52); N, 8.64 (8.38).

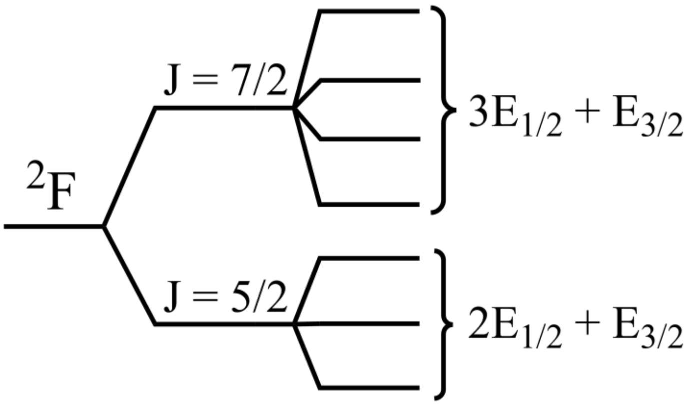

Figure S1. Splitting of the ^2F term due to spin-orbit coupling and crystal field splitting using a D_3' double group treatment (not to scale). Four absorption bands are expected in the NIR region of the spectrum based on transitions from the lowest Stark level of the J = 5/2 manifold to the four Stark levels of the J = 7/2 manifold.

EPR Data

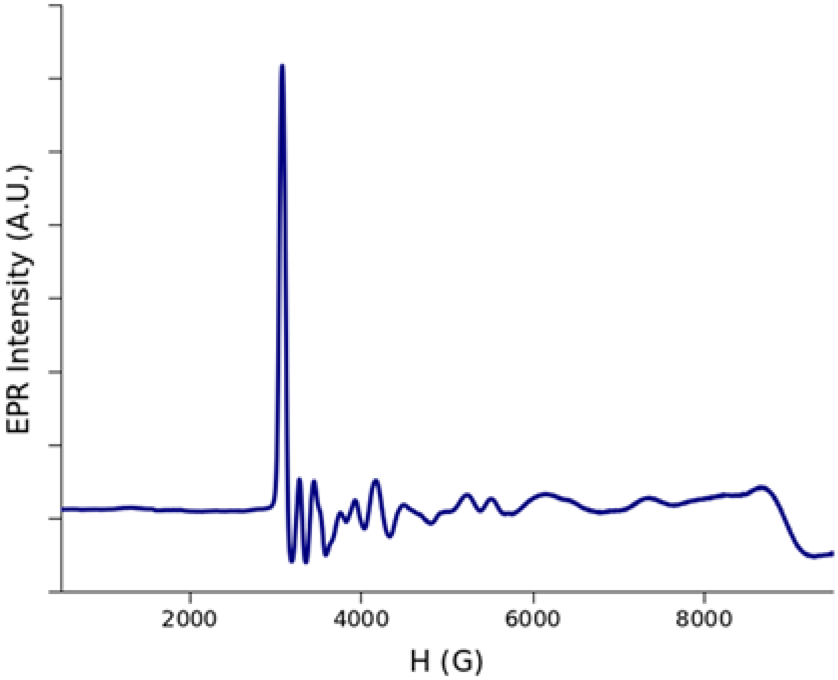

Figure S2. EPR spectrum of **2** as a microcrystalline powder. Parameters: X–band, power = 1.0 mW, T = 5 K, modulation frequency = 100 kHz, modulation amplitude = 20 G.

Magnetism Data

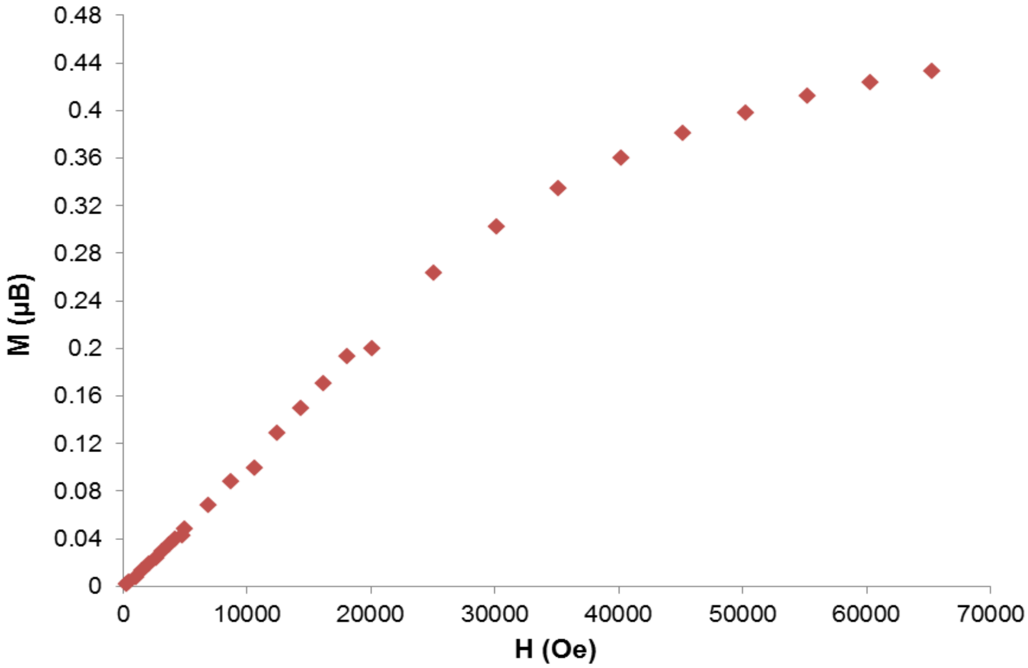

Figure S3. Field dependent magnetic data for **2** collected at T = 2 K.

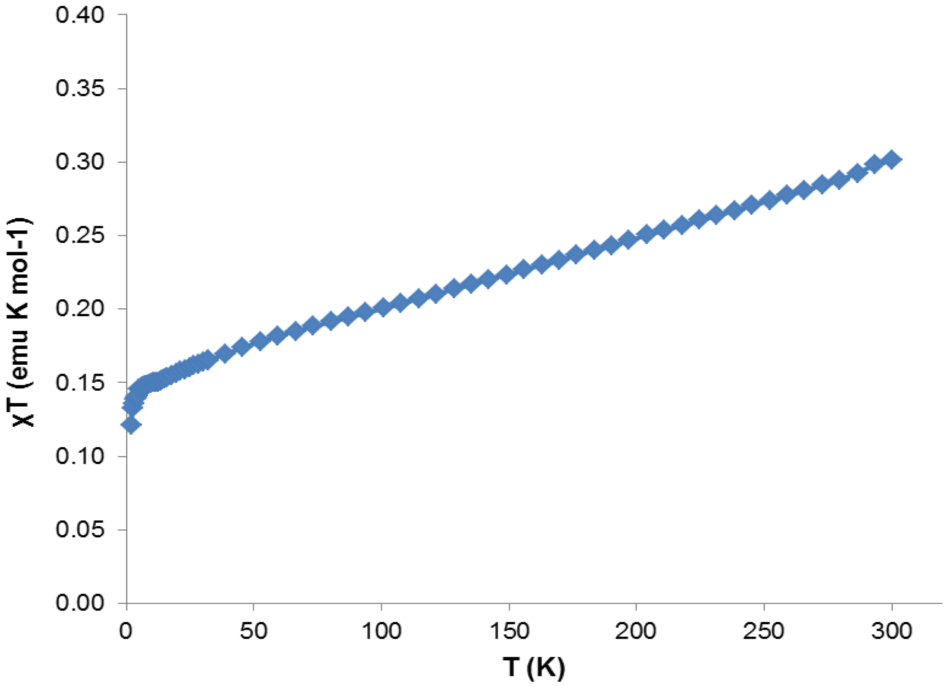

Figure S4. Temperature dependent magnetic data for **2** collected at H = 2 T.

Electrochemical Data

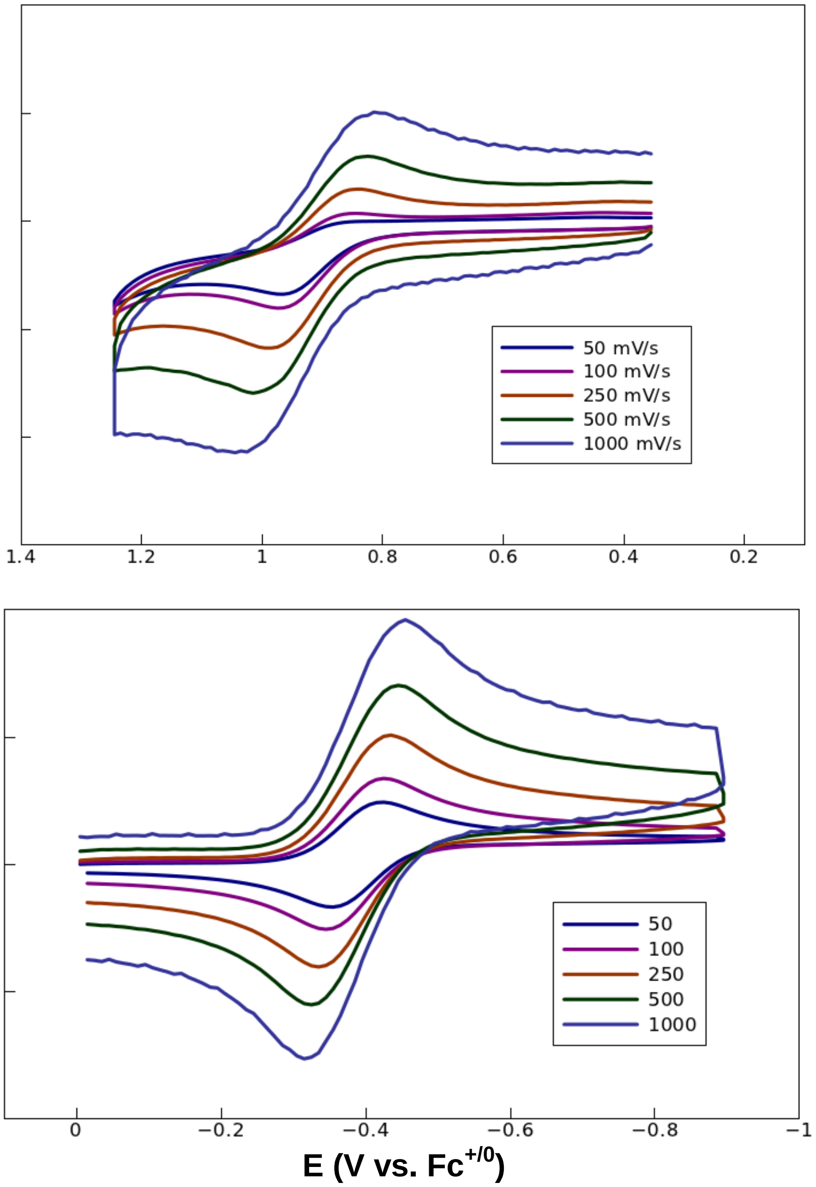

Figure S5. Scan-rate dependence on U(VI/V) (top) and U(V/IV) (bottom) redox couples in the cyclic voltammogram of **2**.

Computational Details

Gaussian 09 Rev. A.02 was used in electronic structure calculations.[10] The B3LYP hybrid DFT method was employed, with a 60-electron small core pseudopotential on uranium with published segmented natural orbital basis set incorporating quasi-relativistic effects,[11] and the 6-31G* basis set on all other atoms. Geometry optimization on **2** was carried out starting from the coordinates of the crystal structure. No restraints were imposed other than spin (doublet). While the molecule exhibits approximate D_3 symmetry, a lower energy C_1 configuration was obtained. The frequency calculation indicated that the geometry was the minimum (no imaginary frequencies), and was in close agreement with the observed IR spectrum (Figure S10). Calculated metal-ligand bond lengths were within 0.05 Å of the crystal structure. Molecular orbitals were rendered with the program Chemcraft v1.6,[12] at an isovalue of 0.03. Mayer bond orders and atomic orbital contributions to individual molecular oribitals were calculated with the AOMix program[13] through fragment molecular orbital analysis, with the following fragments: 1 - U, 2 - Cl_2, 3 $[N(SiMe_3)_2]_3$.

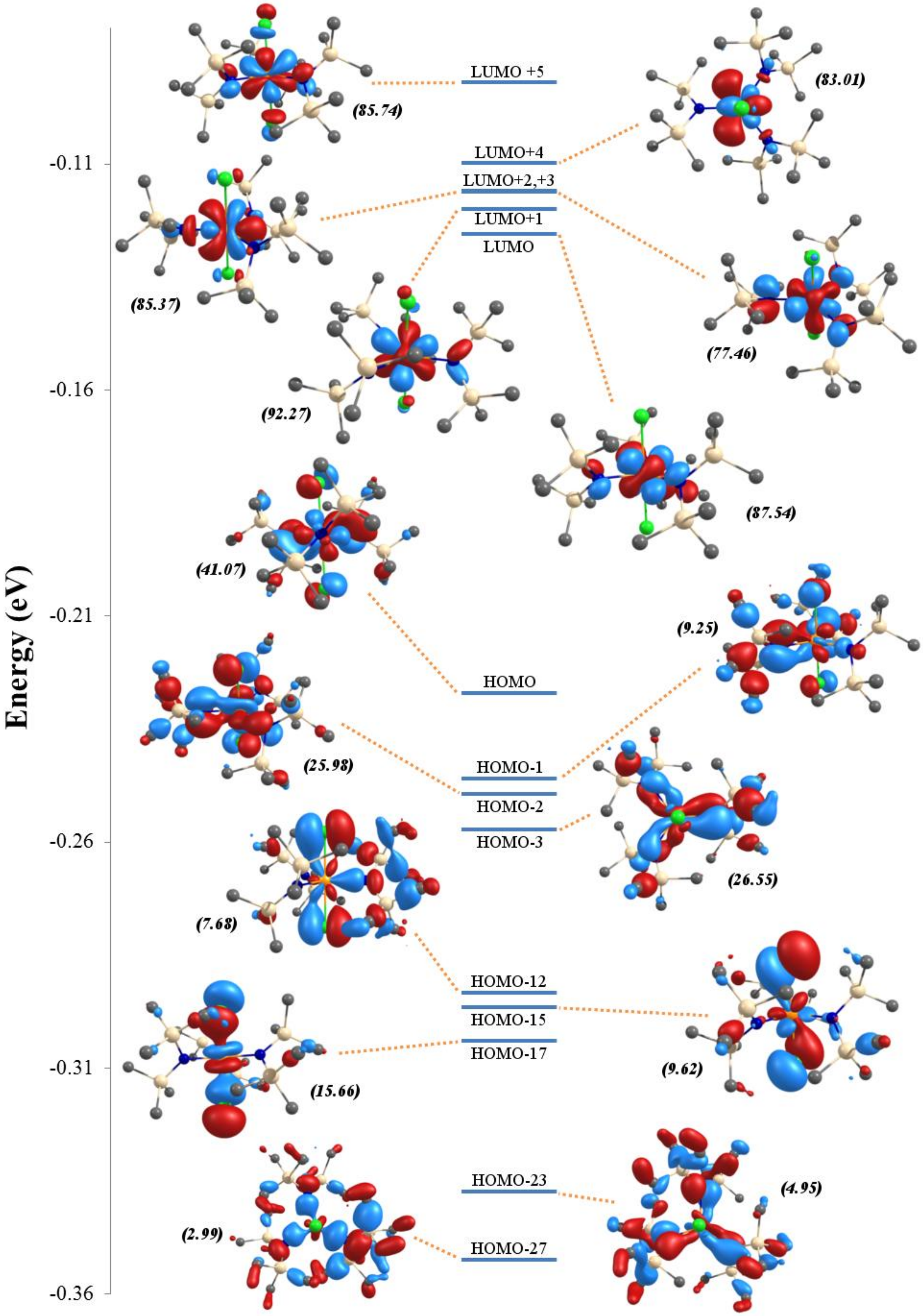

Figure S6. Calculated MO diagram for **2** showing orbitals of primarily uranium f-character. Percent uranium f-character is indicated in parentheses next to each MO.

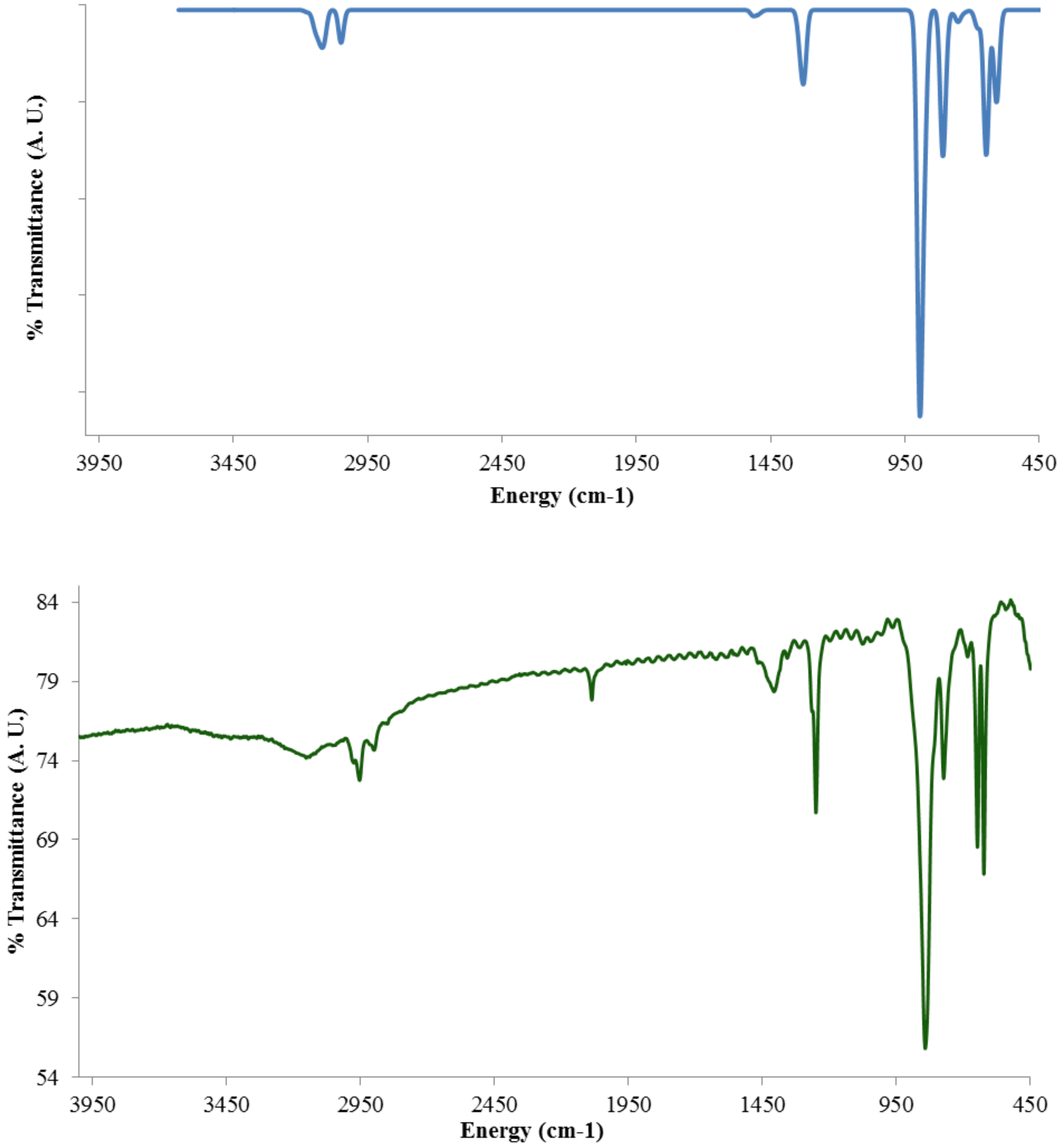

Figure S7. Comparison of calculated (top) and measured (bottom) IR spectrum of **2**. Slight broadening was applied to the predicted lines to better simulate the observed spectrum.

Table S1. Comparison of calculated and structurally characterized bond distances (Å) and angles (°) in **2**.

	Structure (X-ray)	Calculated (DFT)	Δ
U(1)–N(1)	2.1614(16)	2.1954	
U(1)–N(2)	2.1663(15)	2.1956	
U(1)–N(3)	2.1687(16)	2.1862	
U–N (av.)	2.166(2)	2.1924	0.026
U(1)–Cl(1)	2.5704(5)	2.6266	
U(1)–Cl(2)	2.5801(5)	2.6267	
U–Cl (av.)	2.5753(5)	2.6267	0.051
N(1)–U(1)–N(2)	125.52(6)	125.95	
N(1)–U(1)–N(3)	118.71(6)	126.05	
N(2)–U(1)–N(3)	115.74(6)	108.00	
N–U–N (av.)	119.99(7)	120.00	0.01
Cl(1)–U(1)–Cl(2)	179.529(17)	179.42	0.11

Table S2. Coordinates of optimized structure of **2**.

U	0.00139100	-0.13807500	-0.00017200
Cl	0.05661900	-0.15637300	2.62578500
Cl	-0.05337200	-0.14633200	-2.62627500
N	1.77352700	1.15720400	0.03665000
N	0.00556600	-2.32422100	-0.00444700
N	-1.77805800	1.14766400	-0.03220700
Si	-2.07002600	2.53412500	-1.15392100
Si	2.05770500	2.54127200	1.16333000
Si	-1.11246000	-3.28054300	-1.06249500
Si	-3.14357200	0.74911700	1.07840900
Si	1.12766000	-3.27949500	1.05025800
Si	3.14101200	0.77025300	-1.07565700
C	4.82183500	0.83824400	-0.19223300
H	5.09125700	1.82126200	0.20371400
H	5.59323400	0.55654900	-0.92177600
H	4.87153600	0.11673700	0.63136000
C	-3.19863700	1.90135600	2.57630100
H	-2.28763900	1.80005900	3.17518500
H	-4.04675800	1.61858400	3.21434600
H	-3.31871800	2.95512900	2.31011900
C	3.18890700	1.92821000	-2.56930500
H	2.27914100	1.82265200	-3.16931500
H	4.03963800	1.65419700	-3.20768800
H	3.30110400	2.98176300	-2.29878900
C	-2.64666200	-2.28573400	-1.56758300
H	-3.36311900	-2.19344500	-0.74595000
H	-3.13966800	-2.86001600	-2.36410200
H	-2.44559400	-1.29283200	-1.97531500
C	3.09102800	1.98715100	2.65078700
H	2.58244200	1.18980000	3.20194100
H	3.21840500	2.83578300	3.33581600
H	4.08816000	1.63210500	2.37507900
C	-2.97921300	3.96656000	-0.29428100
H	-3.97860700	3.71239800	0.07108000
H	-3.09775200	4.77639600	-1.02638000
H	-2.40757600	4.37123200	0.54858500
C	-4.82432700	0.81043700	0.19437500
H	-5.09861500	1.79305200	-0.19918300
H	-5.59472700	0.52272900	0.92261900
H	-4.86964000	0.09088800	-0.63118200
C	-0.22144200	-3.86128500	-2.62413200
H	0.19701300	-3.01174900	-3.17269400
H	-0.93607200	-4.36785000	-3.28571800
H	0.58814000	-4.56557800	-2.40977800
C	-1.83032500	-4.78169000	-0.14787500
H	-1.09450400	-5.53599500	0.14485400
H	-2.54698600	-5.26995600	-0.82183700
H	-2.38274000	-4.48077300	0.74943600
C	0.47426600	3.31036400	1.85918100
H	-0.16228900	3.76762400	1.09750800

H	0.78943300	4.11124500	2.54238200
H	-0.12714400	2.60455000	2.43427500
C	1.85120600	-4.77489700	0.13066700
H	1.11839100	-5.53158100	-0.16347600
H	2.57064600	-5.26195000	0.80254400
H	2.40140700	-4.46909000	-0.76635200
C	3.03789500	-1.00912200	-1.76376600
H	2.25167600	-1.65490400	-1.36347800
H	3.99338100	-1.51412700	-1.57343200
H	2.87835600	-0.97233100	-2.84599900
C	2.65819200	-2.28007000	1.55757900
H	3.37397800	-2.18324200	0.73589800
H	3.15358700	-2.85441700	2.35257000
H	2.45369100	-1.28889800	1.96783900
C	-3.03069000	-1.03164400	1.76126700
H	-2.24240000	-1.67266800	1.35746900
H	-3.98429300	-1.54044400	1.57145800
H	-2.86913600	-0.99720100	2.84326000
C	0.23968400	-3.86902300	2.61030000
H	-0.18105300	-3.02303800	3.16258000
H	0.95643900	-4.37594400	3.26931200
H	-0.56784700	-4.57503300	2.39380000
C	-3.09901300	1.97941600	-2.64418400
H	-2.58447300	1.18843900	-3.19896100
H	-3.23253900	2.83031200	-3.32522000
H	-4.09350900	1.61566600	-2.37033800
C	-0.49110100	3.31587000	-1.84585600
H	0.14277800	3.77314600	-1.08197600
H	-0.81105100	4.11822200	-2.52508700
H	0.11450100	2.61650100	-2.42442600
C	2.95720900	3.98283500	0.30881600
H	3.95896800	3.73737500	-0.05598700
H	3.06870800	4.79123200	1.04360700
H	2.38363800	4.38586600	-0.53350700

References

[1] (a) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248. (b) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221.

[2] Merbouh, N.; Bobbitt, J. M.; Brückner, C. *Org. Prep. Proced. Int.* **2004**, *36*, 1.

[3] Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[4] Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[5] Sheldrick, G.M. (2008) TWINABS. University of Gottingen, Germany.

[6] Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[7] Sheldrick, G.M. (2008) Acta Cryst. A64,112–122.

[8] Bain, G. A.; Berry, J. F. *J. Chem. Ed.* **2008**, *85*, 532.

[9] Fortier, S.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2010**, *39*, 352.

[10] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[11] (a) Institute for Theoretical Chemistry, University of Cologne, http://www.tc.uni-koeln.de/PP/clickpse.en.html (b) W. Kuechle, M. Dolg, H. Stoll, H. Preuss J. Chem. Phys. 100, 7535 (1994). (c) X. Cao, M. Dolg, H. Stoll, J. Chem. Phys. 118, 487 (2003) (c) X. Cao, M. Dolg, J. Molec. Struct. (Theochem) 673, 203 (2004)

[12] http://www.chemcraftprog.com/

[13] (a) S. I. Gorelsky, *AOMix: Program for Molecular Orbital Analysis*, http://www.sg-chem.net/, University of Ottawa, version 6.5, 2011. (b) S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187–196.