Structure and magnetism of a tetrahedral uranium(III) beta-diketiminate complex

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We describe the functionalisation of the previously reported uranium(III) β-diketiminate complex (BDI)UI$_2$(THF)$_2$ (**1**) with one and two equivalents of a sterically demanding 2,6-di*iso*propylphenolate ligand (ODipp) leading to the formation of two heteroleptic complexes: [(BDI)UI(ODipp)]$_2$ (**2**) and (BDI)U(ODipp)$_2$ (**3**). The latter is a rare example of a tetrahedral uranium(III) complex, and it shows single-molecule magnet behaviour.

Introduction

In recent years, the non-aqueous coordination chemistry of actinides has expanded rapidly.[1] Despite this surge of interest, the supporting ligands used in this field remain limited, and the chemistry is dominated by cyclopentadienyl ligands.[2] Because of this, one focus of current research is to explore other ligand frameworks and how they affect the reactivity and properties (e.g. the magnetism) of the actinide metals.[1] This has led to the development of unique and interesting complexes based on alkyl and aryl ligands,[3] (tripodal) aryloxides,[4] tren-derived ligands,[5] amidinates,[6] amidates,[7] dithiocarboxylates,[8] carbenes,[9] N-heterocyclic carbenes (NHCs),[10] and macrocyclic ligands.[11]

We recently reported the synthesis of actinide complexes with the small-cored macrocyclic tetramethyltetraazaannulene (TMTAA) ligand,[12] which can formally be seen as two β-diketiminate (BDI) ligands tethered together into a macrocyclic ring. By comparison, monomeric BDI ligands, one of the most frequently used supporting ligands in transition metal chemistry,[13] have been the subject of few studies with the actinides (Fig. 1).[14] This is surprising, given that the steric profile of these ligands has been shown to stabilize a variety of low-coordinate or low-valent complexes with metals across the periodic table.[13]

In 2013, Liddle and coworkers reported the synthesis of (BDI)UI$_2$(THF)$_2$ (**1**), a potential starting material for the development of functional low-valent uranium(III) complexes.[14l] However, during further studies of this system, the authors showed that functionalization of uranium(III) BDI complexes can be challenging due to unexpected side reactions. For example, reaction of KN(SiMe$_3$)$_2$ with **1** led to deprotonation of a methyl group on the BDI backbone, resulting in the formation of a dianionic diamide ligand coordinated to a uranium(IV) center.[14l] This backbone methyl deprotonation is a common side reaction for BDI frameworks.[15]

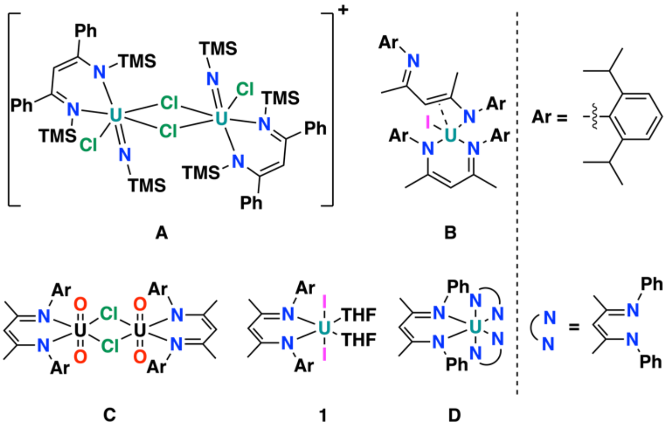
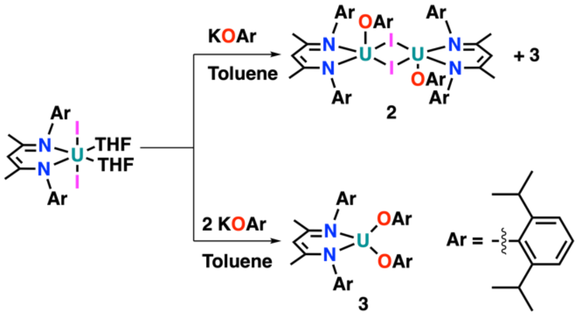


Fig. 1: Selected examples of uranium β-diketiminate (BDI) complexes.

We observed similar difficulties with the functionalization of heteroleptic TMTAA-actinide complexes that could be circumvented by the use of aryloxide ligands.[12a] We therefore hypothesized that oxygen-based donor ligands could offer a new entrance to BDI based chemistry, leading to new synthetic precursors and compounds with potentially interesting magnetic properties.

Results and discussion

Synthesis, Characterization and X-Ray Crystal Structures



Scheme 1: Synthesis of the uranium complexes **2** and **3**.

The reaction between (BDI)UI$_2$(THF)$_2$ (**1**) and one equivalent of the aryloxide ligand salt KODipp resulted in the formation of a mixture of two complexes: the desired mono-aryloxide **2** and what we believed to be the bis-aryloxide complex **3**. As **2** and the impurity showed similar solubility and crystallization properties, the purification process for **2** required at least two crystallization steps using cold hexane, resulting in a low yield of only 28% analytically pure **2**. Use of THF as a solvent resulted

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in similar yields of pure complex **2** after recrystallization. The magnetic moment of **2** was found to be 2.26 μ_B per uranium center in benzene-d_6 at room temperature by the Evans method; this value is at the low end of the range reported for uranium(III) complexes.[16]

X-ray quality single crystals of **2** were obtained from a −40 °C hexane solution. The complex crystallizes on an inversion center in the triclinic space group $P\bar{1}$ with 0.5 hexane molecules in the lattice per formula unit. Complex **2** forms a bis(μ-iodo) dimer in the solid-state (Figure 2) with a uranium-uranium distance of 5.087(1) Å, ruling out any direct interaction between the two atoms. This distance is within the range of previously isolated iodide-bridged dinuclear uranium complexes.[5z, 17] The uranium–ODipp distance U1–O30 was found to be 2.133(6) Å and is comparable to previously reported aryloxide complexes of uranium.[4, 12] Interestingly, in the solid state, the uranium ion in **2** is asymmetrically bound to the two BDI nitrogen atoms, displaying U1–N1 and U1–N2 distances of 2.380(8) Å and 2.450(7) Å. The asymmetric bonding of the uranium ion appears to be related to the electronic structure of the BDI backbone, which exhibits slightly different C1–C2 and C2–C3 distances (1.401(13) and 1.449(13) Å, respectively), indicating partial localization of the double bond in the BDI ligand. A similar trend can also be seen in the C1–N1 (1.328(12) Å) and C3–N2 (1.289(11) Å) distances (see Table S2, ESI, for further details on structural metrics). This is in contrast to previously reported BDI and TMTAA complexes of the actinides,[14] lanthanides,[18] and transition metals,[13] which all display completely delocalized BDI backbones based on solid-state structures. In solution, according to ^{1}H NMR studies, the complex shows time-averaged C_{2v} symmetry (Figure S1) indicating symmetric bonding of the BDI ligand to the uranium center or rapid dynamic behaviour.

We next aimed to prepare **3** directly. Use of 2 equivalents of KODipp in toluene at room temperature resulted in the clean formation of **3** after stirring the reaction mixture overnight. Crystallization from hexane at −40°C gave dark green blocks in 87% isolated yield. The magnetic moment of the complex was found to be 3.02 μ_B in benzene-d_6 at room temperature by the Evans method. Although this is substantially higher than the magnetic moment observed for **2**, it is still within the range reported for uranium(III) complexes.[16] Comparison of the NMR spectra between crude complex **2** and isolated complex **3** unambiguously confirmed that complex **3** is the impurity that arises during the synthesis of complex **2**. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with no solvent molecules in the lattice. The uranium center was found to be in a distorted tetrahedral coordination environment displaying a τ_4' value of 0.85 (Fig. 2).[19] Similar to complex **2**, we found that the electronic structure of the BDI ligand in the solid state can be better described by a localized electronic structure, rather than by a delocalized one (see Table S2, ESI) The uranium–ODipp distances are also comparable to that of **2** and previously reported aryloxide complexes of uranium. The U1–O1–C30 and U1–O2–C42 bond angles were found to be 152.8(2)° and 168.2(2)°; the deviation of linearity in one of the aryloxide ligands is mostly likely caused by packing effects.

Four-coordinate uranium(III) centers are quite rare, and tetrahedral coordination has been previously shown to give rise

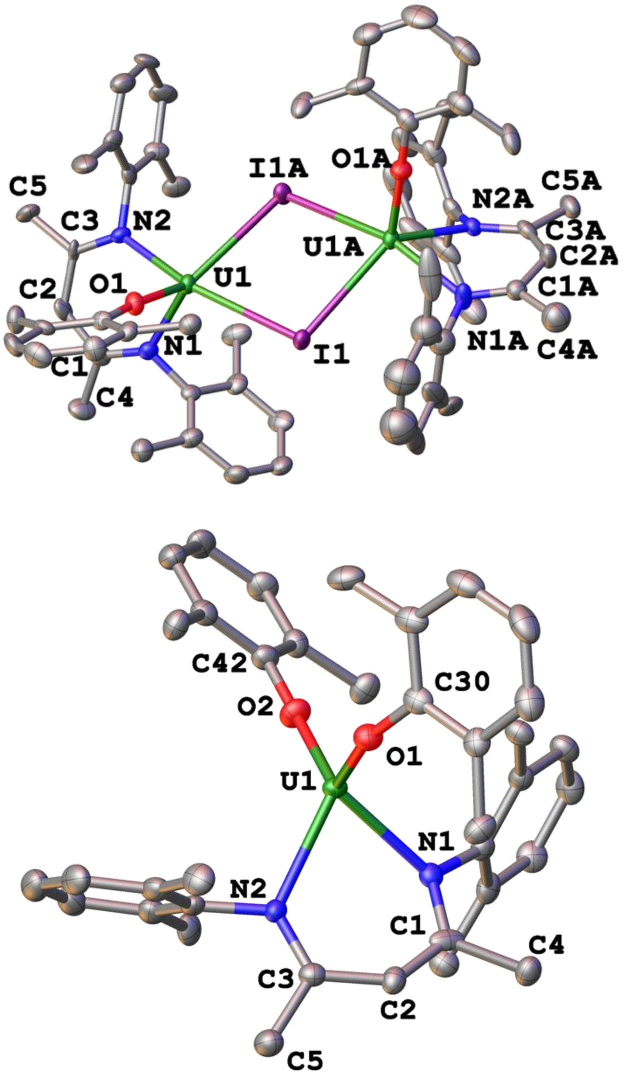

Fig. 2: X-ray crystal structures of complexes **2** (top) and **3** (bottom) with 50% probability ellipsoids Hydrogen atoms, solvent molecules, and methyl groups of the Dipp residues have been omitted for clarity.

to interesting magnetic properties for uranium(III) complexes.[20] We therefore sought to investigate the electronic structure and magnetic properties of complex **3** further through SQUID magnetometry. Variable-temperature dc magnetic susceptibility data were collected for **3** from 3 to 300 K (Fig S3) at 5 kOe and 40 kOe using a two-field correction (see Methods and Materials). The $\chi_M T$ value increases monotonically with temperature and displays a nearly linear temperature dependence above 150 K, indicative of a small temperature-independent paramagnetism (TIP) component. The room temperature $\chi_M T$ value is 1.14 emu K/mol (3.02 μ_B), consistent with the solution-state magnetic moment determined for **3** by the Evans method (3.02 μ_B). The experimental $\chi_M T$ value for **3** falls within the range reported for other uranium(III) complexes and is slightly lower than the expected value of 1.64 emu K/mol for a free uranium(III) ion ($5f^3$)[16]. For comparison, the pseudotetrahedral uranium(III) complexes $[U(OSi(O^tBu)_3)_4]^-$ and $[U(N(SiMe_3)_2)_4]^-$ possess room temperature $\chi_M T$ values of 0.77 and 1.36 emu K/mol, respectively, under an applied magnetic field of 5 kOe.[20] The lower $\chi_M T$ value for

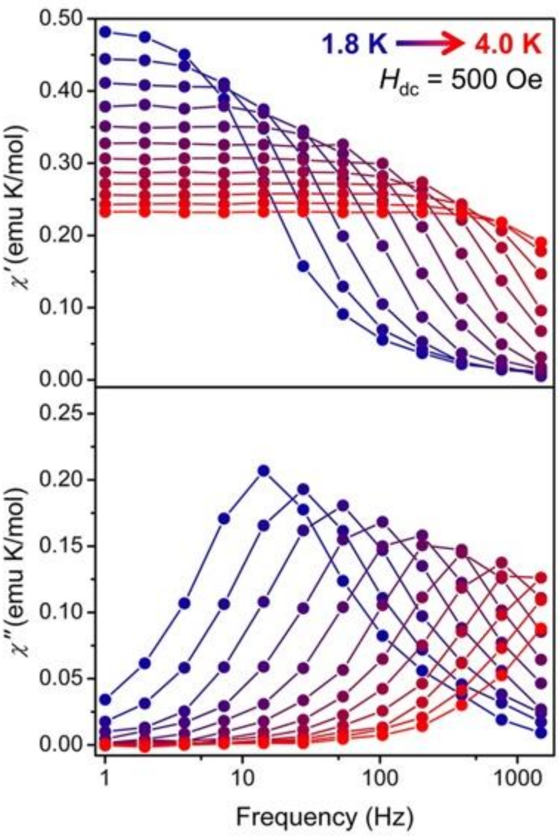

Fig. 3: In-phase (χ_M', top) and out-of-phase (χ_M'', bottom) components of the ac magnetic susceptibility for complex **3** under an applied dc field of 500 Oe at frequencies ranging from 1–1500 Hz and temperatures from 1.8–4 K (0.2 K steps). The colored lines are guides for the eye.

$[U(OSi(O^tBu)_3)_4]^-$ is the result of diminished TIP as compared to $[U(N(SiMe_3)_2)_4]^-$, which may arise from a stronger ligand field in the former complex. The stronger ligand field in $[U(OSi(O^tBu)_3)_4]^-$ is corroborated by density functional theory (DFT) calculations[20]. The room temperature $\chi_M T$ value for **3** falls between the values for $[U(OSi(O^tBu)_3)_4]^-$ and $[U(N(SiMe_3)_2)_4]^-$, which may suggest that complex **3** displays a ligand field strength that is intermediate between that of the latter two complexes.

The magnetic relaxation dynamics of **3** were probed by ac magnetic susceptibility measurements from 2 to 4 K (Fig. 3, S4). Magnetic relaxation times, τ, were extracted from a simultaneous fit of in-phase (χ_M') and out-of-phase (χ_M'') components of the susceptibility to a generalized Debye model (Fig. S5-7). Under zero applied magnetic field, two independent relaxation domains were observed: one process between 1 and 1500 Hz and a second process at higher frequencies, beyond the range of the SQUID magnetometer (Fig. S4). The low-frequency process displays small magnitude χ_M'' values, which indicates that it is a minor component of the overall magnetic relaxation dynamics in **3**. Two independent relaxation domains have been observed previously in uranium(III) complexes and may be caused by intermolecular interactions.[21] Under an applied magnetic field of 500 Oe, only one relaxation process is observed for **3**. An Arrhenius plot of inverse temperature versus the log of τ for this data is linear above 2.6 K (Fig. 4), indicative of magnetic relaxation via a thermally-activated Orbach process.[22] At lower temperatures, the temperature dependence is exponential, which suggests that quantum tunnelling of the magnetization begins to compete with Orbach relaxation.[23] Accordingly, a fit to the data was calculated using Equation 1:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/kT} + \tau_{tunnel}^{-1} \qquad (1)$$

where τ_0 is the attempt time, U_{eff} is the thermal barrier to magnetization reversal, and τ_{tunnel} is the relaxation time for quantum tunnelling. This fit affords $\tau_0 = 3.39(24) \times 10^{-7}$ s, $U_{\text{eff}} = 14.5(1)$ cm^{-1}, and $\tau_{\text{tunnel}} = 1.18(6) \times 10^{-2}$ s.[24] The thermal barrier for **3** is similar to the U_{eff} values determined for $[U(OSi(O^tBu)_3)_4]^-$ and $[U(N(SiMe_3)_2)_4]^-$: 18 and 16 cm^{-1}, respectively.[20]

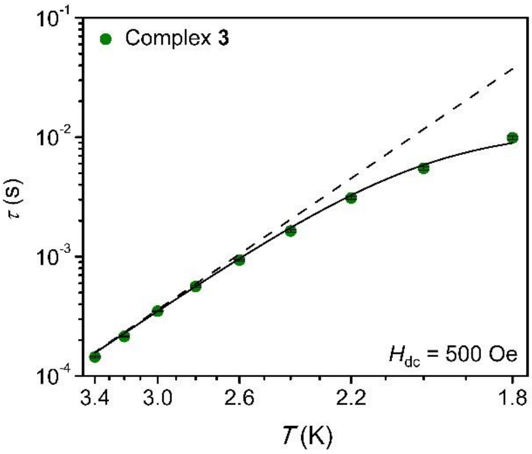

Fig. 4: Plot of magnetic relaxation time (τ, log scale) versus temperature (T, inverse scale) for data collected under an applied dc field of 500 Oe for complex **3**. The solid black line represents the fit to the data, as described in the main text, and the dashed line represents the Orbach relaxation process.

Experimental section

Methods and Materials

The reagents KODipp,[25] and $(BDI)UI_2(THF)_2$ **1**[14l] were prepared according to literature procedures. Celite was dried at 160°C for at least 3 days and then kept under high vacuum for 12 h prior to use. Celite filters were flushed with the corresponding solvent prior to use. All reactions were carried out under N_2 or argon in a Braun Glovebox or using standard Schlenk techniques in solvents degassed by sparging and dried over columns of activated alumina. C_6D_6 was dried over sodium/benzphenone, distilled and degassed by three freeze-pump-thaw cycles prior to their use. NMR spectra were recorded on Bruker AV-600, AV-500, DRX-500, AVB-400, or AV-300 spectrometers with the solvent residual peak as reference points and chemical shifts recorded in units of parts per million (ppm). Magnetic moments were determined by Evans Method[26a] using a sealed capillary of the corresponding NMR solvent as an internal standard. The moments were calculated using the following formulas: $\chi_{Compound} = \chi_{measured} - \chi_{diamagnetic}$ with $\chi_{measured} = \frac{477\Delta f}{2fc}$ (Δf = peak to peak separation in Hz, f = frequency of the spectrometer used and c = concentration of the analyte) and $\mu_{eff} = 2.827 \cdot \sqrt{\chi_{compound}T}$ Diamagnetic corrections were calculated from tabulated values.[26b] Elemental analyses were determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley.

Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Magnetic samples were prepared by adding crystalline powder of the compound (5.90 mg) to a quartz tube, which was subsequently packed with a small amount of quartz wool to hold the sample in place. The tube was then flame sealed under applied vacuum. DC magnetic susceptibility measurements were performed at temperatures ranging from 3–300 K. All data were corrected for the contribution of the quartz wool and the diamagnetic contributions from the core diamagnetism estimated using Pascal's constants.[26b] The magnetic susceptibility was calculated from the difference between the moments at the two fields to remove any saturated ferromagnetic impurity component, that is $\chi_M=(M_2-M_1)/(m_s(H_2-H_1))$, where M_x is the magnetic moment measured at each field H_1=5 kOe (0.5 T) and H_2=40 kOe (4 T), and m_s is the sample mass. AC magnetic measurements were collected between 2–300 K at zero and 500 Oe (0.01 T) in a frequency range from 1–1500 Hz. Uncertainties for magnetic relaxation times and fitting of Arrhenius plots were determined using CC Fit.[24]

X-Ray Crystallography

Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CheXray crystallographic facility. Measurements of all compounds were performed with a Bruker APEX-II area detector using Mo K_α radiation (λ = 0.71073 Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with Bruker APEX2 software (v. 2014.11). Data refinement and reduction were performed with Bruker SAINT (V8.34A). All structures were solved with SHELXT.[27a] Structures were refined using SHELXL-2014 by full matrix least-squares refining on F^2. [27b] Molecular graphics were computed using the OLEX2 software package.[28] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model. Specific details can be found in Tables S1 and S2 in the Supporting Information. CCDC 1991563 and 1991562 contain the CIF-Files for **2** and **3** respectively.

Synthetic Procedure

[(BDI)U(ODipp)I]$_2$ (2)

Complex **1** (1 eq, 0.2 mmol, 210 mg) was dissolved in toluene (10 mL) and stirred until all solids were dissolved. A suspension of KODipp (1 eq, 0.2 mmol, 44 mg) in toluene (5 mL) was added to the solution of **1** dropwise. The mixture gradually turned from dark blue to dark green, and the reaction mixture was stirred at room temperature overnight. The volatiles were then removed *in vacuo*, and the green oily residue was dissolved in hexane (15 mL) and filtered through a pad of Celite. The filtrate was concentrated to a volume of 3 mL and cooled to −40 °C to give green blocks of crude **2**. This crystallization process was repeated one more time, yielding analytically pure crystals of **2** as green blocks (28% yield, 0.056 mmol, 54 mg). Mp ca. 140 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 30.7 (s, 2H), 21.5 (s, 1H), 18.4 (s, 1H), 14.3 (s, 1H), 11.3 (s, 6H), 9.6 (s, 6H), 4.5 (s, 1H), 3.5 (s, 2H), 2.2 (s, 6H), 1.5 (s, 6H), −7.2 (s, 6H), −8.7 (s, 2H), −23.6 (s, 6H), −23.7 (s, 6H), −27.9 (s, 1H). Anal. Calcd (%) for $C_{82}H_{116}N_4O_2I_2U_2$ (**2**): C, 51.30; H, 6.09; N, 2.92. Found: C, 51.60; H, 6.00; N, 2.77. μ_{Eff} = 2.26 μB (Evans method, C_6D_6, 294 K).

(BDI)U(ODipp)$_2$ (3)

Complex **1** (1 eq, 0.2 mmol, 210 mg) was dissolved in toluene (10 mL) and stirred until was all solids were dissolved. A suspension of KODipp (2 eq, 0.2 mmol, 88 mg) in toluene (5 mL) was added to the solution of **1** dropwise. The mixture gradually turned from dark blue to dark green, and the reaction mixture was stirred at room temperature overnight. The volatiles were then removed *in vacuo*, and the green oily residue was dissolved in hexane (15 mL) and filtered through a pad of Celite. The filtrate was concentrated to a volume of 3 mL and cooled to −40 °C, yielding analytically pure crystals of **3** as green blocks (87% yield, 0.175 mmol, 177 mg). Mp ca. 155 °C (decomp.); ^{1}H NMR (600 MHz, C_6D_6, 25°C): δ 21.2 (s, 3H, broad), 20.4 (s, 6H, broad), 16.2 (s, 3H, sharp), −1.5 (s, 1Hm, sharp), −1.8 (s, 4H, sharp), −3.2 (s, 6H, broad), −3.7 (s, 3H, sharp), −6.7 (s, 29H, broad), −14.9 (s, 1H, broad), −35.3 (s, 12H, sharp), −37.9 (s, 6H, broad). Anal. Calcd.(%) for $C_{53}H_{75}N_2O_2U$ (**3**): C, 63.01; H, 7.48; N, 2.77. Found: C, 63.17; H, 7.36; N, 2.64. μ_{eff} = 3.02 μB (Evans method, C_6D_6, 294 K).

Conclusions

In conclusion, we have reported the synthesis and structural characterization of two novel uranium(III) β-diketiminate (BDI) complexes featuring either one or two sterically encumbering aryloxide ligands. Even though the dimeric complex [(BDI)U(ODipp)I]$_2$ (**2**) can be obtained in only low yields, it is a potential starting material for future reactivity investigations, particularly for preparing mixed ligand complexes. Additionally, this work shows that neutral tetrahedral uranium complexes such as (BDI)U(ODipp)$_2$ (**3**) display interesting single-molecule magnet behavior, with a thermal barrier to magnetic relaxation that is slightly smaller than U_{eff} values reported previously for anionic, tetrahedrally-coordinated uranium(III) complexes. The use of different monoanionic ligands in place of ODipp in **3** may offer a route to tune the magnetic properties of tetrahedrally-coordinated uranium(III) complexes in the future. Our findings emphasize that the BDI ligand framework, though still uncommon in f-element chemistry, holds promise for enabling intriguing structural motifs, electronic properties, and reactivity with the actinides.

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Notes and references

1 S.T. Liddle, Angew. Chem. Int. Ed. 2015, **54**, 8604.

2 (a) M.A. Boreen, D.J. Lussier, B.A. Skeel, T.D. Lohrey, F.A. Watt, D.K. Shuh, J.R. Long, S. Hohloch, J. Arnold, *Inorg. Chem.*, 2019, **58**, 16629. (b) M.A. Boreen, G. Rao, D.G. Villarreal, F.A. Watt, D. Britt, S. Hohloch, J. Arnold. *Chem. Commun.*, 2020, **56**, 4535. (c) F.S. Guo, Y.-C. Chen, M.-L. Tong, A. Mansimkkamäki, R.A. Layfield, *Angew. Chem. Int. Ed.*, 2019, **58**, 10163; (d) F.S. Guo, N. Tsoureas, G.-Z. Huang, M.-L. Tong, A. Mansikkamäki, R.A. Layfield, *Angew. Chem. Int. Ed.*, 2020, **59**, 2299. (e) M. Ephritikhine, *Organometallics*, 2013, **32**, 2464; (f) W.J. Evans, *Organometallics,* 2016, **35**, 3088. (g) B.E. Bursten. .J. Strittmatter, *Angew. Chem. Int. Ed.*, 1991, **30**, 1069. (h) O. Walter, *Chem. Eur. J.*, 2019, **25**, 2927. (i) G. Zi, *Chem. Commun.*, 2018, **54**, 7412. (j) M. Sharma and M.S. Eisen, 2008, Metallocene Organoactinide Complexes. In: T.E. Albrecht-Schmitt (eds) Organometallic and Coordination Chemistry of the Actinides. Structure and Bonding, **127**. Springer, Berlin, Heidelberg (k) M.A. Boreen, K.N. McCabe, T.D. Lohrey, F.A. Watt, L. Maron, S. Hohloch, J. Arnold *Inorg. Chem.*, 2020, **59**, DOI: 10.1021/acs.inorgchem.0c01038.

3 (a) E.R. Sigurdson and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 812. (b) L.A. Seaman, J.R. Walensky, G. Wu and T.W. Hayton, *Inorg. Chem.*, 2013, **52**, 3556. (c) S. Fortier, B.C. Melot, G. Wu and T.W. Hayton, *J. Am. Chem. Soc.*, 2009, **131**, 15512. (d) S. Fortier, J.R. Walensky G. Wu and T.W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 11732. (e) S.J. Kraft, P.E. Fanwick and S.C. Bart, *J. Am. Chem. Soc.*, 2012, **134**, 6160. (f) W.G. van der Sluys, C.J. Burns and A.P. Sattelberger, *Organometallics*, 1989, **8**, 855. (g) M.A. Boreen, B.F. Parker, T.D. Lohrey and J. Arnold, *J. Am. Chem. Soc.*, 2016, **138**, 15865.

4 (a) I. Castro-Rodriguez, H. Nakai, L.N. Zakharov, A.L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757. (b) I. Castro-Rodriguez, K. Olsen, P. Gantzel and K. Meyer, *J. Am. Chem. Soc.,* 2003, **125**, 4565. (c) S.C. Bart, C. Anthon, F.W. Heinemann, E. Bill, N.M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536. (d) I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242. (e) B. Kosog, H.S. La Pierre, F.W. Heinemann, S.T. Liddle and K. Meyer, *J. Am. Chem. Soc.*, 2012, **134**, 5284. (f) O.P. Lam and K. Meyer, *Polyhedron,* 2012, **32**, 1. (g) S.C. Bart and K. Meyer, *Structure and Bonding*, 2008, **127**, 119. (h) S.M. Franke, B.L. Tran, F.W. Heinemann, W. Hieringer, D.J. Mindiola and K. Meyer, *Inorg. Chem.*, 2013, **52**, 10552. (i) H.S. La Pierre and K. Meyer, *Prog. Inorg. Chem.*, 2014, **58**, 303. (j) H.S. La Pierre, A. Scheurer, F.W. Heinemann, W. Hieringer and K. Meyer, *Angew. Chem. Int. Ed.*, 2014, **53**, 7158. (k) D.P. Halter, F.W. Heinemann, J. Bachmann and K. Meyer, *Nature*, 2016, **530**, 317. (l) J. Huemmer, F.W. Heinemann and K. Meyer, *Inorg. Chem.*, 2016, **56**, 3201. (m) C.J. Inman, A.S.P. Frey, A.F.R. Kilpatrick, F.G.N. Cloke and S.M. Roe, *Organometallics*, 2017, **36**, 4539. (n) S. Fortier, J.R. Aguilar-Calderón, B. Vlaisavljevich, A.J. Metta-Magaña ´, A.G. Goos, C.E. Botez, *Organometallics*, 2017, **36**, 4591. (m) D.N. Huh, S. Roy, J.W. Ziller, F. Furche, W.J. Evans, *J. Am. Chem. Soc.*, 2019, **141**, 12458.

5 (a) B.M. Gardner and S.T. Liddle, *Chem. Commun.*, 2015, **51**, 10589. (b) A.L. Ward, W.W. Lukens, C.C. Lu and J. Arnold, *J. Am. Chem. Soc.*, 2014, **136**, 3647. (c) D. Patel, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Dalton Trans*, 2013, **42**, 5224. (d) B.M. Gardner, G. Balázs, M. Scheer, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Nature Chem.*, 2015, **7**, 582. (e) B.M. Gardner, J. McMaster, F. Moro, W. Lewis, A.J. Blake and S.T. Liddle, *Chem. Eur. J.*, 2011, **17**, 6909. (f) B.M. Gardner, J. McMaster, W. Lewis and S.T. Liddle, *Chem Commun.*, 2009, 2851. (g) B.M. Gardner, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *J. Am. Chem. Soc.*, 2009, **131**, 10388. (h) D.M. King, F. Tuna, J. McMaster, W. Lewis, A.J. Blake, E.J.L. McInnes and S.T. Liddle, *Angew. Chem. Int. Ed.*, 2013, **52**, 4921. (i) D.M. King, J. McMaster, F. Tuna, E.J.L. McInnes, W. Lewis, A.J. Blake and S.T. Liddle, *J. Am. Chem. Soc.*, 2014, **136**, 5619. (j) D.M. King, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Science*, 2012, **337**, 717. (k) B.M. Gardner, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 7068. (l) B.M. Gardner, G. Balázs, M. Scheer, A.J. Wooles, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 15250. (m) P. Roussel, R. Boaretto, A.J. Kingsley, N.W. Alcock and P. Scott, *J. Chem Soc., Dalton Trans.*, 2002, 1423. (n) P. Roussel, N.W. Alcock, R. Boaretto, A.J. Kingsley, I.J. Munslow, C.J. Sanders and P. Scott, *Inorg. Chem.*, 1999, **38**, 3651. (o) P. Roussel, W. Errington, N. Kaltsoyannis and P. Scott, *J. Organomet. Chem.*, 2001, **635**, 69. (p) P. Roussel and P. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 1070. (q) N. Kaltsoyannis and P. Scott, *Chem. Commun.*, 1998, 1665. (r) P. Roussel, P.B. Hitchcock, N.D. Tinker and P. Scott, *Inorg. Chem.*, 1997, **36**, 5716. (s) P. Roussel, P.B. Hitchcock, N. Tinker and P. Scott, *Chem. Commun.*, 1996, 2053. (t) P. Scott and P.B. Hitchcock, *Polyhedron*, 1994, **13**, 1651. (u) E.P. Wildman, G. Balázs, A.J. Wooles, M. Scheer and S.T. Liddle, *Nature Comm.*, 2017, **8**, 14769. (v) E.P. Wildman, G. Balázs, A.J. Wooles, M. Scheer and S.T. Liddle, *Nature Commun.*, 2016, **7**, 12884. (w) B.M. Gardner, W. Lewis, A.J. Blake and S.T. Liddle, *Organometallics*, 2015, **34**, 2386. (x) B.M. Gardner, P.A. Cleaves, C.R. Kefalidis, J. Fang, L. Maron, W. Lewis, A.J. Blake and S.T. Liddle, *Chem. Sci.*, 2014, **5**, 2489. (y) P. Scott and P.B. Hitchcock, *J. Chem. Soc., Chem. Commun.*, 1995, 579. (z) S. Hohloch, J.R. Pankhurst, E.E. Jaekel, B.F. Parker, D.J. Lussier, M.E. Garner, C.H.Booth, J.B. Love, J. Arnold, *Dalton Trans.*, 2017, **46**, 11615.

6 a) C. Camp, N. Settineri, J. Lefèvre, A.R. Jupp, J. M. Goicoechea, L. Maron and J. Arnold, *Chem. Sci*, 2015, **6**, 6379. b) N.S. Settineri, M.E. Garner and J. Arnold, *J. Am. Chem. Soc.*, 2017, **139**, 6261. C) N. Settineri, J. Arnold, *Chem. Sci.*, 2018, **9**, 2831.

7 M.D. Straub, S. Hohloch and J. Arnold *Dalton Trans.* 2018, **47**, 1772.

8 (a) A.C. Behrle, A.J. Myers, P. Rungthanaphatsophon, W.W. Lukens, C.L. Barnes, J.R. Walensky, *Chem. Commun.*, 2016, **52**, 14373. (b) M.A. Boreen, B.F. Parker, S. Hohloch, B.A. Skeel, J. Arnold, *Dalton Trans.*, 2018,**47**, 96.

9 (a) S.T. Liddle, I.S. Edworthy and P.L. Arnold, *Chem. Soc. Rev.*, 2007, ***36***, 1732. (b) D.P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A.J. Blake and S.T. Liddle, *Nature Chem.*, 2011, **3**, 454. (c) D.P. Mills, O.J. Cooper, F. tuna, E.J.L. McInnes, E.S. Davies, J. MacMaster, F. Moro, W. Lewis, A.J. Blake and S.T. Liddle, *J. Am. Chem. Soc.*, 2012, **134**, 10047. (d) S.T. Liddle, D.P. Mills and A.J. Wooles, *Chem. Soc. Rev.*, 2011, **40**, 2164. (e) O.J. Cooper, D.P. Mills, J. McMaster, F. Moro, E.S. Davies, W. Lewis, A.J. Blake and S.T. Liddle, *Angew. Chem. Int. Ed.*, 2011, **50**, 2383. (f) O.J. Cooper, J. McMaster, W. Lewis, A.J. Blake and S.T. Liddle, *Dalton Trans.*, 2010, **39**, 5074. (g) O.J. Cooper, D.P. Mills, J. McMaster, F. Tuna, E.J.L. McInnes, W. Lewis, A.J. Blake and S.T. Liddle, *Chem. Eur. J.*, 2013, **19**, 7071. (h) S.T. Liddle, D.P. Mills and A.J. Wooles, *Organomet. Chem.*, 2010, **36**, 29. (i) E. Lu, O.J. Cooper, J. McMaster, F. Tuna, E.J.L. McInnes, W. Lewis, A.J. Blake and S.T. Liddle, *Angew. Chem. Int. Ed.*, 2014, **53**, 6696. (j) M. Gregson, E. Lu, F. Tuna, E.J.L. McInnes, C. Hennig, A.C. Scheinost, J. McMaster, W. Lewis, A.J. Blake, A. Kerridge and S.T. Liddle, *Chem. Sci.*, 2016, **7**, 3286. (k) P.L. Arnold and S.T. Liddle, *Chem. Commun.*, 2006, 3959. (l) M. Gregson, E. Lu, D.P. Mills, F. Tuna, E.J.L. McInnes,

C. Hennig, A.C. Scheinost, J. McMaster, W. Lewis, A.J. Blake, A. Kerridge and S.T. Liddle, *Nature Comm.*, 2017, **8,** 14137.

10 (a) M.E. Garner, S. Hohloch, L. Maron and J. Arnold, *Organometallics*, 2016, **35**, 2915. (b) M.E. Garner, S. Hohloch, L. Maron and J. Arnold. *Angew. Chem. Int. Ed.*, 2016, **55**, 13789. (c) M.E. Garner and J. Arnold, *Organometallics*, 2017, **36**, 4511. (d) M.E. Garner, T.D. Lohrey, S. Hohloch, and J. Arnold, *J. Organomet. Chem.,* 2018, **857**, 10.

11 For selected examples see: (a) J. L. Sessler, P. J. Melfi and G. D. Pantos, *Coord. Chem. Rev.*, 2006, **250**, 816; (b) J. L. Sessler, A. E. Vivian, D. Seidel, A. K. Burell, M. Hoehmer, T. D. Mody, A. Gebauer, S. J. Weghorn and V. Lynch, *Coord. Chem. Rev.*, 2001, **216–217**, 411; (c) V. W. Day, T. J. Marks and W. A. Wachter, *J. Am. Chem. Soc.*, 1975, **97**, 4519; (d) J. L. Sessler, W. B. Callaway, S. P. Dudek, R. W. Date and D. W. Bruce, *Inorg. Chem.*, 2004, **43**, 6650; (e) J. L. Sessler, P. J. Melfi, D. Seidel, A. E. V. Gorden, D. K. Ford, P. D. Palmer and C. D. Tait, *Tetrahedron*, 2004, **60**, 11089; (f) I.-T. Ho, J. L. Sessler, S. S. Gambhir and J. V. Jokerst, *Analyst*, 2015, **140**, 3731; (g) J. T. Brewster, Q. He, G. Anguera, M. D. Moore, X.-S. Ke, V. M. Lynch and J. L. Sessler, *Chem. Commun.*, 2017, **53**, 4981; (h) J. L. Sessler, A. E. V. Gorden, D. Seidel, S. Hannah, V. Lynch, P. L. Gordon, R. J. Donohoe, C. D. Tait and D. W. Koegh, *Inorg. Chim. Acta*, 2002, **341**, 54; (i) J. L. Sessler, P. J. Melfi, E. Tomat, W. Callaway, M. T. Huggins, P. L. Gordon, D. W. Koegh, R. W. Date, D. W. Bruce and B. Donnio, J. *Alloys Compd.*, 2006, **418**, 171; (j) P. L. Arnold, A.-F. Pécharman, E. Hollis, A. Yahia, L. Maron, S. Parsons and J. B. Love, *Nat. Chem.*, 2010, **2**, 1056; (k) P. L. Arnold, G. M. Jones, Q.-J. Pan, G. Schreckenbach and J. B. Love, *Dalton Trans.,* 2012, **41**, 6595; (l) P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J.-C. Griveau, R. Caciuffo, N. Magnani, L. Maron, L. Castro, A. Yahia, S. O. Odoh and G. Schreckenbach, *J. Am. Chem. Soc.*, 2013, **135**, 3841; (m) M. Zegke, G. S. Nichol, P. L. Arnold and J. B. Love, *Chem. Commun.*, 2015, **51**, 5876; (n) X.-J. Zheng, N. L. Bell, C. J. Stevens, Y.-X. Zhong, G. Schreckenbach, P. L. Arnold, J. B. Love and Q.-J. Pan, *Dalton Trans.*, 2016, **45**, 15910; (o) P. L. Arnold, J. H. Farnaby, R. C. White, N. Kaltsoyannis, M. G. Gardiner and J. B. Love, *Chem. Sci.*, 2014, **5**, 756; (p) P. L. Arnold, C. J. Stevens, J. H. Farnaby, M. G. Gardiner, G. S. Nichol and J. B. Love, *J. Am. Chem. Soc.*, 2014, **136**, 10218; (q) P. L. Arnold, J. H. Farnaby, M. G. Gardiner and J. B. Love, *Organometallics*, 2015, **34**, 2114; (r) M. S. Dutkiewicz, J. H. Farnaby, C. Apostolidis, E. Colineau, O. Walter, N. Magnani, M. G. Gardiner, J. B. Love, N. Kaltsoyannis, R. Caciuffo and P. L. Arnold, *Nat. Chem.*, 2016, **8**, 797; (s) J. L. Sessler, D. Seidel, A. E. Vivian, V. Lynch, B. L. Scott and D. W. Koegh, *Angew. Chem., Int. Ed.*, 2001, **40**, 591; (t) M. Yang, W. Ding and D. Wang, *New J. Chem.*, 2017, **41**, 63.

12 (a) S.Hohloch, M.E. Garner, B.F. Parker, J. Arnold *Dalton Trans.* 2017, **46**, 13768; (b) S. Hohloch, M.E. Garner, C.H. Booth, W.W. Lukens, C.A. Gould, D.J. Lussier, L. Maron and J. Arnold *Angew. Chem. Int. Ed* 2018, **49**, 16368.

13 (a) S. Hohloch, B.M. Kriegel, R.G. Bergman and J. Arnold *Dalton Trans*. 2016, **45**, 15725. (b) R.L. Webster, *Dalton Trans.*, 2017, **46**, 4483; (c) Y. Liu, J. Li, X.Ma, Z- Yang, H.W. Roesky, *Coord. Chem. Rev.*, 2018, **374**, 387; (d) L. Bourget-Merle, M.F. Lappert, J.R. Severn, *Chem. Rev.*, 2002, **102**, 3031; (e) D.J. Mindiola, *Angew. Chem. Int. Ed.*, 2009, **48**, 6198; (f) K. Huse, C. Wölper, S. Schulz, *Eur. J. Inorg. Chem.*, 2018, 3472.

14 (a) P.B. Hitchcock, M.F. Lappert and D.-S. Liu, *J. Organomet. Chem.* 1995, **488**, 241; (b) P.B. Hitchcock, J. Hu, M.F. Lappert, S. Tian *J. Organomet. Chem.*, 1997, **536-537**, 473; (c) R.J. Wright, P.P. Power, B.L. Scott, J.L. Kiplinger *Organometallics* 2004, **23**, 4801; (d) T.W. Hayton, G. Wu *J. Am. Chem. Soc.* 2008, **130**, 2005; (e) T.W. Hayton, G. Wu *Inorg. Chem.* 2008, **47**, 7415; (f) M.F. Schettini, G. Wu, T.W. Hayton *Inorg. Chem.* 2009, **48**, 11799; (g) M.F. Schettini, G. Wu, T.W. Hayton, *Chem Commun.* 2012, **48**, 1484; (h) F. Dulong, O. Bathily, P. Thuery, M. Ephritikine, T. Cantat *Dalton Trans.* 2012, **41**, 11980; (i) N.E. Travia, M.J. Monreal, B.L. Scott, J.L. Kiplinger *Dalton Trans.* 2012, **41**, 14514; (j) M.J. Monreal, R.J. Wright, D.E. Morris, B.L. Scott, J.T. Golden, P.P. Power, J.L. Kiplinger *Organometallics* 2013, **32**, 1423 ; (k) F. Dulong, P. Thuery, M. Ephritikhine, T. Cantat *Organometallics* 2013, **32**, 1328; (l) A.J. Wooles, W. Lewis, A.J. Blake, S.T. Liddle *Organometallics* 2013, **32**, 5058. (m) J. Riedhammer, J.R. Aguilar-Calderon, M. Miehlich, D.P. Halter, D. Munz, F.W. Heinemann, S. Fortier, K. Meyer, D. Mindiola, *Inorg. Chem.*, 2020, **59**, 2443.

15 C. Camp and J. Arnold *Dalton Trans.* 2016, **45**, 14462.

16 D.R. Kindra, W.J. Evans, *Chem. Rev.*, 2014, **114**, 8865 .

17 A.L. Ward, H.L Buckley, W.W. Lukens, J. Arnold, *J. Am. Chem. Soc.*, 2013, **135**, 13965.

18 (a) S.V. Klemenyeva, M.Y. Afonin, A.S. Bogomyakov, M.T. Gamer, P.W. Roesky, S.N. Konchenko, *Eur. J. Inorg. Chem.*, 2016, 3666. (b) C. Cui, A. Shafir, J.A.R. Schmidt, A.G. Oliver, J. Arnold, *Dalton Trans.*, 2005, 1387. (c) P. Liu, Y. Zhang, Q. Shen, *Organometallics*, 2013, **32**, 1295. (d) J. Zhang, Z. Zhang, Z. Chen, X. Zhou, *Dalton Trans.*, 2012, **41**, 357. (e) Y. Yao, Z. Zhang, H. Peng, Y. Zhang, Q. Shen, J. Lin, *Inorg. Chem.*, 2006, **45**, 2175. (f) Y. Yao, M. Xue, Y. Luo, Z. Zhang, R. Jiao, Y. Zhang, Q. Shen, W. Wong, K. Yu, J. Sun, *J. Organomet. Chem.*, 2003, **678**, 108.

19 A. Okuniewski, D. Rosiak, J. Chojnacki, B. Becker, *Polyheydron,* 2015, **90**, 47.

20 L.C.J. Pereira, C. Camp, J.T. Coutinho, L Chatelain, P. Maldivi, M. Almeida, M. Mazzanti *Inorg. Chem.* 2014, **53**, 11809.

21 J. D. Rinehart, K. R. Meihaus, J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7572.

22 C. B. Finn, R. Orbach, W.P. Wolf, *Proc. Phys. Soc.*, 1961, **77**, 261.

23 S. T. Liddle, J. van Slageren, *Chem. Soc. Rev.*, 2015, **44**, 6655.

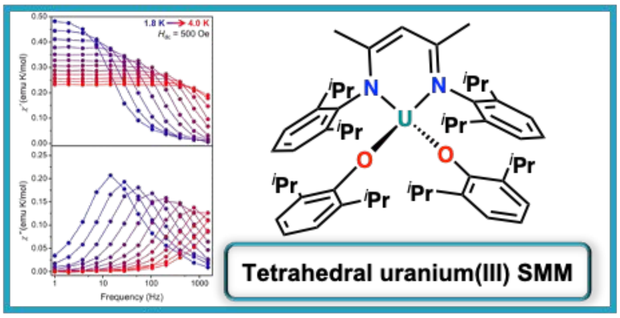
24 D. Reta and N. F. Chilton, *Phys. Chem. Chem. Phys.*, 2019, **21**, 23567.

25 M.J. Monreal, R.K. Thomson, T. Cantat, N.E. Travia, B.L. Scott, J.L. Kiplinger, *Organometallics*, 2011, **30**, 2031.

26 (a) D.F. Evans, *J. Chem. Soc.*, 1959, 2003 (b) G.A. Bain, J.F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.

27 a) Sheldrick, G. M. Acta Crystallogr. Sect. A 2015, 71 (1), 3. b) Sheldrick, G. M. Acta Crystallogr. Sect. A 2008, 64 (1), 112.

28 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339.



A rare tetrahedrally coordinated uranium(III) complex supported by β-diketiminate ligands is synthesized and investigated for its magnetic properties.