Abstract: After more than 50 years, the synthesis and electronic structure of the first and only reported \( \text{U}^0 \) complex \([\text{U}(\text{bipy})_4]^{-}\) (1) has been re-investigated. Additionally, its one-electron reduced product \([\text{Na(THF)}_4][\text{U}(\text{bipy})_4]^{-}\) (2) has been newly discovered. High resolution crystallographic analyses combined with magnetic and computational data show that 1 and its derivative 2 are best described as highly reduced species containing mid-to-high-valent uranium ligated by redox non-innocent ligands.

Prior to the 1940s, the heaviest natural elements known at the time, namely Th–U, were classified as sixth-row transition metals under the belief that their valence electrons sequentially populated 6d-orbitals to give 7s6d electronic configurations. Based upon this and some chemical similarities to 4d and 5d metals, these heavy elements were categorized under Groups 4–6 in the periodic table. However, the discovery of Np and Pu precipitated a paradigm shift in the classification of the heavy metals as neither synthetic element exhibited chemical properties akin to their supposed Group 7a and 8 congeners. \(^1\)

From this divergent chemistry and the highly electropositive nature of these elements, along with the observation that the redox character of Th–Pu is dominated by a 4+ oxidation state, the “actinide concept” was born to appropriately describe the heaviest known elements in terms of 7s6d5f electronic configurations.\(^2,3\)

While the actinide series is now complete and has long since been established, the chemical and electronic properties of the 5f metals continue to not only be a point of technological interest but also fundamental curiosity.\(^4\) The actinides are intriguing from the perspective that these elements exhibit characteristics that seemingly exist in a regime somewhere between that of the lanthanide and transition metals.\(^3,4\) For instance, the later actinides (amically Am–Lr) trend towards a persistent 3+ oxidation state like that found for lanthanides, while the early actinides (e.g., U) display multi-electron chemistry similar to that of d-block metals. Yet, unlike transition metals, the redox chemistry of the early actinides is largely limited to mid-to-high-valent oxidation states with an \(\text{An}^{4+}\) preference. In the case of uranium, its molecular redox chemistry has traditionally been restricted within a three-electron \(\text{U}^{6+}–\text{U}^0\) interchange.\(^5,6\)

Recently, the research groups of Evans and Meyer have reported the extraordinary isolation and characterization of the unequivocal molecular \(\text{U}^0\) compounds \([\text{K}_2(2.2.2\text{-crypt})\{\text{C}_5\text{H}_3\text{SiMe}_3\}_2\text{U}]\) and \([\text{K}_2(2.2.2\text{-crypt})\{\text{H}^{3\text{Me}}\text{ArO})_3\text{mes}]\text{U}\]\(^7\) respectively.\(^7\) Their success calls into question the historically accepted molecular redox limitations of the early actinides, suggesting that even lower oxidation states, namely \(\text{U}^0\) and \(\text{U}^2\), may be accessible under the proper synthetic conditions.

Interestingly, one example of a \(\text{U}^0\) compound has been described in the literature. In 1963, Herzog et al. published the synthesis of \([\text{U}(\text{bipy})_4]\) (bipy = 2,2’-bipyridine) (1) described as a zero-valent uranium species supported by neutral bipy ligands.\(^8\) While the formulation of 1 was confirmed a decade later by X-ray crystallographic analysis,\(^9\) this complex has largely been overlooked as, as far as we can best determine, its report has only been cited once within the last fifty years.\(^10\) It must be noted, though, that the validity of its assignment as zero-valent uranium is challenged by the reported effective magnetic moment of 2.67 \(\mu_\text{B}\) (avg), inconsistent with \(\text{U}^6\) and closer to \(\text{U}^3/\text{U}^0\),\(^10\) as well as the important fact that bipy is the quintessential redox-active ligand. Finally, and quite surprisingly, we have discovered that 1 can be reduced to the one-electron reduction product \([\text{Na(THF)}_4][\text{U}(\text{bipy})_4]^{-}\) (2), thus further convoluting the matter.

The redox non-innocence of bipy complicates formal oxidation state assignments in metal complexes as it can adopt three, localized redox levels: neutral bipy\(^0\), open-shell bipy\(^-\) anion, and closed shell bipy\(^2+\) dianion (Scheme 1).\(^1\) Even in complexes containing redox-limited metals, such as the lanthanides, canonical oxidation state assignments can be nontrivial.\(^11\) For instance, in the [Lu(bipy)\(_4\)] complex, magnetic data support either [Lu\(^0\)(bipy)\(_4\)]\(^+\) or [Lu\(^2+\)(bipy\(^2-\))](bipy \(^-\))(bipy\(_0\))] form with an EPR value \((g = 2.0014)\) suggestive of the latter.\(^12\) In homoleptic transition-metal complexes of the type [M(bipy)\(_3\)],
both metal and ligand make formal oxidation state assignments difficult as shown by Wieghardt et al. As the character of uranium can be considered as intermediate between lanthanide and transition metal, this further obfuscates canonical determinations in \([\text{U(bipy)}_2]\).

In an effort to better understand the electronic structure of this lost complex along with the low-valent chemistry of uranium, we have revisited the synthesis of 1 and provide a definitive oxidation state assignment of both metal and ligand based upon thorough structural and electronic analyses. Moreover, we describe the synthesis, characterization, and electronic structure of the new reduced species 2 which also sheds valuable insight into the unique chemistry of the actinides, especially as it pertains to the transition metal/lanthanide duality of these 5f-elements.

Treatment of a THF solution of UCl₄ with 4 equiv of either \([\text{Li(bipy)}]\) or \([\text{Na(bipy)}]\), prepared in-situ, generates a deep purple mixture from which 1 instantly precipitates as a fine, purple powder \([\text{Eq (1)}]\). Contrary to the original description of its synthesis, we have found 1 to be only sparingly soluble in THF and aromatic solvents such as benzene. Purification of 1 can be accomplished utilizing a modified Soxhlet extractor \([\text{Scheme 1)}\) under refluxing toluene over a one week period from which small, purple crystals of 1-C₆H₆ can be isolated in 56% yield.

Complex 1 is sufficiently soluble in \(\text{C}_6\text{D}_6\) such that its ⁱH NMR spectrum reveals a paramagnetic species that displays four weak but sharp resonances in a 1:1:1:1 ratio ranging from 24.1 to –34.2 ppm, indicating a uniform ligand environment in solution. Importantly, the IR spectrum (KBr pellet) of 1 shows a prominent stretch at 925 cm⁻¹, a clear signature of the bipy⁻ ligand, that strongly suggests the presence of ligand non-innocence in 1, counting its description as a \(\text{U}^\text{IV}\) complex.

The \(\text{C}_{\text{py}}-\text{C}_{\text{py}}\) bond length in 1 is highly sensitive to the ligand charge-level, thus its oxidation state can be readily ascertained by bond metric analysis of X-ray determined structures (Scheme 1). The previously reported structure of 1 suffers from poor resolution that fails the 3σ criterion, precluding any meaningful assessment. Utilizing crystals harvested from the Soxhlet extraction of 1, we have determined a new, synchrotron resolved structure (Figure 1). Complex 1-C₆H₆ crystallizes in the \(\text{P}1\) space group with each ligand found in a crystallographically independent position. The uranium center in 1 adopts distorted cubic coordination geometry.

\[ \text{UCl}_4 + 4 \text{M(bipy)} \rightarrow \text{THF} \rightarrow \text{M}^+ + 4 \text{MCl} \]

FIGURE 1. Molecular structure of 1-C₆H₆.

The \(\text{C}_{\text{py}}-\text{C}_{\text{py}}\) distances of 1.425(4)-35(5) Å in 1 are clear-cut and all within the 1.43 Å range established for the bipy⁻ anion and comparable to those found in \([\text{U}^{\text{IV}}(n\text{BuAr})_2(\text{bipy}^\text{⁻}))))\] \((\text{C}_{\text{py}}-\text{C}_{\text{py}} = 1.429(7), 1.426(7) Å)\). Moreover, the NCCN dihedral angles in 1 range from 0.4–2.2°, consistent with the increased planarity that occurs within the bipy ligand upon one-electron reduction. Thus, based upon the structural evidence alone, 1 is best described not as \(\text{U}^\text{II}\) but as \(\text{U}^\text{IV}\) ligated by four radical bipy monoanions in the form \([\text{U}^{\text{IV}}(\text{bipy}^\text{⁻})]_4\). Notably, this structure differs from the related lanthanide complexes where-in \([\text{Ln}^{\text{III}}(\text{bipy}^\text{⁻}))(\text{bipy}^\text{⁻})(\text{bipy}^\text{⁻})]_2\) \((\text{M} = \text{Sc, Ti, Y})\) found amongst the early d-elements.

During our investigations of 1, we discovered trace amounts of 2 as a crystalline side-product formed in one reaction. Attempts to synthesize 2 by the addition of excess \([\text{Na(bipy)}]\) to suspensions of 1 in THF were unsuccessful, resulting in no observed change. However, addition of \([\text{UCl}_4(\text{THF})_4]\) to a stirring solution of \([\text{Na(bipy)}]\) in THF, prepared from 4 equiv of bipy and 5 equiv of \(\text{Na}^\text{0}\), generates a dark brown-green product mixture from which 2 can be isolated in 30% yield after recrystallization (Eq. (2)).

Complex 2 displays improved solubility properties over 1 as it is highly soluble in THF and pyridine and is stable in these solutions at room temperature for several months. The ¹H NMR spectrum of 2 in \(\text{D}_2\text{O}\)pyridine displays four very broad, para-
magnetically shifted resonances, again in a 1:1:1:1 ratio, signifying ligand equivalence in solution, while its IR spectrum (KBr pellet) is marked by diagnostic bipy \(^-\) stretches (see the Supporting Information).

Crystals of 2:0.5C\(_2\)H\(_6\) (Figure 2), grown from THF/C\(_2\)H\(_6\) mixtures, show a non-interacting cation/anion pair within the P\(\bar{1}\) space group where the uranium retains its distorted cubic coordination geometry, differing from dodecahedral lutetium in [Li(THF)]\_2Lu\(^{\text{bipy}}\)\(^-\).\(^{[12]}\) As with 1, the [U(bipy)\(_4\)]\(^-\) fragment occupies a crystallographically independent position that allows for the localized charge assignment of each bipy ligand. Inspection of the C\(_{py}\)–C\(_{py}\) metric parameters reveals two distinct charge states corresponding to bipy\(^-\) (1.422(5), 1.439(5) \(\AA\)) and bipy\(^2\)\(^-\) (1.379(8), 1.384(7) \(\AA\)) in 2. Consistent with this, the U–N\(_{bipy}\) distances of the bipy\(^-\) ligands (2.53 \(\AA\) (avg)) are longer than the analogous distances of the two bipy\(^2\)\(^-\) ligands (2.47 \(\AA\) (avg)). Altogether, the structural data suggest a U\(^IV\) species formulated as [U\(^{\text{bipy}}\)\(_4\)]\(_2\)(bipy\(^2\)\(_2\))\(_2\) in the solid-state. If true, this is noteworthy as 2 would represent the first instance of an An–bipy\(^-\) compound and the first example of high-valent uranium supported by non-neutral bipy.

**Figure 2.** Molecular structure of 2:0.5C\(_2\)H\(_6\). It must be noted that while the structural data of 1 and 2 are compelling, definitive oxidation state assignments must be made with caution. It has been proposed that strong M–N\(_{bipy}\) interactions, especially those arising from the enhanced \(\pi\)-donating abilities of bipy\(^2\)\(^-\), may distort C\(_{py}\)–C\(_{py}\) distances leading to potential charge-state misinterpretations.\(^{[10b]}\) In order to further corroborate the solid-assignments, the electronic structures of 1 and 2 were examined.

The diagnostic, oxidation-state dependent \(f\rightarrow f\) transition bands of uranium are not visible in the UV/Vis/NIR spectra of 1 and 2. Instead, in both spectra of 1 and 2, these bands are obscured by a comparatively intense, broad absorption in the 600–1000 nm region with an accompanying band found between 300–400 nm,\(^{[15a]}\) signature features of the bipy\(^-\) \(\pi\rightarrow \pi^*\) transitions.\(^{[15]}\)

The magnetic properties of 1 and 2 were investigated using a SQUID magnetometer. The dc magnetic susceptibility measurements of 1 and 2 were performed on crushed polycrystaline samples in the temperature range of 1.9–300 K, under an applied dc field of 1000 Oe (Figure 3). The room temperature \(\chi_M T\) value of 2.37 cm\(^3\)Kmol\(^{-1}\) for 1 strongly suggests the presence of a U\(^{\text{V}}\) ion (\(S = 1\), \(L = 0\)) with four bipy\(^-\) radicals. Upon subtraction of the expected values for four \(S = 1/2\) spins arising from the radical anions (4 \(\times\) 0.375 cm\(^3\)Kmol\(^{-1}\)), the remaining value of 0.87 cm\(^3\)Kmol\(^{-1}\) is well within the reported range for 5\(f\) systems.\(^{[4b, 17]}\) The \(\chi_M T\) product of 1 decreases gradually to about 15 K before decreasing sharply to reach a minimum of 0.1 cm\(^3\)Kmol\(^{-1}\) at 1.9 K. Such a decrease can be attributed to the dominant antiferromagnetic coupling between spin carriers but also to the thermal depopulation of the higher excited states upon decrease of temperature.\(^{[17]}\) The observed small magnetic moment at low temperature is in good agreement with the often seen quenched magnetic moment values for U\(^{IV}\) due to the loss of Kramer degeneracy for the U\(^{IV}\) ion.

In the case of 2, the observed \(\chi_M T\) value of 1.2 cm\(^3\)Kmol\(^{-1}\) is close to the spin only value for three non-interacting \(S = 1/2\) spins (3 \(\times\) 0.375 cm\(^3\)Kmol\(^{-1}\)) which can be attributed to one U\(^{\text{V}}\) ion and two bipy\(^-\) monoradical anions. However, this observed value is slightly below the reported values for U\(^{\text{V}}\) (5\(f\), \(S_{\text{rad}} = 1/2\), \(L = 3\)).\(^{[4b, 16]}\) This could be due to the presence of antiferromagnetic interactions within the molecule through strong \(\pi\)–\(\pi\) interactions between the two bipy\(^-\) radical anions (3.59 \(\AA\)). Alternatively, 2 could be treated as possessing a U\(^{\text{V}}\) ion with one non-interacting \(S = 1/2\) bipy\(^-\) radical written as [U\(^{\text{bipy}}\)\(_4\)(bipy\(^2\)\(_2\))](bipy\(^2\)\(_2\)). In this scenario, the 0.825 cm\(^3\)Kmol\(^{-1}\) U\(^{\text{V}}\) contribution would fall in the low range for a 5\(f\) ion.\(^{[4b]}\) However, as the effective magnetic moments of uranium can fall over a wide range, caution must be exercised when correlating magnetic values to oxidation states.\(^{[4b]}\)

Interestingly, in 2, upon decreasing the temperature, the \(\chi_M T\) decreases gradually indicating dominant antiferromagnetic interactions between the spin carriers. The small \(\chi_M T\) value of 0.1 cm\(^3\)Kmol\(^{-1}\) at 1.9 K is likely due to the presence of non-negligible intermolecular antiferromagnetic interactions between the neighboring molecules. In fact, an intermolecular distance of 3.66 \(\AA\) can be found between the radical anions, which is comparable to the aforementioned intramolecular \(\pi\)–\(\pi\) distance of 3.59 \(\AA\) found in 2.
To further elucidate the electronic structures of 1 and 2, especially to determine spin densities, the complexes were examined through DFT methods using a full atom model for each compound. For 1, geometry optimizations at the singlet, triplet, quintet, and septet multiplicities were calculated to assign the ground state. For 2, the doublet, quartet, and sextet multiplicities were probed with the same objective. Table 1 shows the relative energies calculated for the different states of 1 and 2.

### Table 1. Energy results for the calculated DFT models.

<table>
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<th>Model</th>
<th>Multiplicity</th>
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<td>0</td>
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<tr>
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<tr>
<td></td>
<td>sextet</td>
<td>$-2458.6219742$</td>
<td>12.52</td>
</tr>
</tbody>
</table>

(a) Difference in energy from the septet state with the corresponding energies for the singlet, triplet, and quintet states. (b) Difference in energy from the quartet state with the corresponding energies for the doublet and sextet states.

In the case of 1, the septet state is the lowest in energy by at least 28.1 kcal mol$^{-1}$ as compared to the other calculated spin states (Table 1). In complete agreement with the empirical $U^0$ assignment of 1, the electronic structure of the septet model of 1 shows four unpaired electrons residing in ligand-based MOs (HOMO, HOMO–1, HOMO–2, and HOMO–3), while the other two unpaired electrons reside in metal-based 5f-orbitals (HOMO–4 and HOMO–5; Figure 4). Inspection of the ligand-based MOs shows increased electron density, ranging from 17 to 21%, between the $C_{py}-C_{py}$ bonds of the bipyridine ligands which corresponds to greater $\pi$-bonding character. This is fully consistent with the assigned bipy$^2$– redox level for each ligand, and the calculated $C_{py}-C_{py}$ distances (1.426–1.434 Å, Table S3 in the Supporting Information) agree with those observed in the crystal structure of 1.

For 2, the quartet ($[U^0(\text{bipy})]_2(\text{bipy})^\text{–}$) multiplicity is found to be lower than the doublet ($[U^0(\text{bipy})^\text{–}]_2(\text{bipy})$) and sextet ($[U^0(\text{bipy})^\text{–}]_2(\text{bipy})^\text{–}$) states by 1.47 and 12.52 kcal mol$^{-1}$, respectively (Table 1) and agrees best with the experimental data. Though, close in energy, the doublet spin state for 2 cannot be ruled out as a ground state configuration. Computationally, when treated as a quartet, the one electron reduction of 1 to 2 rearranges the orbital occupancy resulting in electron pairing that gives rise to two bipy$^2$– ligands (HOMO and HOMO–1) and one singly occupied ligand molecular orbital (HOMO–2) while leaving two unpaired electrons in metal-based orbitals (HOMO–3 and HOMO–4). Interestingly, the HOMO possesses a considerable metal contribution of 19.9% (Figure S14 in the Supporting Information). The MO diagram of the quartet state (Figure 5) shows the remaining unpaired ligand electron to be largely localized on a single bipyridine.
Kiplinger et al. have demonstrated that intramolecular metal–ligand electron transfer in \( [\text{U(bipy)}]^{2-} \) to be facile and mediated by coordination geometry, showing that oxidation state assignments in actinide complexes supported by non-innocent ligands is not straightforward and influenced by a number of factors.\(^{[15,16]} \) As such, \( [\text{U}^0(\text{bipy}^2^-)(\text{bipy})]^+ \) or \( [\text{U}^2(\text{bipy}^-)(\text{bipy})]^2- \) are strict canonical forms and \( 2 \) is perhaps better considered in terms of its total spin multiplicity rather than through formal oxidation state assignments. Indeed, at room temperature, the ligands are observed to be magnetically equivalent as shown by its \( ^1\text{H} \) NMR spectrum (vide supra).

Finally, as a means to better understand the solution-phase electronic characteristics of the \([\text{U(bipy)}]^{2-}\) system, the redox properties of \( 2 \) were examined by cyclic voltammetry. In THF at room temperature, the cyclic voltammogram (CV) of \( 2 \) features six distinct redox waves at \(-2.20, -2.40, -2.60, -2.85, -3.01, \) and \(-3.15 \text{ V (vs. Fc}^{2+}, \mbox{Figure 6).}^{[11,16]} \) This observation can only be explained through a combination of stepwise reductions occurring at both the metal and its ligands. Interestingly, the electrochemistry of \( 2 \) is not unlike \([\text{Cr(bipy)}]^{2+}\) which also shows six separate redox waves in its CV.\(^{[10]} \) Of the six waves seen in the CV of \( 2 \), we have only assigned the semi-reversible wave at \( E_{1/2} = -2.20 \text{ V} \) as corresponding to the couple between \( 1 \) and \( 2 \) based upon the resting potential \((\approx -2.32 \text{ V})\). While the CV of \( 2 \) is complicated, it clearly reveals a rich electrochemical platform that details distinct similarities to transition metal congeners.

![Figure 6. Cyclic voltammogram of 2 in THF (vs. Fc\(^{2+}\)).](image)

In conclusion, we have revisited the \([\text{U}^0]^{2-}\) complex \([\text{U(bipy)}]^{2-}\) \((1)\) and described the synthesis of its one electron reduced product \([\text{Na(THF)}]_2[\text{U(bipy)}]_2\) \((2)\). Full crystallographic, magnetic, and theoretical analyses reveal that, contrary to its original description, complex \( 1 \) does not possess a zero-valent uranium center. Instead, both \( 1 \) and \( 2 \) can be described as containing a cationic metal center ligated by non-innocent bipy ligands found at both the bipy\(^-\) and bipy\(^2-\) redox levels. Nearly lost to time, \( 1 \) is especially unique as it represents the first instance of uranium supported by redox non-innocent ligands. The CV of \( 2 \) shows the \([\text{U(bipy)}]^{2-}\) system to be highly electrochemically active, suggesting the character and chemistry of \([\text{U(bipy)}]^{2-}\) is likely closer in line to that found for its transition metal analogues, \([\text{M(bipy)}]^{2-}\), rather than its related lanthanide derivatives \([\text{Ln(bipy)}]_{n}^{2-}\) \((n = 3, 4)\). As Bart and co-workers have recently shown, the chemistry of uranium supported by redox-active ligands can be rich and unique.\(^{[19]} \) Accordingly, we are currently exploring the chemistry of highly reduced \( 1 \) and \( 2 \), especially their potential to perform multi-electron transfer chemistry.

**Supporting Information**

CCDC 1433629 and 1433630 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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