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Radical Anionic versus Neutral 2,2'-Bipyridyl Coordination in Uranium Complexes Supported by Amide and Ketimide Ligands

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The synthesis and characterization of $(bipy)_2U(N[t\text{-}Bu]Ar)_2$ (**1**-$(bipy)_2$, bipy = 2,2'-bipyridyl, Ar = 3,5-$C_6H_3Me_2$), $(bipy)U(N[^1Ad]Ar)_3$ (**2**-bipy), $(bipy)_2U(NC[t\text{-}Bu]Mes)_3$ (**3**-$(bipy)_2$, Mes = 2,4,6-$C_6H_2Me_3$), and $IU(bipy)(NC[t\text{-}Bu]Mes)_3$ (**3**-I-bipy) are reported. X-ray crystallography studies indicate that bipy coordinates as a radical anion in **1**-$(bipy)_2$ and **2**-bipy, and as a neutral ligand in **3**-I-bipy. In **3**-$(bipy)_2$, one of the bipy ligands is best viewed as a radical anion, the other as a neutral ligand. The electronic structure assignments are supported by NMR spectroscopy studies of exchange experiments with 4,4'-dimethyl-2,2'-bipyridyl and also by optical spectroscopy. In all complexes, uranium was assigned a +4 formal oxidation state.

Introduction

Most metals are known to form complexes with 2,2'-bipyridyl (bipy) and for a given metal center multiple oxidation states may be encountered.[1, 2] For an electropositive, reducing metal, the bipy ligand is commonly reduced to its corresponding radical anion,[1-3] with concomitant oxidation of the metal center. Complexes of lanthanides with bipy as a radical anion ligand have been reported increasingly in recent years and examples of both redox-active[4-12] and redox-inactive[3, 13-20] metals are known. Recently, examples for actinides have also been reported: $Tp^*_2U(bipy)$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate),[21] $Cp'_2U(bipy)$ (Cp' = η^5-1,2,4-$(Me_3C)_3C_5H_2)$,[22] and $Cp'_2Th(bipy)$.[23] Other reported complexes of uranium and bipy are consistent with coordination of a neutral bipy ligand.[24-28]

In 2000, we reported the structure and reactivity of inverted sandwich complexes formed between a bridging aromatic hydrocarbon and two uranium centers via $\mu\text{-}\eta^6,\eta^6$ interactions and have the formula $(\mu\text{-}\eta^6,\eta^6\text{-arene})[U(N[R]Ar)_2]_2$ (R = t-Bu or Ad, 1-adamantyl; arene = benzene or toluene; Ar = 3,5-$C_6H_3Me_2$).[29, 30] Later on, analogous complexes supported by ketimide ligands were also isolated and characterized as disodium or dipotassium salts of the formula $M_2(\mu\text{-}\eta^6,\eta^6\text{-arene})[U(NC^tBuMes)_3]_2$ (M = Na or K, Mes = 2,4,6-$C_6H_2Me_3$), and monopotassium salts of the formula $K(\mu\text{-}\eta^6,\eta^6\text{-arene})[U(NC^tBuMes)_3]_2$ (arene = naphthalene, biphenyl, $trans$-stilbene, or p-terphenyl).[31, 32] Those previous reports focused on the synthesis and characterization of those species and highlighted their two-electron per uranium reducing ability. Since our initial examples, others have also reported bridging benzene or toluene uranium complexes and surveyed their reactivity.[33-42] As part of our reactivity study, we decided to investigate the reactivity of arene-bridged inverted sandwich diuranium complexes with bipy to determine the factors influencing the formation of the resulting products, especially the oxidation state of the bipy ligand.

Herein, we report the synthesis and characterization of $(bipy)_2U(N[t\text{-}Bu]Ar)_2$ (**1**-$(bipy)_2$, Ar = 3,5-$C_6H_3Me_2$), $(bipy)U(N[^1Ad]Ar)_3$ (**2**-bipy), $(bipy)_2U(NC[t\text{-}Bu]Mes)_3$ (**3**-$(bipy)_2$, Mes = 2,4,6-$C_6H_2Me_3$), and $IU(bipy)(NC[t\text{-}Bu]Mes)_3$ (**3**-I-bipy). The geometric and electronic structures of these complexes were investigated both in the solid state (X-ray crystallography) and in solution (NMR and UV-vis spectroscopy) in order to assess whether the bipy ligands have neutral or radical anionic character. The complexes discussed here contain a uranium center with a *formal* oxidation state ranging from +2 to +4 if bipy is assumed to be neutral. As is the case with transition metal and lanthanide compounds,[1, 2] the bipy radical anion was encountered for low oxidation states and neutral bipy for the higher oxidation states.

Results and discussion

Syntheses

Compound $(\mu\text{-toluene})[U(N[t\text{-}Bu]Ar)_2]_2$ (**1**$_2$-μ-toluene)[29] reacts with 4 equivalents of bipy to form **1**-$(bipy)_2$ (Eq 1) as a dark brown microcrystalline solid in 71% isolated yield. No *mono*-bipy complexes were observed as intermediates in the synthesis of **1**-$(bipy)_2$, likely a consequence of the open coordination environment created by the presence of only two t-butylanilide ligands per uranium center (as opposed to three such ligands in other uranium complexes reported by our group).[43-45]

$$(1)$$

(2)
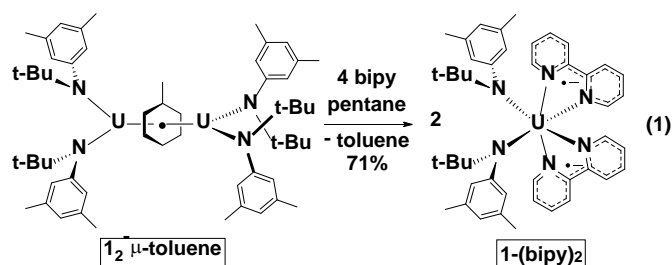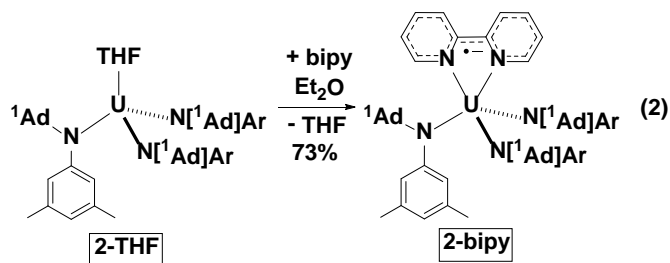
However, when three *N*-adamantylanilide ligands are coordinated to uranium, only the *mono*-bipy complex, **2**-bipy, is formed (Eq 2). The synthesis of **2**-bipy is straightforward and can be accomplished by the reaction of (THF)U(N[¹Ad]Ar)₃ (**2**-THF) with 1 equiv bipy (73% yield, dark brown solid).

(3)
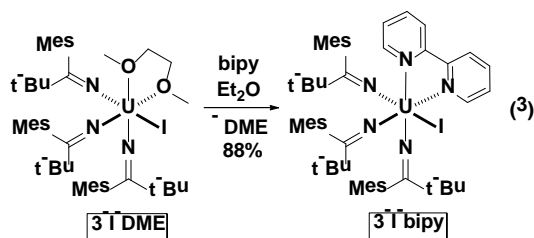
As discussed elsewhere,[31, 32] the supporting ketimide ligand NC[*t*-Bu]Mes has the steric bulk moved one atom further from the uranium center compared to an anilide ligand. The iodide *tris*-ketimide IU(DME)(NC[*t*-Bu]Mes)₃ (**3**-I-DME)[32] incorporates a molecule of DME, while iodide uranium *tris*-anilide complexes do not coordinate Lewis bases.[29] Replacement of DME from **3**-I-DME with bipy led to **3**-I-bipy, which was isolated as a green microcrystalline solid in 90% yield (Eq 3).
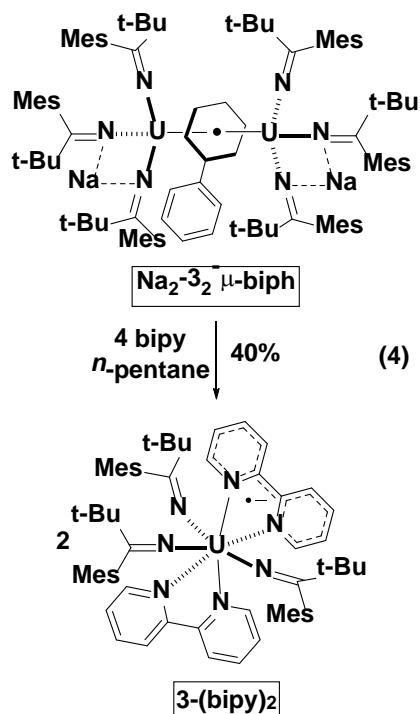
The last compound of the series, **3**-(bipy)₂, was prepared from Na₂(μ-biphenyl)U₂(NC[*t*-Bu]Mes)₆ (Na₂-**3**₂-μ-biph)[31] and

bipy as shown in Eq 4. The reaction of the ketimide diuranium complex Na₂-**3**₂-μ-biph with bipy is more complicated than that of the arene-bridged amide complex **1**₂-μ-toluene. The stoichiometry employed, 4 equivalents of bipy for one arene-bridged dinuclear complex, led to the highest yield of **3**-(bipy)₂. If the only other product of the reaction were M[bipy] (M = Na, K), 6 equivalents of bipy would be necessary. Minor uranium byproducts were observed by investigating the ¹H NMR spectrum of the crude reaction mixture, but those were not identified. Nonetheless, extraction and crystallization from *n*-pentane led to **3**-(bipy)₂ as a dark-brown solid isolated in 40% yield.

X-ray crystallography results

Metrical parameters from X-ray crystal structures can be used to assign the oxidation state of the bipyridyl ligand; such parameters can be associated with donation of electron density into the LUMO of bipy, a π bond (**a** in Figure 1) between the carbon atoms connecting the aromatic rings. Therefore, shortening of the **a** bond and enhanced coplanarity of the two rings are signatures of a bipy ligand coordinated as a radical anion.[4, 46, 47]
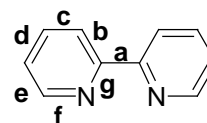
Figure 1. Bond labeling of bipy.

X-ray crystal structures were determined for all four complexes (Figure 2). Acceptance of an electron into the LUMO of bipy would cause the bonds **a**, **c**, and **e** (Figure 1) to shorten and the bonds **b**, **d**, **f**, and **g** to lengthen.[46]

Figure 2. Structural drawing of **1**-(bipy)₂ (top left), **2**-bipy (top right), **3**-(bipy)₂ (bottom left), **3**-I-bipy (bottom right) with thermal ellipsoids at the 50% probability level; hydrogen, solvent atoms and disordered counterparts were removed for clarity.

Table 1. Comparison of distances (Å) in bipy and in discussed complexes.

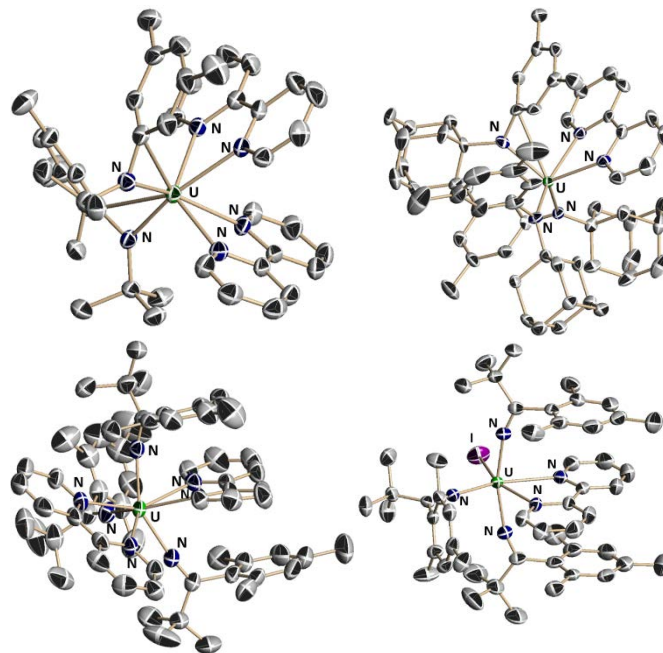| Bond	bipy[46]	**1**-(bipy)$_2$	**2**-bipy	**3**-(bipy)$_2$	**3**-I-bipy
a	1.490(3)	1.429(7); 1.426(7)	1.415(13)	1.471(10); 1.418(10)	1.484(10)
b	1.394(2)	1.409(10); 1.411(10)	1.415(18)	1.396(15); 1.418(13)	1.386(14)
c	1.385(2)	1.368(11); 1.358(11)	1.350(20)	1.353(18); 1.357(17)	1.377(16)
d	1.383(3)	1.395(11); 1.400(11)	1.401(21)	1.374(17); 1.412(18)	1.356(17)
e	1.384(2)	1.353(10); 1.357(10)	1.364(20)	1.381(15); 1.365(16)	1.370(15)
f	1.341(2)	1.353(8); 1.361(8)	1.393(16)	1.324(13); 1.358(13)	1.340(12)
g	1.346(2)	1.388(8); 1.375(8)	1.353(17)	1.352(12); 1.375(11)	1.348(13)

Table 2. Selected distances (Å) and torsion angles (°) in discussed complexes.

Parameter (avg.)	**1**-(bipy)$_2$	**2**-bipy	**3**-(bipy)$_2$	**3**-I-bipy
U-N$_{ligand}$	2.302(6)	2.275(13)	2.263(10)	2.213(9)
U-N$_{bipy}$	2.488(6); 2.454(6)	2.483(10)	2.609(7); 2.528(7)	2.581(7)
N-C-C-N^a	3.2(6); 1.9(6)	3(1)	2.2(9); 2.4(9)	0.90(8)
C-C-C-C^a	5.8(8); 1.9(6)	2(1)	3(1); 5(1)	3(1)

a: torsion angle

Table 3. Optical spectra of bipyridyl complexes (in toluene unless otherwise specified).

Complex	λ_{max} in nm ($\varepsilon \times 10^{-3}$ in M^{-1} cm^{-1})
1-(bipy)$_2$	790 (3.2); 470 (5.1); 415 (7.2); 370 (15.1); 285 (38.8)
2-bipy	891 (3.6); 777 (4.2); 447 (7.1); 370 (17.4); 285 (35.8)
3-(bipy)$_2$	476 (2.8); 423 (4.1); 376 (6.4); 285 (34.4)
3-I-bipy	685 (0.6); 413 (2.7); 307 (12.4)
Na(bipy) in THF[4]	952 (1.3); 833 (1.5); 752 (1.1); 562 (6.5); 532 (6.2); 386 (29.5)

The metrical parameters for the two inequivalent bipy ligands in **1**-(bipy)$_2$ are similar (Table 1) and indicate that both bipy ligands are best considered as radical anions. Similarly, the bipy ligand in **2**-bipy (Table 1) is best viewed as a coordinated radical anion. However, the two bipy ligands in **3**-(bipy)$_2$ have different sets of parameters (Table 1): one of them is consistent with assignment as a radical anion, while the other is consistent with a neutral bipy ligand. Finally, in **3**-I-bipy, the bipy distances suggest the presence of a neutral bipy ligand (Table 1). Interestingly, the neutral bipy ligands in **3**-I-bipy and **3**-(bipy)$_2$ engage in $\pi-\pi$ stacking[48] with the aromatic rings of two ketimide ligands (3.63 and 3.85 Å for **3**-I-bipy and 3.62 and 4.54 Å for **3**-(bipy)$_2$). In all complexes then, uranium can be assigned a +4 formal oxidation state, in agreement with the fact that this oxidation state is encountered most frequently in the organometallic chemistry of uranium.[49]

The distance between uranium and the nitrogen of the supporting ligand (Table 2) can also probe the electronic density present at the uranium center, since it can be compared with corresponding values in non-bipy complexes for which the oxidation state was experimentally estimated by X-ray absorption near-edge structure (XANES) spectroscopy.[30] The average U-N$_{amide}$ distance in **2**-bipy (2.275(13) Å) is closer to the value in IU(N[^{1}Ad]Ar)$_3$ (**2**-I, 2.204(9) Å, +4 oxidation state) than in **2**-THF (2.346(9) Å, +3 oxidation state); in **1**-(bipy)$_2$, this distance is longer (2.302(6) Å), but the amide ligand features a *t*-butyl instead of an adamantyl substituent. For **3**-(bipy)$_2$ and **3**-I-bipy, the average U-N$_{ketimide}$ distances (2.263(10) and 2.213(9) Å, respectively) are similar to the average found in **3**-I-DME (2.189(21) Å). These observations are consistent with the presence of uranium(IV) centers.

The two torsion angles (N-C-C-N and C-C-C-C) between the planes of the two aromatic rings presented in Table 2 have also been used as an indication of the radical anion character of the coordinated bipy ligand. For example, their values are 3° for (Me$_5$C$_5$)$_2$Yb(bipy), in which bipy is considered a radical anion,[4] and 9.94° and 11.80° for UI$_3$(bipy)$_2$(py), in which bipy is

considered a neutral ligand.[24] In all complexes listed in Table 2 the observed values indicate an almost planar bipy molecule, but for **3**-I-bipy and the neutral bipy of **3**-(bipy)$_2$ this could also be a consequence of the $\pi-\pi$ stacking present in the molecules (Figure 2).

NMR spectroscopy studies

All compounds discussed here are paramagnetic, regardless whether bipy is coordinated to the uranium center as a radical anion or as a neutral ligand. Only **1**-(bipy)$_2$ and **2**-bipy have peaks in their ^{1}H NMR spectra that allow variable temperature (VT) studies (Figure 3), for the rest of the compounds the spectra showed relatively broad peaks over a large temperature range. The linear δ versus 1/T plots for **1**-(bipy)$_2$ (Figure 3, -50 to 100 ºC) and **2**-bipy (Figure 3, 20 to 100 ºC) indicate that Curie-Weiss behavior is evident for both species. Accurate determination of δ values below the minimum temperatures indicated was inhibited by excessive peak broadening. Also, some of the shifts corresponding to bipy protons are too broad or not identifiable at lower temperatures. The linear δ versus 1/T plots indicate that no temperature dependent processes occur in solution.[50]

As mentioned above, the bipy-ketimide compounds **3**-(bipy)$_2$ and **3**-I-bipy do not have straightforward ^{1}H NMR spectra, likely a consequence of steric crowding that inhibits rotation of the ancillary ligands in solution (Figure S10). The peaks are broad and some could not be identified. For example, when recording the VT spectra for **3**-I-bipy from 20 to 100 ºC, the peaks broadened and most of them were indistinguishable from the baseline around 40 ºC. In addition, **3**-I-bipy is not very soluble in aromatic solvents and precipitates at temperatures below room temperature. Investigation of ^{1}H NMR spectra of **3**-(bipy)$_2$ as a function of temperature also revealed complicated behavior. At ambient temperature, the number of peaks identifiable (more than 8, 4 for ketimide protons and 4 for bipy protons) indicates that the two ketimide and/or bipy ligands are not equivalent on the NMR time scale due to slow rotation. Some peaks broaden

into the baseline as the temperature was increased, but up to 100 °C, a straightforward spectrum was not obtained. When a spectrum was recorded after returning to room temperature, new peaks were observed, but the decomposition products could not be identified.
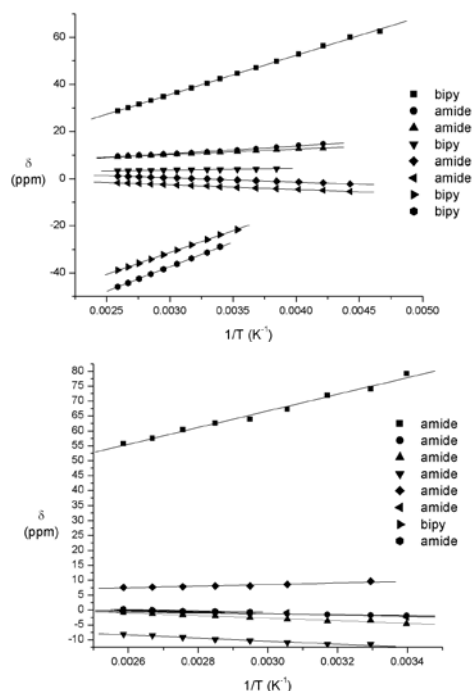

Figure 3. Plots of δ versus 1/T for **1**-(bipy)₂ (top) and **2**-bipy (bottom).

For a series of ytterbocene bipy compounds it was found that a reduced bipy ligand exchanges more slowly with 4,4'-dimethyl-2,2'-bipyridine (dmb) than does a neutral one.[3] Such studies could not be conducted for **3**-I-bipy because of its low solubility in aromatic solvents at room temperature, but were undertaken for the other bipy complexes (Figures S1-7). ^{1}H NMR spectra of solutions of **1**-(bipy)₂ and free bipy or dmb, taken immediately after mixing the two compounds, appeared as the sum of spectra of **1**-(bipy)₂ and bipy or dmb indicating that there is no exchange between the coordinated bipy molecules and free bipy or dmb on the NMR time scale. After three hours, peaks corresponding to **1**-(dmb)₂, independently synthesized and characterized, were visible. Although most of the chemical shifts were not sharp and different enough to allow the identification of more than two uranium compounds, based on the peaks corresponding to some bipy/dmb protons, a third species was also likely present in solution. Since this species shows two sets of peaks for each identifiable proton it was assumed to be the mixed **1**-(bipy)(dmb) compound. The equilibrium between the three species was reached within 5 days with a molar ratio **1**-(bipy)₂ : **1**-(bipy)(dmb) : **1**-(dmb)₂ of approximately 1 : 2 : 1 based on the integration of the peaks mentioned above.

^{1}H NMR spectra of solutions of **2**-bipy and free bipy or dmb also appeared as the sum of the independent spectra of **2**-bipy and free bipy or dmb, when taken shortly after mixing of the compounds. For a solution of **2**-bipy and dmb, although peaks for a new compound could not be observed because of the broadness of signals for **2**-bipy, the appearance of free bipy was not apparent after one day at room temperature, but free bipy did form after an additional day of heating the solution at 80 °C. Interestingly, in (dmb)U(C₅Me₅)(C₈H₈),[25] dmb coordinates as a neutral ligand indicating that the *tris*-amido uranium fragment is more reducing than (C₅Me₅)(C₈H₈).

In contrast to the case of **1**-(bipy)₂ or **2**-bipy and bipy or dmb solutions, investigation by ^{1}H NMR spectroscopy of solutions of **3**-(bipy)₂ and free bipy or dmb indicated that spectra taken within minutes after mixing **3**-(bipy)₂ with bipy or dmb in C₆D₆ were different than the sum of the spectra of the two compounds. A complete assignment of the chemical shifts for these mixtures was not possible due to peak broadening, but the observations made are consistent with the exchange of a bipy ligand with free bipy or dmb.

In similar experiments conducted with ytterbocenes or (Me₅C₅)₂Ca(bipy) it was reported that a neutral bipy ligand exchanged with dmb upon mixing.[4] The VT NMR spectroscopy experiments indicate that there is a slow exchange between **1**-(bipy)₂ and **2**-bipy and bipy or dmb suggesting that the bipy ligands are radical anionic; the fast exchange observed between **3**-(bipy)₂ and bipy or dmb is consistent with the presence of bipy as a neutral ligand.

Absorption spectra

The bipyridyl anion has a diagnostic optical spectrum with three intense (ε ≈ 10³ M⁻¹ cm⁻¹) absorption bands in the 700-1000 nm region.[4] Absorption spectra of **1**-(bipy)₂ and **2**-bipy toluene solutions at 25 °C show high intensity bands (ε ≈ 10³ M⁻¹ cm⁻¹) in the 500-1000 nm region (Figure 4). A comparison with spectra of classical uranium compounds is useful in determining the nature of these bands. Although the absorption spectra of **2**-I or **2**-THF have bands in the 500-1000 nm region,[30] they are not as intense as expected for the bipy radical anion. In accord with other data presented, the high intensity bands observed in the spectra of **1**-(bipy)₂ and **2**-bipy are attributed to transitions of the bipy radical anion (Table 3). Consistent with the presence of bipy coordinated as a neutral ligand in **3**-I-bipy, its UV-vis spectrum lacks the characteristics intense bands in the 700-1000 nm region (Table 3). Such bands are also absent from the UV-vis spectrum of **3**-(bipy)₂, for which X-ray crystallography indicated the presence of one bipy coordinated as a radical anion and one bipy coordinated as a neutral ligand. This finding suggests that under the conditions of the UV-vis experiment the two bipy ligands are equivalent. Similarly, no bands were reported in the region 700-1000 nm from the UV-vis spectrum of LaI₂(bipy)₂(DME), for which X-ray crystallography parameters indicate two equivalent bipy ligands with intermediate character between radical anionic and neutral bipy ligands.[3]
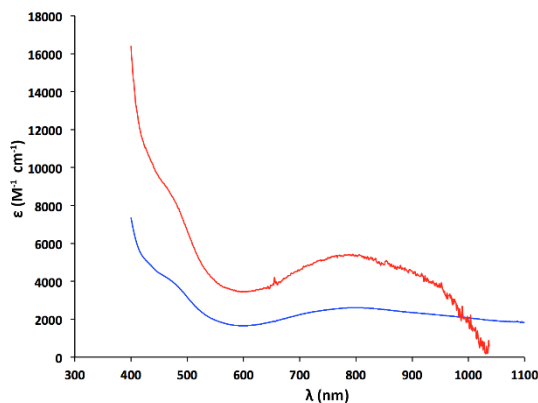
Figure 4. UV-vis absorption spectra of **1**-(bipy)₂ (blue) and **2**-bipy (red) toluene solutions at 25 °C.

The absorption bands discussed above are relevant with respect to assigning the character of bipy as a radical anionic or neutral ligand. In addition, bands present in the UV region (200-400 nm) can be assigned to $\pi \rightarrow \pi^*$ transitions of the arene rings or to ligand to metal charge transfer bands because of their high intensity ($\varepsilon \approx 10^5$ M^{-1} cm^{-1}). Absorption bands present in the visible region (400-800 nm) that have $\varepsilon \approx 10^3$ M^{-1} cm^{-1} could be either f $\rightarrow$ d or charge transfer transitions and they may overlap with transitions due to the radical anionic bipy ligand.

Conclusions

A series of bipyridyl uranium complexes, the *bis-* and *tris*-amidouranium complexes **1**-(bipy)₂ and **2**-bipy and the *tris*-ketimidouranium complexes **3**-(bipy)₂ and **3**-I-bipy, was synthesized and characterized. Their solid-state molecular structures indicate that bipy coordinates as a radical anion in **1**-(bipy)₂ and **2**-bipy, leading to uranium(IV) centers, and as a neutral ligand in **3**-I-bipy, in which uranium was already in the +4 oxidation state. In **3**-(bipy)₂, the crystallographic parameters indicate that one bipy is coordinated as a radical anion, while the other is coordinated as a neutral ligand. These findings are not surprising since the +4 oxidation state is most frequently encountered in the organometallic chemistry of uranium. The radical anionic character of bipy in **1**-(bipy)₂ and **2**-bipy was corroborated by ligand exchange studies, monitored by ¹H NMR spectroscopy, and by absorption spectroscopy.

Experimental

General considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. Anhydrous diethyl ether was purchased from Mallinckrodt; *n*-pentane, *n*-hexane and tetrahydrofuran were purchased from EM Science. Diethyl ether, toluene, benzene, *n*-pentane, and *n*-hexane were dried and deoxygenated by the method of Grubbs.[51] THF was distilled under nitrogen from purple sodium benzophenone ketyl. Distilled solvents were transferred under vacuum into glass bombs before being transferred into a Vacuum Atmospheres dry box. C₆D₆ and toluene-*d*₈ were purchased from Cambridge Isotopes and were degassed and dried over 4 Å sieves. 4 Å sieves, alumina, and Celite were dried *in vacuo* overnight at a temperature just above 200 °C. Compounds **1**₂-μ-toluene,[29] **2**-THF,[30] Na₂-**3**₂-μ-biphenyl,[31] and **3**-I-DME[32] were prepared according to literature methods. 2,2'-Bipyridine and 4,4'-dimethyl-2,2'-bipyridine were dissolved in diethyl ether and THF, respectively, and their solutions passed through alumina. The crystalline solids obtained from concentrated solutions at −35 °C were extensively dried under vacuum (6-12 h) before use. Other chemicals were used as received. ¹H NMR spectra were recorded on Varian XL-300 or Varian INOVA-501 spectrometers at room temperature unless otherwise specified. Chemical shifts are reported with respect to internal or external solvent, 7.16 ppm (C₆D₆). UV-vis spectra were recorded on a HP spectrophotometer from 200 to 1100 nm using matched 1 cm quartz cells; all spectra were obtained using a solvent reference blank. Numerical modeling of all data was done using the program Origin 6.0. CHN analyses were performed by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Synthesis of 1-(bipy)₂. **1**₂-μ-toluene (0.253 g, 0.199 mmol) and bipy (0.124 g, 0.794 mmol, 4 equiv) were each dissolved in 5 mL of toluene and the two solutions were frozen. The thawing bipy solution was added dropwise to the stirring thawing solution of **1**₂-μ-toluene. After 35 min, volatiles were removed under reduced pressure, the product mixture was extracted with 20 mL of *n*-pentane and the extract filtered through Celite. The volatiles were removed under reduced pressure again and the extraction with *n*-pentane repeated. After filtration through Celite and concentration to 10 mL, 0.211 g (0.234 mmol) of the desired product, **1**-(bipy)₂, (59% yield) was obtained as dark brown crystals from cooling the above solution to -35 °C (after three days). A second crop was obtained after ca. two weeks from concentrating the mother liquor and cooling it to -35 °C (0.044 g, 0.049 mmol, total yield of 71%). ¹H NMR (300 MHz, C₆D₆, 22 °C): δ = 41.76 (s, 2H, *bipy*); 11.43 (s, 1H, *p*-Ar); 11.27 (s, 9H, *t-Bu*); 3.80 (s, 2H, *o*-Ar); -0.35 (s, 2H, *bipy*); -3.42 (s, 6H, *Me*-Ar); -23.22 (s, 2H, *bipy*); -28.57 (s, 2H, *bipy*). UV-vis (toluene, 22 °C): λ_max (nm, ε × 10⁻² M⁻¹, cm⁻¹) = 285 (387.9 ± 13.5); 370 (150.7 ± 12.3); 415 (71.8 ± 5.3); 470 (51.1 ± 3.7); 790 (32.3 ± 2.4). Anal. calcd. for C₄₄H₅₂N₆U: C, 58.47; H, 5.76; N, 9.30. Found: C, 58.55; H, 5.92; N, 9.36.

Synthesis of 1-(dmb)₂. A similar procedure as for **1**-(bipy)₂, using 4,4'-dimethyl-2,2'-bipyridyl (dmb) instead of bipy was followed. Yield: 53%. ¹H NMR (300 MHz, C₆D₆, 22 °C): δ = 39.10 (s, 2H, *bipy*); 28.33 (s, 6H, C*H*₃-bipy); 11.45 (s, 9H, *t-Bu*); 11.26 (s, 1H, *p*-Ar); -0.60 (s, 2H, *bipy*); -2.11 (s, 2H, *o*-Ar); -3.39 (s, 6H, *Me*-Ar); -38.17 (s, 2H, *bipy*). Anal. calcd. for C₄₈H₆₀N₆U: C, 60.06; H, 6.26; N, 8.76. Found: C, 59.85; H, 6.25; N, 8.70.

Synthesis of 2-bipy. Compound **2**-THF (0.136 g, 0.12 mmol) and bipy (0.019 g, 0.12 mmol, 1 equiv) were each dissolved in 3 mL of diethyl ether and the two solutions frozen. The thawing bipy solution was added dropwise to the stirring thawing solution of **2**-THF. After 1 h, volatiles were removed under vacuum, the product mixture was extracted with 10 mL of *n*-pentane and the extract filtered through Celite. The volatiles were removed under reduced pressure again and the extraction with *n*-pentane repeated. After filtration through Celite and concentration to 3 mL, 0.103 g (0.09 mmol, 73% yield) of the desired product, **2**-bipy, was obtained as dark brown crystals from cooling the above solution to -35 °C (after five days). ¹H NMR (500 MHz, C₇D₈, 80 °C): δ = 60.39 (s, 1H, *p*-Ar); 7.82 (s, 2H, *o*-Ar); -0.31 (s, 3H, Ad distal C*H*₂); -0.74 (s, 3H, Ad distal C*H*₂); -0.94 (s, 6H, Ad proximal C*H*₂); -1.65 (s, 3H, Ad C*H*); -9.13 (s, 6H, *Me*-Ar). UV-vis (toluene, 22 °C): λ_max (nm, ε × 10⁻² M⁻¹, cm⁻¹) = 285 (304.3 ± 25.9); 388 (107.7 ± 13.7); 426 (48.7 ± 9.2); 482 (33.0 ± 7.7); 850 (17.8 ± 5.7). Anal. calcd. for C₆₄H₈₀N₅U: C, 66.41; H, 6.97; N, 6.05. Found: C, 66.33; H, 6.76; N, 6.45.

Synthesis of 3-(bipy)₂. Na₂-**3**₂-μ-biphenyl (0.115 g, 0.06 mmol) and bipy (0.038 g, 0.24 mmol, 4 equiv) were dissolved each in 3 mL of *n*-pentane and the two solutions were frozen. The thawing bipy solution was added dropwise to the stirring thawing solution of Na₂-**3**₂-μ-biphenyl. After 0.5 h, volatiles were removed under vacuum, the product mixture was extracted with 10 mL of *n*-pentane and the solution filtered through Celite. The volatiles were removed under reduced pressure again and the *n*-pentane extraction repeated. After filtration through Celite and concentration to 3 mL, 0.043 g (0.09 mmol, 31% yield) of the desired product, **3**-(bipy)₂, was obtained as dark brown crystals from cooling the above solution to -35 °C (after six days). ^{1}H NMR (500 MHz, C_7D_8, 80 °C): δ = 19.86 (s), 11.82 (s), 8.68 (s), 8.23 (s), 7.45 (s), 6.71 (s), 6.22 (s), 1.87 (s), -3.14 (s), -3.36 (s). UV-vis (toluene, 22 °C): $λ_{max}$ (nm, ε × 10^{-2} M^{-1}, cm^{-1}) = 476 (2.8); 423 (4.1); 376 (6.4); 285 (34.4). Anal. calcd. for $C_{62}H_{76}N_7U$: C, 64.37; H, 6.57; N, 8.48. Found: C, 64.36; H, 6.75; N, 8.63.

Synthesis of 3-I-bipy. Diethyl ether solutions of **3**-I-DME (1.220 g, 1.149 mmol, 40 mL) and of bipy (0.179 g, 1.149 mmol, 1 equiv, 12 mL) were frozen. The thawing bipy solution was added dropwise to the thawing and stirring uranium solution and the reaction mixture was warmed up to room temperature. After 2 h, the volatiles were removed under reduced pressure, 10 mL of *n*-pentane added to the solid and the slurry filtered. The solid was dried under reduced pressure and it amounted to 1.140 g of **3**-I-bipy (1.011 mmol, 88% yield). ^{1}H NMR (300 MHz, C_6D_6, 80 °C): δ = 44.60 (s), 20.50 (s), 15.34 (s), 7.50 (s), -3.21 (s), -16.80 (s), -19.25 (s). UV-vis (toluene, 22 °C): $λ_{max}$ (nm, ε × 10^{-2} M^{-1}, cm^{-1}) = 307 (123.8 ± 14.9); 413 (26.8 ± 1.1); 685 (5.9 ± 0.1). Anal. calcd. for $C_{52}H_{68}N_5IU$: C, 55.37; H, 6.08; N, 6.21. Found: C, 55.18; H, 6.54; N, 5.74.

Exchange of coordinated bipy with free bipy or dmb. Solutions in C_6D_6 of uranium compounds and free bipy (not exact amounts) were loaded into an NMR tube and their ^{1}H NMR spectra recorded. For the exchange with dmb, ca. 0.01 mmol of uranium compound and stoichiometric amounts of dmb (1 or 2 equiv, depending on the number of coordinated bipy molecules) were dissolved in C_6D_6 or toluene-d_8, and the solutions transferred to an air-free NMR tube. Spectra of these solutions were recorded periodically, as specified in the text.

X-ray crystal structures. The X-ray data collections were carried out on a Siemens Platform three-circle goniometer with a CCD detector using Mo-K□ radiation (λ = 0.71073 Å). The data were processed utilizing the program SAINT supplied by Siemens Industrial Automation, Inc. The structures were solved by direct methods (SHELXTL v5.03, Sheldrick, G. M., and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques.

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Notes and references

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