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Exploring the Redox Properties of Bench-Stable Uranyl(VI) Diamido–Dipyrrin Complexes

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ABSTRACT: The uranyl complexes UO2(OAc)(L) and UO2Cl-(L) of the redox-active, acyclic diamido–dipyrrin anion L are reported and their redox properties explored. Because of the inert nature of the complexes toward hydrolysis and oxidation, synthesis of both the ligands and complexes was conducted under ambient conditions. Voltammetric, electron paramagnetic resonance spectroscopy, and density functional theory studies show that one-electron chemical reduction by the reagent CoCp2 leads to the formation of a dipyrrin radical for both complexes [Cp2Co][UO2(OAc)(L•)] and [Cp2Co][UO2Cl(L•)].

INTRODUCTION

Redox-active ligands, also referred to as redox-noninnocent ligands, continue to fascinate and perplex chemists. While the ability of these ligands to adopt multiple stable oxidation states often hinders analysis of the electronic structures of metal complexes, the reactivity of metals can be expanded by their action as electron reservoirs, altered Lewis acids, and reactive ligand radicals and in enabling ligand-to-substrate electron transfer.1–3 Although the chemistry with transition metals has been vastly explored, there has only recently been a rise in interest of actinide complexes of redox-active ligands, in particular those of uranium.4–6

Uranium is most commonly present as the uranyl(VI) dication UO22+ under ambient conditions. This dioxide adopts a linear [O=U=O]2+ structure in which the axial oxygen atoms (Oax) are strongly bound to the uranium center.7 As a result, UO22+ is very stable in terms of both kinetics and thermodynamics. Even so, the reduction of uranyl(VI) to uranium(IV) via the unstable uranyl(V) cation UO2+ is an important aspect of uranium remediation by immobilization, and significant advances have been made in the isolation and study of reduced uranyl complexes, e.g., in oxometalated and oxosilylated uranyl(V) compounds.8

Uranyl complexes of redox-active ligands, such as Schiff bases,7,9 quinones,4 and pyrroles in, for example, tetraaza[14]-annulenes,10 calix[4]pyrroles,8 and dipyrrins,15–15 have been reported. Because of the added redox character of these ligands, the complexes react differently under reducing conditions. For example, uranyl(VI) complexes of pentadentate N2O2-saldien ligands with various substituents all underwent one-electron uranium reduction to afford the corresponding uranyl(V) complex, regardless of the difference in the substituents.16 In contrast, the uranyl(VI) α-di-imine diphenolate (1) (Figure 1) and uranyl(VI) salophens undergo one-electron reduction of the ligand, leading to ligand-centered radical anions and not the expected uranyl(V) complexes.9,10,17

Figure 1. Structures of uranyl(VI) di-imine and dipyrrin complexes.

Dipyrrins are popular because of their effective absorption of visible light through π−π* transitions, forming colorful and luminescent metal complexes.18,19 Uranyl complexes of dipyrrin ligands can be readily accessed through anhydrous, salt metathesis routes.13 We recently reported the redox behavior of the donor-expanded Schiff-base uranyl(VI) dipyrrin complex 2 (Figure 1) and its contrasting but controlled inner- and outer-sphere redox chemistry. The use of 1 equiv of the outer-sphere reductant CoCp2 resulted in one-electron reduction of the ligand to a dipyrrin radical. The addition of a second equiv of CoCp2 reduced the uranium center to uranyl(V). The reaction of 2 with 1 equiv of the inner-sphere reductant [TiCp2Cl]2 led to the formation of a doubly titanated uranium(IV) complex.14 In addition, the
effects of both the equatorial coordination sphere and axial oxo–ligand bonding in 2 were investigated, showing that it is possible to shift the nonaqueous uranyl(VI/V) and uranyl(V/IV) reduction potentials to values in the range accessible to reductants that are present in uranium remediation processes and in nuclear fuel storage. However, these dipyrin complexes all display air sensitivity and therefore need to be handled accordingly.

This study presents the formation of easy-to-synthesize and bench-stable uranyl complexes of a diamidodipyrrin ligand and an evaluation of their reduction properties. A similar ligand has previously been exploited in the formation of boron and transition-metal complexes, such as nickel, copper, and cobalt, although these studies mainly focused on the rich coordination chemistry of these ligands. We rationalized that the use of these ligands would deliver a uranyl complex that would potentially be resistant toward oxidation reactions and hydrolysis, while maintaining its redox properties.

■ RESULTS AND DISCUSSION

Synthesis and Structures of Uranyl(VI) Complexes.
The synthesis of HL was achieved using a modification of previously reported procedures (Scheme 1). The amination of (trichloroacetyl)pyrrole was conducted in neat, boiling tert-butylamine; however, because of the steric demand of tert-butylamine, the pyrrole amide 4 was synthesized in lower yield compared with the literature derivatives. The second step was an acid-catalyzed condensation that led to formation of the dipyrromethane 5 in 36% yield. In contrast to acyclic Schiff-base dipyrin ligands made previously in our group, 5 did not spontaneously oxidize during its synthesis and required additional oxidant (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ) to form the dipyrin HL, which was readily purified using silica chromatography. The formation of HL was indicated not only by the disappearance of the dipyrrolic proton singlet at 5.86 ppm in the $^1$H NMR spectrum but also by the intensely orange solid obtained, typical of the dipyrin chromophore (see the Supporting Information, SI). The reaction between HL, triethylamine, and 1 equiv of uranyl acetate [UO$_2$O(OAc)$_2$·2H$_2$O] or uranyl chloride [UO$_2$Cl$_2$(THF)$_2$] (THF = tetrahydrofuran) in a mixture of methanol (MeOH) and CHCl$_3$ (1:3, v/v) in air led to rapid color changes from an orange to a dark-pink solution (Scheme 2). The acetate complex UO$_2$(OAc)(L) was obtained in 77% yield as a dark-pink solid, and the chloride UO$_2$Cl(L) was obtained in 91% yield as a dark-reddish-pink solid after aqueous workups. While no additional purification steps were required for UO$_2$(OAc)(L), UO$_2$Cl(L) was heated in chloroform to ensure the formation of a single product. The second product is likely the ion pair [UO$_2$(solvent)(L)][Cl] formed through ready dissociation of the chloride anion. The chloride complex UO$_2$Cl(L) may also be prepared via KL using air-sensitive methods.

Formation of the uranyl complexes was indicated by the disappearance of the pyrrole N–H proton at 12.69 ppm for HL and the downfield shift of the pyrrole peaks in the $^1$H NMR spectra (see the SI). Both complexes adopt C$_{5h}$ symmetry in solution, which is also seen in the $^{19}$F NMR spectra, with three resonances indicating horizontal planar symmetry. In addition, the $^1$H NMR spectrum of UO$_2$(OAc)$_2$(L) contains a broad singlet at 2.17 ppm with an integration of 3H that is assigned to the coordinated acetate ion; this fluxionality of the acetate means that it is not easily identified in the $^{13}$C($^1$H) NMR spectrum. The chloride complex UO$_2$Cl(L) was also prepared under nonaqueous conditions: the reaction between KL (formed in situ by the reaction of HL and KH in THF) and UO$_2$Cl$_2$(THF)$_2$ in THF formed UO$_2$Cl(L) in high yield.

Crystals suitable for X-ray analysis were grown for HL, UO$_2$(OAc)(L) and UO$_2$Cl(L) (Figures 2 and 3). Weakly diffracting orange plates of HL were crystallized from a concentrated dimethyl sulfoxide (DMSO) solution, and so the X-ray structure is reported to show connectivity only. HL did not display any intermolecular hydrogen bonding and instead displayed hydrogen bonding between the amide N4–H and the O3 atom of the DMSO solvate molecule.

Greenish-pink blocks of UO$_2$(OAc)(L) were grown through the slow evaporation of a concentrated THF solution. The asymmetric unit comprises two molecules that differ primarily in the orientation of the monodentate acetate group, supporting the fluxionality of this anion seen in solution by NMR spectroscopy. In the solid state, the complex adopts a distorted pentagonal-bipyrimidal coordination geometry, in which the ONNO donor set of the expanded dipyrin ligand

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**Scheme 1. Synthesis of HL**

![Scheme 1](image1)

“Reaction conditions: (i) neat 1BuNH$_2$, reflux, 16 h; (ii) 0.5 equiv of C$_6$F$_5$CHO, 5 mol % p-TSA, PhCH$_3$, reflux, 16 h; (iii) 1.1 equiv of DDQ, THF, RT, 24 h.

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**Scheme 2. Synthesis of Uranyl Complexes of HL**

![Scheme 2](image2)

“Reaction conditions: (i) 1.1 equiv of UO$_2$(OAc)$_2$·2H$_2$O or UO$_2$Cl$_2$(THF)$_2$, NEt$_3$, MeOH/CHCl$_3$ (1:3, v/v), heated to reflux in air for 16 h; (ii) 1.5 equiv of KH under N$_2$, THF, RT, 16 h, followed by the addition of UO$_2$Cl$_2$(THF)$_2$; (iii) 1 equiv of CoCp$_2$, THF, RT, 16 h.

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**Figure 2.** X-ray crystal structure of HL viewed from the side and top. For clarity, all hydrogen atoms except those involved in hydrogen bonding are omitted (displacement ellipsoids are drawn at 50% probability).
occupies the equatorial positions along with the acetate ligand. This shows ONNO coordination geometry similar to that of Cu(DADPph$_{2}$)$_{2}$Cl (DADPph$_{2}$ = 1,1'-isopropylamido-5-phenyl-4,6-dipyrrinato) in which the equatorial position is occupied by a chloride ligand.\textsuperscript{20} The uranium coordinates to the oxygen atoms of the amide groups, as seen with other uranyl(VI) amide complexes.\textsuperscript{25} The O$_{in}$–U1 and U1–O$_{as}$ bond lengths are 1.774(2) and 1.759(2) Å, respectively, with an O$_{ax}$–U1–O$_{as}$ angle of 177.9(2)$^\circ$ and are fully consistent with uranyl(VI). The U1–N$_{pyrrole}$ bond lengths are 2.514(5) and 2.505(6) Å, the U1–O$_{amide}$ bond lengths are 2.315(1) Å, and the U1–O$_{pyrrole}$ is 2.314(5) Å.

Pink crystals of UO$_2$(Cl$_2$) were grown by the slow evaporation of a THF solution, and the X-ray crystal structure is similar to that of UO$_2$(OAc)$_2$ (L). In this case, the O$_{in}$–U1 and U1–O$_{as}$ bond lengths are 1.774(2) and 1.759(2) Å, respectively, with an O$_{ax}$–U1–O$_{as}$ angle of 177.54(9)$^\circ$. The U1–N$_{pyrrole}$ bond lengths are 2.508(2) and 2.517(2) Å, while the U1–O$_{amide}$ bond lengths are 2.389(2) and 2.406(2) Å. The U1–Cl bond length is 2.7018(6) Å, which is close to the U–Cl bond length of the dipyrrin–diamine analogue 2, 2.710(1) Å.\textsuperscript{14} Both complexes exhibit U–O$_{ax}$ bond lengths and O$_{ax}$–U–O$_{as}$ angles in the range of other unfunctionalized uranyl(VI) complexes, in which an average U–O$_{ax}$ bond of 1.777 Å is seen.\textsuperscript{3} In addition, the U–O$_{amide}$ bond distance is similar to those found in other uranyl(VI) amide complexes (typically 2.34–2.40 Å).\textsuperscript{25}

\textbf{Electrochemistry.} The cyclic voltammograms (CVs) of HL, UO$_2$(OAc)$_2$(L), and UO$_2$Cl$_2$(L) were recorded in acetonitrile (MeCN) at a scan rate of 100 mV s$^{-1}$ (Figure 4). The CV of HL features a quasi-reversible reduction at $E_{1/2}$ = −1.15 V versus ferrocene/ferrocnium (Fc/Fc$^+$) and an irreversible reduction at $E_p$ = −1.99 V versus Fc/Fc$.^\circ$. The first reduction appears reversible when isolated in the CV (Figure 4, dotted line). This feature is significantly less negative than that of the analogous diimine–dipyrrin ligand (seen in 2), which displays a reversible reduction at $E_{1/2}$ = −1.51 V versus Fc/Fc$^+$ in CH$_2$Cl$_2$.\textsuperscript{14} Although the diamide ligand is more easily reduced than the diimine analogue, this is not true of their corresponding complexes. The CV of UO$_2$(OAc)$_2$(L)

Figure 3. X-ray crystal structures of UO$_2$(OAc)$_2$(L) (a and c) and UO$_2$Cl$_2$(L) (b and d) viewed from the side and top. For clarity, all hydrogen atoms except on amide N1 and N4 are omitted (displacement ellipsoids drawn at 50% probability).

Figure 4. Stacked CVs for HL, UO$_2$(OAc)$_2$(L) and UO$_2$Cl$_2$(L). All measured as 1 mM MeCN solutions (0.1 M [Bu$_4$N][PF$_6$] supporting electrolyte, glassy-carbon working electrode, platinum gauze counter electrode, and silver wire quasi-reference electrode). Potentials are referenced against the Fc/Fc$^+$ couple recorded under identical conditions.
[UO₂(OAc)(L⁺)] and [Cp₂Co][UO₂Cl(L⁺)] show a relatively sharp line devoid of hyperfine structure synonymous with the formation of an S = 1/2 species (see the SI). Both compounds show gₘₒₓ = 1.997, a value significantly shifted from that of the free electron (2.0023). These data are consistent with a ligand-centered reduction affording [UO₂(X)(L⁺)]⁻, where the presence of the coordinated uranium(VI) ion not only has instigated the g shift but also broadened the line, obscuring all hyperfine splitting from the various spin-active nuclei in the dipyrrin. No signal for a uranyl(V) complex (UO₂(X)(L⁺)) would be expected to be seen at RT.

**Electronic Spectroscopy.** The absorbance spectra of HL acetate, chloride uranyl complexes UO₂(X)(L), and reduced complexes [Cp₂Co][UO₂(X)(L⁺)] were recorded (Figure 5).

![Figure 5](https://doi.org/10.1021/acs.inorgchem.1c03744)

Figure 5. UV–vis spectra of HL in CH₂Cl₂, UO₂(OAc)(L) and UO₂Cl(L) in THF, and [Cp₂Co][UO₂(OAc)(L⁺)] and [Cp₂Co][UO₂Cl(L⁺)] in pyridine.

HL has a maximum absorbance of 470 nm (ε = 27280 M⁻¹ cm⁻¹) and is similar to the previously synthesized derivatives. Upon metalation to form the uranyl complexes UO₂(X)(L), the easy-to-visualize color change is reflected in the UV–vis spectrum with significant red shifts observed relative to HL; the absorbance is independent of the anion, and both complexes exhibit a maximum absorbance at 546 nm (ε = 82316 M⁻¹ cm⁻¹) along with a second, weaker band at 510 nm and a shoulder at 478 nm. The reduced compounds [Cp₂Co][UO₂(X)(L⁺)] are poorly soluble in THF, and measurements were therefore carried out in pyridine. Both compounds exhibit near-identical spectra. The intense absorption of the dipyrrin chromophore in the UV and visible regions that took place before 300 nm has now shifted dramatically and can be seen just before 400 nm. The maximum absorbance has also shifted to 500 nm (ε = 45700 M⁻¹ cm⁻¹).

**Density Functional Theory (DFT) Calculations.** The occurrence of one-electron reduction of the diamido-dipyrrin ligand and not the uranium center in the uranyl complexes is supported by computational analysis. DFT calculations were undertaken on both UO₂(OAc)(L) and UO₂Cl(L) and their one-electron-reduction products. The former experiments reveal that the lowest unoccupied molecular orbitals (LUMOs) of both complexes are located entirely on the ligand, whereas in contrast, the LUMOs+1 are metal-based, indicating that one-electron reductions should indeed lead to ligand-based radicals (Figure 6). Furthermore, the LUMOs+1 suggest that the second reduction should lead to uranium reduction, i.e., to the formation of uranyl(V) complexes. The singly occupied molecular orbitals (SOMOs) of [UO₂(OAc)-(L⁺)] and [UO₂Cl(L⁺)] are also ligand-based, and the unpaired spin-density maps of both show that the electron density is located entirely on the meso-carbon of the ligand, furthermore confirming the radical character of the ligand after one-electron reduction.

As shown previously, the CV of UO₂Cl(L) exhibits another similar set of reductions, and it was concluded that this was due to the lability of the chloride, forming the ion pair [UO₂(MeCN)(L)][Cl] in solution. A study conducted previously in the group, however, demonstrated that the cation of 2, [UO₂(L⁺)][BAF₂], first undergoes uranyl(V)/uranyl(V) reduction rather than the formation of a ligand radical (L²⁺ = dipyrrin–dimine ligand). Therefore, to ensure that UO₂Cl(L) and [UO₂(MeCN)(L)][Cl] exhibit similar reactivity, the LUMOs of both UO₂Cl(L) and [UO₂(L⁺)]⁺ were compared with those of 2 and [UO₂(L²⁺)]⁺ (see the SI). These calculations show that the LUMOs of both UO₂Cl(L) and UO₂Cl(L²⁺) are ligand-based. While the LUMO of [UO₂(L⁻)]⁺ exhibits both ligand and metal character and results experimentally in uranyl(V)/uranyl(V) reduction, the LUMO of [UO₂(L⁺)]⁺ is fully ligand-based. This supports the theory that the second species seen in the CV is likely the ion pair [UO₂(MeCN)(L)][Cl] and that this compound exhibits similar reactivity to the parent UO₂Cl(L).

**CONCLUSIONS**

The diamido–dipyrrin ligand acts as a tetradentate chelate for the uranyl dication and, because of its low-lying π* molecular orbitals, is a redox-nonninnocent partner in the reduction chemistry of its uranyl complexes. The uranyl complexes UO₂(OAc)(L) and UO₂Cl(L) are both insensitive toward hydrolysis and could therefore be easily prepared and stored on the bench. In addition, both complexes undergo one-
electron reduction when reacted with CoCp₂, leading to ligand radicals rather than uranyl(V) complexes. Although attempts to crystallize the singly reduced complexes were unsuccessful, EPR, cyclic voltammetry, and DFT studies support the presence of a ligand radical. Our current investigations are focused on manipulation of the redox behavior of similar dipyrrin ligands in order to form air-stable uranyl(V) dipyrrin complexes.

**EXPERIMENTAL SECTION**

**General Procedure. Caution!** Depleted uranium (primary isotope 238U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47 × 109 years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert-atmosphere glovebox in a radiation laboratory equipped with α- and β-counting equipment. The syntheses of all air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under an atmosphere of dry argon. Vacuum Atmospheres and MBraun gloveboxes were used to manipulate and store air- and moisture-sensitive compounds under an atmosphere of dried and deoxygenated dinitrogen. The solvents pyridine-d₅ and THF-d₈ were refluxed over potassium metal overnight, trap-to-trap-distilled, and three times free-pump-thaw-degassed prior to use. All glassware was dried in an oven at 160 °C, cooled under 10–3 mbar vacuum, and then purged with argon. Prior to use, all Fisherbrand R 1.2 mm retention glass microfiber filters and stainless-steel cannulae were dried in an oven at 160 °C overnight. All solvents for use with air- and moisture-sensitive compounds were stored in Teflon-tapped ampules containing predried 4 Å molecular sieves. Solvents were collected from a solvent purification system (Innovation Technologies), where they had been passed over a column of molecular sieves for 24 h prior to collection. They were then degassed prior to use and subsequent storage. All chemicals were used as received without any purification, unless otherwise specified. Tetrabutylammonium hexafluorophosphate, [nBu₄N][PF₆], was recrystallized twice from absolute EtOH and further dried for 2 days under vacuum.

1H NMR spectra were recorded on a Bruker AVA400 spectrometer operating at 399.90 MHz, a Bruker AVA500 or a Bruker PRO500 spectrometer operating at 500.12 MHz, or a Bruker AVA600 spectrometer operating at 599.81 MHz. 13C{1H} NMR spectra were recorded on a Bruker AVA400 or a Bruker PRO500 spectrometer operating at 125.76 MHz. 19F{1H} NMR spectra were recorded on a Bruker AVA500 spectrometer operating at 470.59 MHz. Chemical shifts are reported in parts per million. 1H and 13C{1H} NMR spectra are referenced to residual solvent resonances calibrated against an external standard, SiMe₄ (δ = 0 ppm). 19F{1H} NMR spectra are referenced to an external standard, CCl₃F (δ = −152.8 ppm). 13C{1H} NMR spectra are referenced to residual solvent resonances calibrated against an external standard, CCI₆ (δ = −128.0 ppm). 19F{1H} NMR spectra are referenced to an external standard, SiMe₄ (δ = 0 ppm). All spectra were recorded in CCl₄ at 120 °C.

All programs were used within the Supporting Information.

Single-crystal X-ray diffraction data were collected at 120 K on an Oxford Diffraction Xcalibur diffractometer using graphite-monochromated Mo Kα radiation equipped with an Eos CCD detector (λ = 0.71073 Å) or at 120 K on a Supernova Dual Cu at Zero Atlas diffractometer using Cu Kα radiation (λ = 1.5418 Å). Structures were solved using ShelXT direct methods or intrinsic phasing and refined using a full-matrix least-squares refinement on F² using ShelXL. 2D All programs were used within the OLEX suite. All non-hydrogen atoms were treated using anisotropic displacement and H parameters were constrained to parent atoms and refined using a riding model unless otherwise specified. All single-crystal X-ray structures were analyzed and illustrated using Mercury 4.3.1.

Elemental analyses were carried out by Elemental Microanalysis Ltd., measured in duplicate. All Fourier transform infrared (FTIR) spectra were recorded using a JASCO 410 or a JASCO 460 plus spectrometer. Intensities are assigned as w = weak, m = medium, and s = strong. All UV–vis absorption spectra were recorded on a Jasco V-670 spectrometer on a 10 mm quartz cuvette, fitted with a septum for air-sensitive compounds.

**Synthesis. 4.** (Trichloroacetyl)pyrrole (4.8 g, 23 mmol, 1.0 equiv) was added to 50 mL of freshly distilled tert-butylamine, and the mixture was heated to 50 °C for 1 h. The solvent was removed under reduced pressure. The solid was washed with n-hexane (3 × 100 mL), and the remaining white solid was recrystallized from a hot ethanol (EtoH) solution. Yield: 1.42 g (39%). 1H NMR (400 MHz, MeOD-d₄): δ = 6.86 (1H, dd, J = 2.6 and 1.4 Hz), 6.75 (1H, dd, J = 3.7 and 1.4 Hz), 6.12 (1H, dd, J = 3.7 and 2.6 Hz), 1.43 (9H, s). 13C{1H} NMR (101 MHz, MeOD-d₄): δ = 158.51, 126.50, 120.95, 110.34, 108.56, 50.80, 27.90. HRMS (ESI+, MeOH). Calcd for C₇H₆N₄O ([M + H]+): m/z 261.1778. Found: m/z 261.1775 (mass error = −0.007 ppm).

5. (2.4 g, 17.4 mmol, 2.0 equiv) was added to PhCH₃ (80 mL). Pentafluorophenylhexylbenzene (1.5 g, 7.6 mmol, 1.0 equiv) and p-toluenesulfonic acid (p-TSA; 40 mg, 0.23 mmol, 0.03 equiv) were added to the gray suspension before the mixture was set to reflux. After 20 h, the reaction was cooled to RT. The solids were filtered and washed with PhCH₃ (3 × 10 mL). The isolated white solid was recrystallized from n-hexane, resulting in a white powder. Yield: 1.45 g (36%). 1H NMR (400 MHz, DMSO-d₆): δ = 11.33 (2H, s), 7.21 (2H, s, 2H), 6.70 (2H, dd, J = 3.7 and 2.5 Hz), 5.86 (1H, s), 5.73 (2H, t, J = 3.1 Hz), 3.59 (s, 18H). 13C{1H} NMR (101 MHz, DMSO-d₆): δ = 160.81, 146.50, 141.97, 132.71, 127.56, 116.13, 110.54, 108.49, 108.03, 50.87, 32.96, 29.33. 19F{1H} NMR (376 MHz, DMSO-d₆): δ = −141.28 (2F, dd, J = 24.0, 6.9 Hz), −157.60 (1F, t, J = 22.7 Hz), −163.31 (2F, td, J = 23.7 and 7.0 Hz). HRMS (ESI+, MeOH). Calcd for C₂₉H₂₅F₆N₅O ([M + H]+): m/z 511.2126. Found: m/z 511.2110 (mass error = −0.089 ppm). Calcd for C₂₉H₂₉F₆N₅O₂ ([M + Na]+): m/z 533.1943. Found: m/z 533.1928 (mass error = −1.84 ppm). Elem anal. Calcd for C₂₉H₂₉F₆N₅O₂ (MW = 510.2 g mol⁻¹): C, 58.82; H, 5.33; N, 10.97. Found: C, 58.95; H, 5.36; N, 10.85. FTIR (film): v_MAX 1581 cm⁻¹ (C=O=ONH).
127 mg (77%). 1H NMR (400 MHz, MeOH-d$_4$): $\delta_H$ 7.59 (2H, $d, J = 4.5$ Hz), 7.15 (2H, $d, J = 4.5$ Hz), 2.17 (3H, bs), 1.80 (18H, s). 13C($^1$H) NMR (126 MHz, MeOH-d$_4$): $\delta_C$ 169.76, 158.86, 144.80, 143.44, 142.21, 137.67, 137.41, 133.53, 128.46, 119.00, 54.04, 27.70. 19F($^1$H) NMR (376 MHz, MeOH-d$_4$): $\delta_F$ = -141.82 (2F, dd, $d, J = 21.3$ and 5.9 Hz), -155.06 (1F, $d, J = 20.6$ Hz), -163.97 (2F, td, $d, J = 20.7$ and 6.0 Hz). HRMS (ESI$, MeOH$). Calcd for $C_{27}H_{28}F_5N_4O_6U$ ([M + H]$^+$): $m/z$ 837.24314. Found: $m/z$ 837.25460 (mass error = 11.46 ppm). Calcd for $C_{27}H_{27}F_5N_4O_6U$ ([M + Na]$^+$): $m/z$ 859.22830 (mass error = 3.22 ppm). Calcd for $C_{27}H_{25}F_5N_4O_4ClU$ ([M + H]$^+$): $m/z$ 836.24314. Found: $m/z$ 837.24314 (mass error = 11.46 ppm). Calcd for $C_{25}H_{24}ClF_5N_4O_4U$ (MW = 836.24 g mol$^{-1}$): $\epsilon$ = 20812 M$^{-1}$ cm$^{-1}$; $\lambda_{max}$ = 5465 nm, $\epsilon$ = 82316 M$^{-1}$ cm$^{-1}$.

**UO$_2Cl_2$(L). Method A: A solution of HL (131 mg, 0.257 mmol, 1 equiv; in 1.3 MeOH/CHCl$_3$, 150 mL) was added to a solution of $UO_2Cl_2$ (173 mg, 0.283 mmol, 1.1 equiv; in 1 MeOH/CHCl$_3$, 20 mL), after which $\text{NET}_3$ was added (47 µL, 0.334 mmol, 1.3 equiv), causing an immediate color change from orange to red. The reaction mixture was heated to 65 °C and stirred for 18 h, after which the solvent was removed under reduced pressure. The majority of the red solid was redissolved in CH$_2$Cl$_2$ (400 mL) and filtered. The filtrate was washed with H$_2$O (3 × 50 mL), dried with MgSO$_4$, and concentrated to obtain a red solid. The red solid and residue were combined, yielding a red solid. Yield: 189 mg (91%). 1H NMR (400 MHz, MeCN-d$_3$): $\delta_H$ 8.22 (2H, s), 7.46 (2H, $d, J = 4.4$ Hz), 7.19 (2H, $d, J = 4.4$ Hz), 1.76 (18H, s). 13C($^1$H) NMR (126 MHz, MeCN-d$_3$): $\delta_C$ 169.78, 159.02, 144.81, 143.17, 142.42, 138.05, 137.56, 134.23, 132.34, 119.57, 55.02, 27.84. $^{19}$F($^1$H) NMR (376 MHz, MeCN-d$_3$): $\delta_F$ = -140.88 to -143.36, -154.28 to -155.13, -162.18 to -163.97. HRMS (ESI$, MeOH$). Calcd for $C_{25}H_{25}F_5N_4O_4ClU$ ([M + OAc]$^+$): $m/z$ 877.22201. Found: $m/z$ 877.22201 (mass error = 0.33 ppm). Calcd for $C_{27}H_{24}ClF_5N_4O_4U$ (MW = 836.24 g mol$^{-1}$): $\epsilon$ = 45700 M$^{-1}$ cm$^{-1}$; $\lambda_{max}$ = 551 nm, $\epsilon$ = 15470 M$^{-1}$ cm$^{-1}$.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03744.

Full synthetic procedures, X-ray crystallography, DFT calculations, EPR spectroscopy, and electrochemical methods (PDF)

**Accession Codes**

CCDC 2122704–2122706 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**

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REFERENCES

(1) Broere, D. L. J.; Plessius, R.; van der Vlugt, J. I. New avenues for ligand-mediated processes — expanding metal reactivity by the use of redox-active catechol, o-aminophenol and o-phenylenediamine ligands. Chem. Soc. Rev. 2015, 44 (19), 6866–6915.

(2) Dutta, S. K.; Beckmann, U.; Bill, E.; Weyhermüller, T.; Wieghardt, K. 1,2-Bis(pyridine-2-carboxamido)benzen(2−) radials. A Noninnocent Ligand. Syntheses, Structures, and Mechanisms of Formation of [(N-bu2)4[NiFeCN2(N-bpy)(X2)] (X = CN−, N3−) and the Electronic Structures of [MII(bpybox)- (CN)]2 (M = Co, Fe). Inorg. Chem. 2000, 39 (15), 3355–3364.

(3) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. Synthesis and Characterization of a Uranium(III) Complex Containing a Redox-Active 2,2′-Bipyridine Ligand. Inorg. Chem. 2010, 49 (3), 1103–1110.

(4) Coughlin, E. J.; Qiao, Y.; Lapsheva, E.; Zeller, M.; Schelter, E. J.; Bart, S. C. Uranyl Functionalization Mediated by Redox-Active Ligands: Generation of O−C Bonds via Acylation. J. Am. Chem. Soc. 2019, 141 (2), 1016–1026.

(5) Pattenaude, S. A.; Mullane, K. C.; Schelter, E. J.; Ferrer, M. G.; Stein, B. W.; Bone, S. E.; Lezama Pacheco, J. S.; Kozimor, S. A.; Fanwick, P. E.; Zeller, M.; Bart, S. C. Redox-Active vs Redox-Innocent: A Comparison of Uranium Complexes Containing Diamine Ligands. Inorg. Chem. 2018, 57 (11), 6530–6539.

(6) Halter, D. P.; Heinemann, F. W.; Maron, L.; Meyer, K. The role of uranium–arene bonding in H2O reduction catalysis. Nat. Chem. 2018, 10 (3), 259–267.

(7) Crandall, H. W. The Formula of Uranyl Ion. J. Chem. Phys. 1949, 17 (7), 602–606.

(8) Cowie, B. E.; Purkis, J. M.; Austin, J.; Love, J. B.; Arnold, P. L. Thermal and Photocatalytic Reduction and Functionalization Chemistry of the Uranium Dication, [UVO2]2+. Chem. Rev. 2019, 119 (18), 10595–10637.

(9) Herasymchuk, K.; Chiang, L.; Hayes, C. E.; Brown, M. L.; Ovens, J. S.; Patrick, B. O.; Leznoff, D. B.; Storr, T. Synthesis and electronic structure determination of uranium(VI) ligand radical complexes. Dalton Trans. 2016, 45 (31), 12576–12586.

(10) Beiger, C.; Tian, Y.-H.; Barker, B. J.; Boland, K. S.; Scott, B. L.; Batista, E. R.; Kozimor, S. A.; Sessler, J. L. Synthesis and characterization of a tetrathiafulvalene-salphen actinide complex. Dalton Trans. 2013, 42 (19), 6716–6719.

(11) Assafa, M. K.; Pedrick, E. A.; Wakefield, M. E.; Wu, G.; Hayton, T. W. Oxidation of the 14-Membered Macrocyclic Dibenzotetramethyltetraaza[14]annulene upon Ligation to the Uranyl Ion. Inorg. Chem. 2018, 57 (14), 8317–8324.

(12) Kent, G. T.; Murillo, J.; Wu, G.; Fortier, S.; Hayton, T. W. Coordination of Uranyl to the Redox-Active Calix[4]pyrrole Ligand. Inorg. Chem. 2020, 59 (12), 8629–8634.

(13) Bolotoulo, D.; Metta-Magaña, D.; Fortier, S. F-element metalated dipyrrins: synthesis and characterization of a family of uranyl bis(dipyrrinate) complexes. Dalton Trans. 2017, 46 (10), 3284–3294.

(14) Pankhurst, J. R.; Bell, N. L.; Zegke, M.; Platts, L. N.; Lamfsus, C. A.; Maron, L.; Natrajan, L. S.; Sproles, S.; Arnold, P. L.; Love, J. B. Inner-sphere vs. outer-sphere reduction of uranyl supported by a redox-active, donor-expanded dipyrrin. Chem. Sci. 2017, 8 (1), 108–116.

(15) Bell, N. L.; Shaw, B.; Arnold, P. L.; Love, J. B. Uranyl to Uranium(IV) Conversion through Manipulation of Axial and Equatorial Ligands. J. Am. Chem. Soc. 2018, 140 (9), 3378–3384.

(16) Takeyama, T.; Tsushima, S.; Takao, K. Effects of Substituents on the Molecular Structure and Redox Behavior of Uranyl(VI) Complexes with N2O2-Donating Schiff Base Ligands. Inorg. Chem. 2021, 60, 11435.

(17) Takao, K.; Tsushima, S.; Ogura, T.; Tsutomura, T.; Ikeda, Y. Experimental and Theoretical Approaches to Redox Innocence of Ligands in Uranil Complexes: What Is Formal Oxidation State of Uranium in Reductant of Uranyl(VI)? Inorg. Chem. 2014, 53 (11), 5772–5780.

(18) Shikha Singh, R.; Prasad Paitandi, R.; Kumar Gupta, R.; Shankar Pandey, D. Recent developments in metal dipyrrin complexes: Design, synthesis, and applications. Coord. Chem. Rev. 2020, 414, 213269.

(19) Baudron, S. A. Dipyrrin based metal complexes: reactivity and catalysis. Dalton Trans. 2020, 49 (19), 6161–6175.

(20) Thoi, V. S.; Stork, J. R.; Niles, E. T.; Depperman, E. C.; Tierney, D. L.; Cohen, S. M. Diamodipyrilligands with Multiple Metal Bonding Modes. Inorg. Chem. 2008, 47 (22), 10533–10541.

(21) Jacobsen, J. A.; Stork, J. R.; Magde, D.; Cohen, S. M. Hydrogen-bond rigidified BODIPY dyes. Dalton Trans. 2010, 39 (3), 957–962.

(22) Saund, S. S.; Goldschmidt, S. L.; Ng, K.; Stewart, V.; Siegler, M. A.; Thoi, V. S. Exploring ligand non-innocence of coordinatively-versatile diamodipyrilligand covalent complexes. Chem. Commun. 2019, 55 (12), 1825–1828.

(23) Pankhurst, J. R.; Cadenbach, T.; Betz, D.; Finn, C.; Love, J. B. Towards dipyrrins: oxidation and metatallation of acyclic and macrocyclic Schiff-base dipyromethanes. Dalton Trans. 2015, 44 (5), 2066–2070.

(24) Brewster, J. T.; He, Q.; Anguera, G.; Moore, M. D.; Ke, X.-S.; Lynch, V. M.; Sessler, J. L. Synthesis and characterization of a dipyrramethyl–uranil complex. Chem. Commun. 2017, 53 (36), 4981–4984.

(25) Clement, O.; Rapko, B. M.; Hay, B. P. Structural aspects of metal–amide complexes. Coord. Chem. Rev. 1998, 170 (1), 203–243.

(26) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. Chem. Rev. 1996, 96 (2), 877–910.

(27) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

(28) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Chem. 2015, 71, 3–8.

(29) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Adv. 2008, 64, 122.

(30) Dolomanov, O. V.; Boushis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339–341.