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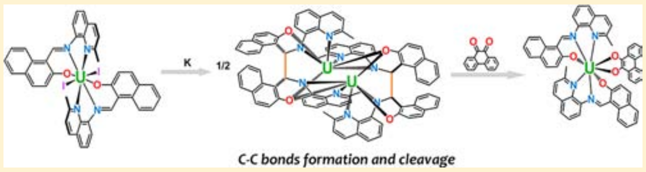
Synthesis of Electron-Rich Uranium(IV) Complexes Supported by Tridentate Schiff Base Ligands and Their Multi-Electron Redox Chemistry

Clément Camp, Julie Andrez, Jacques Pécaut, and Marinella Mazzanti*

Laboratoire de Reconnaissance Ionique et Chimie de Coordination, SCIB, UMR-E CEA/UJF-Grenoble 1, INAC, CEA-Grenoble, 17 rue des Martyrs, Grenoble, F-38054, France

Supporting Information



ABSTRACT: The synthesis, structure, and reactivity of a new complex of U(IV) with the tridentate Schiff base ligand Menaphtquinolen are reported. The reduction of the bis-ligand complexes [$UX_2(^{Me}naphtquinolen)_2$] (X = Cl, (**1-Cl**) ; I (**1-I**)) with potassium metal affords the U(IV) complex of the new tetranionic hexadentate ligand μ-bis-^{Me}naphtquinolen formed through the intramolecular reductive coupling of the imino groups of each ^{Me}naphtquinolen unit. The solid state structure of the [U(μ-bis-^{Me}naphtquinolen)]$_2$ dimer **2** isolated from toluene confirms the presence of a U(IV) complex of the reduced ligand. Reactivity studies with molecular oxygen and 9,10-phenanthrenequinone show that complex **2** can act as a multielectron reducing agent releasing two electrons through the cleavage of the C−C bond to restore the original imino function of the ligand. In the resulting U(IV) and U(VI) complexes [U(9,10-phenanthrenediol)(^{Me}naphtquinolen)$_2$], **3**, and [$UO_2(^{Me}naphtquinolen)_2$], **4**, the restored tridentate Schiff base allows for the coordination of the reduced substrate to the metal. Electrochemical studies of complex **2** show the presence of irreversible ligand centered reduction processes and of a reversible U(IV)/U(III) couple.

INTRODUCTION

Complexes of low valent uranium are attracting increasing interest because they can promote the activation and functionalization of small molecules[1−3] such as CO,[4−9] CO_2,[1,10−17] N_2[18−20] and azides[21−24] in mild conditions. Because of the unique coordination and bonding properties of uranium, its compounds could also provide an attractive alternative to transition metals for the catalytic transformation of small molecules.[4,7,12,25,26]

However, metal based multielectron processes remain uncommon in uranium chemistry[2,27,28] especially in comparison with the d-block metals, the chemistry of low-valent uranium being dominated by single-electron transfers. In this context, the association of uranium to a noninnocent ligand acting as an independent electron reservoir at the same molecule represents an attractive alternative that should render multielectron reactivity possible while stabilizing highly reactive formally low-valent oxidation states. Accordingly, in recent years ligand based redox processes have been increasingly combined with metal centered redox transfers to promote multielectron reductions in uranium complexes.[29−40] In most of these systems the electrons stored on the coordinated aromatic ligands become available to oxidizing substrates either through metal mediated processes or by a sterically induced reduction mechanism.

An alternative ligand-based mechanism for storing and transferring electrons in metal complexes involves the reversible formation and cleavage of C−C bonds in tetradentate Schiff base ligands that can function as two electron reservoir in redox reactions.[41−45]

Multidentate Schiff bases have been extensively used as supporting ligands in the chemistry of d-block metals. In uranium chemistry the use of Schiff base ligands has been mostly limited to the complexation of UO_2^{2+}.[46,47] Recently our group and others have shown that tetradentate and pentadentate Schiff bases are also effective ligands for the stabilization of the elusive pentavalent uranyl.[48−55]

In contrast only very few examples of U(III)[56] and U(IV)[47,57−59] complexes of Schiff base ligands have been reported. Polynucleating hexadentate Schiff bases have been used to promote the formation of heteropolymetallic complexes of U(IV) with 3d metals which show interesting magnetic properties.[60] However, to the best of our knowledge, the study of the redox reactivity of U(IV) Schiff base complexes is limited to one example.[45] We have recently reported redox reactivity studies of U(IV) complexes of the tetradentate ligand salophen (salophen = *N,N′*-disalicylidene-*o*-phenylenediaminate) which demonstrate that the salophen ligand behaves as a redox-active ligand able to store and release up to 4 electrons through the reversible formation and cleavage of one or two C−C bonds.[45]

Here we report a new U(IV) complex supported by a redox-active tridentate Schiff-base ligand ^{Me}naphtquinolen. The tridentate nature of the ligand was chosen to render available two coordination sites at the metal center which were not present in the previously reported salophen system. The presence of available coordination sites should allow the coordination of potential

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substrates to the metal center leading to a better control of the reactivity. Notably, it might favor reaction pathways involving the metal-mediated inner-sphere transfer to the coordinate substrate of the electrons stored upon reduction in the C−C bond. We show that this Schiff base behaves as a redox active ligand when coordinated to U(IV) and that the reduction of the bis-ligand complex of U(IV) proceeds with the reductive coupling of the imino function of the ligand to afford a new U(IV) complex with two electrons stored in a C−C bond. The ligand-based multielectron redox activity of the system was confirmed by reactivity studies of the reduced system with different oxidizing substrates.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. Glassware was dried overnight at 130 °C before use.

^{1}H NMR Experiments. were carried out using NMR tubes adapted with J. Young valves. ^{1}H NMR spectra were recorded on Bruker 200 and 500 MHz and Varian Mercury 400 MHz spectrometers. NMR chemical shifts are reported in ppm with solvent as internal reference.

UV−visible Spectra. UV−vis measurements were carried out with a Varian Cary 50 Probe spectrophotometer in quartz cells (optical path lengths: 1 mm) adapted with Young valves.

Elemental Analyses. Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany.

Starting Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Eurisotop (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, hexane, pyridine, and thf). All reagents were dried under high-vacuum for 7 days prior to use. 9,10-phenanthrenequinone was purified by recrystallization in toluene prior to use. Dry dioxygen was prepared upon storing an O_2 atmosphere upon P_4O_{10} for one week prior to use. Depleted uranium turnings were purchased from the ″Société Industrielle du Combustible Nucléaire″ of Annecy (France). UCl_4[61] and $UI_4(OEt_2)_2$[62] were prepared according to the published procedures.

Caution! Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47 × 10^9 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.

H-^{Me}naphtquinolen. The ligand was prepared by a modified literature procedure.[63,64] A solution of 2-methylquinolin-8-amine (1.0 g, 6.32 mmol, 1 equiv) and 3-hydroxy-2-naphtaldehyde (1.1 g, 6.39 mmol, 1.01 equiv) in 30 mL of anhydrous toluene was stirred in a Dean−Stark setup at 110 °C during 2 days. Then the solvent was removed under vacuum giving an orange-brown solid. This solid was suspended in 100 mL of cyclohexane and heated to reflux. Toluene was added dropwise until most solid was soluble, and the temperature was raised to maintain the reflux. A hot filtration was carried out to remove the black insoluble impurities, and the mixture was cooled down to room temperature, affording red crystals that were filtered and dried under vacuum to give H-^{Me}naphtquinolen (1.38 g, 4.42 mmol, 70% yield).

^{1}H NMR (200 MHz, CDCl3, 298 K): δ = 15.8 (br s, 1H, OH), 9.3 (d, 1H), 8.1 (d, 1H), 8.0 (d, 1H), 7.7−7.4 (m, 7H), 7.3−7.2 (m, 1H), 6.9 (d, 1H), 2.9 (s, 3H, CH_3). ^{13}C NMR (200 MHz, CDCl3, 298 K): δ = 182.3 (C═N), 159.3 (C_{aro}), 145.9 (C_{aro}), 139.5 (C_{aro}), 139.3 (C_{aro}), 136.6 (C_{aro}), 136.0 (C_{aro}), 134.5 (C_{aro}), 129.5 (C_{aro}), 128.4 (C_{aro}), 127.2 (C_{aro}), 126.9 (C_{aro}), 126.7 (C_{aro}), 125.7 (C_{aro}), 124.1 (C_{aro}), 123.6 (C_{aro}), 122.3 (C_{aro}), 118.4 (C_{aro}), 113.2 (C_{aro}), 8.0 (C_{aro}), 25.9 (CH_3). ES-MS: m/z = 313.2 [M+H$^+$].

K-^{Me}naphtquinolen. To a stirring solution of H-^{Me}naphtquinolen (1.2 g, 3.84 mmol, 1 equiv) in 30 mL of anhydrous tetrahydrofuran (THF) was added portion wise potassium hydride (0.15 g, 3.84 mmol, 1 equiv). The solution turned from deep orange to deep red. After 12 h stirring, an orange solid deposited. This solid was filtered and dried under vacuum for 5 h to give K-^{Me}naphtquinolen (0.88 g, 2.51 mmol, 65% yield).

^{1}H NMR (200 MHz, py-d$_5$, 298 K): δ = 9.7 (s, 1H, HC═N), 8.6 (d, 1H), 8.0 (d, 1H), 7.7 (m, 2H), 7.5−7.7 (m, 3H), 7.3−7.0 (m, 4H), 2.5 (s, 3H, CH_3).

$[UCl_2(^{Me}naphtquinolen)_2]$, 1-Cl. A solution of K-^{Me}naphtquinolen (92.3 mg, 0.263 mmol, 2 equiv) in THF (10 mL) was added to UCl_4 (50.0 mg, 0.132 mmol, 1 equiv), and the reaction mixture was stirred at room temperature overnight, affording an orange suspension. The mixture was filtered to remove KCl, the THF volume of the filtrate was reduced to 2 mL, and the solution was layered with hexane. The resulting orange precipitate was filtered and dried under vacuum to afford an orange solid (89.0 mg, 0.096 mmol, 72% yield). ^{1}H NMR (200 MHz, THF-d$_8$, 298 K): δ = 25.7 (s, 2H), 19.4 (d, 2H), 13.0 (d, 2H), 11.8 (d, 2H), 10.1 (t, 2H), 9.7 (t, 2H), 9.5 (m, 2H), 5.6 (s, 6H), 1.0 (d, 2H)-0.4 (t, 2H), −0.8 (m, 2H), −3.0 (d, 2H), −6.1 (s, 2H). Anal. Calcd for $[UCl_2(^{Me}naphtquinolen)_2]$ $C_{42}H_{30}Cl_2N_4O_2U$: C, 54.15; H, 3.25; N, 6.01. Found: C, 54.03; H, 3.41; N, 6.06. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a pyridine solution of $[UCl_2(^{Me}naphtquinolen)_2]$.

Reduction of $[UCl_2(^{Me}naphtquinolen)_2]$, 1-Cl. To a solution of **1-Cl** (24.5 mg, 0.026 mmol, 1 equiv) in THF (4 mL) was added a potassium chunk (2.1 mg, 0.053 mmol, 2 equiv), and the reaction mixture was stirred at room temperature overnight, affording a deep brown suspension. The ^{1}H NMR spectrum (200 MHz, THF-d$_8$, 298 K) recorded for the crude reaction mixture showed that a complex mixture of compounds had formed, among which the resonances of **2** and **2b** could be identified (see Supporting Information).

A suspension of potassium graphite (7.1 mg, 0.053 mmol, 2 equiv) in THF (2 mL) was added to a solution of **1-Cl** (24.5 mg, 0.026 mmol, 1 equiv) in THF (2 mL), and the reaction mixture was stirred at room temperature for 15 min, affording a deep brown suspension. Graphite was removed by centrifugation. The ^{1}H NMR spectrum (200 MHz, THF-d$_8$, 298 K) recorded for the crude reaction mixture (see Supporting Information) showed the formation of **2** and **2b** as the only ^{Me}naphtquinolen-containing species.

$[U(\mu\text{-bis-}^{Me}naphtquinolen)]_2$, 2. A solution of ^{Me}naphtquinolen-K (150.0 mg, 0.428 mmol, 2 equiv) in THF (8 mL) was added to $[UI_4(OEt_2)_2]$ (191.3 mg, 0.214 mmol, 1 equiv), and the reaction mixture was stirred at room temperature overnight, affording a yellowish-brown suspension. Intermediate data for $[UI_2(^{Me}naphtquinolen)_2]$, **1-I**: ^{1}H NMR (200 MHz, pyridine-d$_5$, 298 K): δ = 108.9 (br s, 2H), 37.9 (s, 2H), 37.3 (s, 6H), 31.1 (s, 2H), 29.7 (br s, 2H), 22.1 (s, 2H), 21.6 (s, 2H), 18.0 (br s, 6H), 16.9 (s, 2H), 4.3 (s, 4H), 0.6 (s, 2H), −3.2 (s, 2H) −7.4 (s, 2H). This mixture was added onto potassium chunks and then stirred at room temperature for 12 h. The reaction mixture gradually turned dark olive brown. The mixture was filtered to remove KI, and the filtrate evaporated to dryness. The resulting brown solid was extracted with toluene (12 mL) to give a brown suspension that was filtered. The filtrate was taken to dryness to give $[U(\mu\text{-bis-}^{Me}naphtquinolen)]_2$, **2**, as a brown solid (122.9 mg, 0.071 mmol, 67% yield). ^{1}H NMR (200 MHz, toluene-d$_8$, 298 K): δ = 88.0 (s, 2H), 46.2 (s, 2H), 41.7 (m, 4H), 33.1 (d, 2H), 31.2 (d, 2H), 30.9 (d, 2H), 20.0 (t, 2H), 17.8 (d, 2H), 15.1 (d, 2H), 14.9 (m, 2H), 13.2 (t, 2H), 12.3 (t, 2H), 10.4 (t, 2H), 8.9 (dt, 2H), 7.2 (d, 2H), 5.6 (d, 2H), 5.2 (d, 2H), 2.5 (d, 2H), −3.9 (d, 2H), −5.1 (d, 2H), −5.9 (t, 2H), −7.7 (s, 6H, CH_3), −9.0 (d, 2H), −13.8 (d, 2H), −25.8 (s, 6H, CH_3). Anal. Calcd for **2** $C_{84}H_{60}N_8O_4U_2$: C, 58.61; H, 3.51; N, 6.51. Found: C, 58.37; H, 3.73; N, 6.38. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a toluene solution of **2**.

Upon dissolution of **2** into pyridine, 2 sets of proton signals are observed in solution assigned to the dimeric complex **2** and the monomeric analogue **2b**: ^{1}H NMR (500 MHz, pyridine-d$_5$, 298 K):

Ratio of complexes **2**: **2b**: 3:1 after 30 min, 0.5:1 after 4 days.

Complex **2**: δ = 85.7 (s, 2H), 47.4 (d, 2H), 41.1 (d, 2H), 35.2 (d, 2H), 32.3 (d, 2H), 28.9 (s, 2H), 28.1 (d, 2H), 18.4 (t, 2H), 16.7 (d, 2H), 15.2 (t, 2H), 11.3 (t, 2H), 11.2 (t, 2H), 11.1 (t, 2H), 10.9 (d, 2H), 9.8 (d, 2H),

Table 1. X-ray Crystallographic Data

compound	**1-Cl**·(pyridine)	**2**·(toluene)$_2$	**3**·(pyridine)$_{4.5}$	**4**
formula	C47 H35 N5 O2 Cl2 U	C98 H76 N8 O4 U2	C78.5 H60.5 N8.5 O4 U	C84 H60 N8 O8 U
crystal size [mm]	0.28 × 0.22 × 0.15	0.32 × 0.19 × 0.02	0.25 × 0.10 × 0.02	0.27 × 0.14 × 0.03
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$
V [Å^3]	1977.10(13)	1897.75(15)	12586.6(13)	3319.99(15)
a [Å]	10.0338(4)	11.1583(6)	45.625(2)	16.2723(5)
b [Å]	12.7361(5)	13.4999(7)	15.8387(9)	11.8342(3)
c [Å]	16.6880(7)	13.5383(5)	18.5959(13)	18.1568(5)
α [deg]	101.098(3)	97.421(3)	90	90
β [deg]	101.394(3)	107.177(4)	110.506(5)	108.281(3)
γ [deg]	102.627(3)	98.029(4)	90	90
Z	2	1	8	2
absorption coefficient [mm^{-1}]	4.287	4.324	2.640	4.941
F (000)	988	936	5720	1736
T [K]	150(2)	150(2)	150(2)	150(2)
total no. reflexions	41283	14739	31319	39686
unique reflexions [R(int)]	12067 [0.0592]	7739 [0.0961]	9013 [0.1193]	10126 [0.0740]
final R indices [$I > 2\sigma(I)$]	0.0511	0.0780	0.0623	0.0450
largest diff. peak and hole [e A^{-3}]	5.549 and −2.664	2.983 and −1.895	2.465 and −1.712	1.340 and −1.248
GOF	1.155	0.939	1.063	1.012

8.9 (d, 2H), 8.1 (d, 2H), 6.3 (d, 2H), 5.2 (d, 2H), 0.9 (s, 6H, CH$_3$), −0.7 (d, 2H), −3.8 (t, 2H), −6.7 (d, 2H), −9.5 (d, 2H), −10.0 (d, 2H), −13.9 (s, 6H, CH$_3$).

Complex **2b**: δ = 91.3 (s, 2H), 47.6 (d, 2H), 45.9 (d, 2H), 44.1 (s, 2H), 35.6 (d, 2H), 32.1 (d, 2H), 20.2 (d, 2H), 19.3 (d, 2H), 19.1 (t, 2H), 17.5 (m, 2H), 14.3 (t, 2H), 13.9 (t, 2H), 13.7 (d, 2H), 13.4 (t, 2H), 13.3 (d, 2H), 6.5 (s, 6H, CH$_3$), 5.7 (d, 2H), 4.6 (d, 2H), 3.7 (t, 2H), 2.2 (s, 2H), 1.6 (d, 2H), −5.3 (t, 2H), −5.7 (d, 2H), −7.0 (d, 2H), −11.8 (d, 2H), −15.0 (s, 6H, CH$_3$).

Reaction of 2 with 9,10-Phenanthrenequinone. A toluene (6 mL) 9,10-phenanthrenequinone (12.2 mg, 0.059 mmol, 2 equiv) solution was prepared and added to a toluene (4 mL) solution of complex **2** (50.6 mg, 0.029 mmol, 1 equiv). Immediately the deep brown solution turned yellowish green. The mixture was stirred 3 h before filtration. The brown solid was washed with 2 × 0.5 mL of toluene and dried in vacuo to give [U(9,10-phenanthrenediol)-(^{Me}naphtquinolen)$_2$] **3** as a brown-gold solid (33.8 mg, 0.032 mmol, 54% yield). Similar results were obtained when performing the reaction in pyridine. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated pyridine solution of the complex. ^{1}H NMR (200 MHz, toluene-d$_8$, 298 K): δ = 27.6 (s, 2H), 19.9 (s, 2H), 19.1 (s, 2H), 18.6 (s, 2H), 16.2 (d, 2H), 13.0 (t, 2H), 12.5 (d, 2H), 11.7 (t, 2H), 9.4 (t, 2H), 9.3 (t, 2H), 8.0 (d, 2H), 0.7 (t, 2H), 0.6 (d, 2H), −1.1 (d, 2H), −2.4 (d, 2H), −5.2 (d, 2H), −10.5 (s, 6H). Anal. Calcd for **3**·(toluene$_{0.2}$) $C_{57.2}H_{39.6}N_4O_4U$: C, 63.32; H, 3.68; N, 5.16. Found: C, 63.54; H, 3.85; N, 5.25.

Reaction of 2 with I$_2$. A solution of iodine (2.9 mg, 0.011 mmol, 2 equiv.) in toluene (1 mL) was added dropwise to a stirred solution of **2** (9.7 mg, 0.006 mmol, 1 equiv.) in toluene (0.5 mL). Immediately, the dark brown solution turned pale brown. After 10 min stirring, the crude reaction was taken to dryness and dissolved into pyridine. The ^{1}H NMR spectrum (200 MHz, py-d$_5$, 298 K) recorded for the crude reaction mixture showed that complex **1-I** was restored.

Reaction of 2 with Dry O$_2$. A pyridine (6 mL) solution of complex **2** (58.0 mg, 0.034 mmol, 1 equiv) was transferred into a reaction vessel. The suspension was degassed using a freeze−pump−thaw procedure. Then 1 atm of dry dioxygen was introduced into the flask. Immediately, a color change from dark brown to dark red/orange was observed. The reaction was stirred for 12 h at room temperature before the solvent was removed in vacuo. The solid was washed with toluene (3 × 2 mL), recovered and dried in vacuo to afford **4** as a bright orange solid (42.0 mg, 0.047 mmol, 69% yield). ^{1}H NMR (200 MHz, THF-d$_8$, 298 K): δ = 10.3 (s, 2H, N=CH), 8.5 (d, 2H, H$_{aro}$), 8.2 (d, 2H, H$_{aro}$), 7.9−7.8 (m, 6H, H$_{aro}$), 7.7−7.5 (m, 6H, H$_{aro}$), 7.4 (t, 2H, H$_{aro}$), 7.2 (t, 2H, H$_{aro}$), 6.2 (d, 2H, H$_{aro}$), 3.4 (s, 6H, CH$_3$). Anal. Calcd for **4**·(KI$_{0.25}$) $C_{42}H_{30}N_4O_4UK_{0.25}I_{0.25}$: C, 54.00; H, 3.24; N, 6.00. Found: C, 53.88; H, 3.49; N, 5.98. The presence of KI arises from the residual presence of KI in the batch of complex **2** used in this reaction.

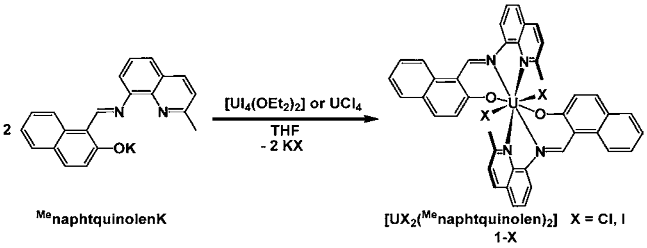
Electrochemical Methods. Cyclic voltammetry data were carried out at room temperature in an argon-filled glovebox described above. Data were collected using a Biologic SP-300 potentiostat connected to a personal computer. All samples were 10 mM in complex with 0.1 M [Bu$_4$N][PF$_6$] supporting electrolyte in pyridine solution. The experiments were carried out with a platinum disk (d = 5 mm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The experiments were repeated on independently synthesized samples to assess the reproducibility of the measurement. Potential calibration was performed at the end of each data collection cycle using the ferrocene/ferrocenium $[(C_5H_5)_2Fe]^{+/0}$ couple as an internal standard.

X-ray Crystallography. Diffraction data were taken using an Oxford-Diffraction XCallibur S kappa geometry diffractometer (Mo−Kα radiation, graphite monochromator, λ = 0.71073 Å). To prevent evaporation of cocrystallized solvent molecules the crystals were coated with light hydrocarbon oil, and the data were collected at 150 K. The cell parameters were obtained with intensities detected on three batches of 5 frames. The crystal-detector distance was 4.5°cm. The number of settings and frames has been established taking in consideration the Laue symmetry of the cell by CrysAlisPro Oxford-diffraction software.[65] A total of 866 for **1-Cl**, 430 for **2**, 377 for **3**, and 498 for **4** narrow data were collected for 1° increments in ω with a 15 s exposure time for **1-Cl**, 100 s for **2**, 200 s for **3**, and 80 s for **4**. Unique intensities detected on all frames using the Oxford-diffraction Red program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the ABSPACK Oxford-diffraction program.[65] Space groups were determined from systematic absences. The structures were solved by direct methods using the SHELXTL 6.14 package.[66] All non-hydrogen atoms were found by difference Fourier syntheses and refined on F^2. For **1-Cl** hydrogen atoms were found by Fourier synthesis and refined except for methyl groups which were fixed in ideal position. For **2**, **3**, and **4** hydrogen atoms were fixed in ideal position. Full crystallographic details for complexes **1**−**4** are given in Table 1.

RESULTS AND DISCUSSION

[UX$_2$(^{Me}naphtquinolen)$_2$] Complexes. Proton NMR spectra of the reaction mixture of 2 equiv of ^{Me}naphtquinolenK and 1 equiv of [UI$_4$(OEt$_2$)$_2$] or [UCl$_4$] in deuterated THF shows only one set of signals assigned to the heteroleptic mononuclear [UX$_2$(^{Me}naphtquinolen)$_2$] **1-X** complexes (Scheme 1) where X = I or Cl respectively. The UV−visible spectra for **1-Cl** and **1-I** display a series of intense absorptions below 450 nm ($\varepsilon \approx$ 25000 L cm^{-1} mol^{-1}) that we assign to ligand-based $\pi-\pi^*$ transitions. The solubility of **1-Cl** in organic solvents (fully soluble in THF, partially soluble in toluene) is much higher than the one of **1-I** (sparingly soluble in THF, insoluble in toluene) facilitating its separation from KX salts. Accordingly, the complex [UCl$_2$(^{Me}naphtquinolen)$_2$] was also isolated pure in high yield. The X-ray structural analysis of **1-Cl** shows that the uranium atom is octa-coordinated by two ^{Me}naphtquinolen and two chloride ligands in a slightly distorted square antiprism possessing a pseudo C_2 axis (Figure 1). The mean values of U−O (2.20(2) Å), U−N (2.6(1) Å), and U−Cl (2.67(4) Å) bond distances (Table 2) are in the range of the ones found in other U(IV) Schiff base complexes,[45,57,58] and bond valence calculations are in agreement with a +IV oxidation state for the metal (see Supporting Information). The ^{Me}naphtquinolen ligands are strongly distorted from planarity with about 70° between the quinoleine and the naphtol planes. This is most probably due to sterical repulsion between the two tridentate ligands in the present coordination environment. The two ^{Me}naphtquinolen ligands are arranged perpendicular to each other with the two halide anions lying on the same face of the square antiprism. This geometry is very different from the one reported for analogous tridentate ligands bound to Yb(III) or Y(III).[67] In the crystal structure of the [L$_2$Ln(N(TMS)$_2$)] (Ln = Yb(III) or Y(III) L = bis(3,5-di-*tert*-butylsalicylidene)-8-aminoquinoline) the two tridentate Schiff bases are almost planar and bind the metal in a parallel fashion. These two binding modes are reminiscent of those found in sandwich and meridional isomers of uranium bis-ligand complexes of tetradentate Schiff bases.[45,57]

Scheme 1. Synthesis of [UX$_2$(^{Me}naphtquinolen)$_2$] 1-X (X = Cl, I)



Synthesis and Structure of [U(μ-bis-^{Me}naphtquinolen)]$_2$. The proton NMR spectrum in THF of the reaction mixture after reduction of the complex **1-I** with 2 equiv of potassium in deuterated THF shows the presence of two sets of 26 signals (ratio 66:34) (see Supporting Information, Figure S.A.3). The proton NMR in toluene of the reaction mixture after removal of THF shows the presence of only one set of 26 signals. Recrystallization from toluene affords the complex [U(μ-bis-^{Me}naphtquinolen)]$_2$ **2** pure in 67% yield (Scheme 2).

The solid state structure of **2** determined by X-ray structural studies is presented in Figure 2. It shows that the dimeric compound **2** is composed of two [U(IV)bis-^{Me}naphtquinolen] complexes bridged by the phenolate oxygens of the two tetra-anionic bis-^{Me}naphtquinolen ligands. The crystal structure is centrosymmetric, with an inversion center located halfway between the two uraniums. Each metal cation is hepta-coordinated in a distorted capped trigonal prismatic environment by the four nitrogen (mean U−N = 2.5(1) Å) and two oxygen atoms from a bis-^{Me}naphtquinolen ligand (mean U−O = 2.3(1) Å) and by a bridging phenolate oxygen form the other [U(IV)-bis-^{Me}naphtquinolen] complex. The two bidentate phenolate bridging ligands hold the two uranium centers in the dimer at 3.7983(8) Å apart (Figure 3). The analysis of the structural parameters of the complex clearly shows that the reduction has occurred on the imino groups of the ligands rather than on the metal ions. Notably, the two electron reduction of the ligand results in the formation of two C−C bonds, 1.64(1) Å long, by intramolecular coupling of the original imino groups. The value of the C−C bond distance is larger than those found in the Na$_2$[U(bis-salophen)] (1.559(7) Å) and [U$_2$(cyclo-salophen)-(py)$_4$] (1.609(5) Å) complexes for the C−C bonds formed after reductive coupling of the imino groups[45] but remains in the range of reported values for C−C bonds. Reductive coupling mediated by low valent uranium has been previously reported for carbonyl compounds,[68] heterocycles,[69] CO,[6] and CS$_2$.[70] The C−N$_{am}$ bond distances (mean C−N$_{am}$ = 1.474(5) Å) of the ligand

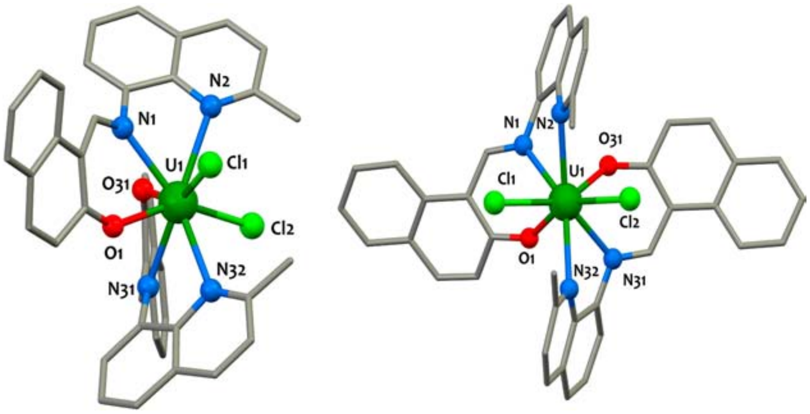
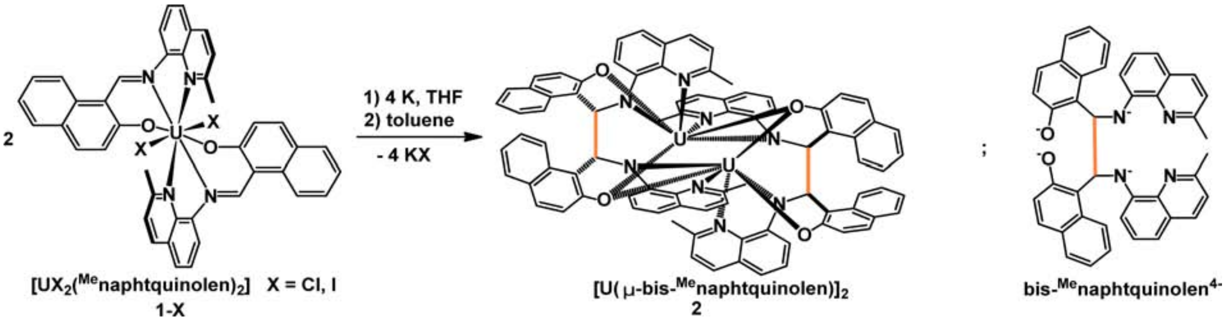


Figure 1. Mercury diagrams (side and top views) of the solid-state molecular structure of [UCl$_2$(^{Me}naphtquinolen)$_2$] in **1-Cl**. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: uranium (deep green), chlorine (bright green), nitrogen (blue), oxygen (red), and carbon (gray).

Table 2. Mean Values of Selected Bond Lengths (Å) in the U(IV) Complexes **1-Cl**, **2**, **3**, and **4**

compound	U–N_{aro}	U–$N_{imino/amido}$	U–$O_{phenolate}$	U–X	C–C_{link}	C–$N_{imino/amido}$
1-Cl	2.70(3)	2.51(3)	2.204(18)	2.67(4)$_{X = Cl}$		1.293(2)
2	2.538(3)	2.36(2)	2.26(10)		1.636(14)	1.474(5)
3	2.58(7)	2.52(2)	2.227(13)	2.26(4)$_{X = O}$		1.294(9)
4	2.646(4)	2.55(2)	2.238(6)	1.776(3)$_{X = O^{2-}}$		1.292(2)

Scheme 2. Synthesis of [U(μ-bis-^{Me}naphtquinolen)]$_2$ **2** and Schematic Representation of the Tetranionic Hexadentate Ligand Bis-^{Me}naphtquinolen^{4-}



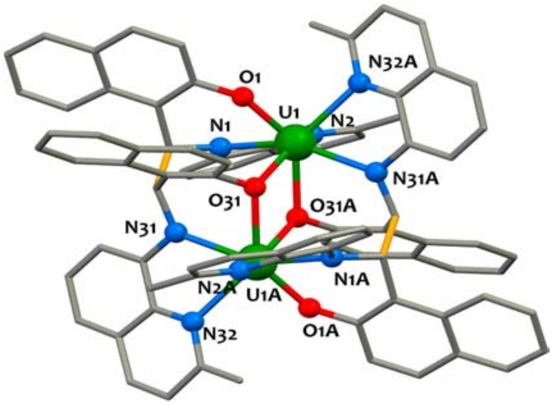


Figure 2. Mercury diagram of the solid-state molecular structure of [U(μ-bis-^{Me}naphtquinolen)]$_2$ in **2**. Hydrogen atoms and solvent molecules are omitted for clarity. The C–C bond formed by reduction of the imine moieties of the ligands is represented in yellow. Color code: uranium (green), nitrogen (blue), oxygen (red), and carbon (gray). (U1A = U1 −*x*+1,−*y*+1,−*z*+2).

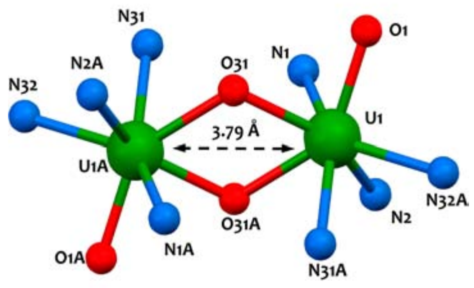
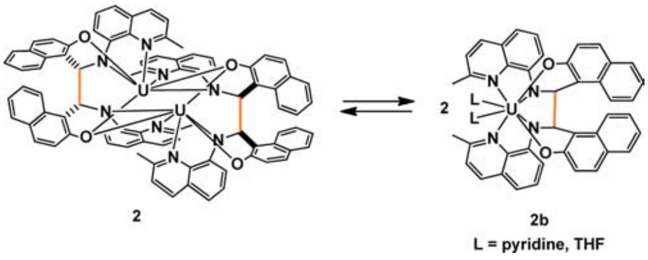


Figure 3. View of the dinuclear core of complex [U(μ-bis-^{Me}naphtquinolen)]$_2$ **2**.

backbone are much longer than the one observed in **1-Cl**, and are in agreement with the presence of two amido groups. This is further confirmed by the analysis of the values of the U–N bond distances, with the U–N_{am} distances in **2** (U–N_{am} = 2.36(2) Å) being significantly shorter than the U–N_{py} distances in **2** (U–N_{py} = 2.538(3) Å) and the U–N_{im} distances in **1-Cl** (U–N_{im} = 2.51(3) Å). This distance compares well with the U–N_{am} (2.387(8) Å) and U–N_{im} (2.624(7) Å) found in Na_2[U(bis-salophen)].[45] Finally, bond valence calculations are in agreement with a +IV oxidation state for the uraniums in **2** (see Supporting Information). The value of the magnetic moment (2.44 μ_β) per uranium measured using the Evans method[71] for a toluene solution of **2** is also in the range of values reported for U(IV) complexes.[30] Thus, the formula [U(μ-bis-^{Me}naphtquinolen)]$_2$ where bis-^{Me}naphtquinolen is a tetra-anionic hexadentate ligand provides a good description of this neutral complex.

Compound **2** is stable for weeks at room temperature in the solid state or in toluene solution under inert atmosphere. In addition to the ligand-based $\pi-\pi^*$ transitions below 450 nm, a long tail absorption extending to 750 nm is observed in the UV–visible spectrum of **2** (see Supporting Information), responsible for its dark-brown color in solution. The proton NMR spectrum of **2** in toluene solution shows only one set of 26 signals assigned to a centrosymmetric dimeric solution species in agreement with the solid state structure of **2**. The ^{1}H NMR spectrum of **2** in deuterated THF or pyridine shows the presence of two sets of 26 resonances indicating that two forms of the complex are present in coordinating polar solvents (Scheme 3). Evaporation of the pyridine and THF solutions and dissolution of the resulting solid in toluene result again in the presence of only one species in the proton NMR spectrum. The monitoring of the ^{1}H NMR spectrum of complex **2** in pyridine solution at different times after dissolution shows that the ratio between the two isomers evolves in time, going from 3:1 after 30 min, to a final stable ratio of 0.5:1 after 4 days. The proton chemical shifts for the initially major species are close to the ones measured for complex **2** in deuterated toluene. This suggests that the initially major species in pyridine solution is a dinuclear complex which with time undergoes a rearrangement in pyridine solution. The second set of 26 resonances could either correspond to a solvent adduct of the dinuclear complex **2** or to a monomeric form of the complex. Pulsed-field-gradient stimulated-echo diffusion NMR spectroscopy (see Supporting Information) was used to measure the diffusion coefficients of both species in pyridine solution. *D* is a function of the molecular weight and has been successfully used to discriminate metallosupramolecular architectures in solution.[72,73] The values measured in pyridine ($(D_A/D_B)^3 = 1.63$; $M_A/M_B = 1.69$) are in agreement with the presence of a mononuclear and a dinuclear complexes in solution. Attempts to isolate crystals of the monomeric complex from pyridine or thf were not successful.

Scheme 3. Equilibrium between the Dimeric and the Monomeric Forms of 2 in Coordinating Solvents



The most probable pathway for the formation of **2** (see Supporting Information) from the reduction of **1** involves the reduction of the two imino group to afford two U(IV) radical anion complexes which then undergo intramolecular C−C coupling. This produces a U(IV) complex of the new hexadentate tetranionic bis-phenolato bis-amido bis-^{Me}naphtquinolen ligand where at least two coordination sites are available at the metal center for solvent or substrate binding. In the absence of coordinating solvents this complex dimerizes through phenolate bridging to yield **2**.

Isolation of a pure product from the reduction of the chloride analogue **1-Cl** with potassium proved more difficult. Proton NMR in deuterated THF of the reaction mixture after reduction of **1-Cl** with 2 equiv of potassium metal shows the presence of several sets of signals. Two sets of signals were assigned to the reduced species **2** and **2b**, the other signals remain unidentified. The presence of additional species can be explained in terms of a competition of an intermolecular C−C coupling process leading to complex mixtures as a result of the presence of the more coordinating chloride ligand. Although the ligands could rearrange in solution, the conformation adopted by the two tridentate ligands in the solid state structure of the complex **1-Cl** with the two carbons of the imino groups situated at a distance of 5.995(6) Å is not favorable to intramolecular C−C bond formation. However, proton NMR studies show that the reduction of **1-Cl** with KC_8 in THF leads cleanly to the formation of complexes **2** and **2b**. These results show that clean ligand based reduction followed by intramolecular C−C coupling is not limited to uranium complexes of tetradentate Schiff bases. However in the case of tridentate Schiff bases the choice of the halide precursor plays an important role in the outcome of the reduction reaction. Moreover, the final complex presents free coordination sites at the metal center which are not available in the previously reported Na_2[U(bis-salophen)] complex obtained from the intramolecular C−C coupling of two reduced imino groups from the $[U(salophen)_2]$ precursor.[42]

Complex **2** provides an interesting precursor for the synthesis of more reduced species. The possibility of further reduction of the metal center in **2** was explored by electrochemical studies.

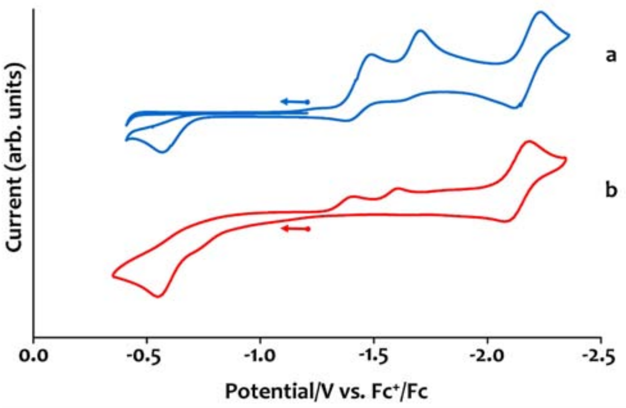


Figure 4. Cyclic voltammogram for 10 mM solutions of (a) **1-I** and (b) **2** in ∼0.1 M $[Bu_4N][PF_6]$ pyridine solution at 100 mV s^{-1} scanrate.

Table 3. Voltammetric Data for 1-I and 2

	ligand-based waves			metal-based wave
compd	E_{pa} (V)	E_{pc1} (V)	E_{pc2} (V)	$E_{1/2}$(V)
1-I	−0.56	−1.45	−1.65	−2.16
2	−0.56	−1.49	−1.70	−2.17

Electrochemistry. Cyclic voltammetry data were collected for complexes **1-I** and **2** in ∼0.1 M $[Bu_4N][PF_6]$ pyridine solution and are presented in Figure 4 and Table 3. All redox potentials are referenced against the $[(C_5H_5)_2Fe]^{+/0}$ redox couple. While the free ligand in K-^{Me}naphtquinolen does not exhibits reduction process in the range −0.5 to −2.4 V (see Supporting Information), the voltammogram of complex **1-I** shows three distinct reduction events. A first reduction process occurs at $E_{pc1} = -1.45$ V and is followed by a reduction at $E_{pc2} = -1.65$ V. These two waves are associated with an irreversible oxidation process occurring at $E_{pa} = -0.56$ V which is not observed when the voltammogram is swept initially from −1.2 V toward the positive direction. These data indicate the presence of a system with a limited degree of chemical reversibility as one could expect because of the formation of the C−C bond after ligand reduction. Finally, a third reversible process is observed at $E_{1/2} = -2.16$ V. Similar redox processes are observed on the voltammogram of the reduced species **2** which can be reversibly reduced at $E_{1/2} = -2.17$ V and irreversibly oxidized at $E_{pa} = -0.56$ V. The latter wave has a shoulder at −0.68 V that can be reasonably assigned to the oxidation of the monomeric form in equilibrium with the dimeric one in pyridine solution. Notably, it has been observed that the intensity of the shoulder was increasing 1 h after dissolution of **2** in pyridine, in agreement with a higher ratio of monomer/dimer in pyridine solution as observed in the NMR studies. The two irreversible reduction waves at $E_{pc1} = -1.49$ V and $E_{pc2} = -1.70$ V are not observed when the voltammogram is swept initially from −1.3 V to the negative direction and are thus associated to the reduction of the oxidation product.

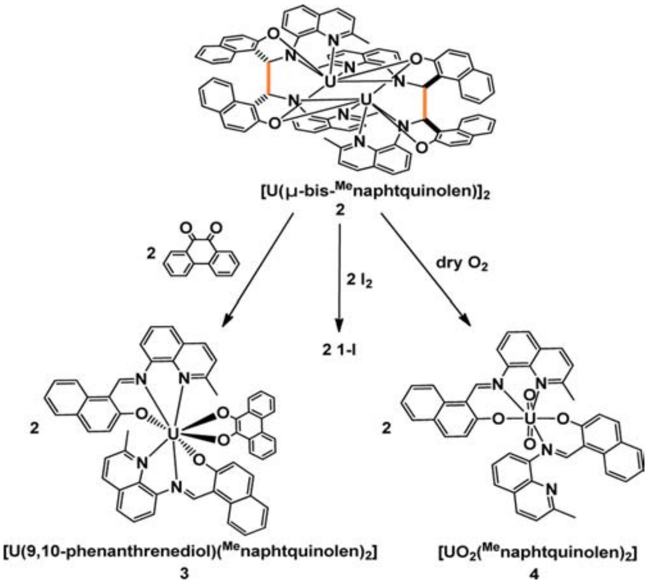
Taking into account that both the ligand and the uranium center are electroactive species, distinguishing ligand-based and metal-based processes is critical. The values of the redox potentials of the first two reduction waves are not compatible with metal based reductions (U(IV)/U(III) and U(III)/U(II)). The pseudoreversible reduction processes in the −1.45 to −1.70 V range probably correspond to two successive one electron transfers to the bis-^{Me}naphtquinolen ligand platform. Thus, the irreversible oxidation occurring at $E_{pa} = -0.56$ V corresponds to the oxidation of the bis-^{Me}naphtquinolen platform, that is, to the oxidative cleavage of the C−C bond.

The irreversibility of the ligand-based processes suggests that the electrochemical reduction is followed by a rapid chemical transformation involving the formation or cleavage of the C−C bond between two reduced imino groups. This process confers a strong stabilization to the system, as is expressed by the much lower potential required for transferring an electron to the ^{Me}naphtquinolen ligand than the one required for oxidizing the bis-^{Me}naphtquinolen platform (ΔEp = 0.9 V).

The reversible wave at $E_{1/2}$ = −2.16 V corresponds to a further reduction of **2** and is attributed to a U(IV)/U(III) couple. This fits with the range of values of redox potentials reported for other U(IV)/U(III) reversible systems.[74−76] Future studies will be directed to identify the chemical conditions allowing the isolation of this reduced species and to investigate its reactivity.

Reactivity of [U(μ-bis-^{Me}naphtquinolen)]$_2$ with Oxidizing Agents. The reaction of [U(μ-bis-^{Me}naphtquinolen)]$_2$ **2** with different oxidizing substrates has been investigated to assess if the electrons stored in the C−C bond can become available. Complex **2** can act as a multielectron reductant when reacted with 9,10-phenanthrenequinone, iodine, or molecular oxygen (Scheme 4).

Scheme 4. Reactivity of [U(μ-^{Me}bis-naphtquinolen)]$_2$ 2 with Oxidizing Agents



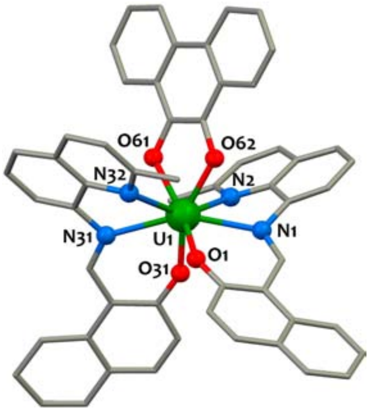


Figure 5. Mercury diagram of the solid-state molecular structure of [U(9,10-phenanthrenediol)(^{Me}naphtquinolen)$_2$] **3**. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: uranium (green), nitrogen (blue), oxygen (red), and carbon (gray).

Complex [U(9,10-phenanthrenediol)(^{Me}naphtquinolen)$_2$] **3** is obtained in 54% yield from the reaction of **2** with 9,10-phenanthrenequinone in toluene. The same reactivity is observed when using pyridine as solvent. The UV−visible spectrum for **3** is very similar to the one of **1-I**, with two strong absorption bands centered at 420 and 334 nm ($\varepsilon \approx 25000$ L cm^{-1} mol^{-1}) that we assign to ligand-based $\pi-\pi^*$ transitions. Notably, the tail absorption extending to 750 nm, characteristic of the reduced form of the ligand, is not present in **3**, in agreement with an oxidation of the ligand platform. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a pyridine solution of **3**, allowing its structural characterization. The molecular structure, as shown in Figure 5, consists of a C_2-symmetric complex where the uranium atom is octa-coordinated in a distorted square antiprismatic fashion by two tridentate monoanionic ^{Me}naphtquinolen ligands and one dianionic 9,10-phenanthrenediol ligand. The reduction of the quinone to its cathecolate form is confirmed by the analysis of the metrical parameters for the ligand. The average U−O$_{9,10\text{-phenanthrenediol}}$ bond distances (2.26(4) Å) are relatively short, as expected for a doubly charged phenolate ligand, and are in the same range of the U−O$_{\text{phenolate}}$ moieties from the ^{Me}naphtquinolen ligand (2.23(1) Å). The C−O bond distances for this ligand (1.359(1) Å) are in agreement with the presence of simple C−O bonds. The imino moieties of the ^{Me}naphtquinolen ligands have been restored, as is illustrated by the short C−N double bond distances (1.294(9) Å) and long U−N bond distances (2.52(1) Å) which compare well with those found in **1-Cl**. The overall neutral charge of the complex and the bond valence sum calculations are in agreement with a +IV oxidation state of the uranium cation in **3**.

The reduction of 9,10-phenanthrenequinone is likely to proceed through the coordination of the substrate to the metal center and disruption of the dimeric structure of **2** followed by the cleavage of the two ligand C−C bonds. Thus each mononuclear uranium(IV) complex [U(μ-bis-^{Me}naphtquinolen)] acts as a two electron reducing agent without undergoing a variation of the oxidation state of the metal center. In contrast to what was observed for the previously reported U(IV) multielectron redox system based on a tetradentate Schiff base, the presence of available coordination sites at the metal center allows a direct coordination of the incoming substrate to the uranium as shown by the structure of the oxidation product. This should provide a more controlled reaction pathway.

Proton NMR studies also show that the reaction of **2** with I_2 in toluene leads to the cleavage of the C−C bond restoring the original Schiff base structure and affords the **1-I** complex demonstrating the chemical reversibility of this redox system.

The number of transferred electrons can be increased when both the ligand and the metal are participating in the electron transfer. The reaction of a dark brown solution of **2** with excess dry oxygen in pyridine (where **2** is mostly present in its monomeric form **2b**) proceeds instantly to give a dark red/orange solution. The ^{1}H NMR spectrum recorded for the reaction mixture shows 13 resonances in the diamagnetic region, in agreement with the presence of the new uranyl(VI) complex [UO_2(^{Me}naphtquinolen)$_2$] **4**.

The solid-state structure of **4**, determined by single crystal X-ray diffraction, is represented in Figure 6. The uranium atom has a pentagonal bipyramidal coordination provided by the two oxo groups in axial positions and five O and N-donor atoms from two ^{Me}naphtquinolen ligands in the equatorial plane.

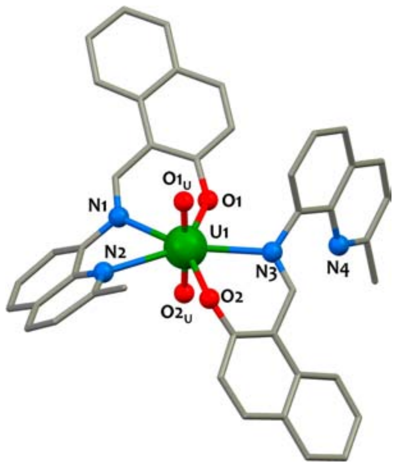


Figure 6. Mercury diagram of the solid-state molecular structure of $[UO_2(^{Me}naphtquinolen)_2]$ **4**. Hydrogen atoms are omitted for clarity. Color code: uranium (green), nitrogen (blue), oxygen (red) and carbon (gray).

While the first ^{Me}naphtquinolen ligand adopts a classical tridentate ONN coordination mode, as found in **1-Cl** and **3**, the second ^{Me}naphtquinolen ligand is bound to the uranium center in a bidentate fashion by the phenolate and the imino group with the nitrogen atom from the quinoline remaining noncoordinated. Pentagonal bipyramid is the most common coordination geometry for uranyl(VI) compounds, higher coordination numbers in the equatorial plane being disfavored for sterical reasons. The $C-N_{im}$ (1.276(6) and 1.308(6) Å) bond distances from both ^{Me}naphtquinolen ligands are in the same range than the ones found in **1-Cl** and **3**, confirming their imino character. $U-N_{im}$, $U-N_{aro}$, and $U-O_{naphtol}$ mean bond distances (respectively 2.547(2), 2.646(4), and 2.238(6) Å) compare well with those found in other uranyl(VI) Schiff base complexes.[47,54]

The uranyl UO_2 group in **4** is nearly linear (O−U−O angle 177.3(1)°) with uranyl bond distances (mean U−O distance 1.776(3) Å) falling in the characteristic range of seven-coordinate hexavalent uranyl complexes.[47,54]

The formation of complex **4** from **2b** provides a rare example of a transfer of 4 electrons from a mononuclear uranium(IV) complex.

■ SUMMARY

Here we have prepared and characterized new examples of U(IV) complexes containing a tridentate Schiff base. Redox reactivity studies show that the reduction of the $[UX_2(^{Me}naphtquinolen)_2]$ halides proceeds cleanly for the iodide precursor while multiple products are formed for the chloride derivative. The reduction leaves the oxidation state of the metal center unchanged and occurs on the imino function of the ligand leading to intramolecular C−C bond formation. The two electrons stored in the resulting amidophenolate U(IV) complex are released in the presence of oxidizing agents. In the U(IV) and U(VI) complexes $[U(9,10\text{-phenanthrenediol})(^{Me}naphtquinolen)_2]$, **3**, and $[UO_2(^{Me}naphtquinolen)_2]$, **4**, obtained respectively in the two- and four-electron reduction of oxidizing substrates, the restored tridentate Schiff base allows for the coordination of the reduced substrate to the metal. Thus tridentate Schiff bases provide a new example of redox active ligands which enable multielectron reductions at a U(IV) center. This shows that ligand centered reductions are not limited to tetradentate Schiff bases, and that controlled ligand centered reactivity can be achieved with lower denticity ligands by a careful choice of the reaction condition and ligand structure. Electrochemical studies suggest that the new U(IV) amidophenolate complex might provide a suitable precursor for the synthesis of highly reactive U(III) complexes. Future studies will be directed to investigate how the ligand structure affects the reducing properties in these systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected ^1H NMR and UV−vis spectra, pulsed-field-gradient stimulated-echo diffusion NMR data, selected cyclovoltammograms, bond valence sum calculations, X-ray crystallographic data, and files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: marinella.mazzanti@cea.fr.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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