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Multielectron Redox Reactions Involving C−C Coupling and Cleavage in Uranium Schiff Base Complexes

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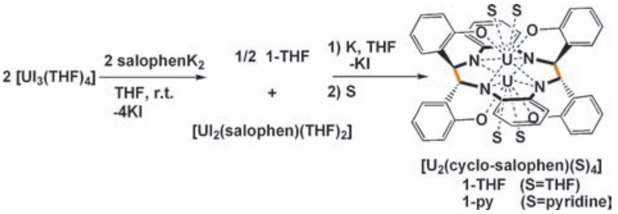
Abstract: The reaction of U(III) with Schiff base ligands and the reduction of U(IV) Schiff base complexes both promote C−C bond formation to afford dinuclear or mononuclear U(IV) amido complexes, which can release up to four electrons to substrates through the oxidative cleavage of the C−C bond.

Scheme 1. Synthesis of **1**



Multielectron redox reactions play a key role in many biological and synthetic catalytic processes.[1−3] Multiple-electron transfer reactions can be achieved from the association of redox-active metal centers and polydentate unsaturated ligands, which can store electrons in a reduced form.[4−16] The interesting reactivity of low-valent uranium toward small molecules such as CO, N_2, CO_2, and H_2O[17−23] renders particularly attractive the development of uranium complexes capable of performing multielectron reductions. Accordingly, the number of complexes associating uranium to redox-active ligands has been growing rapidly in the past few years.[10,24−32] In these reports, reduced actinide species have been stabilized by storing electron density on π-radical ligands. Rarely, coupling of the resulting π-radical ligands resulted in C−C bond formation.[28,32,33] Tetradentate Schiff bases are highly π-delocalized ligands that can provide a convenient way to store electrons in complexes of d-block elements[8] and samarium[9] through metal-assisted reversible reductive coupling of the imino groups. The use of such Schiff base ligands in actinide chemistry has been limited mostly to the chemistry of uranyl(VI),[34] but a few examples of Schiff base complexes of uranyl(V) and uranium(IV) have also been reported.[35−38] Arnold and co-workers[39] recently reported the synthesis of a unique U(III) complex of a macrocyclic Schiff base that was characterized by magnetic studies. Herein we demonstrate that the reaction of trivalent uranium with the tetradentate Schiff base *N*,*N*′-disalicylidene-*o*-phenylenediaminate (salophen) leads not to a U(III) complex but instead to reductive coupling of the Schiff base imino groups and the formation of C−C bonds, which can be cleaved by oxidizing agents. The new dinuclear U(IV) complex [U_2(*cyclo*-salophen)$(THF)_4$] (**1-THF**) containing a macrocyclic octaanionic amido ligand is formed in this reaction. Moreover, the reduction of the U(IV) complex [$U(salophen)_2$][35] leads to intramolecular C−C bond formation between two salophen units rather than to metal reduction.

The 1:1 reaction of $UI_3(THF)_4$ with salophenK_2 in THF yields the dinuclear complex **1-THF** and the U(IV) complex [$U(salophen)I_2(THF)_2$][40] in a 1:2 ratio (Scheme 1). The two complexes were characterized by ^{1}H NMR spectroscopy (Figures S1 and S2 in the Supporting Information) and electrospray ionization mass spectrometry (ESI−MS) (Figure S3). ^{1}H NMR spectroscopy studies showed that further reduction of this mixture with potassium metal yields **1-THF** as the only product (Figure S4). **1-THF** can be obtained in 86% yield from this reaction. Recrystallization of **1-THF** in pyridine yields the analogous pyridinate complex [U_2(*cyclo*-salophen)$(py)_4$] (**1-py**). Structural data were obtained for the derivative **1-py** by single-crystal X-ray diffraction (Figure 1). The structural parameters of **1-py** point unambiguously to the presence of a U(IV) dimer complexed by the octadentate octaanionic amidophenolate macrocyclic ligand *cyclo*-salophen formed from the reductive C−C coupling of the two imino groups of two salophen ligands. Notably, the U−N bond distances (2.39−2.60 Å) are significantly shorter than distances usually found in U(IV) Schiff base complexes (usual range: 2.58−2.65 Å).[36,37] Similarly, the C−N bond lengths [average value: 1.473(4) Å] are much longer than expected for imino moieties (usual range: 1.26−1.31 Å), in agreement with the occurrence of a reduced ligand. This was further confirmed by the sp^3 character of the

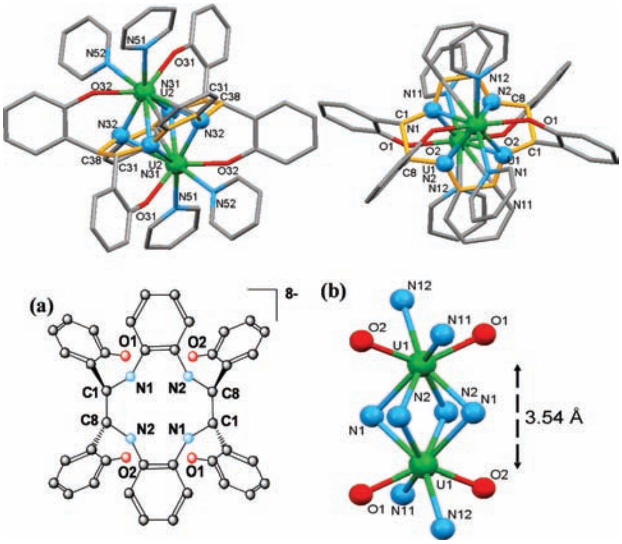


Figure 1. Top: Mercury diagrams of the structure of [U_2(*cyclo*-salophen)$(py)_4$] (**1-py**). Hydrogen atoms and solvent molecules have been omitted for clarity. The macrocyclic ligand core is represented in yellow, uranium in green, nitrogen in blue, oxygen in red, and carbon in gray. Bottom: (a) Drawing and numbering scheme of the *cyclo*-salophen ligand. (b) View of the core of complex **1-py** showing the coordination environment of the two uranium atoms.

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carbons involved in the C−C reductive coupling [average C1−C8−C_{phenol} angle: 110(1)°]. The value of the two resulting C−C distances [1.609(5) Å], although rather long, is in the range of C−C bond lengths found in sterically hindered systems. The resulting dinucleating ligand *cyclo*-salophen (Figure 1a) holds two uranium atoms in close proximity (Figure 1b), with a U−U distance of 3.54(1) Å. Magnetic data were collected over the temperature range 2−300 K for **1-THF** and **1-py**. The similarity of the χ versus T data (Figure S5) is in agreement with the presence of an analogous structure for the two complexes. In general, the magnetic susceptibility of U(IV) compounds displays Curie−Weiss behavior at high temperature and temperature-independent paramagnetism at low temperature.[41] The complexes **1-THF** and **1-py** showed a deviation from this behavior. Such a deviation in U(IV) dimers with a short U−U distance could suggest the presence of a magnetic interaction between the U ions.[41] Future studies will investigate further the presence of a U−U interaction.

The formation of **1-THF** in Scheme 1 is accompanied by the formation of the U(IV) complex [U(salophen)$I_2$$(THF)_2$]. The addition of potassium metal to this mixture allows the reduction of [U(salophen)$I_2$$(THF)_2$], affording the complex **1-THF** in a analytically pure form according to Scheme 1. The formation of **1-THF** probably proceeds through the stepwise (Scheme S1) or simultaneous reduction of four imino groups by four U(III) ions to yield unstable U(IV) complexes of the corresponding radical anions, which rapidly couple to form two C−C bonds. This indicates that $UI_3(THF)_4$ is able to reduce the imino group of the free or U(III)-bound salophen ligand. The fact that the formation of a half-reduced complex (with only one salophen imino group reduced) was not observed is probably due to the low stability of such species and the high stability of the [U(salophen)$I_2$$(THF)_2$] byproduct. Future studies, including cyclic voltametry, will be directed toward elucidating the mechanism leading to the formation of **1**. Preliminary studies have shown that further reduction of complex **1** with potassium leads to the formation of NMR-silent species, which are currently under investigation.

From Scheme 1 it is evident that the reduction of [U(salophen)$I_2$$(THF)_2$] with potassium metal can provide an alternative route for the synthesis of complexes **1-THF** and **1-py**. This observation suggested that the reduction of the bis-ligand complex [U$(salophen)_2$] (**2**) could be used to promote intramolecular C−C coupling between the imino groups of the salophen ligands to afford a mononuclear complex capable of multielectron redox reactions. The formation of C−C coupling promoted by U(IV) complexes associated[28,42] or not[32] with a reducing agent has been previously reported for imidazole, azine, pinacol, and benzophenone ketyl groups but not for imino groups.

Complex **2** is conveniently prepared[35] from the reaction of [$UI_4(PhCN)_4$] with 2 equiv of salophenK_2 in THF. An X-ray diffraction study of **2** revealed the presence of a sandwich structure in which the two salophen ligands adopt a boat conformation, encapsulating the uranium center between the convex sides of the two ligands. The solid-state structure of [U$(salophen)_2$] is presented in Figure 2 together with selected bond distances. The sandwich geometry and the short observed distances between carbon atoms from the imino groups of two different ligands in **2** (C7···C27, 4.51 Å; C14···C34, 4.84 Å) suggested that the intramolecular reductive C−C coupling might be possible.

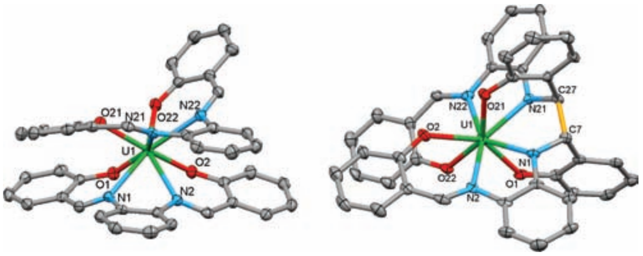
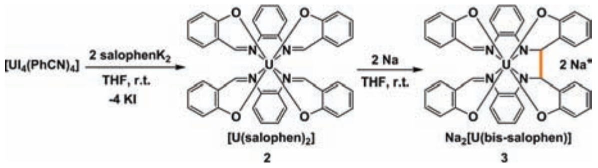


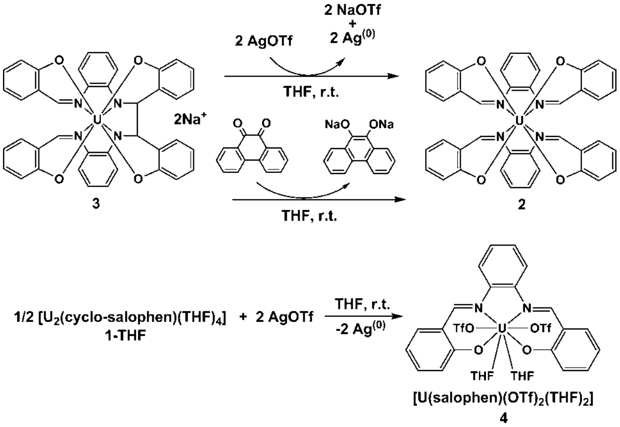
Figure 2. Mercury diagrams showing (left) **2** and (right) the [U(bis-salophen)]$^{2-}$ anion in **3-18C6**, with 30% probability ellipsoids. Hydrogens atoms have been omitted for clarity. U is shown in green, N in blue, O in red, C in gray, and the C−C bond bridging the two original salophen units in yellow). Selected bond distances (Å) in **2**: U1−N1, 2.623(6); U1−N2, 2.645(2); U1−N21, 2.629(6); U1−N22, 2.578(5). In **3-18C6**: U1−N1, 2.393(5); U1−N21, 2.380(5); U1−N2, 2.629(4); U1−N22, 2.619(5); C7−C27, 1.559(7).

Scheme 2. Synthesis of **2** and Its Further Reduction with Sodium To Afford **3**



The reduction was successfully performed by adding 2 equiv of sodium metal per uranium to **2** in THF (Scheme 2). The reduction afforded the reduced complex Na_2[U(bis-salophen)] (**3**) in 86% yield. Single crystals of the complex [Na(18-crown-6)$(py)_2$]$_2$[U(bis-salophen)] (**3-18C6**) suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a pyridine solution of **3** in the presence of excess 18-crown-6. The crystal structure of **3-18C6** shows unambiguously that the reduction occurs on the ligand rather than on the metal, ruling out the presence of a U(II) species in the final mononuclear complex. However, the mechanism of the reduction reaction could involve reduction of the metal followed by electron transfer to the ligand. Thus, the formula Na_2[U(bis-salophen)], where bis-salophen is a hexa-anionic octadentate ligand built from the reductive coupling of two imino groups, one from each salophen ligand, provides a good description of complex **3**. The value of the distance for the C−C bond between C7 and C27 resulting from the reductive coupling of the two salophen ligands [1.559(7) Å] is smaller than the corresponding distance in complex **1-py**. Bond distances and angles involving the C7, C14, C27, and C34 carbon atoms are consistent with sp^3 character for C7 and C27 and with sp^2 character for carbons C14 and C34. The values of the U−N bond distances are consistent[43,44] with the presence of two amido groups and two imino groups, with the U−N_{amido} distances [U1−N1, 2.393(5) Å; U1−N21, 2.380(5) Å] being significantly shorter than the U−N_{imino} distances [U1−N2,

Scheme 3. Two-Electron Reduction by Complex **3** and Four-Electron Reduction by Complex **1**



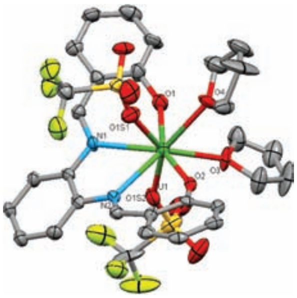


Figure 3. Mercury diagram of the solid-state molecular structure of [U(salophen)(OTf)$_2$(THF)$_2$] (**4**). Hydrogens atoms have been omitted for clarity. Uranium (green), sulfur (yellow), nitrogen (blue), oxygen (red), fluorine (light-green), and carbon (gray) atoms are represented with 30% probability ellipsoids.

2.629(4) Å; U1−N22, 2.619(5) Å]. This confirmed that a partial reduction of the salophen ligands occurred. The bond valence sum analyses of the complexes **1-py** and **3−18C6**, which were performed using the empirical expression and constants proposed by Brown[45] are also in agreement with the presence of uranium(IV) in both complexes (see Tables S15 and S16 in the Supporting Information).

Preliminary reactivity studies were performed on complexes **1-THF** and **3** to probe the ability of their C−C bonds to act as reservoirs of two electrons that can be involved in electron transfers (Scheme 3). The reactions of the mononuclear complex **3** with 2 equiv of the monoelectronic oxidizing agent AgOTf and with 1 equiv of the two-electron oxidizing agent phenanthrenequinone led to the cleavage of the C−C bond in complex **3**, restoring the original Schiff base complex **2**. Systems that can undergo reversible intramolecular C−C bond formation are of high current interest for the development of molecular responsive devices.[46]

Similarly, the reaction of the dimeric complex **1-THF** with 4 equiv of AgOTf led to the cleavage of the two C−C bonds and the disruption of the dinuclear structure, affording the new mononuclear U(IV) complex [U(salophen)(OTf)$_2$(THF)$_2$] (**4**) in which the two imino groups of the salophen ligand have been restored. Complex **4** can be prepared in 56% yield from this reaction. The structure of **4** was confirmed by X-ray diffraction (Figure 3). These reactions show that the complexes **1-THF** and **3** can act as four- and two-electron reducing agents, respectively, through cleavage of the ligand C−C bonds without undergoing a change in the oxidation state of the metal center.

In conclusion, we have shown that the tetradentate Schiff base salophen can be used to stabilize reduced uranium complexes by storing electrons in C−C bonds formed by reductive coupling of the imino groups. The stored electrons can become available to oxidizing agents through cleavage of the C−C bonds. Moreover, the reductive coupling of the Schiff base promoted by low-valent uranium provides an original, convenient route to the synthesis of dinuclear uranium complexes that is well-suited to the study of magnetic interactions and reactivity. Future work will investigate the reactivity of these complexes with different reducing and oxidizing substrates. The wide range of available Schiff bases leads us to anticipate the possibility of tuning the reactivity and magnetic properties in these systems.

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Supporting Information Available: Complete synthetic and experimental details; selected ^{1}H NMR and ESI−MS spectra; magnetic data; tabulated bond valence sum calculations; and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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