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A Versatile Route to Homo- and Heterobimetallic 5f-5f and 3d-5f Complexes Supported by a Redox Active Ligand Framework

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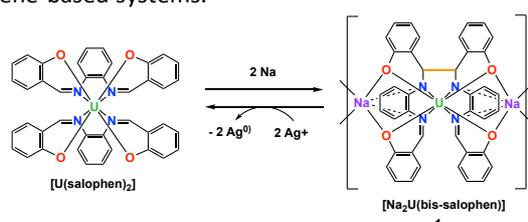
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The salt-elimination reaction of the complex [Na₂U(bis-salophen)] with metal halides provides an entry to the synthesis of well-defined homobimetallic uranium-uranium and rare heterobimetallic uranium-cobalt and uranium-nickel complexes supported by a redox-active dinucleating ligand.

Heterometallic 3d-5f coordination compounds are attracting increasing attention because of their importance in the fundamental understanding of the nature of bonding and metal-metal interaction in 5f elements.¹ Moreover, they offer the possibility to combine the distinct characteristics of f and d block elements to obtain new physical properties and to promote novel chemical reactivity.² Notably the association of uranium with 3d elements led to the discovery of original uranium-3d polymetallic assemblies with unique magnetic properties.³ Moreover, the importance of multimetallic cooperativity in the stoichiometric and catalytic transformation of molecules such as CO₂, CO or CS₂ is increasingly recognized,^{2,4} but most studies have so far focused of heterobimetallic complexes associating early/main group and late d-block metal ions.^{2,5}

To date, only a handful of heterobimetallic complexes that feature d-block and uranium metal centres in close proximity have been reported and their reactivity remains essentially

unexplored.⁶ Moreover, the use of redox active ligands⁷ in the synthesis and reactivity of 5f-3d complexes is so far limited to ferrocene-based systems.^{6c,8}



Recently, we have explored the chemistry of uranium complexes supported by Schiff-base ligands.^{8b,9} We found that the reduction of the [U^{IV}(salophen)₂] complex with Na (Scheme 1),^{9a} affords a U(IV) complex of the new dinucleating bis-salophen ligand via ligand-based reduction.

Scheme 1. C-C bond formation/cleavage in U(IV) Schiff base complexes.

Here we show that the complex [Na₂U(bis-salophen)] (Scheme 1) provides a versatile precursor for the synthesis of homo- and hetero-bimetallic complexes of the redox-active bis-salophen ligand via salt metathesis reaction.

Notably, the addition of one equivalent of [U₄(OEt₂)₂] or UCl₄ onto a THF solution of [Na₂U(bis-salophen)], **1** yields the homobimetallic complexes [U₂(bis-salophen)(S)_n]₂ (S= THF, n =

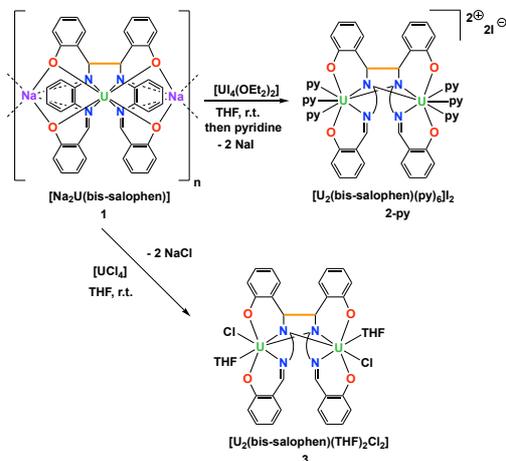
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Electronic Supplementary Information (ESI) available: [Electronic Supplementary Information (ESI) available: [Synthetic details, full crystallographic data, ¹H and ¹³C NMR spectra, ESI/MS spectra are included. CCDC 1539156 (**4-2py**); 1539157 (**2-py**); 1539158 (**5-THF**); 1539159 (**4-3py**); 1539160(**4-THF**); 1539161 (**3**)]. See DOI: 10.1039/x0xx00000x

3, **2-THF**; S = Py, n = 6, **2-py**) (Scheme 2) and $[U_2(\text{bis-salophen})(\text{THF})_2\text{Cl}_2]$, **3**, respectively. ESI/MS spectra of **2-THF** indicate the presence of a dinuclear species in THF solution ($m/z = 1231.1$, corresponding to the $\{[U_2(\text{bis-salophen})]\}^+$ moiety).



Scheme 2. Synthesis of complexes **2-py** and **3**.

Single crystals of $[U_2(\text{bis-salophen})(\text{py})_6]^{2+}$ **2-py** were obtained by recrystallization of **2-THF** from a pyridine/hexane solution while crystals of **3** were obtained from THF/hexane. The ^1H NMR spectra of **2-py** and **3** in pyridine- d_5 and in THF- d_8 solution respectively, display 14 shifted paramagnetic resonances indicating the presence of C_2 -symmetric U(IV) species in agreement with the pseudo- C_2 symmetry found in the solid state structure.

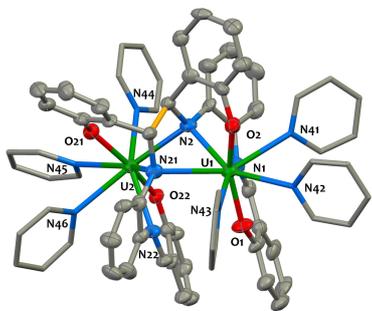
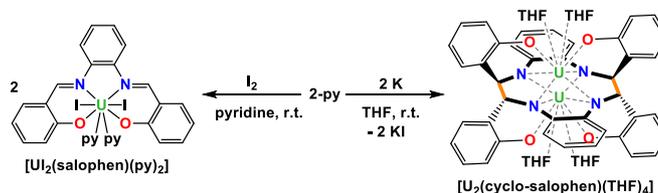


Figure 1. Solid-state structure of the cation $[U_2(\text{bis-salophen})(\text{py})_6]^{2+}$ in **2-py** (50% probability ellipsoids). Hydrogen atoms, counter anions and interstitial solvent molecules have been omitted for clarity.

The solid-state structure of **2-py** consists of isolated ions pairs and the structure of the $[U_2(\text{bis-salophen})(\text{py})_6]^{2+}$ cation is presented in Figure 1. The structure of **3** (see ESI) shows the presence of a neutral complex where a chloride ion binds each uranium cation. In both complexes two U(IV) ions are encapsulated by the octadentate hexaanionic chelating ligand bis-salophen which adopts an helical structure. It is remarkable that upon substitution of the two sodium ions in **1** by a U(IV) cation the hexaanionic ligand bis-salophen unfolds to accommodate a second uranium(IV) ion. These dinuclear

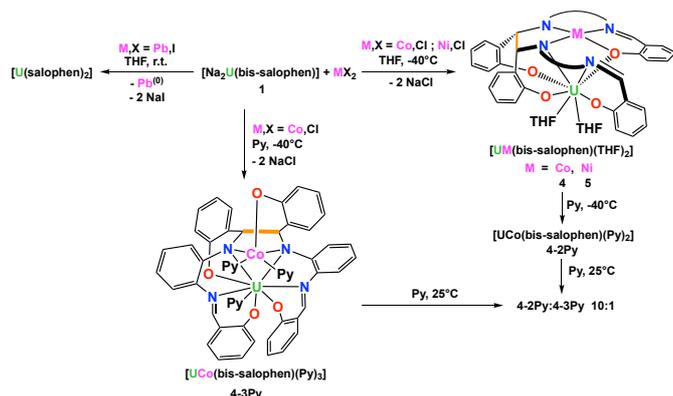
complexes present a pseudo- C_2 axis located between the two uranium ions and the two carbon atoms forming the C-C bond (in orange in scheme 2) connecting the two salophen moieties. Both uranium(IV) centres in **2-py** are eight-coordinated by two phenolate, two amido and one imino moieties from the bis-salophen ligand and three pyridine molecules in a slightly distorted dodecahedral fashion. The two amido moieties of the ligand act as bridging units and are unsymmetrically coordinated to the uranium atoms, the U1-N2 (2.4283(1) Å) and U2-N21 (2.4606(1) Å) bond distances being shorter than those of U1-N21 (2.6603(1) Å) and U2-N2 (2.6643(1) Å), in **2-py** and U1-N2 (2.448(5) Å) and U2-N4 (2.453(5) Å) being shorter than U2-N2 2.610(5) Å and U1-N4 (2.528(5) Å) in **3**. This results in a 4.0241(2) Å and 3.86(1) Å separation of the two uranums in **2-py** and **3** respectively, which is significantly longer than that (3.54(1) Å) observed in the more sterically constrained complex $[U_2(\text{cyclo-salophen})(\text{THF})_4]$.⁶ The U-N_{imino} and the U-N_{amido} average bond distances in complexes **2-py** and **3** are very similar to those found in complex **1**. Similarly the values of the C-C bond distance between the two amido groups in the bis-salophen ligand remain unchanged compare to complex **1**.



Scheme 3. Ligand-based redox reactivity of complex **2-py**.

The two electrons stored in the C-C bond between the two amido groups in **2-py** can become available for the reduction of oxidizing substrates. Notably, treatment of **2-py** with one equivalent of iodine leads to the cleavage of the C-C bond restoring the original Schiff base structure to yield $[U_2(\text{salophen})(\text{py})_2]$ (Scheme 3). However, the homobimetallic complexes **2-py** and **3** do not react with less reactive molecules such as CO_2 or CS_2 .

The reduction of **2-py** and **3** by potassium metal affords the previously reported $[U_2(\text{cyclo-salophen})(\text{THF})_4]$ ^{9a} complex. It should be noted that the complex **2-THF** could not be prepared by reduction of $[U_2(\text{salophen})(\text{THF})_2]$ with one equivalent of potassium, a reaction that only leads to the formation of the fully reduced $[U_2(\text{cyclo-salophen})(\text{THF})_4]$ ^{9a} complex and unreacted precursor.



Scheme 4. Reactivity of **1** with divalent metal halides.

We then extended this versatile synthetic route to access original 3d-5f heterobimetallic complexes. The reaction of **1** with an equimolar amount of MX_2 ($M, X = Co, Cl$; Ni, Cl) in THF or in pyridine affords $[UCo(bis-salophen)(S)_x]$, $S = THF$, $x = 2$, **4-THF**, $S = Py$, $x = 2$, **4-2py**, $S = py$, $x = 3$, **4-3py**, and $[UNi(bis-salophen)(S)_2]$, $S = py$ **5-py**, $S = THF$, in 57–64% yield (Scheme 4). The 1H NMR spectra of complexes **4** and **5** in THF or pyridine display 28 paramagnetic resonances indicating fully asymmetric species in solution. In order to obtain complexes **4** and **5** as the only reaction products the addition of the Co(II) and Ni(III) salts to **1** should be slow. Fast addition of MX_2 salts ($M = Co, Ni$) results in the formation of significant amounts of the oxidation product $[U(salophen)_2]$ and Co(0) or Ni(0). The reactivity of **1** with PbI_2 , does not afford a U-Pb heterobimetallic species but leads quantitatively to the $[U(salophen)_2]$ complex (Scheme 4). This suggests that in order to prepare heterobimetallic complexes from **1** the redox potential of the metal halide precursor has to be compatible with that of **1** ($E_{1/2} = -1.14V$ vs Fc^+/Fc , as determined by Cyclic Voltammetry) to avoid unwanted ligand-based oxidation.

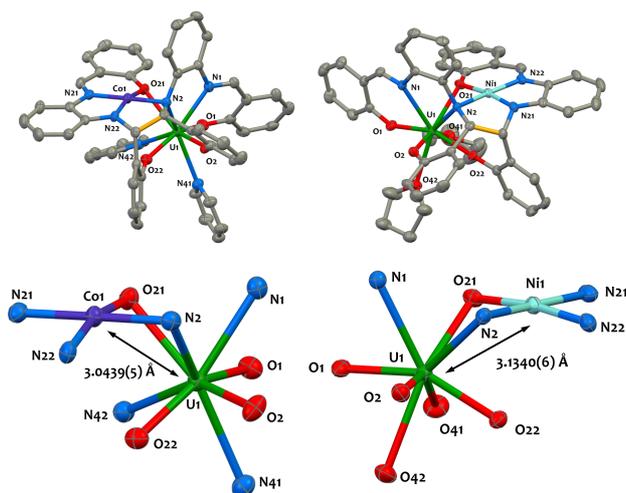


Figure 2. Solid-state molecular structures of **4-2py** (top left) and **5-THF** (top right) (50% probability ellipsoids) and metal coordination spheres in **4-2py** (bottom left) and **5-THF** (bottom right). Hydrogen atoms have been omitted for clarity.

The molecular structures of **4-5** ($S = THF$, **2py**, **3py**) and **5-THF** were determined by X-ray crystallography (Figure 2). Depending on the conditions of crystallization of **4** in pyridine (see supporting) two different types of compounds were isolated (**4-2py** and **4-3py**). These two compounds both exist in solution and display different proton NMR signals. Dissolution of **4-THF** in pyridine affords **4-2py** as a major product. When the reaction of **1** with $CoCl_2$ is carried out in pyridine at $-40^\circ C$ **4-3py** is obtained. **4-3py** partially rearranges to give **4-2py** in pyridine at room temperature. The X-ray crystal structures of the THF and pyridine adducts of $[UCo(bis-salophen)(X)_2]$ ($X = THF$ **4-THF** and $X = pyridine$ **4-2py**) are fairly similar both showing the presence of a four-coordinate square-planar cobalt(II) ion in a ONNN pocket. In contrast, in **4-3py** the cobalt(II) ion is pentacoordinated by one oxygen and two nitrogen atoms of the bis-salophen ligand and two pyridine nitrogens with a square pyramidal geometry. Similarly to what was observed for the formation of the homodinuclear uranium complexes **2-py** and **3**, the bis-salophen ligand unfolds in complexes **4-2py** and **5-THF** to accommodate a 3d metallic ion. The overall final structures are asymmetric and the bis-salophen ligand is highly distorted. All four structures present an octadentate dinucleating bis-salophen ligand that coordinates a 3d (Co(II) or Ni(II)) and one U(IV) ion. The metrical parameters of the ligand are in agreement with the presence of the hexaanionic amidoiminophenolate bis-salophen. The uranium ion is hexacoordinated by the ligand, and its coordination sphere is completed to eight in a distorted square antiprismatic fashion by the coordination of two solvent molecules. The two metallic ions are connected through $\mu-N_{amido}$ and $\mu-O_{phenolate}$ bridging atoms, and lie in remarkably close proximity (U-M distance: 3.0439(5) Å in **4-2py**, and 3.1340(6) Å in **5-THF**). The U-Co bond distance is significantly longer in **4-THF** (3.135 Å) and in **4-3py** (3.183 Å). These U-M distances are significantly shorter than those found in trimeric $U^{IV}Co_2$ (3.68(2) Å) and $U^{IV}Ni_2$ (3.64(1) Å) complexes supported by Schiff bases.^{3a, 10} Arnold and colleagues recently reported the sole examples of U-Ni bonds featuring significantly shorter intermetallic bond distances (2.556(1)–2.520(1) Å).^{6e} The U-Co separation in **4-2py** is larger than the sum of the covalent radii for Co and U (2.81 Å),¹¹ but falls in the range of the three examples of U-Co bonds reported in the literature (3.0319(7)–2.874(3) Å).^{6d, 6h, 6j} Another unexpected feature of the structure of **4-THF**, **5-THF** and **4-2py** is the configuration inversion of one single carbon atom with respect to the $[Na_2U(bis-salophen)]$ complex. This suggests that the C-C bridging bond (in orange in Figure 2) is broken and reformed during the coordination of the Co and Ni cation. This inversion is not observed in the **4-3py** complex.

The geometry adopted by the bis-salophen ligand in the structures of the bimetallic complexes reported here differs significantly from the geometry found in previously reported homobimetallic bis-salophen complexes of Co(II) and Ni(II). In the latter complexes the M(II) metals are bound in independent ONNO pockets of the bis-salophen ligand.¹²

Preliminary studies of the reactivity of the U-Co complex **4-3py** with CS_2 show that the presence of the Co(II) ion leads to an increased reactivity compared to the homodinuclear

complexes **2-py** and **3**. ^1H NMR studies show that the reaction of **4-3py** with 2 equiv of CS_2 leads to cleavage of the C-C bond of the bis-salophen ligand with complete conversion to the $[\text{U}(\text{salophen})_2]$ complex and concomitant formation of a Co(II) compound identified by EPR spectroscopy (see ESI). ^{13}C NMR of the reaction mixture in pyridine- d_5 show a signal at 248 ppm, a value that matches exactly the chemical shift previously reported for $[\text{K}(\text{18-c-6})]\text{C}_2\text{S}_4$ in deuterated pyridine¹³ and suggests that the putative $[\text{Co}(\text{C}_2\text{S}_4)]$ product (that was not previously reported in the literature) is fully dissociated in pyridine. This result indicates that the two electrons stored on the bis-salophen ligand become available for CS_2 reduction in the UCo heterobimetallic complex.

In summary, we reported a new versatile route to unusual heterobimetallic 3d-5f complexes supported by a redox non-innocent ligand. The combination of a redox non-innocent ligand together with uranium-transition metal cooperativity provides an attractive platform to enable multi-electron chemical transformations. Notably, preliminary studies show that in the heterodimetallic UCo complex the electrons stored in the ligand become available for the reduction of CS_2 . Future studies will be directed to expand the reported synthetic strategy to other heterobimetallic systems and to investigate their reactivity.

Acknowledgements

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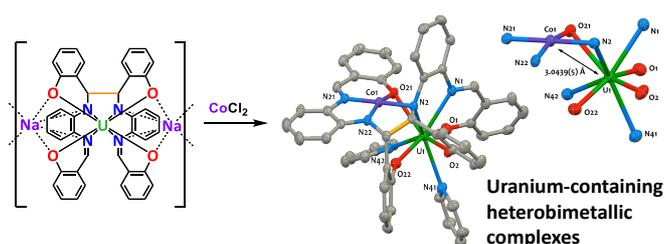
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