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

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The salt-elimination reaction of the complex \([\text{Na}_2\text{U(bis-salophen)}]\) 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.

Heterobimetallic 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. 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. Notably the association of uranium with 3d elements led to the discovery of original uranium-3d polymeric assemblies with unique magnetic properties. Moreover, the importance of multimetallic cooperativity in the stoichiometric and catalytic transformation of molecules such as \(\text{CO}_2\), \(\text{CO}\) or \(\text{CS}_2\) is increasingly recognized, but most studies have so far focused on heterobimetallic complexes associating early/main group and late d-block metal ions.

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. Moreover, the use of redox active ligands in the synthesis and reactivity of 5f-3d complexes is so far limited to ferrocene-based systems.

Recently, we have explored the chemistry of uranium complexes supported by Schiff-base ligands. We found that the reduction of the \([\text{U}^6(\text{salophen})_2]\) complex with \(\text{Na}\) (Scheme 1) affords a \(\text{U}(\text{IV})\) complex of the new dinucleating bis-salophen ligand via ligand-based reduction.

Here we show that the complex \([\text{Na}_3\text{U(bis-salophen)}]\) (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 \([\text{U}_2(\text{OEt}_2)_3]\) or \(\text{UCl}_4\) onto a THF solution of \([\text{Na}_3\text{U(bis-salophen)}]\), 1 yields the homobimetallic complexes \([\text{U}_2(\text{bis-salophen})(\text{S}_2)]_2\) (Scheme 1).
3, 2-THF; S = Py, n = 6, 2-py (Scheme 2) and [U2(bis-salophen)(THF)2Cl2], 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 ([U2(bis-salophen)])+. moeity).

Figure 1. Solid-state structure of the cation [U2(bis-salophen)(py2)]+ 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 [U2(bis-salophen)(py2)]+ 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 octodentate hexaionic 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 hexaionic ligand bis-salophen unfolds to accommodate a second uranium(IV) ion. These dinuclear complexes present a pseudo-C2 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 uranions in 2-py and 3 respectively, which is significantly longer than that (3.54(1) Å) observed in the more sterically constrained complex [U2(cyclo-salophen)(THF)4].6 The U-Nimino and the U-Namide 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.

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 [U2(salophen)(py)2] (Scheme 3). However, the homobimetallic complexes 2-py and 3 do not react with less reactive molecules such as CO2 or CS2.

The reduction of 2-py and 3 by potassium metal affords the previously reported [U2(cyclo-salophen)(THF)4]39a complex. It should be noted that the complex 2-THF could not be prepared by reduction of [U2(salophen)(THF)4] with one equivalent of potassium, a reaction that only leads to the formation of the fully reduced [U2(cyclo-salophen)(THF)4]39a complex and unreacted precursor.

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

Scheme 3. Ligand-based redox reactivity of complex 2-py.
We then extended this versatile synthetic route to access original 3d-5f heterobimetallic complexes. The reaction of 1 with an equimolar amount of MX₂ (M = Co, Cl; Ni, Cl) in THF or in pyridine affords [UCo(bis-salophen)](X)₂, S = THF, x = 2, 4-THF, S = Py, x = 2, 4-2py, S = py, x = 3, 4-3py, and [UNi(bis-salophen)](X)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(II) salts to 1 should be slow. Fast addition of MX₂ salts (M = Co, Ni) results in the formation of significant amounts of the oxidation product [U(salophen)]³⁻ and Co(0) or Ni(0). The reactivity of 1 with PbI₂, does not afford a U-Pb heterobimetallic species but leads quantitatively to the [U(salophen)₂] complex (Scheme 4). This suggests in order to prepare heterobimetallic complexes from 1 the redox potential of the metal halide precursor has to be compatible with that of 1 (E½ = -1.14V vs Fc/Fc⁺, as determined by Cyclic Voltammetry) to avoid unwanted ligand-based oxidation.

The molecular structures of 4-S (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 CoCl₂ is carried out in pyridine at -40°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 an 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 hexanionic 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 metal ions are connected through μ-Namide and μ-Ophenolate 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 U³⁺Co₂ (3.68(2) Å) and U²⁺Ni₂ (3.64(1) Å) complexes supported by Schiff bases.³,¹⁰ 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).⁶ 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).⁶,⁷,⁶,⁶ 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 [Na₂U(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 Cs₂ show that the presence of the Co(II) ion leads to an increased reactivity compared to the homodimetallic
complexes 2-py and 3. 1H NMR studies show that the reaction of 4-3py with 2 equiv of Cs2 leads to cleavage of the C-C bond of the bis-salophen ligand with complete conversion to the [U(salophen)]3 complex and concomitant formation of a (CoI) compound identified by EPR spectroscopy (see ESI). 13C NMR of the reaction mixture in pyridine d5 show a signal at 248 ppm, a value that matches exactly the chemical shift previously reported for [(18-crown-6)Cs]2 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 Cs2 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 heterobimetallic UCo complex the electrons stored in the ligand become available for the reduction of Cs2. Future studies will be directed to expand the reported synthetic strategy to other heterobimetallic systems and to investigate their reactivity.

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References

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