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Uranium(IV) Imidazolin-2-iminato Complexes: A New Class of Actinide Complexes

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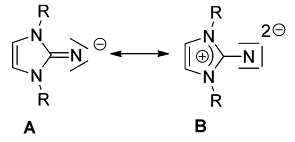
Supporting Information

ABSTRACT: Acid−base reactions between imidazolin-2-imines ($\mathrm{Im^RNH}$) and $[\mathrm{U(NMeEt)_4}]$ selectively afforded uranium(IV) imidazolin-2-iminato complexes of the type $[\mathrm{U(NIm^{\mathit{t}Bu})_4}]$ (**1**), $[\mathrm{U(NIm^{Mes})_3(NMeEt)}]$ (**2**), and $[\mathrm{U(NIm^{Dipp})_2(NMeEt)_2}]$ (**3**) depending on the steric demand of the substituents in the 1 and 3 positions of the imidazole heterocycle (R = *t*Bu, Mes, Dipp). This new class of actinide complexes displays short U−N bonds and nearly linear U−N−C bond angles, suggesting a U−N bond order higher than 1, as well as extraordinarily high catalytic activity in the polymerization of *ε*-caprolactone.

The coordination chemistry of imidazolin-2-iminato ligands toward transition and rare-earth metals has been extensively studied during the past decade,[1−3] and these nitrogen donors have become firmly established in organometallic chemistry and homogeneous catalysis,[4] most notably with regard to their use as ancillary ligands in olefin polymerization and as alkyne metathesis catalysts.[5,6] Owing to the ability of the imidazolium ring to effectively stabilize a positive charge,[7] imidazolin-2-iminato systems ($\mathrm{Im^RN}$) can be described by the two limiting resonance structures **A** and **B** (Scheme 1), with the latter revealing their propensity to act as $2\sigma,4\pi$-electron donors, in particular toward early transition metals in a high oxidation state. Consequently, the resulting metal complexes, e.g., with lanthanide(III) (lanthanide Ln = Sc, Y, Gd, Lu),[3] titanium(IV),[2,5] zirconium(IV), vanadium(V), molybdenum(VI), tungsten(VI),[6] and rhenium(VII), usually display very short metal (M)−N bonds together with large and almost linear M−N−C angles.[8]

Scheme 1. Resonance Structures for Imidazolin-2-iminato Ligands



In view of our long-standing experience in organoactinide chemistry,[9] we had anticipated that these characteristics also qualify imidazolin-2-iminato ligands for complexation of the actinides, with strong M−N interaction and multiple-bond character expected, for instance, in thorium(IV) and uranium(IV) complexes. However, our initial attempts to produce imidazolin-2-iminatouranium complexes by the reaction of $[(\mathrm{C_5Me_5})_2\mathrm{UCl_2}]$ with the silylated imine $\mathrm{Im^{\mathit{t}Bu}NSiMe_3}$ proved unsuccessful, and oxidation with formation of a uranium(V) complex containing a ring-opened and partially hydrogenated imidazoline moiety was observed instead.[10] This called for an alternative approach for the introduction of imidazolin-2-iminato ligands.

The preparation of imidazolin-2-iminato uranium(IV) complexes was carried out by the slow addition of a tetrahydrofuran (THF) solution of the $\mathrm{Im^RNH}$ ligand to a THF solution of the homoleptic $[\mathrm{U(NMeEt)_4}]$[11] at −78 °C. After stirring for 18 h at room temperature, the complex was isolated by extraction with hexane and recrystallization from a toluene solution at −60 °C in moderate-to-high yields.

Surprisingly, the number of imidazolin-2-iminato ligands attached to the uranium center could not be varied by changing the stoichiometry of the starting materials or by adjusting the reaction conditions, suggesting thermodynamic control of the acid−base reaction. Moreover, the number of imidazolin-2-iminato ligands attached to the metal atom shows a strong dependence on the steric bulk of the substituent R on the ligand backbone. While the sterically encumbering diisopropylphenyl (Dipp) substituent only allowed the coordination of two ligands, the slightly smaller mesityl substituent afforded the coordination of three ligands to the metal, whereas the *tert*-butyl-substituted ligand exclusively afforded the homoleptic uranium(IV) complex (Scheme 2).

The chemistry of uranium(IV) ketimide complexes has reached a high level of sophistication during the past decade, shedding light on the fundamental differences in bonding (participation of 5f orbitals), physical properties, and reactivity between transition metals and actinides.[12] The structural similarity of complexes **1**−**3** to uranium(IV) ketimides indicated by similar U−N bond lengths and U−N−C bond angles suggests significant donation of the ligand π electrons to the empty orbitals of the metal center.

The homoleptic complex **1** (Figure 1) crystallized in the monoclinic space group $P2_1/n$, with a ligand cone angle of 76°.[13] The similar U−N bond lengths [2.185(4) Å for U−N10, 2.188(4) Å for U−N7, 2.188(4) Å for U−N1, and 2.197(4) Å for

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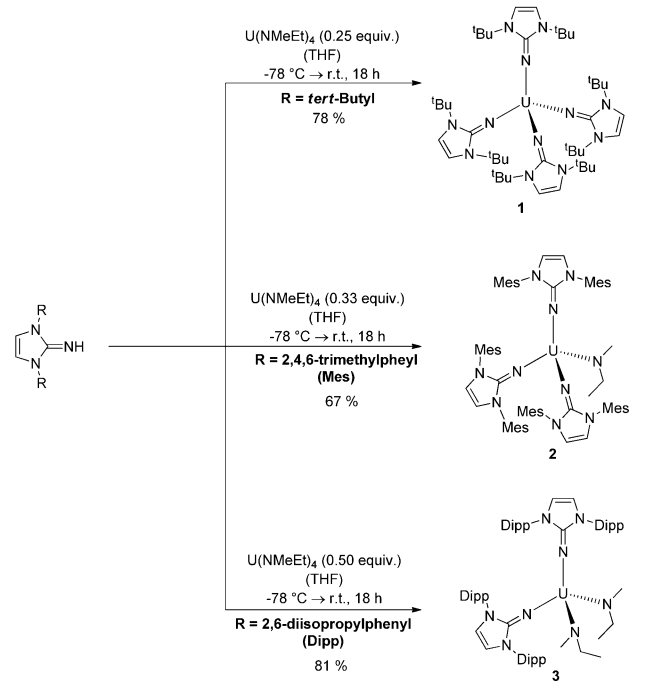
Scheme 2. Synthesis of Complexes 1−3



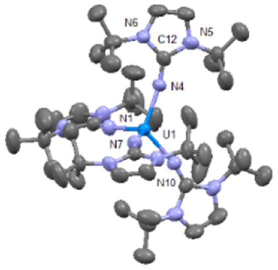


Figure 1. Molecular structure of **1**. Color code: U, green; N, blue; C, gray. Hydrogen atoms are omitted for clarity.

U−N4] and the N−U−N bond angles [119.80(15)° for N7−U−N1, 104.42(15)° for N10−U−N7, 104.94(3)° for N10−U−N1, 106.2516° for N7−U−N4, and 103.38(15)° for N1−U−N4] suggest equal interactions between the partially filled orbitals of the metal center with the corresponding valence orbitals of the ligand.

The different N−U−N bond angles in this homoleptic complex are presumably due to different packing deformation forces in the crystal. Interestingly, the U−N−C bond angles are nearly linear with values of 165.0(4)° for U−N7−C23, 166.3(4)° for U−N4−C12, 168.4(4)° for U−N10−C34, and 167.4(3)° for U−N1−C1, suggesting substantial π character to the U−N bond. Moreover, the bond lengths and angles in **1** are comparable to those of Kiplinger's uranium(IV) ketimide complexes, which exhibit short U−N bonds [2.179(6)−2.185(5) Å] and nearly linear U−N−C bond angles [173.4(6)−176.5(5)°].[12] The U−N bond lengths are significantly shorter than the U−N bond lengths in uranium(IV) amido complexes,[14] further substantiating a partial double-bond character of the U−N bond in the respective complexes.[12e]

We have carried out variable-temperature NMR studies for complex **1**, which show linear chemical shift displacement as a function of the temperature, indicative of Curie−Weiss behavior for a uranium(IV) complex.[15]

Compound **2** (Figure 2) crystallizes in the triclinic space group $P\bar{1}$, with a slightly smaller imidazolin-2-iminato ligand cone angle than that of **1** (70°). The U−N bond lengths are similar to those observed in complex **1**, with 2.174(11) Å for U−N1, 2.177(11) Å for U−N10, 2.226(8) Å for U−N4, and 2.239(7) Å for U−N7. The geometry of the U−N−C linkage depends on the substituent of the nitrogen atom. The U−N1−C1, U−N4−C22, and U−N7−C43 angles have values of 167.9(9)°, 155.6(8)°, and 165.0(8)°, respectively, and the U−N10−C64 angle is bent with a value of 114.9(15)°. The similarity of all U−N bond lengths indicates that the amido group is also partially donating π electron density to empty orbitals of the metal atom. This interaction induces a trigonal-planar geometry around the N$_{\text{amido}}$ bond (sum of angles 360°).

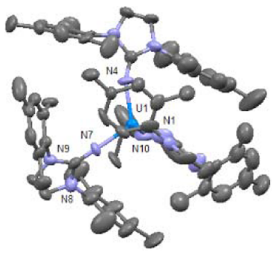


Figure 2. Molecular structure of **2**. Color code: U, green; N, blue; C, gray. Hydrogen atoms are omitted for clarity.

Compound **3** (Figure 3) crystallizes in the monoclinic space group $C2/c$ and exhibits an imidazolin-2-iminato ligand cone angle of 67°. The U−N bond lengths for both imidazolin-2-iminato ligands are nearly identical with U−N1 = 2.182(4) Å and U−N4 = 2.186(4) Å. The U−N bond to the amido nitrogen atoms is slightly longer with 2.214(5) Å for U−N7 and 2.216(5) Å for U−N8, respectively. The U−N1−C1 and U−N4−C28 angles of 170.4(4)° and 172.3(4)° are close to linearity, corroborating again the higher bond order of the U−N bonds.

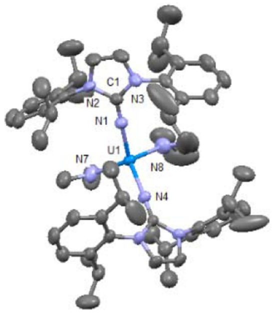


Figure 3. Molecular structure of **3**. Color code: U, green; N, blue; C, gray. Only one of the two molecules in the unit cell is shown. Hydrogen atoms are omitted for clarity.

The increasing π character of the U−N bond may also lead to a decreasing π character of the N−C$_{\text{ipso}}$ bond, distinguishable in the elongation of the same in the corresponding metal-bound imidazolin-2-iminato ligand, in comparison to the double bond of the free ligand. However, in the uranium imidazolin-2-iminato complexes **1−3**, no elongation of the N−C$_{\text{ipso}}$ bond was observed. This is consistent with Kiplinger's results in structurally similar uranium(IV) ketimide complexes.[12]

The uranium complexes **1−3** were analyzed by UV−vis spectroscopy, exhibiting molar absorptivity values of ε_1 = 573 M^{-1}·cm^{-1} (λ_1 = 442 nm) and ε_2 = 854 M^{-1}·cm^{-1} (λ_2 = 356 nm) for complex **1**, $\varepsilon_1 = 563$ $M^{-1}\cdot cm^{-1}$ ($\lambda_1 = 500$ nm) and $\varepsilon_2 = 1073$ $M^{-1}\cdot cm^{-1}$ ($\lambda_2 = 343$ nm) for **2**, and $\varepsilon = 1155$ $M^{-1}\cdot cm^{-1}$ ($\lambda = 377$ nm) for **3**, respectively, which are comparable to the reported uranium ketimido complexes.[12c]

Because of the high oxophilicity of the early actinides, there are not many examples for catalytic reactions involving oxygen-containing substrates.[16] However, previous studies have shown that certain thorium and uranium complexes are active in the polymerization of cyclic esters, such as L-lactide and ε-caprolactone.[17] The electrophilic uranium complexes **1**−**3** are expected to exhibit a slightly higher electron density on the uranium(IV) center in comparison to uranium(IV) complexes with fewer electron-donating ligands because of the high nucleophilic nature of the imidazolin-2-iminato ligands. Therefore, the metal center will be slightly less electrophilic, which will presumably decrease its oxophilicity.

A lower oxophilicity of the metal center may lead to a more rapid insertion of an oxygen-containing substrate (activity), instead of formation of a thermodynamically stable uranium−oxo species, making it less available for any further reaction and therefore decreasing its catalytic activity. Therefore, a delicate equilibrium must be reached between the number of ancillary ligands (steric hindrance) and the electron density at the metal center, in order to achieve a very active catalyst toward a specific substrate like ε-caprolactone. Although a large variety of organometallic complexes have shown high activities in the polymerization of cyclic esters,[18] complex **3** showed an extremely high activity in the formation of polycaprolactone (PCL) at room temperature (activity = 7.0×10^6 g(PCL)$\cdot mol^{-1}\cdot h^{-1}$) with a molecular weight of $M_w = 517800$ Da and a polydispersity of 1.8. Interestingly, complexes **1** and **2** showed lower catalytic activities and were sufficiently active only at 90 °C [complex **1**, 7880 g(PCL)$\cdot mol^{-1}\cdot h^{-1}$; complex **2**, 5312 g(PCL)$\cdot mol^{-1}\cdot h^{-1}$], which is comparable to the activity found for the homoleptic $U(NMeEt)_4$ [3500 g(PCL)$\cdot mol^{-1}\cdot h^{-1}$ at 90 °C]. For complex **3**, 2 equiv of the free amine were obtained after protonolysis with the α-hydrogen of the caprolactone, starting polymerization.

In summary, this work introduces the synthesis and characterization of a new family of imidazolin-2-iminato actinide complexes. The stoichiometry of the formed complexes depends strongly on the steric properties of the ligand. The complexes showed in all cases short $U{-}N_{imidazoline}$ bonds and almost linear U−N−C orientations. Preliminary results for the polymerization of ε-caprolactone showed extraordinarily high catalytic activities for complex **3**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis and characterization of complex **1**−**3** as well as for the polymerization of ε-caprolactone, CIF files, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors and everyone gave approval to the final version.

Notes

The authors declare no competing financial interest.

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