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Uranium Pyrrolylamine Complexes Featuring a Trigonal Binding Pocket and Interligand Noncovalent Interactions

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S *Supporting Information*

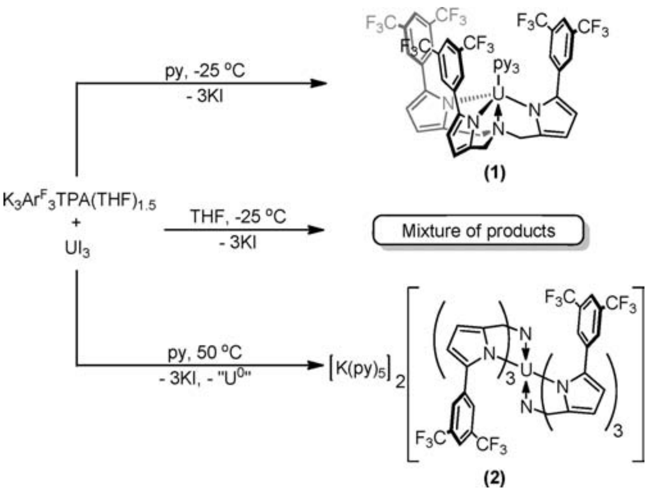
ABSTRACT: The syntheses of tri- and tetravalent uranium complexes of the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand [$\mathrm{Ar^F}$ = 3,5-bis(trifluoromethyl)phenyl; TPA = tris(pyrrolyl-α-methyl-amine)] are described. Interligand noncovalent interactions between arene groups within the complexes are detected both in the solid state and in solution.

The incorporation of noncovalent interactions into the secondary coordination sphere of metal complexes is a proven strategy for stabilizing reactive fragments and effecting new chemistry.[1,2] Because the metal–ligand bonding in many f-block complexes is largely ionic and nondirectional,[3] we postulated that noncovalent interactions between ligands could promote directed coordination chemistry at f-block ions by providing *collective secondary structures*.[4] The use of collective secondary structures could contribute to several research themes including the stabilization of uranium(III) and uranium(V) complexes that are prone to disproportionation,[5,6] the isolation of complexes of reactive small-molecule fragments at f-block ions,[7] and the mitigation of kinetic factors, such as large inner-sphere electron-transfer reorganization energy, which impede the oxidation of cerium(III) compounds.[8]

As a first step to probe these ideas, we set out to prepare complexes showing attractive noncovalent interactions between ligands in the coordination sphere of a uranium ion that could be detected in the solid state using X-ray crystallography and in solution using NMR spectroscopy. We reasoned that a well-defined molecular pocket at a metal ion picketed by electron-deficient arene groups could bind aryl-based ligands cooperatively through dative and arene–arene interactions. The C_3-symmetric $\mathrm{Ar_3TPA^{3-}}$ and other tris(pyrrolyl) ligands have recently been used in transition-metal chemistry for small-molecule activation[9] and magnetism studies.[10,11] Herein we report the synthesis of uranium complexes of the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand [$\mathrm{Ar^F}$ = 3,5-bis(trifluoromethyl)phenyl; TPA = tris-(pyrrolyl-α-methylamine)]. In contrast to related transition-metal complexes of the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand, the uranium complexes form trigonal frameworks with three open-coordination sites. The uranium complexes show evidence for arene–arene interactions[12] between the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand and pyridyl ligands in the solid state and in solution.

Green-black $\mathrm{U^{III}(Ar^FTPA)(py)_3}$ (**1**) was produced from the slow addition of a dilute tetrahydrofuran (THF) solution of $\mathrm{K_3Ar^F{}_3TPA(THF)_{1.5}}$ to a stirred solution of $\mathrm{UI_3}$ in a mixture of 20 mL of THF and 0.5 mL of pyridine at −25 °C (Scheme 1). The product was obtained in 55% yield following crystallization. The moderate yield of the complex is due to its solubility in organic solvents. Attempts to synthesize a THF analogue of **1** failed, generating only mixtures of intractable products in the absence of pyridine. The X-ray structure of **1** (Figure 1) displays a seven-coordinate, C_3-symmetric geometry at the $\mathrm{U^{III}}$ ion, where the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand binds in a tetradentate fashion and three pyridine molecules complete the coordination sphere. The $\mathrm{U^{III}}$ ion in **1** is displaced ~0.86 Å above the plane of the pyrrolyl nitrogen atoms, in contrast to the ~0.4–0.7 Å displacements observed in transition-metal TPA complexes.[9–11,13]

Scheme 1. Syntheses of Complexes 1 and 2



The U–$\mathrm{N_{pyrrolyl}}$ bond lengths in **1** are long at an average distance of 2.602(6) Å. Reported $\mathrm{U^{III}}$–$\mathrm{N_{pyrrolyl}}$ bonds in calix[4]pyrrole complexes are ~2.52 Å.[14,15] The long U–$\mathrm{N_{pyrrolyl}}$ distances are presumably the result of a poor fit of the $\mathrm{U^{III}}$ ion with three bound pyridines into the pocket of the $\mathrm{Ar^FTPA^{3-}}$ ligand. Notably, each pyridine ligand is found in an offset face-to-face orientation with respect to an adjacent $\mathrm{Ar^F}$ substituent on the $\mathrm{Ar^F{}_3TPA^{3-}}$ ligand at an observed pyridine–$\mathrm{Ar^F}$ interaryl–centroid distance of ~3.5 Å. These metrics

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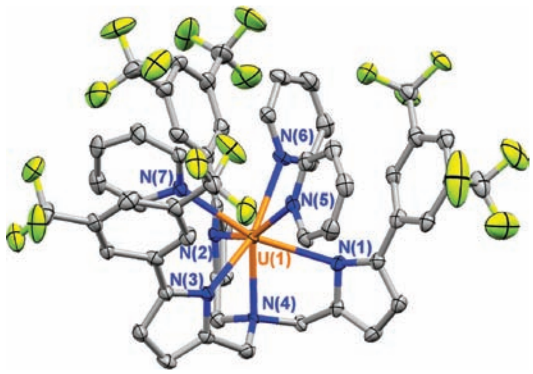


Figure 1. Thermal ellipsoid plot of **1** at 50% probability. Hydrogen atoms and interstitial solvents are omitted for clarity. Bond lengths (Å) and angles (deg): U−N(1) 2.605(6), U−N(2) 2.595(5), U−N(3) 2.605(6), U−N(4) 2.561(5), U−N(5) 2.641(6), U−N(6) 2.653(6), U−N(7) 2.632(6); N(4)−U−N(1) 71.1(2), N(4)−U−N(2) 70.8(2), N(4)−U−N(3) 69.9(2), N(4)−U−N(5) 130.0(2), N(4)−U−N(6) 128.7(2), N(4)−U−N(7) 128.5(2).

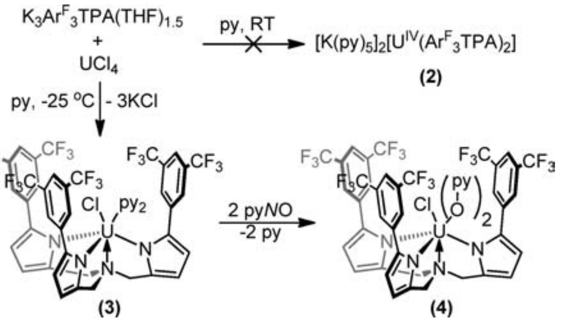
support the presence of face-to-face interarene interactions between the pyridine ligands and Ar^F substituents. Face-to-face arene−arene interactions are typically ~3.5 Å[16] but can be expected to be longer with more bulky substituents. The assignment of the ^1H NMR spectrum of **1** confirms the C_3 symmetry of the complex in solution at room temperature because eight resonances are observed as expected. A single, sharp resonance is observed in the ^{19}F NMR spectrum at −65.8 ppm, consistent with a symmetric ligand environment. Magnetism measurements carried out on **1** displayed a room temperature magnetic moment of 2.91 μ_B, typical for the $5f^3$ electronic configuration of a U^{III} ion.[17] Variable-temperature and low-temperature/variable-field magnetism studies also supported the assignment of **1** as a uranium(III) complex (see Figures S17 and S18 in the Supporting Information). Electronic structure calculations performed on the optimized geometry of **1** demonstrate that the valence 5f orbitals are largely uninvolved in bonding in this complex (see Supporting Information).

Following the same reaction conditions for the synthesis of **1** but performing the addition at room temperature resulted in the formation of the bright-yellow complex $[K(py)_5]_2[U^{IV}(Ar^F{}_3TPA)_2]$ (**2**; Scheme 1). Heating at 50 °C rapidly produced **2** as the major product. Generation of this uranium(IV) product from a uranium(III) starting material implicates a disproportionation pathway ($4U^{III} \rightarrow 3U^{IV} + U^0$).[18] Crystallization from diethyl ether provided **2** in 52% yield. The crystal structure of **2** (Figure S2 in the Supporting Information) shows tetradentate coordination of the U^{IV} ion by each of the two $Ar^F{}_3TPA^{3-}$ ligands in an eight-coordinate, pseudocubic geometry. This structure also contains interarene interactions between all of the Ar^F and pyrrolyl groups. The arms of the two $Ar^F{}_3TPA^{3-}$ ligands interdigitate such that each Ar^F ring is aligned with an adjacent pyrrolyl ring with an average Ar^F centroid to pyrrolyl centroid distance of ~3.7 Å. The U^{IV} ion in **2** is displaced ~1.0 Å above each plane of three pyrrolyl nitrogen atoms.

The ^1H NMR spectrum of **2** in pyridine-d_5 at room temperature displays six resonances in a 2:1:1:1:1:1 ratio. Five resonances are expected based on the equivalency of the six Ar^F pyrrolylmethylene arms of the two ligands. The appearance of a sixth resonance is rationalized on the basis that the *o*-hydrogen atoms on the Ar^F substituents are inequivalent on the NMR time scale. The ^{19}F NMR spectrum supports this assignment. It displays two broad peaks in a 1:1 integration due to hindered rotation of the Ar^F rings nestled into the cleft of the adjacent ligand. It is evident that the self-complementary arrangement of arene groups in the structure of **2** contributes to the formation of the 1:2 complex. Noting the tendency of **2** to form from UI_3, we attempted to prepare it directly from UCl_4.

The addition of $K_3Ar^F{}_3TPA(THF)_{1.5}$ to a solution of UCl_4 in THF/pyridine at −25 °C produced red $U^{IV}(Ar^F{}_3TPA)(py)_2Cl$ (**3**; Scheme 2). Surprisingly, performing this reaction at room temperature led to no observable formation of **2** even when 2 equiv of $K_3Ar^F{}_3TPA(THF)_{1.5}$ was added (Scheme 2). In our hands, complex **2** was only accessible through a disproportionation reaction of the uranium(III) starting material. As in the study of **1**, attempts to prepare the analogous THF adduct of **3** in the absence of pyridine were unsuccessful.

Scheme 2. Syntheses of Complexes 3 and 4 and Failed Synthesis of 2 from UCl_4



The structure of **3** reveals a seven-coordinate geometry (Figure S3 in the Supporting Information). The average $U-N_{pyrrolyl}$ bond length in **3** is 2.375(9) Å, ~0.23 Å shorter than the related distances in **1** and slightly shorter than the previously reported U^{IV}−pyrrolyl bond lengths in calix[4]-pyrrole complexes.[14] In complex **3**, one pyridine ligand is sandwiched between two Ar^F rings at an average Ar^F centroid to pyridine centroid distance of ~3.6 Å. The second pyridine ligand shows no short interarene distances with the Ar^F groups. The U^{IV} ion lies ~0.87 Å above the plane of the three pyrrolyl nitrogen atoms, nearly identical with **1**. Magnetic susceptibility measurements carried out on **3** displayed a room temperature magnetic moment of 3.32 μ_B and variable-temperature and -field responses typical for a $5f^2$ ion.[17]

The number of ^1H and ^{19}F NMR resonances of **3** is highly dependent on the temperature as well as the solvent (Figure 3). In pyridine-d_5, five $Ar^F{}_3TPA$ ligand resonances are observed for **3** in the ^1H NMR spectrum between −23 and +62 °C, indicating that the complex is effectively C_3-symmetric in a pyridine-d_5 solution at room temperature. These peaks appear sharp at higher temperature and broaden at lower temperature, until they can no longer be observed below −23 °C (Figure S14 in the Supporting Information). The absence of resonances observed for bound pyridine and the effective C_3 symmetry is consistent with fast exchange of the pyridine ligands with pyridine-d_5. Similar behavior is observed in ^{19}F NMR, where a single sharp peak broadens at lower temperature. Spectra collected for **3** in toluene-d_8 exhibit more complicated features. At room temperature, the ^1H NMR spectrum displays a number of broad, overlapping peaks, consistent with an

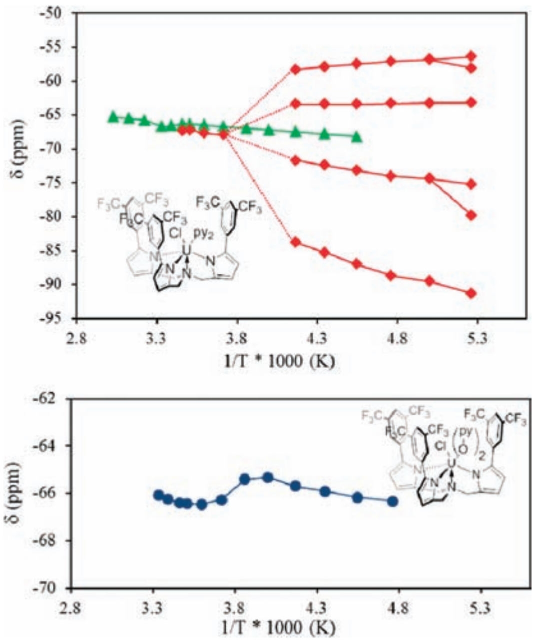


Figure 3. Variable-temperature ^{19}F NMR data for complexes **3** (top) and **4** (bottom). Lines are provided as a guide for the eye. Dotted lines indicate the region around coalescence.

unsymmetric ligand environment. Below room temperature, multiple decoalescence processes are evident in the ^{19}F NMR spectrum (Figure S16 in the Supporting Information). The appearance of multiple decoalescence processes in the variable-temperature NMR experiment suggests that the molecule adopts multiple low-energy conformations that readily equilibrate. These conformations likely correspond to interactions between the Ar^F rings and the pyridine ligands. To further investigate the role of interarene interactions in **3**, we prepared a second Lewis base adduct of **3**.

The addition of 2 equiv of pyridine *N*-oxide (py-O) to **3** leads to the immediate formation of green-yellow $U^{IV}(Ar^F{}_3TPA)(py\text{-}O)_2Cl$ (**4**). Complex **4** was obtained by crystallization at −25 °C from a concentrated solution in toluene layered with hexane in 90% yield, and the structure was determined. A similar local geometry at the U^{IV} ion is observed in **4** as in **3** (Figure S4 in the Supporting Information), but there is an elongation (~0.07 Å) of the $U-N_{pyrrolyl}$ bonds in **4** consistent with the increased electron-donating nature of the py-O ligand relative to pyridine. The major difference in the solid-state structures of **3** and **4** is that the py-O ligands in **4** are unable to orient into the same interarene interactions with the Ar^F rings because of extension of the aryl group of the py-O ligand out of the trigonal pocket. Importantly, the absence of interarene interactions in **4** results in a significant change in the ^{1}H NMR spectrum of **4** relative to **3**. Apart from broadening of the single ^{19}F NMR signal at ~280 K, complex **4** is C_3-symmetric in toluene-d_8 between room temperature and −50 °C. No decoalescence of the ^{19}F NMR peak for **4** into multiple peaks was observed, signifying equivalent chemical environments of the Ar^F rings on the NMR time scale.

In summary, we have shown that uranium(III) and uranium(IV) complexes of the $Ar^F{}_3TPA^{3-}$ ligand possess interligand noncovalent interactions with pyridine ligands bound within a trigonal pocket. We expect that directed interligand noncovalent stabilization will be a generally applicable strategy for manipulation of reactive uranium centers. We are currently expanding upon these initial findings in the context of small-molecule activation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files (CIFs), full experimental details, computational details and data, ^{1}H and ^{19}F NMR spectra, and magnetism data. This material is available free of charge via the Internet at http://pubs.acs.org.

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