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Uranium (III) Scorpionates: Synthesis and Structure of $[(Tp^{Me_2})_2U\{N(C_6H_5)_2\}]$ and $[(Tp^{Me_2})_2U\{N(SiMe_3)_2\}]$

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Reaction of $[(Tp^{Me_2})_2UI]$ with KNR_2 (R = C_6H_5, $SiMe_3$) in tetrahydrofuran (THF) afforded the monomeric trivalent actinide amide complexes $[(Tp^{Me_2})_2U\{N(C_6H_5)_2\}]$, **1**, and $[(Tp^{Me_2})_2U\{N(SiMe_3)_2\}]$, **2**. The complexes have been fully characterized by spectroscopic methods and their structures were confirmed by X-ray crystallographic studies. In the solid state **1** and **2** exhibit distorted pentagonal bipyramidal geometries. The U–NR_2 bond lengths in both complexes are the same but in complex **2** the greater steric demands of the $N(SiMe_3)_2$ ligand led to elongated U–N(pz) bonds, especially those opposite the amido ligand.

Introduction

The exploration of the molecular chemistry of uranium(III) owes much to the availability of a convenient starting material, $[UI_3(THF)_4]$,[1] and to the introduction of the pentamethylcyclopentadienyl group, C_5Me_5, as a stabilizing and solubilizing ancillary ligand.[2] However, in the past few years there has been increased interest in other alternative ligand systems,[3] including the polypyrazolyl borate or "scorpionate" ligands, a sobriquet coined by Trofimenko to relate the tridentate coordination behavior of these ligands to the simple analogy of a scorpion grabbing its prey with two claws and completing the attack with its stinger-terminated overarching tail.[4]

For the past few years we and Sella had investigated the chemistry of samarium and neodymium systems anchored by the hydrotris(3,5-dimethylpyrazolyl)borate scorpionate ligand, $(Tp^{Me_2})^-$, and we have reported the synthesis of a variety of compounds, such as the halides $[(Tp^{Me_2})_2SmX]$ (X = F, Cl, Br, I),[5] aryloxides $[(Tp^{Me_2})_2SmOR]$ (R = Ph, Ph-4-Bu^t, C_6H_2-2,4,6-Me_3, C_5H_4N),[6–8] diphenylamide $[(Tp^{Me_2})_2Sm(NPh_2)]$,[7] phenylalkynide $[(Tp^{Me_2})_2Sm(CCPh)]$,[9] cyclopentadienide $[(Tp^{Me_2})_2Sm(Cp)]$,[10] and related neodymium complexes.[11]

With the availability of $[(Tp^{Me_2})_2UI]$,[12] we decided to explore the chemistry of this system to assess whether it could be a useful precursor for a range of trivalent uranium

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$[(Tp^{Me_2})_2U(ER)]$ compounds and, if so, to compare their nature to the $[(C_5Me_5)_2U(ER)]$ analogues. Ultimately we intend to look for differences between the lanthanide and uranium chemistry that could reflect differences in accessible oxidation states and in metal−ligand bond polarity. Here we describe the preparation and full characterization of the scorpionate supported uranium(III) amides $[(Tp^{Me_2})_2U(NR_2)]$ (R = C_6H_5 (**1**); $SiMe_3$ (**2**)).

Results and Discussion

Metathesis of $[(Tp^{Me_2})_2UI]$ with one equivalent of either $KN(C_6H_5)_2$ or $KN(SiMe_3)_2$ in THF proceeds readily and yields respectively, after simple workup, $[(Tp^{Me_2})_2U\{N(C_6H_5)_2\}]$ (**1**) and $[(Tp^{Me_2})_2U\{N(SiMe_3)_2\}]$ (**2**). The compounds are obtained as black, air-sensitive powders in moderate yield (eq 1) with small amounts of $[(Tp^{Me_2})_2U(dmpz)]$ (dmpz = 3,5-dimethylpyrazolyl) formed as a byproduct. The latter compound could be separated from **1** or **2** by extraction with *n*-hexane, due to its high solubility in this solvent. The compounds are soluble in aromatic and ether type solvents, but poorly soluble in aliphatic hydrocarbons. The elemental analyses and the spectroscopic data are in full accord with the molecular formulation.

$$[(Tp^{Me_2})_2UI] + KR_2 \xrightarrow{THF} [(Tp^{Me_2})_2U(NR_2)] + KI$$
$$(R = C_6H_5,\ \mathbf{1};\ SiMe_3,\ \mathbf{2}) \quad (1)$$

The IR spectra of **1** and **2** show the ν(B−H) stretching modes at 2540 and 2560 cm^{-1}, respectively, typical of κ^3 coordination modes for both Tp^{Me_2} ligands.[10,13] Like its samarium analogue, the ^1H NMR spectrum of **1** at room temperature exhibited six equal intensity Tp^{Me_2} methyl and three 4-H singlets, consistent with a nonfluxional C_2 symmetric coordination sphere, as observed in the solid (vide infra). The ^1H NMR spectrum of **2** at room temperature exhibits a similar pattern of singlets with chemical shifts varying, in most cases, less than 2 ppm compared to **1**, in the relatively wide +25 to −50 ppm window, suggesting very similar structures for **1** and **2**. The resonance of the trimethylsilyl protons for **2** is a singlet at 0.64 ppm. In the case of **1**, at 20 °C only two resonances were observed for the diphenylamide protons, due to fortuitous overlap of the *m*- and *p*-protons. By raising the temperature of the sample to 40 °C this resonance splits in two, due to the different dependences of the chemical shifts with changing temperature. The UV−vis spectra of **1** and **2** in THF show several weak absorption bands in the near-IR region, very similar to those found in other uranium(III) polypyrazolylborate compounds.[14]

The diphenylamide complex **1** crystallized from a THF/toluene mixture in the space group $C2/c$ with a molecule of toluene in the lattice. Crystals of $\mathbf{1}\cdot C_7H_8$ are isomorphous with those of the previously reported $[(Tp^{Me_2})_2Sm(NPh_2)]$ compound.[7] Crystallized instead by slow evaporation of a THF solution, the bis(trimethylsilyl)amide complex **2** packs in the space group $P\overline{1}$ with 2.5 molecules of THF in the lattice. Although not isomorphous with one another, both $[(Tp^{Me_2})_2U(NR_2)]$ complexes display structures which are very similar in many respects. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are given in Table 1. Complex **1** has a crystallographic imposed 2-fold axis, passing through the uranium and N(1) atoms. Complex **2** lacks the crystallographic 2-fold axis; however, it too approximates C_2 symmetry in the solid state supporting the assignment of a nonfluxional C_2 coordination sphere in solution by ^1H NMR data. For clarity of discussion both complexes have been given similar labeling schemes, where the symmetry related

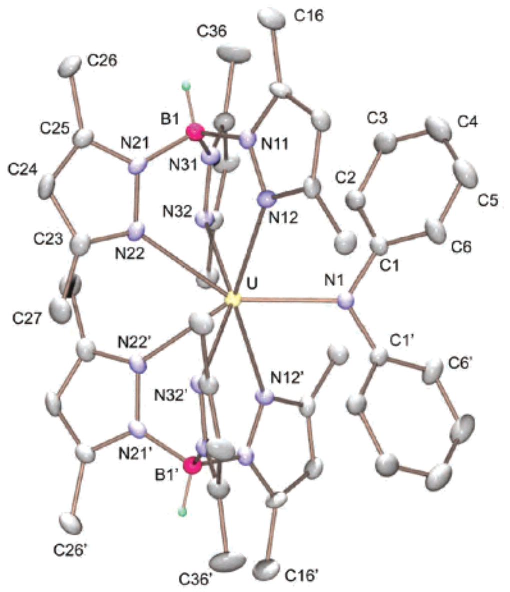

Figure 1. Molecular structure diagram of $[(Tp^{Me_2})_2U(NPh_2)]\cdot C_7H_8$ using 20% probability ellipsoids.

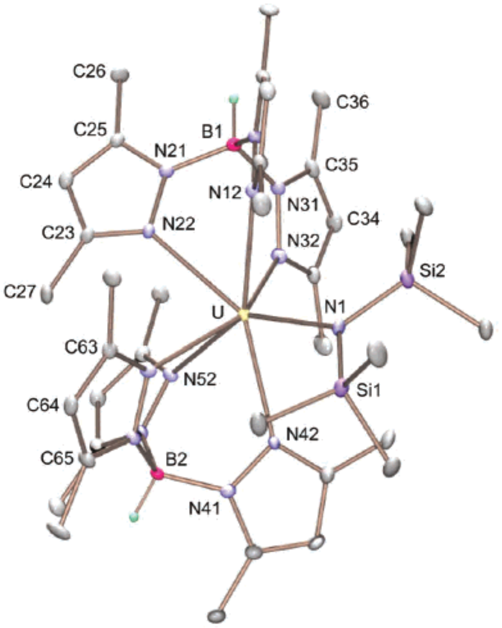

Figure 2. Molecular structure diagram of $[(Tp^{Me_2})_2U\{N(SiMe_3)_2\}]\cdot 2.5\ C_4H_8O$ using 20% probability ellipsoids.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{1}\cdot C_7H_8$ and $\mathbf{2}\cdot 2.5\ C_4H_8O$

parameter	$1\cdot C_7H_8$	$2\cdot 2.5\ C_4H_8O$
U−N1	2.489(9)	2.480(6)
U−N12	2.625(6)	2.681(6)
U−N22	2.695(7)	2.754(6)
U−N32	2.544(6)	2.542(5)
U−N42		2.674(6)
U−N52		2.802(6)
U−N62		2.555(5)
B1−U−B1′ (B2)	151.9(3)	138.49(18)
N1−U−N12	74.08(15)	77.98(19)
N1−U−N42		79.70(19)
N1−U−N32	105.50(15)	108.06(19)
N1−U−N62		107.14(19)
N1−U−N22	142.27(14)	144.78(18)
N1−U−N52		145.88(19)
N12−U−N22	68.2(2)	67.01(17)
N12−U−N32	86.0(2)	82.82(17)
N22−U−N32	70.85(19)	72.29(18)
N22−U−N22′ (N52)	75.5(3)	69.2(2)
N32−U−N32′ (N62)	149.0(3)	144.79(19)

atoms 1x′, 2x′, and 3x′ of **1** correspond to atoms 4x, 5x, and 6x in structure **2**. Both compounds adopt distorted pentagonal bipyramidal geometries, with N(32) and N(32′)/N(62) occupying the axial sites (N(32)−U−N(32′)/N(62) angles of 149.0(3)° and 144.8(2)°, respectively). In both structures the U−N(axial) distances (**1** 2.544(6), and **2** 2.549(5) Å) are shorter than those in the equatorial girdle (**1** 2.66(1), and **2** 2.73(2) Å; average). Although, the meaning of the average is less clear in **2** due to its more distorted nature as reflected in the large range of U−N(eq) values, 2.674−2.802 Å, and the more severe bending of the two Tp^{Me_2} ligands. The B−U−B angles in **2** and **1** are 138.5(2)° and 151.9(3)°, respectively; the latter is close to the 152.0(4)° and 151.6(2)° observed in the respective Sm and Nd analogous $[(Tp^{Me_2})_2Ln(NPh_2)]$ complexes.[7,11] The more distorted nature of **2** can be traced to the bulkier nature of the $N(SiMe_3)_2$ ligand compared to NPh_2, or perhaps more appropriately to the less structurally accommodating features of the former. As evident in Figure 1, the NPh_2 ligand is so positioned that Ph groups nestle between pyrazolyl rings 1 and 3 of the scorpionate ligands, allowing for relatively normal κ^3 bonding of the Tp^{Me_2} ligands. Similar arrangements are seen in the $[(Tp^{Me_2})_2Ln(NPh_2)]$ (Ln = Sm, Nd) analogues. Although the arrangement of the $SiMe_3$ groups in **2** is similar, the bulky $SiMe_3$ group does not permit such favorable intercalation between the pyrazolyl rings. Since the $U-NR_2$ bond lengths in **1** and **2** are the same (2.489(9) and 2.480(6) Å, respectively), the Tp^{Me_2} ligands in **2** not only twist and bend back but slip away to relieve the steric congestion and this leads to a significant lengthening of the U−N(22) (2.754(6) Å) and U−N(52) (2.802(6) Å) bonds opposite the $N(SiMe_3)_2$ ligand.

It is noteworthy that despite the shorter radii of seven-coordinate Sm(III) and Nd(III) (ca. 0.07 and 0.04 Å) compared to U(III),[15] the respective Ln-NPh_2 distances, 2.435(11) Å and 2.480(5) Å, in the $[(Tp^{Me_2})_2Ln(NPh_2)]$ complexes are similar to the $U-NR_2$ distances in **1** and **2**, indicating that steric congestion is more severe in the former complexes. In fact we and Sella were unsuccessful in preparing the scorpionate supported $Ln-N(SiMe_3)_2$ (Ln = Sm, Nd) derivatives, reflecting the delicate balance at play between size of the metal and steric size of the ligand. In contrast, both $[(C_5Me_5)_2U\{N(SiMe_3)_2\}]$[16] and $[(C_5Me_5)_2Sm\{N(SiMe_3)_2\}]$[17] complexes, containing the less bulky C_5Me_5 supporting ligands, are stable and exhibit slightly shorter $M-NR_2$ distances (2.352(2) Å and 2.301(3) Å, respectively) than the 2.480(6) Å distance observed in **2**.

Conclusions

$[(Tp^{Me_2})_2UI]$ provides a convenient entry into a new class of uranium(III) complexes. Salt metathesis of $[(Tp^{Me_2})_2UI]$ with one equivalent of $KNPh_2$ or $KN(SiMe_3)_2$ affords the corresponding scorpionate supported amide complexes $[(Tp^{Me_2})_2U(NR_2)]$ (R = Ph, $SiMe_3$). In the solid state the complexes display pentagonal bipyramidal geometry, as observed for the analogous $[(Tp^{Me_2})_2Ln(NPh_2)]$ (Sm and Nd) complexes. The successful synthesis of $[(Tp^{Me_2})_2U\{N(SiMe_3)_2\}]$, an amido derivative that could not be obtained for samarium or neodymium, reflects the delicate balance at play between size of metal and steric size of ligand. The reactivity of the uranium amide complexes is under investigation and derivative chemistry of uranium(III) based on scorpionate ligands will be reported in due course.

Experimental Section

All operations were performed using standard Schlenk line and drybox techniques under an inert atmosphere of nitrogen. THF, toluene, and *n*-hexane were dried by standard methods and degassed prior to use. Benzene-d_6 was dried over Na and distilled. $[(Tp^{Me_2})_2UI]$ was synthesized by reported methods.[12] **Safety Note:** Depleted uranium and many associated daughter nuclei are radioactive. Working with uranium requires appropriate training and facilities. $KNPh_2$ was prepared by reacting freshly sublimed $HNPh_2$ with a small excess of KH in THF. $KN(SiMe_3)_2$ was purchased from Aldrich. ^1H NMR spectra were recorded on a Varian INOVA-300 spectrometer and referenced internally using the residual solvent resonances relative to tetramethylsilane (benzene-d_6, 7.15 ppm). IR spectra were recorded on a Perkin-Elmer 577 spectrometer. UV−vis-near IR spectra were recorded on a Varian Cary 5G spectrophotometer using 1 cm quartz cells. Carbon, hydrogen, and nitrogen analyses were performed in-house using an EA110 CE Instruments automatic analyzer.

$[(Tp^{Me_2})_2U(NPh_2)]$ (1). A solution of $KNPh_2$ (68 mg, 0.33 mmol) in THF was slowly added to a solution of $[(Tp^{Me_2})_2UI]$ (315 mg, 0.33 mmol) in the same solvent, at room temperature. After the mixture was stirred overnight, the precipitate of KI was removed and the solution was evaporated to dryness. The solid was washed with several portions of hexane to extract the green $[(Tp^{Me_2})_2U(dmpz)]$ that was formed during the reaction in small amounts. The remaining black solid was vacuum-dried. Yield: 75% (245 mg, 0.25 mmol). Anal. Calcd for $C_{42}H_{54}N_{13}B_2U$: C, 50.41; H, 5.44; N, 18.20. Found: C, 50.64; H, 5.27; N, 17.33. IR (Nujol, cm^{-1}): 2540 (B−H). UV−vis (in THF, nm): 520(sh), 554, 628, 678(sh), 752(sh), 854, 888(sh) 934, 1015(sh), 1174, 1209, 1231, 1263. ^1H NMR

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Table 2. Summary of Crystallographic Data for $\mathbf{1}\cdot C_7H_8$ and $\mathbf{2}\cdot 2.5\ C_4H_8O$

compound	$\mathbf{1}\cdot C_7H_8$	$\mathbf{2}\cdot 2.5\ C_4H_8O$
formula	$C_{49}H_{62}B_2N_{13}U$	$C_{46}H_{82}B_2N_{13}O_{2.5}Si_2U$
formula weight	1092.77	1173.08
cryst dimensions (mm)	0.75 × 0.18 × 0.15	0.26 × 0.12 × 0.12
cryst syst	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
unit cell parameters		
a (Å)	16.760(3)	10.779 (2)
b (Å)	16.996(2)	16.163 (3)
c (Å)	17.581(2)	16.736 (3)
α (deg)		82.681 (4)
β (deg)	98.63(2)	79.948 (4)
γ(deg)		71.766 (4)
V (Å^3)	4951(1)	2718.5 (9)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.466	1.433
μ (mm^{-1})	3.326	3.087
refln/restr/param	4338/0/308	11084/10/605
$R_1(F^2)$	0.0561	0.0524
$wR_2(F^2)$	0.1025	0.1249
GOF	1.043	1.014
$\Delta\rho$ min(max) (e Å^{-3})	0.923(−0.918)	2.328(−1.891)

(C_6D_6, 20 °C): δ 21.89 (2H, s, 4-*H*), 20.72 (6H, s, C*H*$_3$), 11.91 (2H, s, 4-*H*), 8.41 (6H, $H_m + H_p$), 4.04 (6H, s, C*H*$_3$), 2.33 (6H, s, C*H*$_3$), −2.41 (6H, s, C*H*$_3$), −3.7 (4H, br, H_o), −13.71 (2H, s, 4-*H*), −14.04 (6H, s, C*H*$_3$), −42.22 (6H, s, C*H*$_3$).

[(Tp^{Me_2})$_2$U{N(SiMe$_3$)$_2$}] (2). The reaction was carried out analogously to the preparation of **1**, utilizing 226 mg (0.24 mmol) of [(Tp^{Me_2})$_2$UI] and 47 mg (0.24 mmol) of KN(SiMe$_3$)$_2$. Yield: 77% (183 mg, 0.18 mmol). Anal. Calcd for $C_{36}H_{62}B_2N_{13}Si_2U$: C, 43.55; H, 6.30; N, 18.34. Found: C, 43.47; H, 6.71; N, 18.42. IR (Nujol, cm^{-1}): (B−H) 2560. UV−vis (in THF, nm): 510(sh), 641, 842, 928, 1018, 1107, 1154, 1174, 1199, 1229, 1254(sh), 1265. ^{1}H NMR (C_6D_6, 20 °C): δ 22.33 (2H, s, 4-*H*), 19.65 (6H, s, C*H*$_3$), 10.64 (2H, s, 4-*H*), 5.03 (6H, s, C*H*$_3$), 0.64 (18H, s, *SiMe*$_3$), −0.33 (6H, s, C*H*$_3$), −0.93 (6H, s, C*H*$_3$), −12.18 (6H, s, C*H*$_3$), −12.84 (2H, s, 4-*H*), −46.58 (6H, s, C*H*$_3$).

X-ray Crystallographic Analysis of 1. Black irregular plates of $\mathbf{1}\cdot C_7H_8$ were grown from a THF/toluene mixture and kept at −10 °C. The crystals were immersed in Nujol and mounted in thin-walled glass capillaries in a nitrogen filled glovebox. Data were collected at room temperature on an Enraf-Nonius CAD4-diffractometer, with graphite-monochromated Mo Kα radiation, using the ω-2θ scan technique. The data were corrected for Lorentz and polarization effects,[18] for linear decay, and empirically for absorption by Ψ scans. Table 2 summarizes the crystallographic data. The structure was solved by Patterson methods and successive difference Fourier techniques,[19] and refined by full-matrix least squares refinement on F^2 using SHELXL-97.[20] A severely disordered toluene solvent molecule near a center of symmetry was localized in the asymmetric unit. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, except the solvent carbon atoms. The contributions of the hydrogen atoms were included at calculated positions (except those of the solvent molecules). Atomic scattering factors and anomalous dispersion terms were taken from ref 19. The illustration was made with a POV-Ray rendering generated from ORTEP-3 instructions.[21]

X-ray Crystallographic Analysis of 2. Black prisms of $\mathbf{2}\cdot 2.5\ C_4H_8O$ were grown from slow evaporation of a THF solution kept at −30 °C. The crystals were immersed in Paratone-N oil and one was selected using a glass fiber and transferred to the cold nitrogen stream bathed goniometer head. Data were collected at −80 °C on a Bruker P4/RA/SMART 1000 CCD diffractometer, with graphite-monochromated Mo Kα radiation, using φ rotations and ω scans.[22] Unit cell parameters were obtained from a least-squares refinement of 4023 centered reflections from the data collection. The lack of systematic absences indicated the space group to be $P\bar{1}$ (No. 2). The data were corrected for absorption through use of the face-indexed Gaussian integration. Table 2 summarizes the crystallographic data. The structure of **2** was solved using the program DIRDIF-96[23] and refinement was completed using the program SHELXL-93.[24] Two full-occupancy well behaved, as well as a half-occupancy severely disordered tetrahydrofuran solvent molecules were localized in the asymmetric unit. The latter was found to be rotationally disordered as well as disordered about the inversion center ($^1/_2$, $^1/_2$, $^1/_2$); the bond distances were fixed at 1.50 Å and the 1,3 distances were fixed at 2.40 Å. Each of the atoms (C30S, C31S, C32S, C33S, C34S, O30S, O31S, O32S, O33S, and O34S) of this inversion/rotation-disordered THF molecule was refined as 80% carbon/20% oxygen with an occupancy factor of 0.5 and with a common isotropic displacement parameter. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, except the disordered solvent atoms. Hydrogen atoms were assigned positions based on the geometries of their attached carbons, and were given thermal parameters of 20% greater than those of the attached carbons. The disordered solvent's hydrogen atoms were included with an occupancy factor of 0.4. The final model for **2** refined to values of $R_1(F^2) = 0.0524$ (for 8612 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1249$ (for 11084 independent data with $[F_o^2 \geq -3\sigma(F_o^2)]$). The largest peak and hole in the final difference Fourier map have densities of 2.328 and −1.891 e$^-$ Å^{-3}, respectively, and are without chemical significance. The illustration was made with a POV-Ray rendering generated from ORTEP-3 instructions.[21]

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Supporting Information Available: X-ray crystallographic data in CIF format for **1** and **2** including tables of final atomic coordinates, thermal parameters, and interatomic distances, angles, and torsional angles are available free of charge via the Internet at http://pubs.acs.org. These files have also been deposited with the Cambridge Crystallographic Data Centre (www: http://www.ccdccam.ac.uk), CCDC Nos. 240356 and 240357.

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