Unique Uranium(III) Cations Anchored by Polydentate Sulfur-Based Ligands: Synthesis and Structure of $[U\{H(R)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$ (R = H, Ph)

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Received June 28, 2001

Poly(pyrazolyl)borates have been extensively used in studies of structure and reactivity issues that are relevant to many different areas.[1] The synthetic utility of these ligands, together with cyclopentadienyls, cyclooctatetraenyl, and borohydrides, has contributed to the development of lanthanide and actinide chemistry.[2,3] Uranium has been the most studied 5f element, but almost all the complexes structurally characterized are neutral. Examples of cationic U (III, IV and V) complexes anchored by those ligands are rare.[4−6]

We and others have been studying the chemistry of U(III) with bis(pyrazolyl)borates, with different substituents at the 3- and 5-positions of the pyrazolyl rings and with different groups coordinated to the boron atom.[7] The structurally characterized compounds are neutral, and the number of ligands coordinated to the metal depends very much on the nature of the substituents at the 3-position of the rings.[7] Taking into account that, so far, the coordination chemistry of U does not involve the use of polydentate soft donor ligands as anchors, we decided to investigate how the chemistry of this metal center is affected by replacing a hard donor set by a significantly softer one. Specifically, we decided to replace two pyrazolyl rings in dihydrobis(pyrazolyl)borates by two (2-mercapto-1-methylimidazolyl) rings. Here we wish to report the synthesis and structural characterization of the cationic complexes $[U\{H(R)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$ (R = H (**1**) and R = Ph (**2**)), which are unprecedented cationic U(III) complexes anchored by poly(thioimidazolyl)borate ligands.

In both complexes, the dihydrobis(thioimidazolyl)borate ligand, $[H(R)B(tim^{Me})_2]^-$, acts as a tridentate ligand to the metal center through the two thione sulfurs and one agostic hydrogen. This coordination mode is analogous to what has been observed with the harder congeners, $[H_2B(pz^*)_2]^-$, (pz* = pz, 3,5Me$_2$-pz, 3^{t}Bu,5Me-pz), previously reported.[7] In contrast, the number of poly(pyrazolyl)borates that it is possible to coordinate to the metal center is completely different from what has been observed for **1** and **2**. Previously, some uranium compounds with M−S bonds have been described, but these compounds were supported by cyclopentadienyl, poly(pyrazolyl)borate, or cyclooctatetraene ligands.[8] Complexes **1** and **2** can be prepared by reacting $UI_3(THF)_4$[9] with $M[H(R)B(tim^{Me})_2]$ (M = Na and R = H, M = Li and R = Ph)[10] and with $TlBPh_4$ in THF, in the molar ratio 1:2:1, and are obtained as red-brown solids, leading to prismatic crystals after recrystallization from THF/*n*-hexane (yield: **1**, 50%; **2**, 60%) (Scheme 1).[11]

Spectroscopic data[12] and the solid state structural analysis[13] are in accord with the formulation $[U\{\kappa^3\text{-}H(R)B(tim^{Me})_2\}_2(THF)_3]$-

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[11] Synthesis of **1** and **2**: A THF solution (20 mL) of $Na[H(H)B(tim^{Me})_2]$ (200 mg, 0.764 mmol) or $Li[H(Ph)B(tim^{Me})_2]\cdot THF$ (301 mg, 0.764 mmol) was added to a blue slurry of $UI_3(THF)_4$ (346 mg, 0.382 mmol) in the same solvent (25 mL). The mixture was stirred overnight at room temperature, resulting in the complete precipitation of a red solid. The red solid was filtered off and washed several times with THF. The solid was suspended in THF, and $TlBPh_4$ (200 mg, 0.382 mmol) in THF was added dropwise. After the mixture was stirred (2 days for **1** and overnight for **2**), a red-brown solution was obtained, which was separated from the yellow TlI by filtration. The supernatant was vacuum-dried to give a red-brown powder. Analytically pure samples were obtained by recrystallization from THF/hexane (**1**, 50% yield; **2**, 60% yield).

[12] Complex **1**: IR (cm^{-1}) 2380 (V br, (ν(B−H)), 1575 (ν(C=C), BPh$_4$), 1015 (ν_{asym}(C−O−C), thf), 860 (ν_{sym}(C−O−C), thf); ^{1}H NMR (300 MHz, thf-d_8, 20 °C, δ (ppm)) 7.35 (8 H, br, *o*-Ph), 6.89 (8H, m, *m*-Ph), 6.73 (4H, m, *p*-Ph), 6.56 (4H, br, C−H), 4.62 (4H, br, C−H), 3.78 (12H, br, Me); ^{1}H NMR (300 MHz, C_5H_5N-d_5, 20 °C, δ (ppm)) 7.90 (8H, s, *o*-Ph), 7.13 (8H, m, *m*-Ph), 6.96 (4H, *p*-Ph), 5.62 (4H, s, C−H), 4.18 (12H, s, Me), 3.62 (12H, thf), 1.58 (12H, thf). Complex **2**: IR (cm^{-1}) 2320 (ν(B−H···U)), 1575 (ν(C=C), BPh$_4$), 1550 (ν(C=C), Ph−B), 1020 (ν_{asym}(C−O−C), thf), 860 (ν_{sym}(C−O−C), thf); ^{1}H NMR (300 MHz, C_5H_5N-d_5, 20 °C, δ (ppm)) 8.05 (8H, s, *o*-Ph), 7.27 (8H, t, *m*-Ph), 7.09 (4H, t, *p*-Ph), 6.59 (4H, t, Ph), 6.34 (2H, t, Ph), 5.54 (4H, d, Ph), 5.49 (4H, br, C−H), 4.25 (12H, br, Me), 3.62 (12H, thf), 1.59 (12H, thf); ^{1}H NMR (300 MHz, C_5H_5N-d_5, −33 °C, δ (ppm)) 8.19 (2H, s, C−H), 8.07 (8H, s, *o*-Ph), 7.29 (8H, t, *m*-Ph), 7.09 (4H, t, *p*-Ph), 6.66 (2H, s, C−H), 6.37 (4H, t, Ph), 6.00 (2H, t, Ph), 5.72 (2H, s, C−H), 5.49 (6H, s, Me), 5.13 (4H, br, Ph), 4.89 (2H, s, C−H), 3.57 (12H, thf), 3.43 (6H, s, Me), 1.50 (12H, thf); ^{1}H NMR (300 MHz, CH_3CN-d_3, 20 °C, δ (ppm)) 7.86 (4H, s, C−H), 7.43 (8H, s, *o*-Ph), 7.16 (8H, t, *m*-Ph), 7.00 (4H, t, *p*-Ph), 6.44 (4H, t, Ph), 6.05 (2H, t, Ph), 5.11 (12H, s, Me), 4.98 (4H, d, Ph), 3.68 (12H, thf), 1.95 (12H, thf).

10.1021/ic0106827 CCC: $20.00

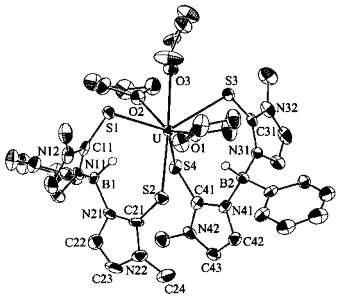
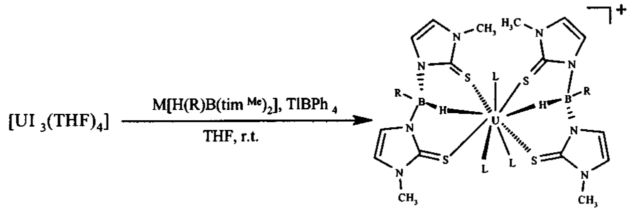


Figure 1. ORTEP view of the cation of $[U\{\kappa^3\text{-Ph(H)B(tim}^{Me})_2\}_2(THF)_3][BPh_4]$ (**2**) with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): U−S(1) 2.912(3), U−S(2) 2.932(3), U−S(3) 2.937(3), U−S(4) 2.929(3), U−O(1) 2.541(7), U−O(2) 2.528(7), U−O(3) 2.621(7), S(1)−U−S(2), 87.8(1), S(4)−U−S(3), 84.6(1).

Scheme 1



(L=THF, R=H (**1**), Ph (**2**))

$[BPh_4]$ (R = H (**1**) and R = Ph (**2**)). The compounds are soluble in tetrahydrofuran, **2** being much more soluble than **1**. They are also soluble in other coordinating solvents, such as acetonitrile and pyridine, with replacement of the THF by those neutral molecules. The compounds $[U\{\kappa^3\text{-H(R)B(tim}^{Me})_2\}_2(L)_3][BPh_4]$ (R = H or Ph and L = C_5H_5N (**3**), CH_3CN (**4**)) are easily obtained by stirring, for a while, **1** or **2** in the respective solvents. The presence of B−H···U agostic interactions was confirmed by X-ray diffraction analysis.[13] For **1**, despite the poor quality of the crystal, which did not provide an accurate data set, the overall structure is unambiguously defined. For $[U\{\kappa^3\text{-H(Ph)B(tim}^{Me})_2\}_2(THF)_3][BPh_4]$, **2**, the crystallographic data is of higher quality, and an ORTEP drawing is shown in Figure 1.

The thioimidazolyl ligands coordinate through the thione sulfur atoms and one of the hydrogen atoms attached to the boron, so that each ligand consists of two six-membered and one eight-membered chelate rings. The eight-membered rings adopt a "boatlike" configuration, which allows for a shorter distance between the metal and the B−H group. In both cations, the U(III) center is formally nine-coordinate, in a distorted tricapped trigonal prismatic geometry. A pair of sulfur atoms from each thioimidazolyl ligand and one THF oxygen atom define the triangular faces of the prism, and the square faces are capped by the remaining THF oxygen atoms and by the two B−H···U agostic interactions. The two triangular faces are almost parallel, the angle between the planes being 5.7° for **2**.

The U···B distances are, for **2**, 3.547(13) and 3.616(3) Å, and the corresponding U−H bonds of 2.61 and 2.71 Å were calculated by positioning the H(B) atoms at their idealized positions.[13] As no f-element compounds are known with eight-membered chelate rings, with or without agostic interactions, no value of U···B separation is known for comparison. Agostic interactions in U(III) complexes were first observed with dihydrobis(pyrazolyl)borate ligands[7] and, more recently, in the seven-coordinate $[UI_2\{\kappa^3\text{-H}(\mu\text{-H})B(3^tBu,5Me\text{-pz})_2\}(THF)_2]$[7c] and $[UI\{\kappa^3\text{-H}(\mu\text{-H})B(3^tBu,5Me\text{-pz})(3Me,5^tBu\text{-pz})\}_2]$[14] complexes as well. However, the U−B separations that have been invoked as a reference in the six-membered UN_4B chelate rings could not be used as such in the eight-membered $U(SCN)_2B$ rings, due to their greater size. Thus, only U−H distances could be compared: in **2**, these distances average 2.66 Å, which is at the low end range observed in the last two mentioned U(III) complexes (2.68−2.79 Å).[7c,14]

The oxygen atom of the THF in the capping site is at a longer distance from the metal (for **2**, U−O3, 2.621(7); U−O2, 2.528(7); U−O1, 2.541(7) Å). The average U−S bond distance in **2** is 2.928(11) Å. The C−S bond distances span from 1.668(12) to 1.726(12) Å, with an average value of 1.71(3) Å, comparing well with the corresponding bond distances in the homoleptic complex $[Zn\{H_2B(tim^{Me})_2\}_2]$.[10b] The C−S lengths are intermediate between a single and a double bond, and this indicates a partial reduction of the π character of the C−S bond.[15] Although the large standard deviations of the molecular parameters of **1** prevented any comparison of bond lengths and angles with **2**, both structures are similar.

The ^1H NMR spectra of **1** and **2** display a single set of three signals for the four thioimidazolyl groups, in the ratio 12:4:4. The resonances due to the counterion appear as three signals, near the diamagnetic region, integrating eight, eight, and four protons each. The aromatic rings in **2** appear also as two triplets and one doublet. Taking into account the structure found in the solid state, the simple pattern obtained in the ^1H NMR indicates a fluxional behavior for these compounds, as is generally observed for other U(III) compounds with poly(pyrazolyl)borates.[7] Only for **2** was a static spectrum obtained, and the pattern indicates the magnetic equivalence of the two ligands.

In conclusion, we have shown that the soft $(H(R)B(tim^{Me})_2)$ ligands are good anchors for f elements, namely, for U(III), acting as tridentate chelators through the sulfur atoms and through an agostic interaction. The type of complex isolated and fully characterized, $[U\{\kappa^3\text{-H(R)B(tim}^{Me})_2\}_2(THF)_3][BPh_4]$ (**1** and **2**), is completely different from what has been obtained with the analogous $[(H(R)B(pz^*)_2]^-$ (R = H, Ph), exemplifying the changes in chemistry that can be achieved simply by altering the donors within a given skeleton. The labile THF can be easily removed, leading to a significant accessibility to the metal center, thus opening the way to a new class of uranium compounds anchored on polydentate sulfur donor ligands, that may be useful to enter into the chemistry of U(III), but also into the chemistry of U(IV) or U(V) by electron transfer reactions. The chemistry of **1** and **2** is under active investigation.

Acknowledgment. This work has been partially supported by PRAXIS XXI (2/2.1/QUI/454/94). L.M. thanks FCT for a Ph.D. grant. The authors thank Professor R. Andersen for fruitful discussions.

Supporting Information Available: ORTEP drawings (PDF) and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0106827

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(13) Crystal data: complex **1**, $C_{52}H_{68}B_3N_8S_4O_3U\cdot OC_4H_8$, MW = 1323.95, triclinic, $P\bar{1}$, $a = 12.818(4)$ Å, $b = 16.290(3)$ Å, $c = 18.355(10)$ Å, $\alpha = 113.09(3)°$, $\beta = 106.39(3)°$, $\gamma = 97.91(2)°$, $V = 3246(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.355$ Mg/m^3, μ(Mo Kα) = 2.676 mm^{-1}, 7951 unique reflections ($I > 0$), 662 parameters, R1 = 0.1092, wR2 = 0.2489 for 5431 reflections with $I > 2\sigma(I)$; complex **2**, $C_{64}H_{76}B_3N_8O_3S_4U$, MW = 1404.03, monoclinic, $P2_1/c$, $a = 15.792(2)$ Å, $b = 18.071(3)$ Å, $c = 22.989(4)$ Å, $\beta = 100.09(1)°$, $V = 6459(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.444$ Mg/m^3, μ(Mo Kα) = 2.693 mm^{-1}, 11532 unique reflections ($I > 0$), 747 parameters, R1 = 0.0763, wR2 = 0.1050 for 7241 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically (except the solvent atoms in **1**), and the hydrogen atoms were introduced in calculated positions (for the BH hydrogen atoms, a fixed B−H bond length of 1.01 Å was used). The data were collected at room temperature with Mo Kα radiation on an Enraf Nonius CAD4 diffractometer.

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