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New Dicarbollide Complexes of Uranium

Daniel Rabinovich,* Chereé M. Haswell, Brian L. Scott, Rebecca L. Miller, Jon B. Nielsen, and Kent D. Abney*

Los Alamos National Laboratory, Chemical Science and Technology Division, CST-11, Mail Stop J514,
Los Alamos, New Mexico 87545

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The synthesis and reactivity studies of organoactinide complexes containing the dicarbollide ligand ($C_2B_9H_{11}{}^{2-}$) are remarkably underdeveloped. The derivative $[U(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]^{2-}$, prepared and structurally characterized by Raymond almost 20 years ago,[1] is the only anionic complex known in this class.[2,3] In view of our current interest in comparing the chemistry of anionic dicarbollide derivatives of the actinides with that of the related neutral or cationic cyclopentadienyl analogues,[4] and since reactivity studies for $[U(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]^{2-}$ were very limited, we set out to explore new dicarbollide complexes of uranium(III) and uranium(IV). A summary of our initial efforts is presented herein.

The reaction of an acetonitrile solution of $UBr_4(NCMe)_4$[5] with 2 equiv of the dicarbollide reagent $Li_2C_2B_9H_{11}$[6] resulted in the clean formation (as observed by ^{11}B NMR spectroscopy) of the bis(dicarbollide) complex $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (eq 1).

$$UBr_4(NCMe)_4 + 2Li_2C_2B_9H_{11} \xrightarrow[-2LiBr]{MeCN} Li_2[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2] \quad (1)$$

Interestingly, when the reaction was performed in THF, the derivative $[Li(THF)_4]_2[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ precipitated as a bright orange microcrystalline solid, and was isolated in 70% yield by filtration from the reaction mixture. The product is extremely air- and moisture-sensitive, but is stable for months when stored at −30 °C under an inert atmosphere. Characterization of $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ included ^1H and ^{11}B NMR spectroscopy.[7] The ^{11}B NMR spectrum of $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ exhibits six resonances in the ratio 1:2:2:2:1:1 spread over a range of nearly 500 ppm, typical of paramagnetic [*e.g.*, Cr(III), Fe(III), Co(II)] metallacarborane complexes.[8]

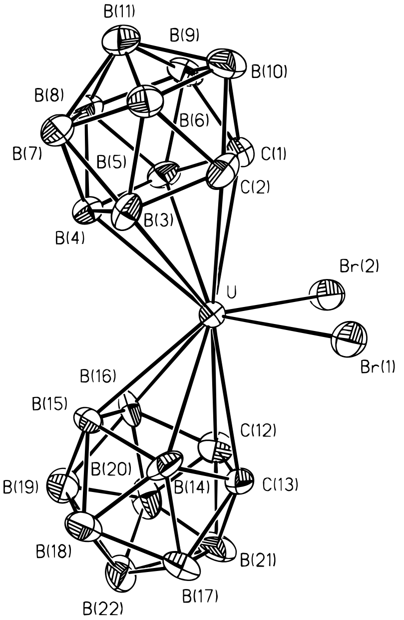

Figure 1. Molecular structure of $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (thermal ellipsoids at 35% probability level).

In agreement with Raymond's observations for the formation of $[U(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]^{2-}$,[1] no intermediates such as $[U(\eta^5\text{-}C_2B_9H_{11})Br_3(THF)_n]^-$ were detected by ^{11}B NMR spectroscopy during the reaction of $UBr_4(NCMe)_4$ with various dicarbollide salts, even if only 1 equiv of $C_2B_9H_{11}{}^{2-}$ was used. In contrast, the deep purple uranium(III) mono(dicarbollide) complex $[Li(TMEDA)][U(\eta^5\text{-}C_2B_9H_{11})I_2(THF)_2]$ was isolated in 70% yield from the reaction of a royal-blue THF solution of $UI_3(THF)_4$[9] with 1 equiv of $Li_2C_2B_9H_{11}$ in the presence of tetramethylethylenediamine (eq 2).[10,11]

$$UI_3(THF)_4 + Li_2C_2B_9H_{11} \xrightarrow[-LiI]{THF\ TMEDA} [Li(TMEDA)][U(\eta^5\text{-}C_2B_9H_{11})I_2(THF)_2] \quad (2)$$

Moreover, the reaction of $[U(\eta^5\text{-}C_2B_9H_{11})I_2(THF)_2]^-$ with a second 1 equiv of $C_2B_9H_{11}{}^{2-}$ produced the green uranium(III) bis(dicarbollide) complex $[U(\eta^5\text{-}C_2B_9H_{11})_2I(THF)]^{2-}$, isolated as the TMEDA adduct [Li-

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(7) ^1H NMR (CD_3CN, 250.13 MHz): δ 60.1 (m, 2 B−*H*), 54.1 (s, 4 C−*H*), 50.4 (m, 4 B−*H*), 43.3 (m, 4 B−*H*), 41.8 (m, 2 B−*H*), −47.9 (br s, 2 B−*H*), −92.2 (br s, 4 B−*H*). ^{11}B NMR [CH_3CN, 80.21 MHz, chemical shifts relative to $BF_3\cdot Et_2O$ (δ = 0)]: δ 515 (br s, $\Delta\nu_{1/2}$ = 231 Hz, 2 B), 468 (br s, $\Delta\nu_{1/2}$ = 225 Hz, 4 B), 90 (d, $^1J_{B-H}$ = 144 Hz, 4 B), 77 (d, $^1J_{B-H}$ = 133 Hz, 4 B), 72 (d, $^1J_{B-H}$ = 151 Hz, 2 B), 52 (d, $^1J_{B-H}$ = 131 Hz, 2 B). Anal. Calcd for $C_{36}H_{86}B_{18}Br_2Li_2O_8U$: C, 34.5; H, 6.9. Found: C, 34.6; H, 7.0.

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(10) $^{11}B\{^1H\}$ NMR (THF, 80.21 MHz): δ 571 (br s, 1 B), 447 (br s, 2 B), 51 (s, 2 B), 48 (s, 2 B), −5 (s, 1 B), −19 (s, 1 B). Anal. Calcd for $C_{16}H_{43}B_9I_2LiN_2O_2U$: C, 21.6; H, 4.9; N, 3.1. Found: C, 21.4; H, 4.8; N, 3.4.

(11) The complex salts $[K(18\text{-crown-}6)][U(\eta^5\text{-}C_2B_9H_{11})I_2(THF)_2]$ and $[(Ph_3P)_2N][U(\eta^5\text{-}C_2R_2B_9H_9)I_2(THF)_2]$ (R = H, Me) have been isolated similarly from the reactions of $UI_3(THF)_4$ with $K_2C_2B_9H_{11}\cdot 0.5dme$[11a] and $[(Ph_3P)_2N](TlC_2R_2B_9H_9)$,[11b] respectively. (a) Prepared by double deprotonation of the diacid $C_2B_9H_{13}$ with KH in dimethoxyethane (dme). Anal. Calcd for $C_4H_{16}B_9K_2O$: C, 18.8; H, 6.3. Found: C, 18.8; H, 6.3. Rabinovich, D.; Abney, K. D. Unpublished results. (b) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178−1179.

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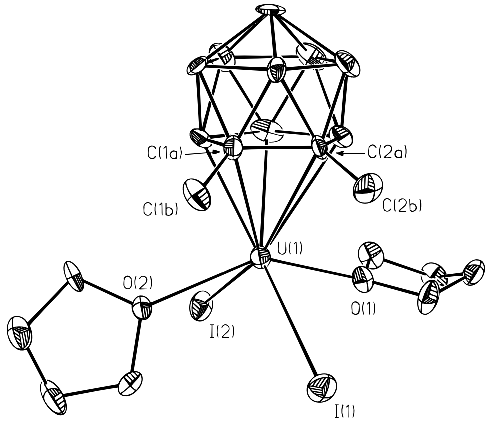

Figure 2. Molecular structure of $[U(\eta^5\text{-}C_2Me_2B_9H_9)I_2(THF)_2]^-$ (thermal ellipsoids at 35% probability level).

$(TMEDA)]_2[U(\eta^5\text{-}C_2B_9H_{11})_2I(THF)]\cdot 2TMEDA$ following an analogous procedure.[12]

The molecular structures of $[Li(THF)_4]_2[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$[13] and of the related dimethyldicarbollide complex $[(Ph_3P)_2N][U(\eta^5\text{-}C_2Me_2B_9H_9)I_2(THF)_2]$[14] were determined by single-crystal X-ray diffraction. The bis(dicarbollide) complex $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (Figure 1) displays a "bent-metallocene" structure and is isostructural with the dichloro analogue.[15] Significantly, the boron and carbon atoms within the dicarbollide ligands were distinguished from each other in the dibromide complex, whereas the ligands are disordered in the dichloride analogue.[1,15]

The mono(dicarbollide) complex $[U(\eta^5\text{-}C_2Me_2B_9H_9)I_2(THF)_2]^-$ adopts a four-legged piano stool structure in the solid state (Figure 2), with *transoid* pairs of iodide and THF ligands [I(1)−U−I(2) = 110.95(4)°, O(1)−U−O(2) = 145.8(3)°]. Thus, it is related to a variety of "half-sandwich" transition metal dicarbollide derivatives[2,16] and also to the actinide cyclooctatetraene complexes $(COT)AnCl_2L_2$ (An = Th, U; L = THF, py).[17] The U−X bond lengths in the new dicarbollide complexes [2.8397(14) and 2.8293(14) Å for X = Br, 3.1328(12) and 3.1534(13) Å for X = I] are similar to those reported for other complexes containing terminal U−Br[18] and U−I bonds,[9,19] and the rest of the interatomic distances also appear to be normal.

In summary, a series of new anionic mono- and bis(dicarbollide) complexes of uranium(III) and uranium(IV) have been isolated and characterized by a combination of analytical, spectroscopic, and X-ray diffraction techniques. Reactivity studies of these complexes are in progress.

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Supporting Information Available: Tables of crystal and intensity collection data, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates and ORTEP drawings for $[Li(THF)_4]_2[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ and $[(Ph_3P)_2N][U(\eta^5\text{-}C_2Me_2B_9H_9)I_2(THF)_2]$ (31 pages). Ordering information is given on any current masthead page.

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(12) $^{11}B\{^1H\}$ NMR (THF, 80.21 MHz): δ 583 (br s, 1 B), 466 (br s, 2 B), 68 (s, 2 B), 64 (s, 2 B), 19 (s, 2 B). Anal. Calcd for $C_{32}H_{94}B_{18}ILi_2N_8OU$: C, 32.6; H, 8.0; N, 9.5. Found: C, 33.1; H, 8.0; N, 10.1.

(13) Crystal data (at −90 °C): monoclinic space group *Cc* (No. 9), a = 26.192(6) Å, b = 11.120(2) Å, c = 20.094(3) Å, β = 103.191(8)°, d_{calcd} = 1.461 g/cm^3, Z = 4, R1 = 0.0449, R2$_w$ = 0.0734.

(14) Crystal data (at −90 °C): monoclinic space group $P2_1/n$ (No. 14), a = 8.838(2) Å, b = 34.504(7) Å, c = 17.692(4) Å, β = 102.48(3)°, d_{calcd} = 1.683 g/cm^3, Z = 4, R1 = 0.0571, R2$_w$ = 0.0951.

(15) We have redetermined the structure of $[Li(THF)_4]_2[U(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]$ and found it to be virtually identical to that previously reported (see ref 1). Crystal data (at −90 °C): monoclinic space group *Cc* (No. 9), a = 26.250(6) Å, b = 10.910(2) Å, c = 20.081(3) Å, β = 102.934(9)°, V = 5605(2) Å^3, d_{calcd} = 1.380 g/cm^3, Z = 4, R1 = 0.0574, R2$_w$ = 0.1095.

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