J|A|C|S
COMMUNICATIONS

Published on Web 03/30/2004

Formation of Inclusion Organoactinide Complexes with Boron-Containing Macrocycles

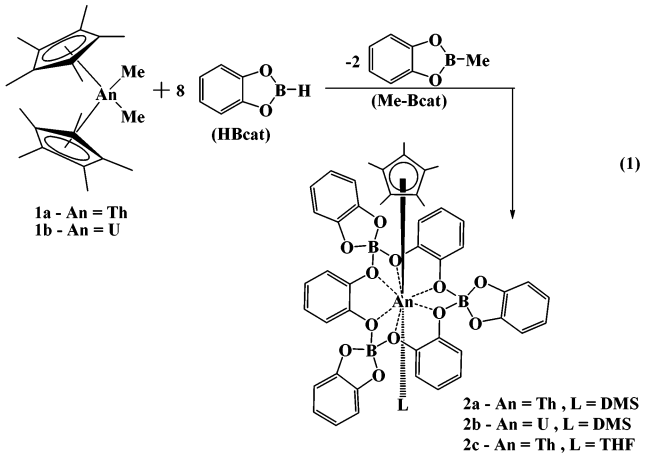
Eyal Barnea, Tamer Andrea, Moshe Kapon, and Moris S. Eisen*

Department of Chemistry and Institute of Catalysis Science and Technology, Technion—Israel Institute of Technology, Haifa 32000, Israel

Received January 8, 2004; E-mail: chmoris@tx.technion.ac.il

Introducing a metal ion into a macrocyclic system can be performed following two major pathways. The first method involves the reaction of the metal ion with a macrocycle (such as crown ethers, porphirins, etc.),[1] whereas the second method creates the macrocycle around the metal center during the reaction.[2] Actinide metals in macrocyclic complexes are of great interest due to their large ionic size and high positive charge. Since high coordination numbers characterize their coordination chemistry, they may serve as templates to the construction of macrocyclic organic molecules.[3] For example, uranyl chloride condenses phthalonitrile to form a 20-membered macrocycle.[4] Crown ethers are known to bind the actinides, but in contrast to lanthanide complexes,[5] only seven actinide complexes where the metal is encapsulated within the macrocycle are known.[6] In most cases, the macrocycle occupies the second (outer) coordination sphere and is not directly bonded to the metal.[7,8]

In this contribution we report the synthesis and crystal structure of 15-membered, hexaoxo, trianionic ligation systems for organoactinides, built from catechol and catecholborate units around the actinide centers,[9,10] with an overall structure of a hexagonal bipyramid geometry.[11]



(1)

The synthesis of complex **2** (**2a** = Th, **2b** = U), shown in eq 1, was accomplished by reacting the complex $(Cp^*)_2AnMe_2$ (Cp^* = pentamethylcyclopentadienyl, An = Th = **1a**, U = **1b**) with an excess of catecholborane (HBcat) that contains 5% dimethyl sulfide (DMS)[12] in benzene at room temperature for 24 h. The first step of the reaction involves the reaction of complex **1** with 2 equiv of HBcat to form Me-Bcat. This product was confirmed by ^{1}H NMR and GC/MS measurements of the crude reaction mixture.[13,14]

Complex **2a** crystallizes in the triclinic space-group *P*-1 with a unit cell of dimensions a = 14.517(2) Å, b = 14.562(2) Å, c = 16.604(3) Å, α = 68.92(7)°, β = 82.40(7)°, γ = 87.83(9)° (Figure 1). The thorium atom is positioned slightly above the center of a concave hexagonal plane described by the six binding oxygen atoms. The deviation of the thorium atom from this plane is 0.5754 Å. The average Th−O bond length (2.457 Å) is slightly higher than that of the tetrakis(catecholato)thorium complexes (2.419 Å).[9] A Cp* ligand rests in the apical position with an average Th−C(Cp*) bond length of 2.766 Å (similar to the average Th−C(Cp*) bond length in complex **1a**, 2.780 Å). Each two catechol units are bridged by a catecholborate fragment disposed perpendicularly to the macrocycle and slightly bent away from the Cp* ligand. The concave shape of the macrocycle is a result of steric interaction between the borate fragments and the Cp* ligand. The DMS ligand, also positioned in an apical position, shows a Th−S bond length (3.0866 Å) longer than that in all known complexes having a Th−S single bond.[15] Complex **2b** is isolobal and isostructural to complex **2a** and crystallizes in the monoclinic space group *P*21/*n* with unit cell dimensions a = 17.383(3) Å, b = 16.774(4) Å, c = 18.284(4) Å, β = 107.86(7)°. The average U−O, U−C(Cp*), and U−S bond lengths are 2.435, 2.705 and 2.9943 Å, respectively. The longer bonds in complex **2a** as compared to those bonds in complex **2b** indicate a larger ionic character of the U(IV) complex.[16]

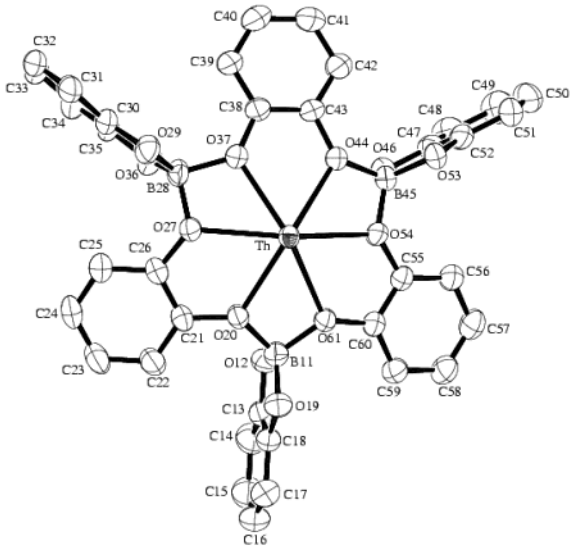


Figure 1. Ellipsoid representation of the molecular structure of complex **2a**. Apical Cp* and DMS ligands were removed for clarity.

Replacement of the DMS ligand by THF was accomplished by heating a THF solution of complex **2a** to 70 °C for 12 h followed by crystallization.[17] Complex **2c** crystallizes in the monoclinic space group *P*21/*c* with unit cell dimensions a = 9.770(2) Å, b = 21.172(3) Å, c = 24.294(4) Å, β = 97.14(7)°. The complex is isostructural to complex **2a**. The Th−O(THF) bond length (2.583 Å) is shorter than the Th−S bond of complex **2a** but longer than the average Th−O(macrocycle) bond length (2.449 Å). An attempt

10.1021/ja0498843 CCC: $27.50

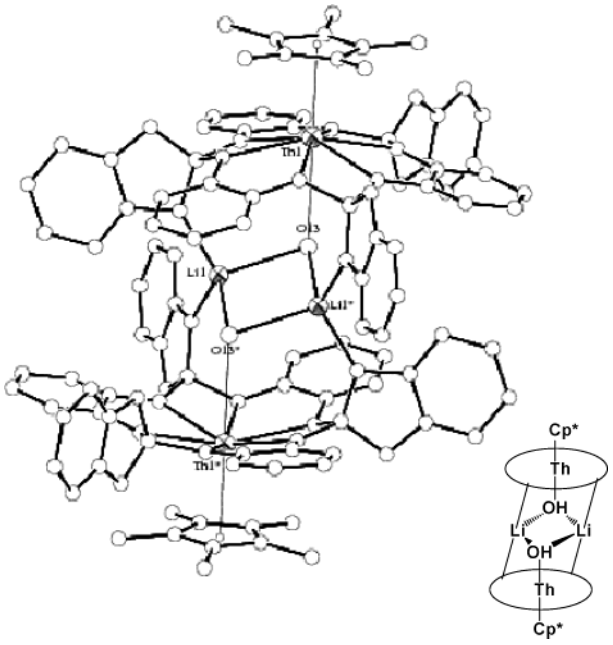


Figure 2. Crystal structure and schematic view of complex **3**.

to remove the Cp* ligand or eject the metal ion from the macrocycle by adding an equimolar amount of water resulted in the decomposition of the complex to yield catechol and other unidentified byproducts. In addition, reaction of complex **2a** with equimolar amounts of complex **1b** did not afford the transmetalation product.

Replacement of the DMS ligand was performed by reacting complex **1a** containing 4.5% of LiOH with an excess of HBcat to form the dimeric crystalline product **3**. Complex **3** crystallizes in the monoclinic space group $P21/n$ with unit cell dimensions $a = 17.192(5)$ Å, $b = 16.451(5)$ Å, $c = 18.700(6)$ Å, $\beta = 111.16(13)°$. X-ray diffraction (Figure 2) revealed an interesting structure, where two macrocycles are connected with two LiOH molecules. Each OH group is bonded to a thorium atom in the apical position, while the Li atom bonds, in addition to the two OH groups, two oxygens of two borate fragments. The Cp* ring centeroid-Th−OH angle is almost linear (177.52(13)°), and the two Cp* ligands are essentially parallel (an angle of 179.7° between the two ring's planes). The two macrocycles are in a staggered position and have a horizontal shift of 2.957 Å along the mean plane defined by the six binding oxygens. ^{1}H NMR of complex **3** in THF was identical to that of complex **2c**, which suggests that **3** is not stable as a dimer in solution and decomposes to give **2c**.

Attempts to prepare similar complexes by reacting HBcat with $Cp^*_2ZrMe_2$, **4**, or $Me_2SiCp''_2Th(^nBu)_2$, **5** (Cp″ = tetramethylcyclopentadienyl), did not yield the desired product. For complex **4**, the formation of Me-Bcat was observed but no macrocycle was formed. It seems that the macrocycle formation requires the presence of the 5f orbitals for the six planar coordination sites.[18] For complex **5**, only the formation of ^{n}Bu-Bcat was observed. It seems that the bridged Cp″ does not dissociate from the complex as compared to complex **2a**, impeding the formation of the macrocycle. Reaction of complex **1a** with pinacolborane (HBpin) produced only $B_2(pin)_3$, a known degradation product of HBpin.[19] In addition, for a 1:1 mixture of HBcat and HBpin with complex **1a**, only the formation of Me-Bcat was observed.

In conclusion, we present the synthesis and crystal structure of the first organoactinides (Th(IV) and U(IV)) complexes bearing the new planar hexaoxo, trianionic, 15-membered macrocyclic ligation systems.

Acknowledgment. This research was supported by the Israel Science Foundation Administered by the Israel Academy of Science and Humanities under Contract 83/01-1.

Supporting Information Available: Experimental section, including the synthesis and ^{1}H, ^{13}C, and ^{11}B NMR analysis of complexes **2a**−**c** and **3**, and a listing of crystallographic data and processing descriptions for the crystal structure of complexes **2a**−**c** and **3** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Constable, E. C. *Coordination Chemistry of Macrocyclic Compounds*; Academic: San Diego, CA, 1999. (b) Dietrich, B.; Viout, P.; Lehn, J. M. *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supra Molecular Chemistry*; VCH: Weinheim, Germany, 1993.
(2) (a) Gerbeleu, N. V.; Arion, V. B. In *Complex Formation and Stereochemistry of Coordination Compounds*; Buslaev, Yu., Ed.; Nova Science Publishers: Commack, NY, 1996; p 133. (b) Hoss, R.; Vögtle, F. *Angew. Chem., Int. Ed*. **1994**, *33*, 375.
(3) Alexander, V. *Chem. Rev*. **1995**, *95*, 273.
(4) (a) Day, V. W.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc*. **1975**, *97*, 4519. (b) Marks, T. J.; Stojakovic, R. D. *J. Am. Chem. Soc*. **1978**, *100*, 1695.
(5) Meyer, G. *J. Alloys Compounds* **2000**, *300*, 113.
(6) Thuéry, P.; Keller, N.; Lance, M.; Vigner, J. D.; Nierlich, M. *New J. Chem*. **1995**, *19*, 619 and references therein. Rogers, R. D.; Bauer, C. B. In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Atwood, J. L., Davis, J. E. D., Macnicol, D. D., Vogtle, F., Eds.; Pergamon: Oxford, 1996; pp 1, 315 and references therein. For NpO_2^{+2} crown ether inclusion complex, see: Clark, D. L.; Keogh, D. W.; Palmer, P. D.; Scott, B. L.; Tait, C. D. *Angew. Chem., Int. Ed*. **1998**, *37*, 164.
(7) (a) For crown ether complexes of the actinindes where the macrocycle occupies the second coordination sphere, see: Kannan, S.; Shanmugasundara, R, S.; Fun, H. K. *Polyhedron* **2001**, *20*, 2145 and references therein. (b) For open-chain crown ether complexes of the actinides, see: Rogers, R. D.; Bond, A. H.; Witt, M. M. *Inorg. Chem*. **1991**, *182*, 9.
(8) Hexaaza macrocycle, azacrowns, calixarene, and macrocyclic schiff base complexes of the actinides are also known. See: (a) Jacques, V.; Desreux, J. F. *Inorg. Chem*. **1996**, *35*, 7205. (b) Sessler, J. L.; Mody, T. D.; Lynch, V. *Inorg. Chem*. **1992**, *31*, 529 and references therein.
(9) Crystal structures of actinide complexes bearing the homoleptic catechol unit $Na_4[An(C_6H_4O_2)_4]\cdot 21H_2O$ are known. See: Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc*. **1978**, *100*, 7882.
(10) For a review on boron-containing macrocycles, see: Höpfl, H. *Struct. Bonding* **2002**, *103*, 1.
(11) Hexagonal bipyramid complexes of the actinides are known, mostly for dioxoactinides, where the two oxygens occupy the apical positions. See ref 6 and also: Li, Y.; Burns, P. C. *J. Sol. State Chem*. **2002**, 166, 219 and references therein.
(12) Commercial HBcat from Aldrich contains DMS; the DMS:HBcat ratio is 1:10.
(13) Cp*H was not observed in the reaction mixture, and therefore we suggest that the other byproducts are $Cp^*\text{-}BH_2$ and B_2H_6, to complete the stoichiometric reaction.
(14) HBcat is known to degrade in the presence of phosphines to form $B_2(cat)_3$, which is a structural fragment of the macrocycle presented here. See: Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem*. **1993**, *32*, 2175.
(15) Th−S bond length of known complexes vary from 2.768 to 3.053 Å. See: Wrobleski, D. A.; Cromer, D. T.; Ortiz, J. V.; Rauchfuss, T. B.; Ryan, R. R.; Sattelberger, A. P. *J. Am. Chem. Soc*. **1986**, *108*, 174 and refs cited therein.
(16) Shannon, R. D. *Acta Crystallogr*. **1976**, *A32*, 751.
(17) Reaction of complex **1a** with freshly prepared Hbcat·THF produced only Me-Bcat, probably because of the strong THF−HBcat interactions that prevent the formation of the macrocycle.
(18) Early transition metal and lanthanide complexes are known to catalyze the hydroboration of alkenes with HBcat without the formation of macrocyclic complexes. See: (a) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal., A.: Chem*. **1995**, *95*, 121. (b) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc*. **1992**, *114*, 9220.
(19) Clegg, W.; Scott, A. J.; Dai, C.; Lesley, G.; Marder, T. B.; Norman, N. C.; Farrugia, L. G. *Acta Crystallogr*. **1996**, *C52*, 2545.

JA0498843