DOE/ER/13529--7

DE93 005291

Report on Progress

U. S. Department of Energy

Grant Number DE-FG02-86ER13529

"Molecular Orbital Studies of the Bonding in Heavy Element Organometallics"

Professor Bruce E. Bursten, Principal Investigator

Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

Date: December 4, 1992

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

I. Technological Advances

A number of technological advances in our laboratories have allowed us to expand our studies of actinide systems during the previous grant period. We have developed expertise in the use and administration of our Digital Equipment DECstation 3100 UNIX-based worksystem, which was requested as an equipment item in our last DOE grant application. The access to this extremely powerful stand-alone computer, as well as its facility in tying into the Cray supercomputer at the Ohio Supercomputer Center, has allowed us to expand our computational vistas greatly. In the past, we have been largely restricted to using the quasirelativistic $X\alpha$ scattered-wave ($X\alpha$-SW) molecular orbital method[1,2] for our investigations of actinide electronic structure. While this method has been very useful to us, it does employ some severe approximations, which are inherent to the method and have been necessary due to computational limitations. The access to more powerful computers has allowed us to use more sophisticated, albeit more complex, electronic structure methods in our investigations.

We have continued to invest time in improving our computational capabilities. Our LDF code, which employs the discrete variational $X\alpha$ (DV-$X\alpha$) method of Ellis,[3] has been updated to include a more sophisticated basis function expansion and the evaluation of total and binding energies for molecules. The code has also been enhanced to exploit the vector architecture of the Cray supercomputer, dramatically reducing the cost of our calculations. Personnel additions to our group during the last grant period have contributed knowledge of ab initio methods, and we have gained some experience in the application of these methods to large actinide systems. We plan to continue refining our electronic structure methodologies during the next grant period.

Although the DECstation 3100 has been a most effective workstation during the prior grant period, it is also out of date with respect to computing and graphics capabilities. We therefore are requesting funding to upgrade this workstation to a DECstation 5000 Model 133, which is a much more powerful workstation. As can be seen in the Budget Justification, the incremental cost for this upgrade is relatively low. It is also noteworthy that no funding is requested for supercomputer time. All of the necessary time on the Cray supercomputer at the OSC will be provided by the PI's grant-in-time from the OSC.

II. Tris(cyclopentadienyl) Actinide Complexes

A major focus of study during the past grant period was the series of organoactinide compounds containing three Cp (pentahapto cyclopentadienyl or modified cyclopentadienyl) ligands.[4] These studies, which have primarily employed the Xα–SW molecular orbital method with quasirelativistic corrections, can be broken down into two basic areas: investigations of the "base-free" compounds Cp_3An, and investigations of the interaction of Cp_3An compounds with a fourth ligand. The first area provides a convenient yet realistic molecular framework in which to compare the electronic structures of compounds of several different actinide elements, including the transplutonium elements.[5] In this series we have thus far investigated compounds spanning the actinide series from Th through Cf,[6,7] and have compared the bonding in the actinide systems to that in analogous transition metal and lanthanide complexes.[8] The second area, which is closely related to the first, allows us to investigate the interaction of actinide compounds with small molecules, to study multiple bonding between an actinide metal and main group atoms, and to compare directly two different oxidation states [An(III) and An(IV)] within a common structural framework.

Cp_3M complexes. In our studies of base-free Cp_3An complexes, we addressed the qualitative differences between the interaction of the C_{3v} (η^5-$C_5H_5)_3$ ligand set with d-block and f-block metals.[6,8] Symmetry constraints allowed us to conclude that a transition metal should be an inappropriate template about which to place three Cp ligands because of the inability of the metal atom to stabilize a high energy a_2 orbital of the ligand set; this observation was originally made by Moffitt in the paper reporting the first synthesis of Cp_3UCl.[9] Because there is an f orbital of a_2 symmetry, there is no such restriction on the interaction of the ligand set with either a lanthanide or actinide center. In fact, this observation fits in nicely with our general observation that ligand interaction with actinide centers is dominated by donation into the metal d orbitals, except when such donation is prevented by symmetry.[4] We find that the preference for donation into the An 6d orbitals is dictated by the greater radial extension of the 6d orbital relative to the 5f orbitals, an effect that is even more dramatic in comparing the 5d and 4f orbitals of lanthanide complexes.[8]

We also noted that the actinide $6d_{z^2}$ orbital, while able to interact with the Cp_3 ligand set by symmetry, has poor overlap with the ligands and is relatively unaffected by them. As a result, the energy of the $6d_{z^2}$ orbital relative to that of the 5f orbitals is highly dependent on the atomic orbital energetics of the actinide center. We examined these effects for a series of Cp_3An complexes, with An = Th through Cf.[6,7] One aspect of this study that was of extreme interest was the ground electron configurations of these complexes. We found that the Th $6d_{z^2}$ orbital in Cp_3Th resides below the 5f manifold. As a result, the one metal-based electron in this Th(III) complex is housed in an orbital that is predominantly 6d rather than 5f in character. This result was consistent with the experimental observations of Edelstein, Lappert, et al., who analyzed the EPR spectrum of Cp''_3Th ($Cp'' = \eta^5$-1,3-$(Me_3Si)_2C_5H_3$) and found it consistent with a $6d^1$ electron configuration.[10] Similar calculations on Cp_3U led to the interesting conclusion that the $6d^15f^2$ and $5f^3$ electron configurations were very nearly degenerate. We and others[11] believe that this may be an incorrect conclusion that may result from the rather crude treatment of relativistic effects in the quasirelativistic $X\alpha$-SW method, and that Cp_3U is an excellent candidate for study by more sophisticated electronic structure methods.

We also reported a comparison of the bonding in the series of Cp_3An complexes (An = U through Cf) to that in the analogous Cp_3Ln complexes.[8] The energies of the 4f and 5d orbitals of the early lanthanide complexes resemble those of the 5f and 6d orbitals of the complexes of the middle actinide elements, while the orbital energies of the complexes of the late lanthanide elements are similar to those of the late actinides. We believe these results to be consistent with the "lanthanide-like" behavior of the later actinide elements. The 5d orbitals of the lanthanides and the 6d orbitals of the actinides have about the same capability to bond to the Cp ligands. However, the 4f orbitals of the lanthanides do not interact with the ligands to the same extent as the 5f orbitals of the actinides, which can be attributed to the differences in the radial extension and energies of the two sets of orbitals. Due to its relatively higher energy, the 6s orbital of the lanthanide metals is not involved in any bonding interaction.

When a Lewis base L is added to a Cp_3An complex, forming Cp_3AnL, the interaction of L with the actinide primarily involves the An $6d_{z^2}$ orbital. This interaction destabilizes the $6d_{z^2}$ orbital to an energy well above that of the 5f orbitals for all the actinide elements. Thus, all Cp_3UL complexes have $5f^3$ electron configurations. Likewise, we predict that if a Lewis base is added to Cp''_3Th, the ground electron configuration will change from $6d^1$ to

$5f^1$.[6] Although no Cp_3ThL complexes are known, Edelstein and coworkers have recently examined the analogous lanthanide complexes Cp_3Ce and Cp_3CeL.[12] Both of these complexes have $5d^1$ electron configurations, but the separation between the states with $5d^1$ and $4f^1$ electron configurations decreases substantially upon addition of L, in accord with our prediction.

In conjunction with our studies on Cp_3An compounds of the transplutonium elements, we also investigated the electronic structures of the closely related $AnCl_3$ series (Cl is isolobal with Cp) where An = Th, Pa, U, Np, Pu, Am, Cm, Bk, and Cf.[7] These were the first reported electronic structure calculations on transplutonium complexes in their most common trivalent oxidation state. The Cl ligands contributes considerably less electron density to the metal center than do the Cp ligands. Nevertheless, the same general trends are observed across the actinide series as were observed in the Cp_3An study. The An 5f orbital energies decrease across the actinide series while the 6d orbital energies remain nearly constant. This change in 5f orbital energies is much more pronounced in the $AnCl_3$ series as the metal centers are much less electron rich relative to the Cp_3An series. The electron density reduction also manifests itself in a decreased diffuseness of the An 5f orbitals in the $AnCl_3$ complexes relative to the Cp_3An complexes. Therefore, the use of Cl as a model for Cp provides a reasonable qualitative picture of trends across the actinide series.

Cp_3ML complexes. Our interest in Cp_3An compounds was initially sparked by the vast number and variety of Cp_3UL compounds. Compounds have been characterized where L is a neutral two electron σ donor, an anionic two electron σ donor, a neutral π acid ligand, an anionic π basic ligand, or even an anionic organometallic fragment.[13] There have also been several reports of multiple bonding between Cp_3U and main group atoms such as carbon and nitrogen.[14]

We have investigated Cp_3UL compounds where L is a π-neutral (H), π-acidic (CO, NO), or π-basic ligand (OH).[8] We find that in all of these compounds the σ bonding interaction is essentially the same: electron density is donated from the σ orbital of the fourth ligand into an uranium orbital that is primarily $6d_{z^2}$ in character with minor contributions from the $5f_{z^3}$ orbital, the $7p_z$ orbital, and the 7s orbital. As was the case when no fourth ligand was bound to Cp_3U, the 5f orbitals in the model compound Cp_3U-H are clustered in a narrow (0.13eV) energy band (with the exception of the 5f a_2 orbital). We took the absence of orbital splitting as further evidence of the minor role that the 5f orbitals play in metal-ligand σ bonding.

When a ligand with π bonding capability is bound to a Cp_3U fragment, we have found that the 5f orbitals play **a significant role. We analyzed** the bonding in the first molecular actinide carbonyl complex **that is stable** at room temperature, Cp'_3UCO ($Cp' = \eta^5$-$C_5H_4SiMe_3$), which was reported by Andersen and coworkers in 1986.[15] The infrared spectroscopy of this compound indicates significant metal-to-ligand back-donation. Our calculations on the model Cp_3UCO compound[16] showed significant carbonyl 2π character in the metal-based HOMO, with the uranium portion deriving entirely from the 5f orbitals. Interaction with the CO ligand stabilizes this orbital below the remaining 5f orbitals, giving theoretical corroboration of extensive U 5f → CO 2π back-bonding. We also investigated the possibility of the formation of the O-bound isocarbonyl complex Cp_3UOC. In contrast to Cp_3UCO, Cp_3UOC shows no π back-bonding interaction, inconsistent with the experimentally observed results. Also, the OC σ bonding orbital lies at a much lower energy than that of CO which causes it to interact with the filled U 6p orbitals to yield no net bonding. Upon the basis of these calculations, we believe that Cp_3UOC

would be unstable relative to Cp_3UCO.

As an extension of our studies on the interaction of Cp_3U with π acceptor ligands, we have investigated the electronic structure of the unknown nitrosyl adduct Cp_3UNO. We find that, as is the case in transition metal systems,[17] NO is a poorer σ donor than CO while being a superior π acceptor. The energy of the NO 2π orbital is lowered sufficiently relative to that of CO to make it nearly isoenergetic with the U 5f orbitals. As a result, the NO contribution to the HOMO of Cp_3UNO is ca. 2.5 times greater than the CO contribution to the HOMO of Cp_3UCO, i.e. NO is acting as a far superior backbonding ligand. The U contribution is nearly pure 5f and hence only the extent, and not the nature, of the U → L backbonding is affected by the change in L.

Investigation of Cp_3UOH reveals that Cp_3U can serve as a π acceptor as well as a π donor. The hydroxide ligand has occupied π orbitals that are lower in energy than the U 5f and 6d orbitals. These orbitals are capable of acting as electron donors to the metal complex. It is indeed found that the 1π orbitals of the OH ligand are donating significantly to the uranium atom. Interestingly, the donation is primarily into the U 6d orbitals, as was the case for σ donation, but the interaction also contains a significant contribution from the 5f orbitals. Consistent with the 5f participation in this interaction, the $5f\pi$ set of orbitals are destabilized above the other 5f orbitals and contain a small contribution from the OH ligand.

III. Actinide-Containing Molecules with Metal-Metal Bonds

We have had a continuing interest in the prospects of finding molecules that contain direct metal-metal bonds involving an actinide center. This is a largely unexplored area that is beginning to receive a large amount of attention from synthetic chemists in the field. There is, of course, a very rich chemistry in transition metal complexes that contain metal-metal bonds.[18] We have been interested in drawing correspondences between the transition elements and the actinides, in the hopes that the existence of new actinide-containing materials could be predicted.

Actinide-Actinide Bonds. In 1984 we published the results of $X\alpha$-SW calculations on the hypothetical naked metal dimers U_2 and Np_2.[19] These were the first such calculations on molecules with actinide-actinide bonds, and proved to be very instructive. The calculations indicated that U_2, like Mo_2,[20] contains a formal metal-metal sextuple bond wherein there were strong interactions between the 5f orbitals of the two uranium centers.

Because the $X\alpha$-SW method can not be used reliably to calculate the total energy of molecules, we have recently addressed the bonding in U_2 by using ab initio methods,[21] which have become sophisticated enough to handle molecules this large with a reasonably accurate treatment of the relativistic corrections. The COLUMBUS program system,[22] including relativistic core potentials (RCP's), was used to peform self-consistent field (SCF), multi-configuration SCF (MCSCF), and single- and multi-reference configuration interaction (SRCI and MRCI) calculations on U_2. Potential energy curves were obtained for 25 electronic states of U_2. Spin-orbit CI calculations were also conducted, but the change in energy due to spin-orbit splitting is negligible for the states considered. Our calculations reveal that the intuitive picture of metal-metal bonding based on transition metal analogues is insufficient for actinide multiple bonding, and that the simple description of U_2 provided by nonrelativistic $X\alpha$-SW molecular orbital calculations is incomplete.

Two groups of states, both exhibiting potential energy minima, were identified for U_2. The first have short bond distances (2.0 - 2.5 Å), low electronic spin, and bonding interactions involving 7s, 6d, and 5f atomic orbitals. These states, whose electronic structure is similar to that predicted for U_2 by our approximate molecular orbital calculations, appear to be metastable states with energies at least 340 kJ/mol above the separated atoms. The second set of electronic states of U_2 arise from purely 6d-orbital bonding, with the 5f orbitals remaining essentially atomic. These somewhat surprising states have long bond distances (3.0 - 3.5 Å), high electronic spins, and energies considerably lower than the short-bond-length states and the separated atoms. The ground state has been tentatively identified as a $^{13}A_g$ ($^{13}\Sigma_g^+$) state with a potential energy minimum at 3.0 Å. The $^{13}\Sigma_g^+$ state is bound by 160 kJ/mol at the SRCI level.

In addition to providing an essential foundation for understanding actinide-actinide bonding, the diuranium investigation also allowed us to develop expertise in the application of ab initio quantum chemical methods to actinide complexes. Only a handful of research groups are conducting ab initio calculations on organoactinide complexes,[23] and reports of such computational studies are still relatively rare in the chemical literature. Computer technology has advanced to the point that ab initio approaches are not only feasible but desirable, and we feel that ab initio methods, along with the increasingly popular density functional approaches, will prove invaluable for understanding the rich chemistry of actinide metal systems.

We have also investigated the possibility of forming direct uranium-to-uranium bonds in dimers of f^1 U(V), compounds that might be analogous to Mo(V) and W(V) dimers.[24] The structurally characterized dimer $U_{(}OR)_{10}$,[25] which does not contain a direct U-U bond, was investigated via quasirelativistic Xα-SW calculations. We observed that the more contracted nature of the U 5f orbitals relative to the 4d and 5d orbitals of Mo and W, respectively, is largely responsible for the lack of metal-metal bonding in the uranium dimer.

We also investigated the bonding in the hypothetical dimer [$CpUO_2$], a model based on known transition metal chemistry. Based on our calculations, we think that there is a possibility that this compound would contain a direct U-U bond, and we have encouraged our colleagues in the synthetic actinide community to attempt the synthesis of this molecule.

Actinide-Transition Metal Bonds. In 1985, the first molecules containing direct, unsupported actinide–transition metal bonds were reported by Marks, et al.[26] These heterobimetallic complexes, such as $Cp^*_2(I)Th-RuCp(CO)_2$, contained a direct bond between an early actinide element and a late transition metal. As such, they were analogous to "early–late" complexes within the transition metals, such as the $Cp_2(X)Zr-RuCp(CO)_2$ complexes reported by Casey et al.[27]

We investigated the bonding in both the Th–Ru and Zr–Ru heterobimetallic systems by using Xα–SW MO calculations.[28] We found that the bonding of the $RuCp(CO)_2$ fragment to both the early transition metal and to the early actinide system were quite similar to one another. The metal–metal bond was extremely polarized, to the point that the best description of the metal–metal bonding was as an anionic $RuCp(CO)_2^-$ fragment interacting with a cationic $Cp_2(X)M^+$ (M = Zr, Th) fragment. Our description of the $RuCp(CO)_2$ fragment as an "organometallic pseudohalide" has been an extremely useful one to synthetic practicioners in the field.[29] Consistent with our model for the bonding in actinide complexes, the donation from the Ru fragment to Th was predominantly into the Th 6d, rather than 5f, orbitals.

IV. Applications of the DV-Xα Method to Trivalent Actinide Chemistry

As mentioned earlier, we are shifting our LDF studies of actinide electronic structure from the quasirelativistic Xα–SW method to the fully relativistic DV–Xα technique. The major class of compounds that we have used to test this methodology is three-coordinate actinide(III) complexes. We have begun studies of the nature of the metal-ligand interactions in the systems MX_3 (M = Th, U, Pu; X = H, CH_3, NH_2, OH) with a number of useful results.[30] This work has reaffirmed the primacy of metal-based 7s and 6d orbitals in actinide-ligand bonding interactions. The actinide f orbitals are relegated to a secondary role in which they serve primarily as acceptors of ligand π electron density, consistent with the conclusions drawn from our earlier Xα-SW studies. The symmetry constraints of three-coordination have helped to reveal the interplay between these ligand field interactions and the coupling of electron orbital and spin angular momentum. One of our most important conclusions, which will be discussed later, is that a ligand field can selectively decouple these angular momenta in orbitals in which the ligand field interaction is strong, with significant spectral and magnetic consequences. As will be described below, we plan to use our experience with the DV-Xα methodology to address the optical spectroscopy of actinide complexes as well as the bonding in a number of systems.

V. Recognitions

We are gratified that our contributions to actinide chemistry have been recognized in the form of invited talks and papers. During the last grant period, the PI was invited to present 14 seminars on actinide chemistry at universities and national laboratories, and to present talks at 9 national and international conferences. We also received several invitations to contribute review articles on our research in actinide chemistry, including invited reviews in 1991 for Angewandte Chemie, the leading German chemical journal, and Chemical Reviews, the major review journal of the American Chemical Society.

References

1. Case, D. A. Annu. Rev. Phys. Chem. 1982, 33, 151.

2. Wood, J. H.; Boring, A. M. Phys. Rev. B 1978, 18, 2701.

3. (a) Averill, F. W.; Ellis, D. E. J. Chem. Phys. 1973, 59, 6411. (b) Rosen, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. J. Chem. Phys. 1976, 65, 3629.

4. Bursten, B. E.; Strittmatter, R. J. Angew. Chem. Int. Ed. Engl. 1991, 30, 1069.

5. (a) Baumgartner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. Angew. Chem., Int. Ed. Engl. 1965, 4, 878. (b) Baumgartner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. Angew. Chem., Int. Ed. Engl. 1966, 5, 134–135. (c) Baumgartner, F.; Fischer, E. O.; Billich, H.; Dornberger, E.; Kanellakopulos, B.; Roth, W.; Steiglitz, L. J. Organomet. Chem. 1970, 22, C17–C19. (d) Laubereau, P.; Burns, J. Inorg. Nucl. Chem. Lett. 1970, 6, 141–150. (e) Laubereau, P.; Burns, J. Inorg. Chem. 1970, 9, 1091–1095.

6. Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. J. Am. Chem. Soc. 1989, 111, 2756.

7. Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. J. Less-Common Met. 1989, 149, 207.

8. Strittmatter, R. J.; Bursten, B. E. J. Am. Chem. Soc. 1991, 113, 552.

9. W. Moffitt, discussion in: Reynolds, L. T.; Wilkinson, G. J. Inorg. Nucl. Chem. 1956, 2, 246.

10. Kot, W. K.; Shalimoff, G. V.; Edelstein, N. M.; Edelman, M. A.; Lappert, M. F. J. Am. Chem. Soc. 1988, 110, 986–987.

11. N. M. Edelstein, personal communication.

12. Kot, W. K.; Edelstein, N.; Lappert, M. F. Abstracts of Papers, 203rd National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1992; NUCL 102.

13. Marks, T. J.; Ernst, R. D. in Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982.

14. (a) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. J. Am. Chem. Soc. 1981, 103, 3589. (b) Brennan, J. G.; Andersen, R. A. J. Am. Chem. Soc. 1985, 107, 514. (c) Cramer, R. E.; Edelmann, F.; Mori, A. L.; Roth, S.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. Organometallics 1988, 7, 841.

15. Brennan, J. G.; Andersen, R. A.; Robbins, J. L. J. Am. Chem. Soc. 1986, 108, 335-336.

16. Bursten, B. E.; Strittmatter, R. J. J. Am. Chem. Soc. 1987, 109, 6606-6608.

17. Bursten, B. E.; Gatter, M. G. J. Am. Chem. Soc. 1984, 106, 2554.

18. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry," 5th Ed., Wiley: New York, 1988.

19. Bursten, B. E.; Ozin, G. A. Inorg. Chem. 1984, 23, 2910.

20. Bursten, B. E.; Cotton, F. A.; Hall, M. B. J. Am. Chem. Soc. 1980, 102, 6348.

21. Pepper, M; Bursten, B. E. J. Am. Chem. Soc. 1990, 112, 7803.

22. (a) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. Int. J. Quantum Chem., Quantum Chem. Symp. 1981, 15, 91. (b) Shepard, R.; Shavitt, I.; Simons, J. J. Chem. Phys. 1982, 76, 543. (c) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J.-G. Int. J. Quantum Chem., Quantum Chem. Symp. 1988, 22, 149. (d) Hsu, H. L.; Pitzer. R. M.; Davidson, E. R. J. Chem. Phys. 1976, 65, 609.

23. Some recent examples: (a) Chang, A. H. H.; Pitzer, R. M. J. Am. Chem. Soc. 1989, 111, 2500. (b) Ortiz, J. V.; Hay, P. J.; Martin, R. L. J. Am. Chem. Soc. 1992, 114, 2736.

24. Cayton, R. H.; Novo-Gradac, K. J.; Bursten, B. E. Inorg. Chem. 1991, 30, 2265.

25. Cotton, F. A.; Marler, D. O.; Schwotzer, W. Inorg. Chem. 1984, 23, 4211.

26. Sternal, R. S.; Brock, C. P.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8270.

27. Casey, C. P.; Jordan, R. F.; Rheingold, A. L. J. Am. Chem. Soc. 1983, 105, 665.

28. Bursten, B. E.; Novo-Gradac, K. J. J. Am. Chem. Soc. 1987, 109, 904.

29. Sternal, R. S.; Marks, T. J. Organometallics 1987, 6, 2621.

30. Schneider, W. F.; Strittmatter, R. J.; Bursten, B. E.; Ellis, D. E., in Density Functional Methods in Chemistry; Labanowski, J. K.; Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991; p. 247-260.

DATE FILMED

01/21/93