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Electronic Structure of Transition Metal Clusters and Actinide Complexes and Their Reactivity

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"Electronic Structure of Transition Metal Clusters and Actinide Complexes and Their Reactivity"

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Our research in this area since October 2007 has resulted in seven completed publications[1-7] and more papers of the completed work are in progress. Our work during this period principally focused on actinide complexes with secondary emphasis on spectroscopic properties and electronic structure of metal complexes. As the publications are available online with all of the details of the results, tables and figures, we are providing here only a brief summary of major highlights, in each of the categories.

Electronic Structure of Actinide Complexes.

We have carried out a number of actinide complexes in aqueous solution; as such complexes are of considerable importance in our understanding of behavior of actinide species in the environment and high level nuclear wastes. A major highlight of our work during this period is experimental-theoretical collaboration on curium (III) complexes with mutli-dentate ligands with Professor Nitsche and coworkers at LBNL. Our focus was on Cu(III) complexes with ligands that have both carboxylic and phosphoric acid groups so that relative binding strengths of the two ligands can be assessed as a with varying pH. Experimental studies have revealed intriguing trends that could not be explained. We have also studied aqueous complexes of U(VI), NP(VI) and Pu(VI) with OH^-.

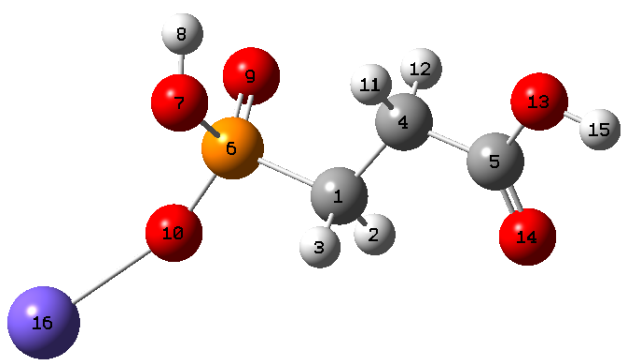
Extensive *ab inito* computations have been carried out to study the equilibrium structure, infrared spectra, and bonding characteristics of a variety of hydrated $NpO_2(CO_3)_m^{q-}$ complexes by considering the solvent as a polarizable dielectric continuum as well as the corresponding anhydrate complexes in the gas-phase.[3] The computed structural parameters and vibrational results at the MP2 level in aqueous solution are in good agreement with Clark et al.'s experiments and provide realistic pictures of the neptunyl complexes in an aqueous environment. Our computed hydration energies reveal that the complex with water molecules directly bound to it yields the best results. Our analysis of the nature of the bonding of neptunyl complexes provides insight into the nature of 6d and 5f-bonding in actinide complexes.We have studied the electronic and spectroscopic properties of plutonyl di and tri carbonate complexes of the types $PuO_2[CO_3]_2$ and $PuO_2[CO_3]_3Ca_3$ using coupled cluster (CC) and other techniques.[4] In particular the structures, and select vibrational spectra, electron density and molecular orbital contour plots of plutonium(VI) complexes of environmental importance such as $[PuO_2(CO_3)_2]^{2-}$ and $[PuO_2(CO_3)_3]^{4-}$ were computed. We have shown that Ca^{2+} is efficacious in gas-phase modeling of electronic and spectroscopic properties of multiply charged plutonyl di and tricarbonate anions through complexes such as $PuO_2(CO_3)_2Ca$ and $[PuO_2(CO_3)_3Ca_3]^{2+}$. Our computed equilibrium geometries and vibrational spectra of these species agree quite well with the EXAFS and Raman data available on related complexes. We have obtained the electron density plots and molecular orbital plots. The results of our computations at the DFT, MP2 and CCSD levels show that the computed geometries and vibrational frequencies are in reasonable agreement among these theoretical levels. We have also compared our computed properties with the available experimental data on the plutonyl carbonate complexes in solutions and solid phases. Our computed geometries for the various interatomic distances at both MP2 and DFT levels agree quite well with the experimental EXAFS results of Clark et al..

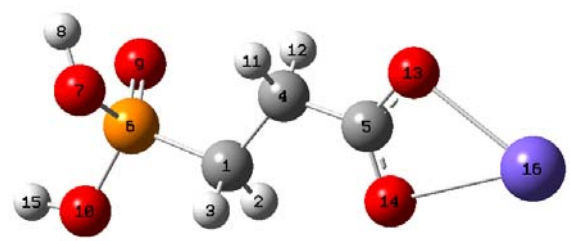
A joint experimental-theoretical study[6] was carried out on curium (III) complexes with multidentate ligands such as phosphonic acid (PPA) which has both carboxylic and phosphoric acid groups to explain the observed dramatic variations in the nature of the observed complexes as a function of pH. Theoretical studies of CmH_2PPA^{2+} and $CmHPPA^+$ complees were carried out in aqueous solution. All possible isomers in the gas phase and aqueous solution have been

calculated. The effects of the aqueous solvent in the configuration preferences of CmH_2PPA^{2+} and $CmHPPA^{+}$ have been investigated. The free energies of solvation were predicted using a self-consistent reaction-field model and a combined discrete-continuum model. Results provided by the different methods were compared and discussed.

Spectroscopic studies on Cm(III) aquoion were carried out by a fluorescence emission spectroscopy at Berkeley, which revealed a band maximum at 593.8 nm. There is a pronounced red-shift of the emission as a result of the complex formation with the PPA molecule, accompanied by an increase in the fluorescence emission lifetime from 65 μs for the Cm(III) aquoion. The TRLFS (time-resolved laser-induced fluorescence spectroscopy) spectra have also been obtained for Cm(III) and PPA species. The PPA molecule can interact with metal ions via the oxygen atoms from the phosphate group and the carboxylate group, thus relative competition of the two groups and their binding propensities with Cm(III) were the central objectives.

Geometries and energy differences of CmH_2PPA^{2+} in aqueous solution were computed using the IEFPCM continuum solvation model and the combined discrete-continuum model at the DFT/B3LYP level. The theoretical results by inclusion of the continuum solvent models produce a relative stabilization of CmH_2PPA^{2+} in aqueous solution. The equilibrium geometries are presented in Fig. 1 and the corresponding geometries of $HPPA^{2-}$ with Cm(III) were also optimized. The conformational free energy difference (ΔG_{conf}) in solution was estimated by adding solvation free energy $\Delta\Delta G_{sol}$ to the gas-phase energy . $\Delta G_{conf} \approx \Delta E + \Delta\Delta G_{sol}$. The calculation with the SCRF model, surprisingly, indicates that the most stable structure is the monodentate phosphate complexation (Cm-P, Fig. 1a) which is the least stable structure in the gas phase. The second stable structure is the bidentate carboxylate complexation (Cm-C2, Fig. 1b), followed by bidentate complexation (Cm-CP2, Fig. 1e). The monodentate carboxylate complexation is even higher in energy in aqueous solution, which is not a stable structure in the gas phase. The tridentate complexation which is the most stable structure in the gas phase is 35.3 kcal/mol higher in energy than the monodentate phosphate complexation. We have also optimized geometries of (a) $Cm[H_2PPA]_2^{+}$ and (b) $Cm[HPPA]_2^{-}$ in aqueous solution.



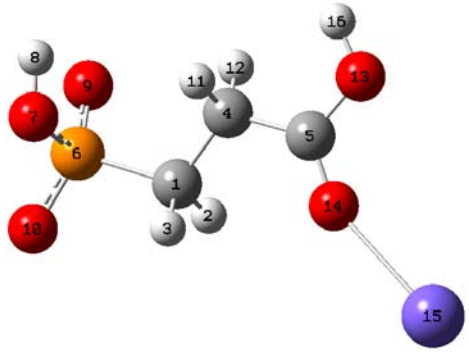


(a) Cm-P ($\Delta\Delta G_{conf}$ = 0.00 kcal/mol)

P_6-O_7: 1.626
P_6-O_9: 1.493
P_6-O_{10}: 1.534
Cm_{16}-O_{10}: 2.331
P_6-C_1: 1.826
C_5-O_{13}: 1.347
C_5-O_{14}: 1.216
C_1-C_4: 1.533
C_4-C_5: 1.518

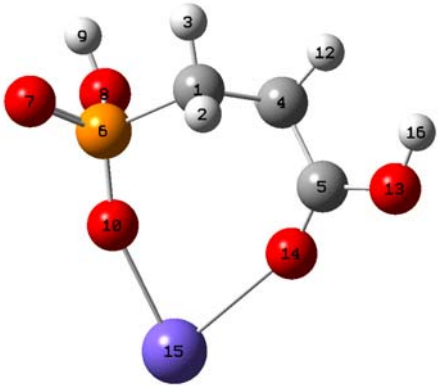
(b) Cm-C2

P_6-O_7: 1.604
P_6-O_9: 1.482
P_6-O_{10}: 1.596
P_6-C_1: 1.809
C_5-O_{13}: 1.277
C_5-O_{14}: 1.263
C_1-C_4: 1.535
C_4-C_5: 1.525
Cm_{16}-O_{13}: 2.498
Cm_{16}-O_{14}: 2.637



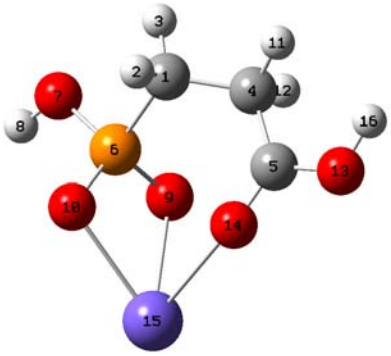
(c) Cm-C ($\Delta\Delta G_{conf}$ = 17.17 kcal/mol)

P_6-O_7: 1.646
P_6-O_9: 1.505
P_6-O_{10}: 1.501
P_6-C_1: 1.842
C_5-O_{13}: 1.331
C_5-O_{14}: 1.229
C_1-C_4: 1.530
C_4-C_5: 1.512
Cm_{15}-O_{14}: 2.582



(d) Cm-CP ($\Delta\Delta G_{conf}$ = 7.09 kcal/mol)

P_6-O_7: 1.490
P_6-O_8: 1.621
P_6-O_{10}: 1.529
P_6-C_1: 1.830
C_5-O_{13}: 1.331
C_5-O_{14}: 1.227
C_1-C_4: 1.553
C_4-C_5: 1.517
Cm_{15}-O_{10}: 2.340
Cm_{15}-O_{14}: 2.572



P_6-O_7: 1.598
P_6-O_9: 1.527
P_6-O_{10}: 1.526
P_6-C_1: 1.826
C_5-O_{13}: 1.328
C_5-O_{14}: 1.227
C_1-C_4: 1.538
C_4-C_5: 1.516
Cm_{15}-O_9: 2.499
Cm_{15}-O_{10}: 2.480
Cm_{15}-O_{14}: 2.598

(e) Cm-CP2 ($\Delta\Delta G_{conf}$ = 18.74 kcal/mol)

We find that the ordering of the calculated conformational Gibbs energies in solution is different from the ordering of energies from the pure continuum model. The tridentate complex Cm-CP2 is the most stable structure in aqueous solution. The next are Cm-P and Cm-C2. Cm-P and Cm-C are not stable structures in the gas phase. Aqueous solution geometries were used in the calculations of gas phase energies. There are significant changes on geometries after solvation in aqueous solution. The conformational Gibbs energy of Cm-P2 is only ca. 6 kcal/mol larger than that of Cm-C2. The carboxylate complexation is capable of displacing the phosphate binding in aqueous solution. Cm-CP is even more unstable. The most stable structure is the tridentate complex Cm-CP2. This might explain the experimental observation that the lifetime of $CmHPPA^+$ is 160 μs while the lifetime of CmH_2PPA^{2+} is 112 μs. $CmHPPA^+$ binds less coordinated water molecules than CmH_2PPA^{2+} in solution.

Extensive *ab initio* calculations have been carried out to study equilibrium structures, vibrational frequencies, and bond characters of hydrated $UO_2(OH)^+$, $UO_2(OH)_2$, $NpO_2(OH)$, and $PuO_2(OH)^+$ complexes in aqueous solution and the gas phase.[7] The structures have been further optimized by considering long-range solvent effects as a polarizable continuum dielectric model. The hydrolysis reaction Gibbs energy of $UO_2(H_2O)_5^{2+}$ is computed to be 8.11 kcal/mol at the MP2 level in good agreement with experiments. Our results reveal that it is necessary to include water molecules bound to the complex for proper treatment of the hydrated complex and the dielectric cavity. Structural reoptimization of the complex in a dielectric cavity seems inevitable to seek subtle structural variations in the solvent and to correlate with the observed spectra and thermodynamic properties in the aqueous environment.

The optimized structure of some of these complexes is not the same in the gaps phase and aqueous solution illustrating the importance of carrying out these computations in solution. Our results also show that the bulk effects are important on the vibrational frequencies of hydrated actinyl hydroxide complexes, especially the $UO_2(OH)_2(H_2O)_3$ and $NpO_2(OH)(H_2O)_4$. They were found to be four-coordinated in the first coordination shell and one water molecule in the second shell in the gas phase, whereas their solvation structures are five-coordinated in the first coordination shell in the continuum PCM model. Moreover, with the equilibrium geometries reoptimized in aqueous solution, the computed Gibbs energy of hydrolysis reaction of $UO_2(H_2O)_5^{2+}$ in solution is 7.27 kcal/mol, which is in good agreement with the experimental value. It is also necessary to include water molecules bound to the complex in the first hydration sphere for proper treatment of the hydrated complex and the dielectric cavity.
phase (left) and aqueous solution (right).

Proposed Plan.

We plan to continue our works on environmental actinide complexes and transition metal species. We are investigating Cm(III) complexes with other ligands such as OH^- and CO_3^{2-} in collaboration with Professor Nitsche and his coworkers who are carrying out EXAFS and time-resolved xray fluorescence studies of such curium(III) complexes in solution. Likewise structures and properties of Bk(III) complexes remain unknown at this time and one often has to rely on analogous lanthanide complexes, which often results in erroneous deductions, as transplutonium complexes tend to behave quite differently from the lanthanide analogs due to relativistic effects. The observed behavior of these complexes as a function of pH is far from understood. Moreover there is a scarcity of thermodynamic solvation energy data on Bk(III) and Am(III) species which occur not only in high level nuclear wastes but also in nuclear reactor reactions during fission process. There have been some exciting experimental findings concerning proton transfers in actinide water complexes. At present there are no theoretical studies to provide insight into these species. We also propose to continue our work on transition metal species and these actinide with specific focus on spectroscopic properties, geometries, Gibbs Free energies in solutions and potential energy curves.

Publications from the DOE BES Grant Oct 2007-Present

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2. Suo, B.; Balasubramanian, K., Spectroscopic constants and potential energy curves of yttrium carbide (YC). *Journal of Chemical Physics* **126**, 224305 (2007) [PDF]

3. Balasubramanian, K and Z. Cao, "Theoretical Studies on Structures of Neptunyl Carbonates: $NpO_2(CO_3)_m(H_2O)_n^q$ (m =1-3, n = 0-3) in Aqueous Solution**",** *Inorganic Chemistry***,** 46, 10510-10519 (2007)

4. Balasubramanian, K. and D. Chaudhuri, "Computational modeling of environmental plutonyl mono-, di- andtricarbonate complexes with Ca counterions: Structures and spectra: $PuO_2(CO_3)_2^{2-}$, $PuO_2(CO_3)_2Ca$, and $PuO_2(CO_3)_3Ca_3$, Chemical Physics Letters, *450, Issues 4-6, Pages 196-202, 2008.*

5. Balasubramanian, K., and Cao, Z., "Geometries and energy separations of electronic states of In_3N, InN_3, and their ions", J. Theoretical and Computational Chemistry, 2008.

6. Cao, Z., Balasubramanian, K., Calvert, M., Nitsche, H., "Solvation effects on the isomeric preference of binding of Curium^{3+} with phosphocarboxylic acid multidentate ligands: mH_2PPA^{2+} and $CmHPPA^+$", Manuscript to be submitted

7. Cao, Z., Balasubramanian, K., "Unusual Structures and Energetics of U(VI), NP(VI) and Pu(VI) complexes with OH^- in aqueous solution: $UO_2(OH)(H_2O)_4^+$, $UO_2(OH)_2(H_2O)_3$, $NpO_2(OH)(H_2O)_4$, and $PuO_2(OH)(H_2O)_4^+$ complexes", in prep.