

Bimetallic Lanthanide and Actinide Metallocene Hydrides

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1 Abstract

2 Introduction

The valence electrons on lanthanide and actinide cations were thought to not participate in bonding due to the limited radial extent of the f -orbitals. However, recent studies in Ln^{2+} complexes revealed that ligand field splitting can lower the energy of d -orbitals and lead to the formation of bimetallic lanthanide and actinide complexes. The aim of this experiment is to investigate the possibility of Y-Y bonding in the recently synthesized bimetallic complex $[(\text{Cp})_2\text{Y}(\mu\text{-H})]_2$.

3 Methods

3.1 Statement of the Models

In a lanthanide, the $4f$ orbitals are much closer to the nuclei compared to the $5d$ orbital. Electrons removed from the system will come from the $5d$ atomic orbital first, increasing the energy of the orbital while not affecting the $4f$ atomic orbital as much. As the oxidation state increases, the energy separation between the two orbitals decreases.

Orbital localization is expected to have no effect on the total energy of a molecule, nor the molecular structure. The orbital energies are expected to increase when localization is applied.

3.2 Computational Details

A DFT calculation was performed on B_2H_6 using the TPSSH functional and def2-SVP basis sets. The diborane molecule was assigned D_{2h} symmetry. The canonical Kohn-Sham molecular orbitals were then plotted and assigned. The

diborane symmetry was then lowered to C_1 and Boys localization was performed. The resulting molecular orbitals were then plotted and assigned as well.

Ground state optimizations of $[(Cp)_2Y(\mu-H)]_2$ and its monoanion were performed at the TPSSh level using def2-SVP basis sets. Solvation of the complexes in THF was simulated with a dielectric constant of 7.58. The HOMO-LUMO gaps of different spin states were analyzed to determine which one the molecule would be in. The spin states of the complexes was used to determine whether the complex would be EPR active. Frontier orbitals were visualized to determine whether metal-metal bonding was observed.

4 Results and Discussion

The HOMO-LUMO gap of the neutral singlet complex is +4.29684 eV, whereas the neutral triplet complex yielded a negative gap. A doublet state was the only reasonable spin state for the monoanion complex without exciting the electron. The closed shell spin state of the neutral complex makes it EPR inactive, whereas the lone electron on the monoanion makes it EPR active. The bond length between the metal centers in the complex were determined to be 354.55 pm and 346.19 pm for the neutral and monoanion complex, respectively. This corresponds to a 0.724% error in the neutral complex and a 0.344% error in the monoanion complex when compared to (). The frontier orbitals of the monoanion complex suggest metal-metal bonding.

5 Conclusions

Appendix

Structure	HOMO-LUMO Gap (eV)
Anion	+0.74691
Neutral Singlet	+4.29684
Neutral Triplet	-2.38537
Neutral Closed	+4.29805
Structure	Y-Y Distance (pm)
Neutral	354.55
Neutral Exp	352
Anion	347.19
Anion Exp	346