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 lignad 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 $[(Cp)_2Y(\mu-H)]_2$.

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 fom 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 increaes, 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. Boys localization was performed after lowering to C_1 symmetry. The canonical Kohn-Sham molecular orbitals and Boys localized orbitals were plotted.

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 deterime whether metal-metal bonding was observe

4 Results and Discussion

Table 1:

| Orbital | Canonical | | | Localized | | |
	Assignment	Energy (eV)	Visualization	Assignment	Energy (eV)	Visualization
HOMO (1b2g)	$\pi^*_{\mathrm{p-p}}$	-8.514		$\sigma^*_{\mathrm{s-p}}$	-10.726	
HOMO-1 (3ag)	$\sigma_{\mathrm{p-p}}$	-9.867		$\sigma^*_{\mathrm{s-p}}$	-10.726	
HOMO-2 (1b3u)	$\pi_{\mathrm{p-p}}$	-10.156		$\sigma^*_{\mathrm{s-p}}$	-10.726	
HOMO-3 (1b2u)	$\pi_{\mathrm{p-p}}$	-11.516		$\sigma^*_{\mathrm{s-p}}$	-10.726	
HOMO-4 (2b1u)	$\sigma^*_{\mathrm{s-s}}$	-12.067		$\sigma^*_{\mathrm{s-p}}$	-13.927	
HOMO-5 (2ag)	$\sigma_{\mathrm{s-s}}$	-17.747		$\sigma^*_{\mathrm{s-p}}$	-13.927	

The HOMO-LUMO gap of the neutral singlet complex was +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 doublet state had a smaller HOMO-LUMO gap than the neutral closed-shell complex of +0.74691 eV, and the excited quartet state also had a negative gap. 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 354.55pm and 346.19pm for the neutral and monoanion complex, respectively. This corresponds to a 0.724% error and a 0.344% error respectively when compared to Dumas et al. [1]
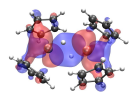
5 Conclusions

References

[1] dumas Megan T. Dumas et al. "Synthesis and reductive chemistry of bimetallic and trimetallic rare- 2 earth metallocene hydrides with (C5H4SiMe3)1- ligands". In: J. Organomet. Chem. 849-850 3 (2017), pp. 38–47. doi: 10.1016/j.jorganchem.2017.05.057.

84a α   (–0.555 eV)
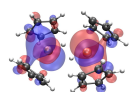
83a α   (–1.302 eV)

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