
Theoretical Study on Lanthanide Metal Organometallic Compounds

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Abstract: Organometallic sandwich complexes exhibit a number of potential structural and electronic properties and attract the attention of many researchers in recent years. In this paper, we systematically studied the structure and stability of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb) complexes using density functional theory calculations. It is found that the $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb) complexes have high C_{8v} point symmetry structure and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ are typical "sandwich" structure. The stability of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ is explained by the calculation of binding energy and HOMO-LUMO gap. The study of binding energy shows $\text{Eu}(\text{C}_8\text{H}_8)^-$, $\text{Eu}(\text{C}_8\text{H}_8)_2^-$, $\text{Ho}(\text{C}_8\text{H}_8)^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ have significantly high binding energy and exhibit high thermodynamic stability. The HOMO-LUMO gaps of $\text{Ho}(\text{C}_8\text{H}_8)^-$, $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ are 2.016, 3.117 and 3.098 eV, respectively, which are obviously higher than other complexes. The result implies that these three complexes are more stable than other complexes. Besides, the comparison of experimental and theoretical vertical electron detachment energy (VDE) of $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ is presented in this paper. The relative error (between theoretical and experimental) of vertical electron detachment energies of sandwich complexes $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ is in the range of 3.7-9.3%, indicating that the theoretical and experimental results are in good agreement.

Keywords: Density Functional Theory, Geometric Structure, Stability, Lanthanide

1. Introduction

The interactions of organic molecules with metal atoms are garnering more and more interest in many areas of modern technology due to their geometries and electronic properties. Several experimental [1-5] and theoretical [6-9] works have been devoted to studying the structure and property of organometallic complexes. Transition metal atoms supported on benzene attract the special attention of scientists for many years, one of the more interesting findings of Kaya and coworkers showed that for the 3d transition metal, the early elements (Sc - V) interact with benzene to form multiple-decker sandwich structures, while the later elements (Fe - Ni) form rice-ball structures [10]. We reported the early transition metal V and the late transition metal Co reaction with benzene molecules based on the density functional theory [11], and the result is consistent with the prediction of Kaya et al. Rao and co-worker studied the structures, spectroscopy and magnetism of transition metal-benzene association complexes [12, 13]. The abundant structural variety and physical chemistry properties exhibited by the transition

metal-benzene complexes have stimulated a growing interest of researcher in metal organic complexes.

Recently, using the 1,3,5,7-cyclooctatetraene (C_8H_8 , COT) as ligands occur in many studies of the interaction of organic molecules with metal atoms [14-18]. Yang and coworkers have obtained the first high-resolution electron spectra of lanthanide complexes with benzene and cyclooctatetraene molecules and determined the metal-ligand bonding and electronic states of these systems by combing the ZEKE measurements with MP2 calculations [15]. Kaya and coworker [16] employed experimental techniques such as mass spectrometry, photoionization spectroscopy and photoelectron spectroscopy and obtained the spectroscopic data of neutral and anionic $\text{Ln}_n(\text{C}_8\text{H}_8)_m$ complexes. The monomer and the dimer with Ce and COT have been studied by H. Bolvin and coworkers using first-principle quantum chemistry methods [17].

Previous studies mainly focus on the neutral sandwich complexes, and there are few reports on charged complexes. The purpose of this paper is to report the structure and stability of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb).

The bond energy, HOMO-LUMO gap, Vertical electron detachment energy (VDE) was calculated. The results showed that $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) have high C_{8v} point symmetry structure, and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ are typical "sandwich" structure. $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Eu}$ and Ho) has a obviously higher binding energy and HOMO-LUMO gap, which suggests that these complexes are more stable than others.

2. Theoretical Methods

The ground state of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb) complexes were determined by means of general gradient approximation to density functional theory (DFT) using GAUSSIAN 09 program [19]. In the recent literature, B3LYP [20-22] has been successfully applied to the study of metal-organic complexes, so in this paper, we also use B3LYP functional to carry out the following calculations. The triple- ζ basis sets, 6-31+G(d), were used for C and H, and the Stuttgart relativistic small effective core potentials and the valence basis sets were used for Ln atoms [23-27]. Different possible spin multiplicities were also considered for each of these structural isomers to determine the preferred spin states of these complexes. Spin-restricted hybrid DFT calculations were employed for the singlet state, while spin-unrestricted hybrid DFT calculations were employed for all other electronic states. Vibrational frequency calculations were performed to ascertain the stability of lowest energy isomers. Thus, the reported states in structural figure are true local minima since they have real frequencies.

3. Results and Discussion

3.1. Geometric Structures of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb)

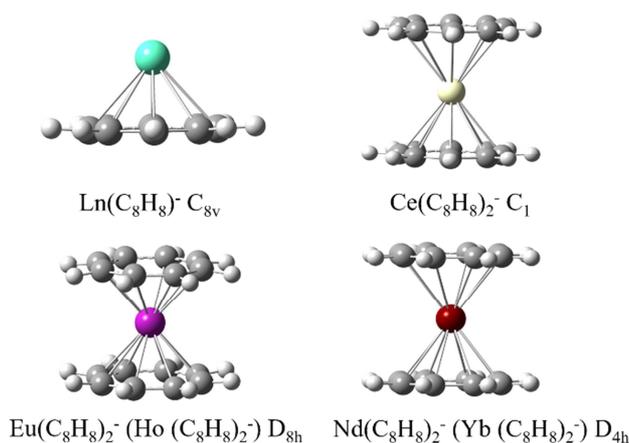


Figure 1. Structure and point group symmetry of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb).

The optimized structures and point group symmetries of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) obtained by B3LYP functional are displayed in Figure 1. All the ground states prefer the low spin multiplicity. From Figure 1, structure $\text{Ln}(\text{C}_8\text{H}_8)^-$ are all C_{8v} point symmetry for $\text{Ln}=\text{Ce},$

$\text{Nd}, \text{Eu}, \text{Ho}$ and Yb . In previous studies, Yang reported a C_{8v} structure for neutral and cationic $\text{Gd}(\text{C}_8\text{H}_8)$ [15]. The result shows that Lanthanide atom reaction with COT molecules prefers the high point symmetry. The Ln-C bond lengths are 2.788 Å for $\text{Ce}(\text{C}_8\text{H}_8)^-$ and $\text{Eu}(\text{C}_8\text{H}_8)^-$, 2.715 Å for $\text{Ho}(\text{C}_8\text{H}_8)^-$, 2.859 Å for $\text{Nd}(\text{C}_8\text{H}_8)^-$, 2.732 Å for $\text{Yb}(\text{C}_8\text{H}_8)^-$, respectively. For $\text{Ce}(\text{C}_8\text{H}_8)^-$ and $\text{Eu}(\text{C}_8\text{H}_8)^-$, and the C-C and C-H bond lengths are about 1.418 and 1.093 Å in the ground doublet structure, respectively. For $\text{Ho}(\text{C}_8\text{H}_8)^-$, the C-C bond length are 1.416 and 1.089 Å, respectively. The C-C bond length is 1.419 Å for $\text{Nd}(\text{C}_8\text{H}_8)^-$ and 1.421 Å for $\text{Yb}(\text{C}_8\text{H}_8)^-$, and the C-H bond length is about 1.091 Å for the two clusters. The lowest-energy structures of $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) are sandwich structures. The point symmetry is C_1 for $\text{Ce}(\text{C}_8\text{H}_8)_2^-$ and D_{4h} for $\text{Nd}(\text{C}_8\text{H}_8)_2^-$ and $\text{Yb}(\text{C}_8\text{H}_8)_2^-$, respectively. $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ are ideal sandwich structure with D_{8h} point symmetry. For $\text{Ce}(\text{C}_8\text{H}_8)_2^-$, $\text{Nd}(\text{C}_8\text{H}_8)_2^-$ and $\text{Yb}(\text{C}_8\text{H}_8)_2^-$, initial structure with D_{8h} symmetry is also considered in the present calculation and the result found it is either not the local minimum structure with imaginary frequency or does not converge. The Ln-C bond length is about 3.04, 3.00, 2.82, 2.78 and 2.72 Å for $\text{Ce}(\text{C}_8\text{H}_8)_2^-$, $\text{Nd}(\text{C}_8\text{H}_8)_2^-$, $\text{Yb}(\text{C}_8\text{H}_8)_2^-$, $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$, respectively. The C-C bond lengths are in the range of 1.40-1.43 Å and the C-H bond length is about 1.09 Å for the lowest-energy structures of $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb). The calculated spin state is different with the prediction by Kaya. In present calculation, the total energy increases with the spin multiplicity.

Table 1. The calculated VDEs of $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) anion complexes, unit in eV.

system	calc
$\text{Ce}(\text{C}_8\text{H}_8)^-$	0.605
$\text{Nd}(\text{C}_8\text{H}_8)^-$	0.767
$\text{Eu}(\text{C}_8\text{H}_8)^-$	0.815
$\text{Ho}(\text{C}_8\text{H}_8)^-$	0.854
$\text{Yb}(\text{C}_8\text{H}_8)^-$	1.773

Table 2. The calculated and experimental VDEs of $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) anion complexes, unit in eV.

system	calc	Expt ^a	Relative error (%)
$\text{Ce}(\text{C}_8\text{H}_8)_2^-$	2.293	2.45	6.5
$\text{Nd}(\text{C}_8\text{H}_8)_2^-$	2.336	2.43	3.7
$\text{Eu}(\text{C}_8\text{H}_8)_2^-$	2.303	2.14	7.5
$\text{Ho}(\text{C}_8\text{H}_8)_2^-$	2.220	2.34	5.1
$\text{Yb}(\text{C}_8\text{H}_8)_2^-$	2.330	2.13	9.3

^a From ref. [16]

3.2. Vertical Electron Detachment Energies

The vertical electron detachment energy VDE is calculated in Tables 1 and 2. The vertical electron detachment energy is defined as the energy difference between the neutral clusters at optimized anion geometry clusters and optimized anion clusters, $\text{VDE} = E_{(\text{neutral at optimized anion geometry})} - E_{(\text{optimized anion})}$. If one assumes that electron detachment are one electron processes, then the final spin multiplicities will differ by ± 1 from the spin multiplicity of the initial states involved in the process. So,

when the anionic complex loses an electron and becomes a neutral species, we consider the spin multiplicity plus one or minus one in the VDE calculation. For the VDE values calculated in both cases, the smaller one is selected. Tables 1 and 2 present the calculated VDE results for $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb), and the experimental values of $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ are also listed in Table 2 in order to compare with the theoretical results. From Table 1, the VDEs of $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}$ and Ho) are close, but the VDE value for $\text{Yb}(\text{C}_8\text{H}_8)^-$ is relatively high. Unfortunately, we have not found the relevant experimental results for $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb). From Table 2, the calculated VDEs of $\text{Ce}(\text{C}_8\text{H}_8)_2^-$ are 2.293 eV, which is a little smaller than experimental data 2.45 eV. The relative error is 6.5%. For $\text{Nd}(\text{C}_8\text{H}_8)_2^-$, the calculated VDE 2.336 eV is in good agreement with the experimental value 2.43 eV, and the relative error is 3.7%. For $\text{Ho}(\text{C}_8\text{H}_8)_2^-$, the calculated VDE also match well with experimental value of 2.34 eV and the relative error is 5.1%. As

$$E_b(\text{Ln}(\text{C}_8\text{H}_8)^-) = E(\text{Ln}) + E(\text{C}_8\text{H}_8^-) - E(\text{Ln}(\text{C}_8\text{H}_8)^-) \quad (1)$$

$$E_b(\text{Ln}(\text{C}_8\text{H}_8)_2^-) = [E(\text{Ln}) + E(\text{C}_8\text{H}_8^-) + E(\text{C}_8\text{H}_8) - E(\text{Ln}(\text{C}_8\text{H}_8)_2^-)]/2 \quad (2)$$

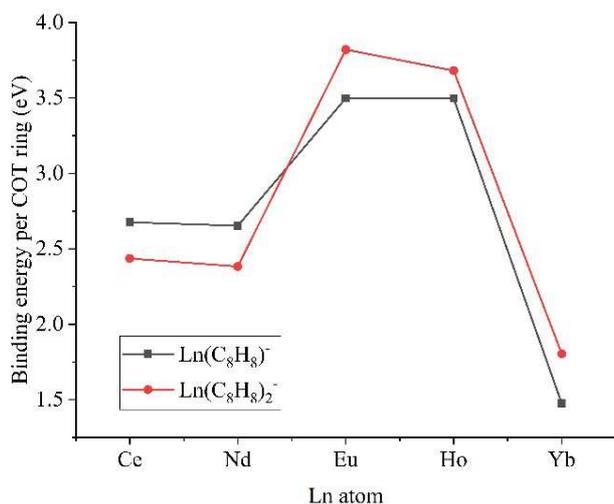


Figure 2. Binding energy per COT ring of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb).

Table 3. The binding energy and HOMO-LUMO gap of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) anion complexes, unit in eV.

System	HOMO-LUMO gap	Binding energy
$\text{Ce}(\text{C}_8\text{H}_8)^-$	1.214	2.676
$\text{Nd}(\text{C}_8\text{H}_8)^-$	1.313	2.653
$\text{Eu}(\text{C}_8\text{H}_8)^-$	1.613	3.499
$\text{Ho}(\text{C}_8\text{H}_8)^-$	2.016	3.497
$\text{Yb}(\text{C}_8\text{H}_8)^-$	1.866	1.476
$\text{Ce}(\text{C}_8\text{H}_8)_2^-$	1.061	2.436
$\text{Nd}(\text{C}_8\text{H}_8)_2^-$	1.099	2.383
$\text{Eu}(\text{C}_8\text{H}_8)_2^-$	3.117	3.821
$\text{Ho}(\text{C}_8\text{H}_8)_2^-$	3.098	3.681
$\text{Yb}(\text{C}_8\text{H}_8)_2^-$	1.128	1.805

Where $E(\text{Ln})$, $E(\text{C}_8\text{H}_8^-)$, $E(\text{C}_8\text{H}_8)$, $E(\text{Ln}(\text{C}_8\text{H}_8)^-)$ and $E(\text{Ln}(\text{C}_8\text{H}_8)_2^-)$ are the energies of Lanthanide atoms, C_8H_8^- , C_8H_8 , $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$, respectively. As displayed in Figure 2 and Table 3, the binding energies of

for $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Yb}(\text{C}_8\text{H}_8)_2^-$, two calculated values (2.303 and 2.330 eV) are both slightly smaller than the experimental values (2.14 and 2.13 eV), and the relative error is 7.5% for $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and 9.3% for $\text{Yb}(\text{C}_8\text{H}_8)_2^-$, respectively. In general, the calculated VDE results of the five complexes are in agreement with the experimental data. The calculated values of $\text{Ce}(\text{C}_8\text{H}_8)_2^-$, $\text{Nd}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ are higher than the experimental results, while the VDE of $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ are lower than the experiments. The relative error is in the range of 3.7-9.3%, and the relative error of the $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ complex is slightly larger than that of the other complexes.

3.3. Binding Energy

The average binding energy per COT ring of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) complexes is computed using the equations (1) and (2):

these complexes are in range of 1.467-3.821 eV, when $\text{Ln} = \text{Eu}$ and Ho , the binding energy of complexes $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ is about 3.5 eV, which is the largest among all complexes. When $\text{Ln} = \text{Ce}$ and Nd , the binding energy is about 2.5 eV, followed by energy of $\text{Ln} = \text{Eu}$ and Ho . The binding energy of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$, 1.476 and 1.805 per COT ring, is the smallest of all. Compared with the binding energies of these complexes, the stability of Eu-COT and Ho-COT is obviously higher than that of other complexes, showing that they are thermodynamically stable enough again decomposing into small fragments.

3.4. HOMO-LUMO Gap

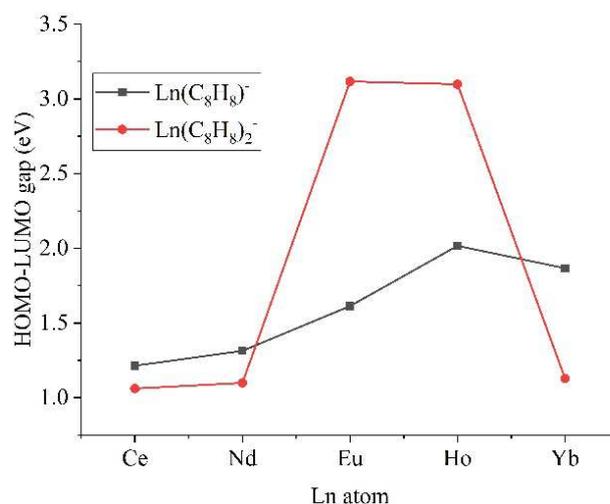


Figure 3. HOMO-LUMO gap of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb).

The energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO Gap) reflects the kinetic stability of these complexes. The HOMO-LUMO gap of the lowest-energy

$\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) structures is presented as a function of Ln ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$ and Yb) atom in Figure 3. The data of HOMO-LUMO gap is given in Table 3. As shown in Figure 3 and Table 3, the HOMO-LUMO gaps of $\text{Ln}(\text{C}_8\text{H}_8)^-$ increase almost linearly with the Ln atom from Ce-Ho, and then decrease a little at $\text{Ln} = \text{Yb}$. $\text{Ho}(\text{C}_8\text{H}_8)^-$ have larger HOMO-LUMO gap, which infers that the $\text{Ho}(\text{C}_8\text{H}_8)^-$ complex have relatively large kinetic stabilities. For $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ complex, compared to the $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln} = \text{Ce}, \text{Nd}$ and Yb), the HOMO-LUMO gaps of $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ are significantly higher. This also implies that $\text{Eu}(\text{C}_8\text{H}_8)_2^-$ and $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ are more stable than other complexes. In fact, the values of HOMO-LUMO gaps of all the $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ complexes studied here are of significant magnitude, indicating that these complexes are relatively stable.

4. Conclusion

The structure and stability of $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb) complexes are investigated using density functional theory calculations. The $\text{Ln}(\text{C}_8\text{H}_8)^-$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$ and Yb) complexes have high C_{8v} point symmetry structure and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ are typical "sandwich" structure. $\text{Ln}(\text{C}_8\text{H}_8)^-$ and $\text{Ln}(\text{C}_8\text{H}_8)_2^-$ ($\text{Ln} = \text{Eu}$ and Ho) has a obviously higher binding energy and HOMO-LUMO gap, which suggests that these complexes are more stable than others. Vertical electron detachment energies were calculated, which are in agreement with experimental results. The relative error is in the range of 3.7-9.3%. The agreement between experimental and theoretical VDE indicates the feasibility of the density functional theory calculations. It is hoped that further studies, both theoretical and experimental, will reveal more structural, electronic and optical properties of sandwich compounds.

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