

# Determination Structure-Property of Lanthanide Organometallic Sandwich Compounds Using Density Functional Theory

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**Abstract:** Organometallic compounds composed of metal atoms and organic molecular rings have unique physical and chemical properties, and show attractive applications in optoelectronic devices, catalysts, biosensors and so on. In this paper, the structure and photoelectron spectra of a series of organometallic compounds  $\text{Ln}(\text{C}_8\text{H}_8)_2$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$  and  $\text{Yb}$ ) have been systematically studied by using two functional B3LYP and BPW91 based on the density functional theory. The results show organometallic complexes  $\text{Ln}(\text{C}_8\text{H}_8)_2$  are typical "sandwich" structure. Both  $\text{Eu}(\text{C}_8\text{H}_8)_2$  and  $\text{Ho}(\text{C}_8\text{H}_8)_2$  have perfect "sandwich" structure with high  $D_{8h}$  point symmetry.  $\text{Nd}(\text{C}_8\text{H}_8)_2$  and  $\text{Yb}(\text{C}_8\text{H}_8)_2$  possess  $D_{4h}$  point symmetry.  $\text{Ce}(\text{C}_8\text{H}_8)_2$  is a distorted "sandwich" structure with  $C_1$  point symmetry. Generalized Koopmans' theorem is applied to simulate the photoelectron spectra, and the results are in agreement with the experiments.

**Keywords:** Density Functional Theory, Photoelectron Spectrum, Lanthanide, Sandwich Structure

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## 1. Introduction

Studies of organometallic complexes, consisting of metal atoms interacting with organic molecules have attracted much attention for both experimentalists [1-8] and theoreticians [9-17]. In particular, transition metal-organic complexes have been of considerable interest in many areas of modern technology [18-27]. Several experimental and theoretical works have been devoted to studying the geometries and the electronic structures of transition metal atoms supported on organic molecules. A considerable amount of reports on the structural, electronic and magnetic properties have been provided on transition metal-organic complexes. For example, the stability of the sandwich structure has been confirmed for  $\text{V}_n(\text{C}_6\text{H}_6)_{n+1}^+$  complexes by ion mobility measurements and collision induced dissociation experiment [23]. The combined use of Stern-Gerlach molecular beam deflection experiments and density functional theory (DFT) computations has revealed magnetic nature of multidecked  $\text{V}_n\text{Bz}_{n+1}$  sandwich clusters [20, 25]. Anion photoelectron spectroscopic experiments and density functional theory calculations have been used to study the equilibrium geometries, electronic

structure and magnetic properties of  $\text{Co}_m(\text{pyrene})_n$  [26] and  $\text{Co}_m(\text{coronene})$  [27] complexes.

Although early investigations of metal ion-organic molecules focused primarily on first-row transition metals, recent studies have proceeded to examine rare earth ions [28-33]. Organolanthanide compounds are currently receiving considerable interest in many areas recently. Many reports showed the structure of Lanthanide atoms supported on benzene [11, 34], fullerenes [35] and cyclooctatetraene [2, 36-37] as the ligand species are highly symmetric sandwich compound. Ab initio study of metal-ring bonding in the bislanthanide and -actinide complexes  $\text{M}(\text{C}_8\text{H}_8)_2$  ( $\text{M} = \text{La}, \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Lu}, \text{Th}, \text{U}$ ) are performed by Dolg and coworker [11]. Kaya and coworker [2] generated the sandwich structures for  $\text{Ln}_n(\text{C}_8\text{H}_8)_m$  by a combination of mass spectrometry, photoionization spectroscopy, and photoelectron spectroscopy methods, and the spectroscopic data are obtained for neutral and anionic  $\text{Ln}_n(\text{C}_8\text{H}_8)_m$  complexes. The photoelectron spectra observed in their experiments showed a pattern of peaks corresponding to  $\text{Ln}(\text{C}_8\text{H}_8)_2$  anion, but there has been no direct spectroscopic confirmation of these structures.

In the present study, the ground state geometric structures of organometallic complexes of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$  and  $\text{Yb}$ ) are obtained. The photoelectron spectra are investigated in theory to compare the previously published experimental PES spectra, simultaneously, the calculated vertical detachment energies are compared with the experimental data.

## 2. Theoretical Methods

The ground state structures of the  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$  and  $\text{Yb}$ ) complexes were determined using GAUSSIAN 09 program [38]. Based on the recent literatures on the metal-organic complexes, both B3LYP [39-41] and BPW91 [42, 43] functionals have been used to study metal-organic complexes [4, 26-27, 44-45], and each of the functions has its own advantages and disadvantages on structure prediction of different cluster systems. In this paper, two functionals (B3LYP and BPW91) are employed to study the structures and electronic properties of the  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$  and  $\text{Yb}$ ) complexes. The triple- $\zeta$  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 [36, 46-48]. The convergence criterion was used for the total energy with  $10^{-8}$  a.u. The configurations are regarded as optimized when the maximum force, the root-mean-square (RMS) force, the maximum displacement of atoms, and the RMS displacement of atoms have magnitudes less than 0.0045, 0.0003, 0.0018, and 0.0012 a. u, respectively. Different possible spin multiplicities were also considered for each of these structural isomers to determine the preferred spin states of these complexes.

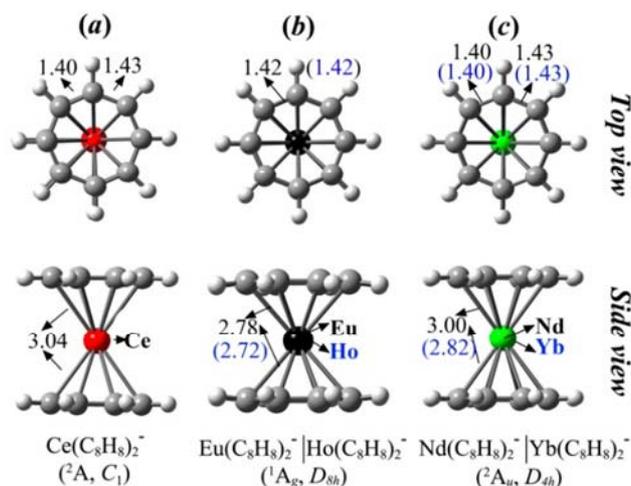
Vertical electron detachment energies (VDEs) were calculated using the generalized Koopmans' theorem by adding a correction term to the eigenvalues of the anion [49]. The correction term was calculated as  $\delta E = E_1 - E_2 - \epsilon_{\text{HOMO}}$ , where  $E_1$  and  $E_2$  are the total energies of the anion and neutral, respectively, in their ground states at the anion equilibrium geometry and  $\epsilon_{\text{HOMO}}$  corresponds to the eigenvalue of the highest occupied molecular orbital (HOMO) of the anion.

## 3. Results and Discussion

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

The geometric structures of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$  and  $\text{Yb}$ ) obtained by the two functionals is similar, and the spin multiplicities, electronic states and point group symmetries are identical to each other by the two functionals. Thus, in the following discussion, we illustrate the geometric structure of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$  and  $\text{Yb}$ ) as represented by the results of B3LYP functional. The geometric structures, point group symmetries and electronic states of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$  and  $\text{Yb}$ ) calculated by B3LYP functional are shown in Figure 1. The spin

multiplicities, electronic states and the relative energies respect to the lowest-energy structure are shown in Table 1.



**Figure 1.** Structure, point group symmetry, electronic state of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Ho}, \text{Nd}$  and  $\text{Yb}$ ) by B3LYP functional: (a)  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$  ( ${}^2\text{A}, \text{C}_1$ )  $\text{Eu}(\text{C}_8\text{H}_8)_2^- / \text{Ho}(\text{C}_8\text{H}_8)_2^-$  (c)  $\text{Nd}(\text{C}_8\text{H}_8)_2^- / \text{Yb}(\text{C}_8\text{H}_8)_2^-$ .

**Table 1.** The spin multiplicities ( $M$ ), electronic states ( $S$ ) and relative energies ( $\Delta E$ ) respect to the lowest-energy structure of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}$  and  $\text{Yb}$ ) by B3LYP functional.

No.	System	M	S	$\Delta E$ (eV)
1	$\text{Ce}(\text{C}_8\text{H}_8)_2^-$	2	${}^2\text{A}$	0.000
2		4	${}^4\text{A}$	2.296
3		6	${}^6\text{A}$	5.406
4	$\text{Nd}(\text{C}_8\text{H}_8)_2^-$	2	${}^2\text{A}_u$	0.000
5		4	${}^4\text{A}$	2.258
6		6	${}^6\text{A}$	5.481
7	$\text{Ho}(\text{C}_8\text{H}_8)_2^-$	1	${}^1\text{A}_g$	0.000
8		3	${}^3\text{A}_u$	2.263
9		5	${}^5\text{A}_g$	5.090
10	$\text{Eu}(\text{C}_8\text{H}_8)_2^-$	1	${}^1\text{A}_g$	0.000
11		3	${}^3\text{A}_u$	2.248
12		5	${}^5\text{A}_g$	4.973
13		7	${}^7\text{A}_u$	8.793
14	$\text{Yb}(\text{C}_8\text{H}_8)_2^-$	2	${}^2\text{A}_u$	0.000
15		4	${}^4\text{A}_u$	2.300
16		6	${}^6\text{A}_u$	5.410

From Figure 1, 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  $\text{Yb}$ ) are sandwich structures. All the ground states prefer the low spin multiplicity. For the  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$ , the lowest-energy structure is a doublet with the  $\text{C}_1$  point symmetry. The Ce-C bond length of  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$  is about 3.04 Å. The C-C bond lengths are in the range of 1.40-1.43 Å. The C-H bond length of  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$  is about 1.09 Å. The perfect doublet geometry with  $\text{D}_{8h}$  symmetry was found in the present work but with one imaginary frequency of  $1700 \text{ cm}^{-1}$ . The similar quartet and sextet are found to be less stable lying 2.296 and 5.406 eV higher in energy than doublet ground state. The  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$  has relatively high  $\text{D}_{4h}$  point symmetry with doublet spin state. The same symmetry structure is also found for  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ . The Ln-C bond length is 3.00 Å for  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$  and 2.82 Å for  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ , respectively. Initial structure with  $\text{D}_{8h}$  symmetry is also considered in the present calculation and the result found it is

not the local minimum structure with imaginary frequency of  $1732\text{ cm}^{-1}$  for  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$ . For  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ , the perfect sandwich geometry either did not converge or converged to ground state structure. The corresponding quartet and sextet are found to be higher in energy by 2.258 and 5.481 eV for  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$  and 2.300 and 5.410 eV for  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ , 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. The two cyclooctatetraene rings are bonded symmetrically to the Ln atom. The Ln-C bond lengths is 2.78 and 2.72 Å for  $\text{Eu}(\text{C}_8\text{H}_8)_2^-$  and  $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ , respectively. The spin multiplicity of  $\text{Eu}(\text{C}_8\text{H}_8)_2^-$  and  $\text{Ho}(\text{C}_8\text{H}_8)_2^-$  is predicted to be singlet, and the high spin multiplicity is also calculated at the same level. The calculated relative energies are less stable than ground state of  $\text{Eu}(\text{C}_8\text{H}_8)_2^-$  by 2.248, 4.973 and 8.793 eV for triplet, quintet and septet, respectively. For  $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ , the triplet and quintet are less stable than singlet by 2.263 and 5.090 eV, respectively. The calculated spin state is different with the prediction by Kaya. In present calculation, the total energy increases with the spin multiplicity.

### 3.2. Vertical Electron Detachment Energies by B3LYP and BPW91 Functionals

The vertical electron detachment energy VDE is calculated by two functionals and the theoretical results are given in Table 2.

**Table 2.** The calculated and experimental VDEs of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  (Ln = Ce, Nd, Eu, Ho and Yb) anion complexes by B3LYP and BPW91 functional, unit in eV.

No.	System	B3LYP	BPW91	Expt <sup>a</sup>
1	$\text{Ce}(\text{C}_8\text{H}_8)_2^-$	2.293	2.206	2.45
2	$\text{Nd}(\text{C}_8\text{H}_8)_2^-$	2.336	2.197	2.43
3	$\text{Ho}(\text{C}_8\text{H}_8)_2^-$	2.220	2.106	2.34
4	$\text{Eu}(\text{C}_8\text{H}_8)_2^-$	2.303	2.164	2.14
5	$\text{Yb}(\text{C}_8\text{H}_8)_2^-$	2.330	2.208	2.13

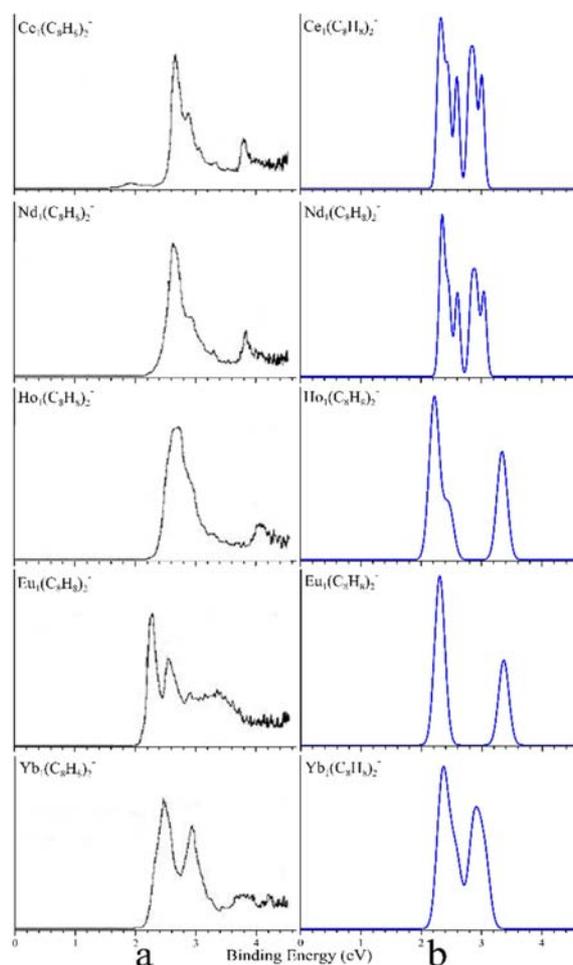
<sup>a</sup>From ref. [2]

The vertical electron detachment energy is defined as the energy difference between the neutral clusters at optimized anion geometry clusters and optimized anion clusters,  $\text{VDE} = E_{(\text{neutral at optimized anion geometry})} - E_{(\text{optimized anion})}$ . When the anionic complex loses an electron and becomes a neutral species, both the spin multiplicity plus one and minus one are considered in the VDE calculation. From Table 2, the calculated VDEs by B3LYP functional are close to the results by BPW91 calculation, and they are in agreement with the experiments. The calculated VDEs of  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$  are 2.293 and 2.206 eV by B3LYP and BPW91, respectively. The value is slightly smaller than experimental result of 2.45 eV, but the result by B3LYP is closer to the experiment. The calculated VDE 2.336 eV of  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$  by B3LYP functional match well with experimental value of 2.43 eV, and the value calculated by BPW91 is a little smaller than experimental data. For  $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ , two calculation are both slightly smaller than the experimental values, but the B3LYP calculation is closer to the experimental results. As for  $\text{Eu}(\text{C}_8\text{H}_8)_2^-$  and  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ , the VDE of B3LYP results are 2.303 and 2.330 eV, which are

larger than experiments, and BPW91 calculation agree well with the experimental values. In general, the result by two functional has its advantages and disadvantages, For  $\text{Ce}(\text{C}_8\text{H}_8)_2^-$ ,  $\text{Nd}(\text{C}_8\text{H}_8)_2^-$  and  $\text{Ho}(\text{C}_8\text{H}_8)_2^-$ , B3LYP calculation results are closer to experiments than BPW91 calculations, while for  $\text{Eu}(\text{C}_8\text{H}_8)_2^-$  and  $\text{Yb}(\text{C}_8\text{H}_8)_2^-$ , the results calculated by BPW91 functional are better agreement with experimental data than those by B3LYP.

### 3.3. Comparison of Computed Spectra with the Experimental Photoelectron Spectra Results

In order to further understand the electronic properties of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  (Ln = Ce, Nd, Eu, Ho and Yb) and in view of the similarity of the results obtained by the two calculations, we select the B3LYP calculation results as a representative to simulate the photoelectron spectra of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  (Ln = Ce, Nd, Eu, Ho and Yb) anion complexes. The experimental and theoretical photoelectron spectra of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  (Ln = Ce, Nd, Eu, Ho and Yb) anion complexes are provided in Figure 2.



**Figure 2.** Comparison of the experimental and computed photoelectron spectra, (a) experimental photoelectron spectra from ref. [2] (b) computed photoelectron spectra by B3LYP functional.

From Figure 2, it can be seen that the photoelectron spectra of  $\text{Ln}(\text{C}_8\text{H}_8)_2^-$  (Ln = Ce, Nd, Ho) are similar in the range of 0.0-4.0 eV. There are two obvious peaks located around the

binding energy of 2.5 and 3.5 eV, respectively. In addition, there are three small peaks beside the first peak. The first VDE of  $\text{Ce}(\text{C}_8\text{H}_8)_2$  measured by Kaya is 2.45 eV, Nakajima also obtained the photoelectron spectrum of  $\text{Ce}(\text{C}_8\text{H}_8)_2$  at 355, 266 and 213 nm. The first measured VDE is 2.60 eV [36]. The present calculated values of VDE by two functionals are 2.293 and 2.206 eV, respectively, and the value is closer to the result of Kaya but a little lower than that of Nakajima. The present calculation predicted the first VDE corresponding to the transition from the anion doublet to neutral singlet. Other measured transitions in experiment occur at 2.66, 2.84, 3.09 and 3.51 eV. The calculation in the present work shows that the photoelectron spectrum of  $\text{Ce}(\text{C}_8\text{H}_8)_2$  has four spectral features located at 2.30, 2.60, 2.89, 3.01 eV. The measured first VDE of  $\text{Nd}(\text{C}_8\text{H}_8)_2$  is 2.43 eV. The first transition energy from the anion doublet to the neutral singlet is calculated to be 2.34 eV, which is in agreement with the experiment. The spectrum of  $\text{Nd}(\text{C}_8\text{H}_8)_2$  shows three small peaks centered at 2.72, 2.81 and 3.09 eV, and the little bit big peak is located at 3.54 eV. Theoretical calculations show that the higher transition energies occur at 2.61, 2.84 and 3.01 eV. For  $\text{Ce}(\text{C}_8\text{H}_8)_2$  and  $\text{Nd}(\text{C}_8\text{H}_8)_2$ , the second peak (~3.5 eV) is not obtained in present work, which may due to the coexistence of isomers in gas cluster beam. As for  $\text{Ho}(\text{C}_8\text{H}_8)_2$ , Figure 2 shows the theoretical photoelectron spectrum with two obvious peaks is consistent with the experimental ones. The calculated first VDE is 2.22 eV, which is in agreement with the experiment. The second peak position calculation is located at 3.5 eV, which is consistent with the experimental result of 3.75 eV. The photoelectron spectrum of  $\text{Eu}(\text{C}_8\text{H}_8)_2$  shows two obvious peaks centered at 2.14 and 2.68 eV. The first VDE corresponding to transition from the anion singlet to the neutral doublet is calculated to be 2.30 eV, which is in agreement with the experimental value. The theoretical spectrum of  $\text{Eu}(\text{C}_8\text{H}_8)_2$  resemble the experimental one, except for being shifted to higher electron binding energies. The similar pattern of transitions implied the sandwich structure of  $\text{Eu}(\text{C}_8\text{H}_8)_2$  and the shift to higher electron binding energies can be interpreted as the theoretical and experimental errors. Good agreement is found in experimental and theoretical spectra for  $\text{Yb}(\text{C}_8\text{H}_8)_2$ . As shown in Figure 2, the comparison between the simulated and experimental spectra of  $\text{Yb}(\text{C}_8\text{H}_8)_2$  shows the same peaks and spectral features at the same electron binding energies. The structure prediction of cluster by using photoelectron spectroscopy simulation associated with density functional theory calculation has realized the unification of the experiment and theory, theoretical information could provide theoretical basis and support for experimental measurement, meanwhile, the experimental measurement will also be able to verify the availability of theoretical prediction. It is hoped that present study will provide some guiding significance for the observation of gas-phase organometallic compound.

## 4. Conclusion

The structural and electronic properties of  $\text{Ln}(\text{C}_8\text{H}_8)_2$  (Ln

= Ce, Eu, Ho, Nd and Yb) are investigated using a combined experimental photoelectron spectra and theoretical density functional calculations. The results show  $\text{Ln}(\text{C}_8\text{H}_8)_2$  species are sandwich structure with  $C_1$  point symmetry for  $\text{Ce}(\text{C}_8\text{H}_8)_2$ . A ideal sandwich structure occurs on  $\text{Eu}(\text{C}_8\text{H}_8)_2$  and  $\text{Ho}(\text{C}_8\text{H}_8)_2$ , while a slight departure from the perfect structure is definitive on the ground state  $\text{Nd}(\text{C}_8\text{H}_8)_2$  and  $\text{Yb}(\text{C}_8\text{H}_8)_2$ , showing  $D_{4h}$  point symmetry. Vertical electron detachment energies were calculated using two functionals B3LYP and BPW91, which are in agreement with experimental results. The theoretical photoelectron spectra are simulated using generalized koopmans' theorem, and the results are discussed and compared with the experiments. The agreement between experimental and theoretical photoelectron spectra can give confidence in the assigned ground state for the complexes considered in the present paper and provide an example for evaluating the accuracies of various DFT methods. It is hoped that the present research can provide theoretical guidance for future experimental observations.

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