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 Ln(C₈H₈)₂⁻ (Ln = Ce, Eu, Ho, Nd and Yb) have been systematically studied by using two functional B3LYP and BPW91 based on the density functional theory. The results show organometallic complexes Ln(C₈H₈)₂⁻ are typical "sandwich" structure. Both Eu(C₈H₈)₂⁻ and Ho(C₈H₈)₂⁻ have perfect "sandwich" structure with high D₈h point symmetry. Nd(C₈H₈)₂⁻ and Yb(C₈H₈)₂⁻ possess D₄h point symmetry. Ce(C₈H₈)₂⁻ is a distorted "sandwich" structure with C₁ 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

1. Introduction

Studies of organometallic complexes, consisting 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 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 V₆(C₆H₆)₆⁺ 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 V₆B₂n⁺ 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 Co₉(pyrene)₉ [26] and Co₉(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 M(C₈H₈)₂ (M = La, Ce, Nd, Gd, Tb, Lu, Th, U) are performed by Dolg and coworker [11]. Kaya and coworker [2] generated the sandwich structures for Ln₉(C₈H₈)₉ by a combination of mass spectrometry, photoionization spectroscopy, and photoelectron spectroscopy methods, and the spectroscopic data are obtained for neutral and anionic Ln₉(C₈H₈)₉ complexes. The photoelectron spectra observed in their experiments showed a pattern of peaks corresponding to Ln(C₈H₈)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 used for \(\text{Ln}\) atoms [36, 46-48]. The maximal displacement of atoms, and the RMS displacement 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 \(\text{Ln}(\text{C}_8\text{H}_8)_2\) (\(\text{Ln} = \text{Ce}, \text{Nd}, \text{Eu}, \text{Ho} \) and \(\text{Yb}\) ) by B3LYP functional: (a) \(\text{Ce}(\text{C}_8\text{H}_8)_2\); (b) \(\text{Eu}(\text{C}_8\text{H}_8)_2\); (c) \(\text{Nd}(\text{C}_8\text{H}_8)_2\); (d) \(\text{Yb}(\text{C}_8\text{H}_8)_2\).](image)

![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.](table)

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

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 Ce(\text{C}_8\text{H}_8)_2, the lowest-energy structure is a doublet with the \(C_1\) point symmetry. The Ce-C bond length of 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 Ce(\text{C}_8\text{H}_8)_2 is about 1.09 Å. The perfect doublet geometry with \(D_\infty h\) symmetry was found in the present work but with one imaginary frequency of 1700 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 Nd(\text{C}_8\text{H}_8)_2 has relatively high \(D_\infty h\) point symmetry with doublet spin state. The same symmetry structure is also found for Yb(\text{C}_8\text{H}_8)_2. The Ln-C bond length is 3.00 Å for Nd(\text{C}_8\text{H}_8)_2 and 2.82 Å for Yb(\text{C}_8\text{H}_8)_2, respectively. Initial structure with \(D_\infty h\) symmetry is also considered in the present calculation and the result found it is
not the local minimum structure with imaginary frequency of 1732 cm\(^{-1}\) for Nd(C\(_8\)H\(_8\)). For Yb(C\(_8\)H\(_8\)), the perfect sandwich geometry either did not converge or converged to a ground state structure. The corresponding quartet and sextet are found to be higher in energy by 2.258 and 5.481 eV for Nd(C\(_8\)H\(_8\)), and 2.300 and 5.410 eV for Yb(C\(_8\)H\(_8\)), respectively. Eu(C\(_8\)H\(_8\)) and Ho(C\(_8\)H\(_8\)) 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 Eu(C\(_8\)H\(_8\)) and Ho(C\(_8\)H\(_8\)), respectively. Eu(C\(_8\)H\(_8\)) and Ho(C\(_8\)H\(_8\)) are 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 Eu(C\(_8\)H\(_8\)) by 2.248, 4.973 and 8.793 eV for triplet, quintet and septet, respectively. For Ho(C\(_8\)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>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>B3LYP</th>
<th>BPW91</th>
<th>Expt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ce(C(_8)H(_8))(_2)</td>
<td>2.293</td>
<td>2.206</td>
<td>2.45</td>
</tr>
<tr>
<td>2</td>
<td>Nd(C(_8)H(_8))(_2)</td>
<td>2.336</td>
<td>2.197</td>
<td>2.43</td>
</tr>
<tr>
<td>3</td>
<td>Ho(C(_8)H(_8))(_2)</td>
<td>2.220</td>
<td>2.106</td>
<td>2.34</td>
</tr>
<tr>
<td>4</td>
<td>Eu(C(_8)H(_8))(_2)</td>
<td>2.303</td>
<td>2.164</td>
<td>2.14</td>
</tr>
<tr>
<td>5</td>
<td>Yb(C(_8)H(_8))(_2)</td>
<td>2.330</td>
<td>2.208</td>
<td>2.13</td>
</tr>
</tbody>
</table>

*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, 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 Ce(C\(_8\)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 Nd(C\(_8\)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 Ho(C\(_8\)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 Eu(C\(_8\)H\(_8\))\(_2\) and Yb(C\(_8\)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 Ce(C\(_8\)H\(_8\))\(_2\), Nd(C\(_8\)H\(_8\))\(_2\) and Ho(C\(_8\)H\(_8\))\(_2\), B3LYP calculation results are closer to experiments than BPW91 calculations, while for Eu(C\(_8\)H\(_8\))\(_2\) and Yb(C\(_8\)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 Ln(C\(_8\)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 Ln(C\(_8\)H\(_8\))\(_2\) (Ln = Ce, Nd, Eu, Ho and Yb) anion complexes. The experimental and theoretical photoelectron spectra of Ln(C\(_8\)H\(_8\))\(_2\) (Ln = Ce, Nd, Eu, Ho and Yb) anion complexes are provided in Figure 2.

From Figure 2, it can be seen that the photoelectron spectra of Ln(C\(_8\)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 Ce(C₈H₁₇)₂ measured by Kaya is 2.45 eV, Nakajima also obtained the photoelectron spectrum of Ce(C₈H₁₇)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 measurements 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 Ce(C₈H₁₇)₂ has four spectral features located at 2.30, 2.60, 2.89, 3.01 eV. The measured first VDE of Nd(C₈H₁₇)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 Nd(C₈H₁₇)₂ shows three small peaks centered at 2.72, 2.81 and 3.09 eV, and the little 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 Ce(C₈H₁₇)₂ and Nd(C₈H₁₇)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 Ho(C₈H₁₇)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 Eu(C₈H₁₇)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 Eu(C₈H₁₇)₂ resemble the experimental one, except for being shifted to higher electron binding energies. The similar pattern of transitions implied the sandwich structure of Eu(C₈H₁₇)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 Yb(C₈H₁₇)₂. As shown in Figure 2, the comparison between the simulated and experimental spectra of Yb(C₈H₁₇)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 Ln(C₈H₁₇)₂⁻ (Ln = Ce, Eu, Ho, Nd and Yb) are investigated using a combined experimental photoelectron spectra and theoretical density functional calculations. The results show Ln(C₈H₁₇)₂ species are sandwich structure with C₁ point symmetry for Ce(C₈H₁₇)₂. A ideal sandwich structure occurs on Eu(C₈H₁₇)₂ and Ho(C₈H₁₇)₂, while a slight departure from the perfect structure is definitive on the ground state Nd(C₈H₁₇)₂ and Yb(C₈H₁₇)₂, showing D₈ₜ 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.

Acknowledgments

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