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The Oxidation State of Ce in the Sandwich Molecule Cerocene

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The sandwich molecule cerocene has been formulated as a complex between the Ce\(^{4+}\) ion (Xe core, 4f\(^0\)) and two planar cyclooctatetraene dianions [C\(_8\)H\(_8\)]\(^2-\). This compound is an air-sensitive, brown-black material characterized by two strong absorption bands in the visible region which have been assigned as ligand to metal charge transfer transitions.\(^1,2\) Subsequently the proposed structure was confirmed by an X-ray structural study on the substituted cerocene [Ce(MeC\(_8\)H\(_7\))]\(_2\).\(^3\) Recently two more substituted cerocene analogs have been synthesized and one of these compounds has been structurally characterized.\(^4\) The synthesis and stability of cerocene has been noted as being quite remarkable because the Ce\(^{4+}\) ion is a strong oxidizing agent and the cyclooctatetraene dianion [C\(_8\)H\(_8\)]\(^2-\) is a strong reducing agent.\(^2,5\) Quasi-relativistic X\(\alpha\) scattered-wave calculations for thorocene (Th[C\(_8\)H\(_8\)]\(_2\)), uranocene (U[C\(_8\)H\(_8\)]\(_2\)), and cerocene showed strong covalent bonding in all three molecules, although cerocene was the most ionic.\(^6\) Later, theoretical calculations by Neumann and Fulde suggested that the Ce ion in cerocene is trivalent and the ground state of cerocene is a Ce\(^{3+}\)[(C\(_8\)H\(_8\))]\(^3-\) species.\(^7\) The basis for these calculations came from an analogy between the cerocene molecule and the observed Kondo effect in cerium metallic solids. The necessary conditions for the Kondo effect in a cerium alloy are strong correlations between the Ce f orbitals (strong Coulomb repulsion), and a weak hybridization between the 4f orbitals of Ce and the conduction electrons of the alloy. In cerocene the hybridization should occur with the \(\pi\) electrons of the two [C\(_8\)H\(_8\)]\(^2-\) ions.\(^8\)

Sophisticated \textit{ab initio} calculations by Dolg \textit{et al.} have supported the earlier idea that cerocene is a trivalent Ce\(^{3+}\) compound (Xe core, 4f\(^1\)) complexed by two [C\(_8\)H\(_8\)]\(^{-1.5}\) ions.\(^9,10\) In this picture the 4f\(^1\) electron is in a localized Ce\(^{3+}\) 4f orbital of e\(_{2u}\) symmetry (D\(_{8h}\) point group) and there are three electrons in the highest-occupied ligand-based \(\pi\) molecular orbital, also of e\(_{2u}\) symmetry, which are delocalized over both eight-membered rings. The unpaired electron on the metal atom is coupled with an unpaired
electron in the ligand orbitals to form a $4f_{e2u}^{1} \pi_{e2u}^{3}$ singlet ground state with the triplet excited state approximately 0.5 eV higher in energy. Configuration interaction couples the $4f_{e2u}^{1} \pi_{e2u}^{3}$ singlet state with the higher energy $4f_{e2u}^{0} \pi_{e2u}^{4}$ singlet state so that the final ground configuration consists of approximately 83% of the $4f_{e2u}^{1} \pi_{e2u}^{3}$ and 17% $4f_{e2u}^{0} \pi_{e2u}^{4}$ configurations. Because of this singlet ground state, cerocene in this trivalent formulation will be diamagnetic or show weak, temperature-independent paramagnetism. Thus it is very difficult to distinguish between the tetravalent and the trivalent models on the basis of magnetic measurements.

One method for determining the oxidation state of an atom is X-ray absorption near edge structure (XANES) where the absorption is measured below and above a characteristic X-ray elemental edge. The energy at which the absorption edge occurs can be correlated with the oxidation state of the metal. The edge energy is also somewhat sensitive to the coordination number and type of atoms surrounding the element of interest. For Ce ions, both the L and K edges have been utilized to determine oxidation state. Recent measurements of Ce XANES have determined the Ce oxidation state in a cerium-exchanged Preyssler's heteropolyanion and in a mixed Pr, Ce high temperature superconductor. In the latter work a shift in the K edge energy of 7 eV to higher energy was found for the tetravalent standard CeO$_2$ relative to the trivalent standard CeF$_3$. In this letter we report measurements of the XANES spectra of various substituted cerocenes, related trivalent cerocene salts, and some Ce standard compounds in order to determine the formal oxidation state of the Ce ion in substituted cerocenes.

The samples used in these experiments are numbered and listed in Table 1. The compounds of Ce[1,4(TMS)$_2$C$_8$H$_6$]$_2$ and Ce[1,3,6(TMS)$_3$C$_8$H$_5$]$_2$ were prepared following the work of Kilimann et al. and Burton et al. as was the Li[Ce[1,3,6(TMS)$_3$C$_8$H$_5$]$_2$] salt. K[Ce(C$_8$H$_8$)$_2$] was synthesized following the work of Hodgson et al. Other Ce compounds used as standards were purchased commercially or prepared from literature references. Since a number of the Ce organometallic compounds are air-sensitive, the solution samples were prepared on a Schlenk line where appropriate. The solution samples were sealed in thin-walled 10 mm OD tubes which were used directly on the beamline. The concentration of Ce in these samples was between 0.05 M - 0.3 M. Stable solid samples were finely ground, diluted with polystyrene beads to an absorption density of approximately 40 mg/cm$^2$, and sealed with mylar tape in a 1.5 mm thick Al holder which had a slot of 5 mm by 25 mm.
Cerium K edge X-ray absorption spectra (at approximately 40.443 keV) were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 4-2 (unfocussed) under dedicated ring conditions (3.0 GeV, 50 - 100 mA) using a Si (400) double crystal monochromator. All spectra were collected in the transmission geometry using Ar-filled ionization chambers and a vertical slit of 0.8 mm. Edge data were collected from each sample at ambient temperature, and if more than one scan was taken, the data were averaged. Data reduction and XANES analyses were done using the appropriate routines from the EXAFSPAK suite of programs developed by G. George of SSRL. The spectra were energy calibrated by simultaneously measuring the spectrum from a reference sample of solid CeB₆, defining its first inflection point as 40.443 keV. The edge energies for all the remaining samples were determined subsequently by taking the maximum of the first derivative of the absorption edge. XANES spectra of some representative samples are shown in Figure 1.

The convolution of the Ce K edge natural linewidth (15.1 eV) and the Si (400) monochromator (17.5 eV) gives an overall energy resolution of ~ 23 eV, which broadens the fine structure in the XANES region. However this broadening does not diminish the precision of the edge energy determinations which is estimated to be ±0.5 eV for the Ce standards and ±1.0 eV for the cerocene type complexes.

Figure 2 shows the K edge shifts of the numbered samples (Table 1) relative to the Ce standard, CeB₆. The data fall into two different regions characterized by the two formal oxidation states, Ce³⁺ and Ce⁴⁺. The separation between these two regions is greater than 7 eV. The compounds Ce[1,4(TMS)₂C₈H₆]₂ and Ce[1,3,6(TMS)₃C₈H₅]₂ are definitely in the Ce³⁺ region. The spread of the data points in the Ce³⁺ region is of the order of 5 eV with Ce[(Me₃C)₂C₅H₃]₃, Li[Ce[1,3,6(TMS)₃C₈H₅]₂], and K[Ce(C₈H₈)₂] at the extreme electron-rich end (close to 0.0 eV in Figure 2) and the aqueous Ce³⁺ ion plus Ce[1,4(TMS)₂C₈H₆]₂ and Ce[1,3,6(TMS)₃C₈H₅]₂ around 4.5 - 5 eV. The difference between the cerocenes and their trivalent salts appears significant. Formally we may write the configuration of the salts as 4f¹e₂u²e₂u⁴. As stated above, the neutral cerocenes are believed to have a ground configuration best regarded as a mixture of 4f¹e₂u²e₂u³ and 4f⁰e₂u⁴. It may well be that the ca. 20% contribution of the formally Ce⁴⁺ latter configuration is responsible for the difference in edge energies between the neutral cerocenes and their Li/K salts.
The XANES spectra in this paper give the assignment of the oxidation state of the Ce ion in substituted cerocene molecules as trivalent. The Ce ion in the substituted cerocenes appears to be less electron-rich than in their alkali metal salts as shown by a 4.5 eV shift toward higher oxidation state of their X-ray K edges. This argument is supported by structural data which show the Ce - ring centroid distance for the substituted cerocenes is ~ 1.97 Å as compared to ~ 2.07 Å for the K(COT)₂Ce diglyme salt. Our experimental results therefore support the conclusion of the sophisticated ab initio calculations that the cerocene ground configuration should be formulated primarily as a 4f₁e₂uπe₂u₃ singlet.

Acknowledgments

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References


Figure captions

Figure 1. Representative K edge spectra of Ce compounds: thick line, CeO₂; thin line, Ce[(Me₃C)₂C₅H₃]₃; dotted line, Ce[1,4(TMS)₂C₈H₆]₂; dashed line, Li{Ce[1,4(TMS)₂C₈H₆]₂}.

Figure 2. K-edge shifts of the Ce compounds relative to CeB₆. The numbering of the samples is given in Table 1.

Table 1. Numbering and characteristics of Ce samples

<table>
<thead>
<tr>
<th>Number</th>
<th>Compound</th>
<th>Type of sample</th>
<th>Color</th>
<th>Reference</th>
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<tr>
<td>1</td>
<td>CeO₂</td>
<td>Solid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ce(NH₄)₄(SO₄)₄·2H₂O</td>
<td>Solid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ce(NH₄)₄(SO₄)₄·2H₂O</td>
<td>1.6 M HNO₃ solution</td>
<td>Yellow</td>
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<td>4</td>
<td>Ce(CH₃C(O)Cl;IC(O)CH₃)₄</td>
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<td>5</td>
<td>CeCl₃·6H₂O</td>
<td>Solid</td>
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<td></td>
</tr>
<tr>
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<td>CeF₃</td>
<td>Solid</td>
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<td></td>
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<tr>
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<td>Solid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>10</td>
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<td>THF solution</td>
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<td>11</td>
<td>Ce[(Me₃C)₂C₅H₃]₃</td>
<td>Toluene solution</td>
<td>Purple</td>
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<td>12</td>
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<td>1.6 M HNO₃ solution</td>
<td>Colorless</td>
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<td>13</td>
<td>Ce₂(SO₄)₃</td>
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<tr>
<td>14</td>
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<td>1.6 M HNO₃ solution</td>
<td>Colorless</td>
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<tr>
<td>15</td>
<td>Ce(NO₃)₃</td>
<td>1.2 M HCl solution</td>
<td>Colorless</td>
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<tr>
<td>16</td>
<td>Ce[1,4(TMS)₂C₈H₆]₂</td>
<td>Toluene solution</td>
<td>Deep purple</td>
<td>4</td>
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<tr>
<td>17</td>
<td>Ce[1,3,6(TMS)₃C₈H₅]₂</td>
<td>Toluene solution</td>
<td>Deep purple</td>
<td>4</td>
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<tr>
<td>18</td>
<td>Li{Ce[1,4(TMS)₂C₈H₆]₂}</td>
<td>Toluene solution</td>
<td>Dark green</td>
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<td>19</td>
<td>K{Ce(C₈H₈)₂}</td>
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<td>Light green</td>
<td>14</td>
</tr>
<tr>
<td>Standard</td>
<td>CeB₆</td>
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Figure 1  Edelstein, et al.
Figure 2 Edelstein, et al.