XAFS Study of the Local Structure of Some Lanthanoid(III) Complexes

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Abstract. Two types of lanthanoid(III) complexes were synthesized: type I complexes - Ln(III) (Ln = Sm, Eu, Tb, Dy) anthrarufinate complexes using anthrarufin (1,5-dihydroxy-9,10-anthraquinone) as the ligands, and type II complexes - Ln(III)-transition(d-block) metal(II) bi-nuclear complexes. The local structures of these complexes were studied by EXAFS spectroscopy. We found that there is a good linear correlation between the ionic radii of Ln(III) and the Ln-O distances for the type I complexes, and for type II complexes the interatomic distances between Gd and coordinated oxygen atoms of the bi-nuclear complex are shorter than those of the Gd mononuclear complex.

Keywords: EXAFS, Lanthanoid complexes,
PACS: 61.10.Ht

INTRODUCTION

The local structures of a series of the lanthanoid, Ln(III), chloranilate and bromanilate complexes have been studied by EXAFS (extended X-ray absorption fine structure) spectroscopy [1-6], IR spectroscopy and thermal analysis [7]. From the thermal analysis and temperature dependent EXAFS studies, interesting results obtained are that coordinated or lattice waters are found in these complexes, and that the atomic distances between Ln(III) and coordinated oxygens depend on the coordination number or the Ln(III) ionic radius. The compounds with Ln(III) have also been studied as useful materials, such as superconductors, NMR shift reagents, and catalysts for many types of chemical syntheses. In the electronic configurations, Ln(III) are classified as inner transition (f-block) metals, and f-electrons are considered to rarely take part in the chemical bond due to the strong shielding by 5s and 5p electrons which are located in outer shell regions. But recently the magnetic interaction between f- and d-electrons has been discussed in the literature [8].

Here we have studied the local structures of two types of complexes by EXAFS spectroscopy. The first type of complexes (type I) are the Ln(III) (Sm, Eu, Tb, Dy) anthrarufinates; this type of complexes are newly synthesized complexes. The second type of complexes (type II) are the Ln(III)-transition(d-block) metal(II) bi-nuclear complexes.

EXPERIMENT AND DATA ANALYSES

Type I Complex: Anthrarufin Ln(III) complexes were synthesized from the following reaction.

\[
2\text{LnCl}_3\cdot n\text{H}_2\text{O} + 3\text{C}_1\text{4O}_4\text{H}_8 + 6\text{NaOH(aq)} \rightarrow \text{Ln}_2(\text{C}_1\text{4O}_4\text{H}_6)_3\cdot n\text{H}_2\text{O} + 6\text{NaCl(aq)}
\]

where lanthanoid trichloride (0.003 mol) and anthrarufin (1,5-dihydroxy-9,10-anthraquinone) (0.01mol) were dissolved in alkaline solution with pH = 13, and heated about one hour at 100 °C. The reaction mixture was cooled and left to rest about 12 hours. After this, the precipitate was filtered, rinsed completely by hot water and dried. The complex structures are given in Fig. 1.

Type II Complex: The Gd(III)-Ni(II) bi-nuclear complex of N,N’-ethylene bis (3-hydroxy salicylaldimine), with the ligand abbreviated as H₂osalen, was synthesized by a one step template reaction [9,10]. A methanol solution (2 ml) of NiCl₂
(0.2 g) and GdCl₃·6H₂O (0.56 g) was added to 60 ml methanol with 2,3-dihydroxybenzaldehyde (0.41 g). After the drop-wise addition of ethylene diamine (0.09 g), the reactant solution was refluxed for about three hours, concentrated to 30 ml and by adding 30 ml of water, precipitates were obtained. The precipitates filtered from the solution were successively rinsed with water, methanol and diethyl ether. The Gd(III) mononuclear complex was also synthesized by a similar method. The complex structures are given in Fig. 2 and the complexes are abbreviated as (a) Gd(III) osalen and (b) Gd(III)-Ni(II) osalen, respectively.

EXAFS Spectra: The Ln(III) L₃-edge X-ray absorption spectra were obtained at BL-10B and BL-7C of Photon Factory in KEK. The energy and current of the storage ring was 2.5 GeV and 250-400 mA, respectively. The X-ray absorption spectra were recorded in transmission mode using ionization chamber detectors.

The EXAFS function, χ(k), was extracted from the absorption spectra and was Fourier transformed by the program of XANADU code [11]. In order to obtain the structural parameters, the EXAFS function was fitted by non-linear least-square method [4-6].

RESULTS AND DISCUSSION

Type I Complex: The k²-weighted EXAFS χ(k) spectra of the type I complexes are given in Fig. 3. The corresponding Fourier transforms (FT) of the complexes for the k-range from 3 to 12 Å⁻¹. We found one peak clearly in the range of 2.0 to 2.5 Å that represented back-scattering from oxygen atoms of the coordinated anthrarufin carbonyl groups. The atomic distances and the coordination numbers are shown in Table 1. The relationship between the ionic radii of Ln(III) and the r(Ln-O) distance obtained by EXAFS analysis is shown in Fig. 5. It is interesting to see that a good linear relationship was obtained. These type I complexes are considered to have two kinds of complex structures (Fig. 1). One is a flat sheet linked by Ln(III), with two waters coordinated to the lanthanoid. Another is a three-dimensional net work seen for the Ln(III) chloranilate and bromanilate complexes [6]. Unfortunately the present EXAFS results cannot distinguish these two possibilities for the coordination of Ln(III) anthrarufinate complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>r / Å</th>
<th>N</th>
<th>σ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm(III)</td>
<td>2.51</td>
<td>6.5</td>
<td>0.10</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>2.48</td>
<td>6.8</td>
<td>0.10</td>
</tr>
<tr>
<td>Tb(III)</td>
<td>2.43</td>
<td>6.9</td>
<td>0.11</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>2.39</td>
<td>6.8</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The error is ±0.02 Å for r and ±10% for N.

Type II Complex: The k²-weighted EXAFS χ(k) spectra of the Gd(III)-Ni(II) bi-nuclear and Gd(III)
mono-nuclear complexes are given in Fig. 6. The corresponding FTs of two Gd(III) complexes for the k-range from 3 to 12 Å⁻¹ are shown in Fig. 7. For Gd osalen we found one apparent peak in the range of 2.0-3.5 Å that is responsible for the back-scattering from the oxygen atoms numbered in Fig. 2.

**FIGURE 6.** The $k^2$-weighted EXAFS $\chi(k)$ spectra for Gd(III) mono-nuclear and Gd(III)-Ni(II) bi-nuclear complexes.

For Gd-Ni osalen, on the other hand, we see that there are two peaks in the range of 2.0-4.0 Å; the first intense peak is from oxygen atoms being similar to those in Gd osalen, and the second peak is due to Ni and Gd atoms. In the second peak, a small contribution from carbon atoms is also included. We need more precise information, however, in order to conclude the fourth peak’s origin.

Table 2 shows the structural parameters for the Gd mononuclear complex. In this r-range there is no carbon contribution. In our model, 2 oxygen atoms are coordinated to Gd atoms at a distance of 2.47 Å, therefore about 5.5 water molecules are coordinated to Gd in this complex.

**TABLE 2.** Structural parameters of Gd and coordinating oxygen atoms for Gd osalen complex.

<table>
<thead>
<tr>
<th>r / Å</th>
<th>N</th>
<th>σ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd-O(1,2)</td>
<td>2.38</td>
<td>2.0</td>
</tr>
<tr>
<td>Gd-O(3,4)</td>
<td>2.47</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Table 3 shows the results for the Gd-Ni bi-nuclear complex. In order to obtain convergence in the curve-fitting calculations, the values of N for Gd-Gd had to be fixed as 2. The Gd-O(1,2) distances for Gd-Ni osalen is shorter (2.34 Å) than that for Gd osalen (2.38 Å, Table 2). This change is reliable within the error. The contraction of bond distance is observed only for the short Gd-O(1,2); the interatomic distances of Gd-O(3,4) for these two complexes are almost the same (~2.46 Å).

The coordination number of Gd-Ni is 1.1±0.1 and this is the value expected from the model (Fig.2). In Gd osalen, the Gd-O(1,2) distance is longer than that of Gd-Ni osalen, i.e., the ligand-chelating cage is compressed by the addition of Ni metal into the Gd complex.

**FIGURE 7.** FTs of EXAFS for the Gd(III) mono-nuclear and Gd(III)-Ni(II) bi-nuclear complexes.

**TABLE 3.** Structural parameters of Gd and coordinating atoms for Gd-Ni osalen complex.

<table>
<thead>
<tr>
<th>r / Å</th>
<th>N</th>
<th>σ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd-O(1,2)</td>
<td>2.34</td>
<td>2</td>
</tr>
<tr>
<td>Gd-O(3,4)</td>
<td>2.46</td>
<td>5.9</td>
</tr>
<tr>
<td>Gd-Ni</td>
<td>3.49</td>
<td>1.1</td>
</tr>
<tr>
<td>Gd-Gd</td>
<td>3.71</td>
<td>2*</td>
</tr>
<tr>
<td>Gd-C</td>
<td>3.74</td>
<td>4*</td>
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</table>

*These values are fixed according to the model.

**REFERENCES**