

Structural studies of lanthanide(III) complexes with oxydiacetic acid and iminodiacetic acid in aqueous solution by EXAFS

Hirokazu Narita,¹ Tsuyoshi Yaita,¹ Shinichi Suzuki,¹ Konomi Takai,¹ Shoichi Tachimori,¹ Haruhiko Motohashi²

¹Research Group for Separation Chemistry, Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-1195, Japan, and ²Spring-8 Service, Mikazuki-cho, Sayo-gun, Hyogo, 679-5143, Japan. E-mail: narita@mummy.tokai.jaeri.go.jp

The local structure of the trivalent lanthanide (Ln(III)) complexes with oxydiacetic acid (ODA) and iminodiacetic acid (IDA) in aqueous solution was investigated by EXAFS spectroscopy. The coordination number and the bond distance were obtained by the detailed EXAFS analysis. The coordination number of Ln(III) in both the Ln-ODA and -IDA systems decreases from nine for lighter Ln(III) to eight for heavier Ln(III). The bond distances of ether O atoms from Ln(III) in the Ln(ODA)₃³⁻ complexes are shorter than those of N atoms in the Ln(IDA)₃³⁻ ones.

Keywords: lanthanide, oxydiacetic acid, iminodiacetic acid, EXAFS.

1. Introduction

Polycarboxylates have been attracted in not only separation and purification of lanthanides but also fundamental chemistry of their lanthanide complexes. Among the compounds, ODA and IDA have been studied extensively. In aqueous solution, many studies show that the tris tridentate complexes are dominant at pH > 6 and [ODA] / [Ln] > 3 for the [Ln(ODA)₃]³⁻, and at pH > 8 and [IDA] / [Ln] > 3~5 for the [Ln(IDA)₃]³⁻ (Grenth, *et al.*, 1972a, 1972b; Foster, *et al.*, 1983; Albin, *et al.*, 1985). However, the detailed structural parameters of these complexes in aqueous solution have not been determined yet. Therefore, we carried out the structural analysis of Ln complexes with ODA and IDA by EXAFS.

2. Experimental

The concentrations of the ligands and Ln(III) were fixed at 0.5 mol dm⁻³ and 0.1 mol dm⁻³, respectively, for all the samples. The pH of the sample solutions was adjusted at 6.5 for the Ln-ODA system and 8.5 for the Ln-IDA system. Under these conditions, the Ln(ODA)₃³⁻ and Ln(IDA)₃³⁻ complexes are predominant. All the sample solutions were sealed in a polyethylene bag with a Teflon spacer of a suitable thickness to appropriate edge jump. Transmission EXAFS data at lanthanide L_{III} edges were collected at the BL-27B station of the Photon Factory in the High Energy Accelerator Organization (2.5 GeV, 200-400 mA) using a Si(111) monochromator at room temperature. Experimental data were analyzed by the XAFS data analysis software package WINXAS 97 (Resler, 1997). Since the effect of multi-electron excitations (Chalboy, *et al.*, 1993; Solera, *et al.*, 1994) was negligibly small in the obtained spectra, we performed the EXAFS analysis without further correction. The EXAFS threshold energy, E_0 , was defined as the maximum in the first derivative of the absorption edge. The EXAFS data were fit using theoretical phases and amplitudes calculated by the program FEFF7 (Zabinsky, *et al.*, 1995). The Na₃[Ln(ODA)₃]·2NaClO₄·6H₂O complexes (Albertsson, 1970) were used for the FEFF calculation of model compounds. No single crystal structures of tris IDA complexes with Ln(III) have been

reported. Therefore, the hypothetical tris IDA complexes, which the

Table 1

Structural parameters obtained from the EXAFS fits to the Fourier filtered peak at ca. 2 Å using 1 shell model.

	ODA					IDA ^a				
	CN ^b	r(Å) ^c	σ ^{2d}	ΔE ₀ ^e	R ^f	CN ^b	r(Å) ^c	σ ^{2d}	ΔE ₀ ^e	R ^f
Nd	9.4	2.47	0.009	-2.3	0.082	9.4	2.49	0.01	-2.6	0.12
Sm	8.7	2.44	0.007	-2.2	0.14	9.2	2.45	0.01	-3.0	0.19
Eu	9 ^g	2.43	0.008	-0.41	0.13	9 ^g	2.43	0.01	-0.63	0.16
Gd	9.5	2.41	0.008	-0.8	0.10	9.4	2.42	0.01	-0.95	0.12
Tb	8.3	2.40	0.008	-2.3	0.14	8.1	2.40	0.01	-3.6	0.22
Dy	8.4	2.38	0.008	-2.7	0.049	8.4	2.39	0.01	-3.5	0.049
Ho	8.4	2.37	0.009	-2.8	0.14	8.5	2.37	0.01	-3.8	0.22
Er	8.0	2.35	0.008	-3.4	0.12	7.7	2.35	0.009	-4.4	0.15
Tm	8.1	2.35	0.008	-3.4	0.11	8.0	2.35	0.01	-4.3	0.17
Yb	7.9	2.33	0.008	-2.2	0.10	8.0	2.33	0.01	-3.2	0.17
Lu	8.0	2.33	0.008	-0.46	0.074	8.2	2.32	0.01	-2.2	0.18

^a N atoms were treated as O atoms.; ^b the total coordination number of Ln(III) ion; ^c the average bond distance(Å); ^d Debye-Waller factor squared(Å²); ^e the shift in threshold energy(eV); ^f residual: $R = \sum |k^3 \chi(k)_{\text{obs}} - k^3 \chi(k)_{\text{calc}}| / \sum k^3 \chi(k)_{\text{obs}}$; ^g fixed parameters.

ether O atoms in the Na₃[Ln(ODA)₃]·2NaClO₄·6H₂O were replaced by N atoms, were taken as model compounds of the Ln-IDA system. The dominant paths obtained from FEFF7 calculation for the model compounds are single-scattering (SS) Ln-O(carboxylate, coordinating to Ln(III), cc), SS Ln-O(ether, e), SS Ln-C(carboxylate, c), SS Ln-C(ether, e), SS Ln-O(carboxylate, uncoordinating to Ln(III), cu), multiple-scattering (MS) Ln-C(c)-O(cu), 3legs, and MS Ln-O(cc)-O(cu), 3legs. The values of the amplitude reduction factor, S_0^2 , for the Ln-ODA and Ln-IDA systems were fixed at 0.91 and 0.82, respectively, during the fits. These S_0^2 values were determined by using the spectra for the Eu-ODA and Eu-IDA systems, the coordination number being assumed to be nine. Because a number of reliable structural studies of the Eu-ODA and the Eu-IDA systems in aqueous solution indicates the nine coordinated europium complexes under the same condition as this work, as described previously. The fits were performed in two times for each sample: (i) the filtered EXAFS spectra of the 1st peak (ca. 2 Å) in the Fourier transforms (FTs) were fit using 1 shell. All the parameters except S_0^2 were floated. (ii) the total EXAFS spectra were fit using above dominant path. The coordination number of each shell and the shift in threshold energy, ΔE_0 , was fixed on the basis of the results of (i). The 1st peak was fit using 2 shells (O(cc) and O(cc) or N). The Debye-Waller factor, σ , and bond distance, r , were floated.

3. Results and Discussion

We first carried out the EXAFS fits about the pronounced 1st peak (ca. 2 Å) in the FTs of k^3 -weighted EXAFS for the Ln-ODA and the Ln-IDA systems. This peak indicates the local structure around Ln(III), corresponding to the Ln-O and/or Ln-N interactions. In this fit, the total coordination number of Ln(III), and the average distance for the Ln-O(cc) and Ln-O(e) or Ln-N bonds are determined. Table 1 shows the total coordination number and the average distance. The total coordination number of Ln(III) in both the tris ODA and tris IDA complexes changes from nine for the lighter Ln(III) to eight for the heavier Ln(III). The average distance of Ln-O and/or Ln-N bonds decreases with a decrease in the ionic radius. These trends are in good agreement with those for the aqua Ln(III) complexes (Yamaguchi, *et al.*, 1988).

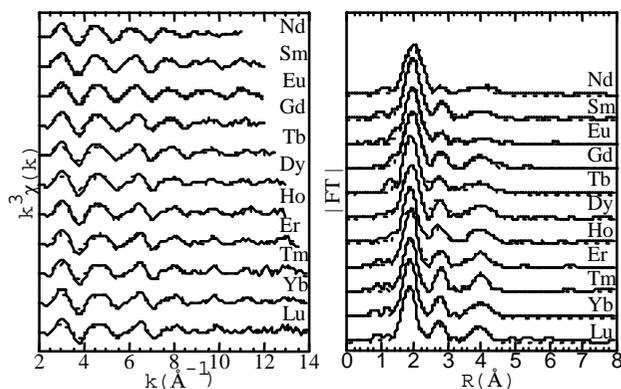


Figure 1

Raw Ln L_{III} -edge k^3 -weighted EXAFS data (A) and corresponding FTs (B) for the tris ODA complexes. experimental data (solid line); theoretical fit (dotted line)

On the basis of the results of the 1 shell fits, the fits to the raw EXAFS spectra and corresponding FTs were performed using all the dominant paths. Figures 1 and 2 show the experimental data and the theoretical fits in the Ln-ODA and -IDA systems, respectively. It has been shown that the lighter Ln complexes (Nd-Gd) are nine coordinated ones and the heavier Ln ones (Tb-Lu) are eight coordinated ones. Therefore, the number of O(e) or N atoms was fixed at three for all the complexes, and that of the O(cc) atoms was at six for the lighter ones and at five for the heavier Ln ones. The fitting results for the bond distances of Ln-O(cc), Ln-O(e) and Ln-N with ionic radius of Ln(III) (eight coordinated) (Shannon,

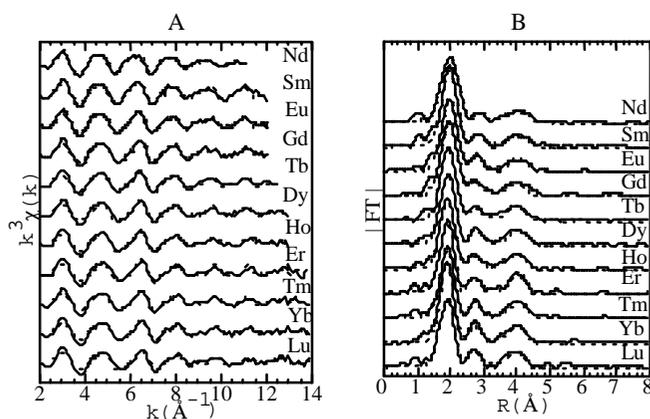


Figure 2

Raw Ln L_{III} -edge k^3 -weighted EXAFS data (A) and corresponding FTs (B) for the tris IDA complexes. experimental data (solid line); theoretical fit (dotted line)

1976) are shown in Fig. 3. Two remarkable features are found: the Ln-O(cc) bond distances are shorter than the Ln-O(e) / -N ones; the Ln-N ones are longer than Ln-O(e) ones. These trends are consistent with the analogous single crystal complexes (Albertson, 1970; Oskarsson, 1971).

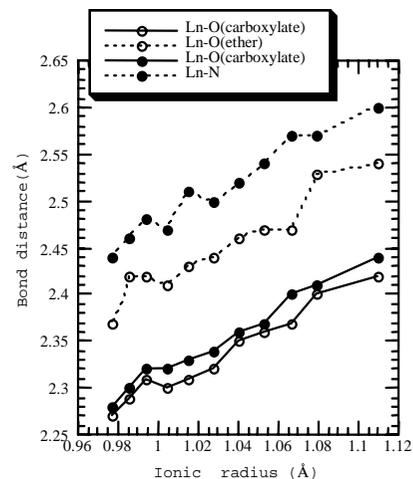


Figure 3

The relation between the bond distances and ionic radius of Ln(III). Open circles: the tris ODA complexes. Closed circles: tris IDA complexes. Debye-Waller factor $\sigma^2(\text{\AA}^2)$:

The tris ODA complexes (O(carboxylate);O(ether)

Nd(0.003;0.001)Sm(0.003;0.001)Eu(0.005;0.002)Gd(0.004;0.001)Tb(0.002;0.001)Dy(0.003;0.001)Ho(0.003;0.001)Er(0.003;0.002)Tm(0.003;0.002)Yb(0.002;0.001)Lu(0.005;0.003)

The tris IDA complexes (O(carboxylate);N)

Nd(0.004;0.001)Sm(0.003;0.001)Eu(0.003;0.001)Gd(0.006;0.003)Tb(0.002;0.001)Dy(0.004;0.001)Ho(0.002;0.001)Er(0.003;0.001)Tm(0.003;0.001)Yb(0.003;0.001)Lu(0.004;0.002)

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