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## Dehydration processes for lanthanoid(III) chloranilate complexes studied by EXAFS

Takafumi Miyanaga\* and Susumu Sudoh

*Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561, Japan, E-mail: takaf@cc.hirosaki-u.ac.jp*

Temperature dependences of the local structures of chloranilate complexes of Pr(III), Nd(III), Tb(III), and Er(III) were studied by EXAFS (extended X-ray absorption fine structure) in order to reveal the process of the dehydration for the coordinated water molecules. The coordination number around central lanthanoid(III) ion was reduced stepwise as temperature increases, which behaviour depends on the kind of central lanthanoid(III) ion. Accompanying the decrease of the coordination numbers, the interatomic distances between central lanthanoid(III) ion and oxygen atoms in a first shell decrease.

**Keywords:** EXAFS, Lanthanoid Complex, Dehydration Process

### 1. Introduction

It is well-known that a good knowledge of the structure is needed to allow a thorough interpretation of the various physical and chemical properties, e.g. magnetic property, of polynuclear complexes [Verdaguer *et al.*, 1980]. However frequently, these compounds are prepared as polycrystalline powders which are not suitable for X-ray structure study. On the other hand, EXAFS (extended X-ray absorption fine structure) technique is powerful for structural study of such a polycrystalline powder and even for liquid state samples.

In this paper, we have measured temperature dependent EXAFS data for Pr(III), Nd(III), Tb(III) and Er(III) complexes and discuss about the dehydration process for lanthanoid(III) complexes more generally and consistently. To understand the dehydration process is important for not only the syntheses of organometallic compounds but also the adsorption and desorption process in the molecules.

### 2. Experimental and Data analysis

The lanthanoid(III) complexes  $(Ln_2(C_6O_4Cl_2)_3 \cdot nH_2O)$ , Ln=Er, Tb, Nd, Pr) were prepared from aqueous solutions of chloranilic acid and Ln(III) trichloride hydrate in molar ratio 3:1. The

precipitates were filtered, washed with hot water to remove unreacted chloranilic acid completely, and dried under vacuum.  $L_{III}$ -edge X-ray absorption spectra were obtained at BL 7C of the Photon Factory in KEK (Tsukuba). Si(111) double crystal monochromator was used. An energy and current of the storage ring are 2.5 GeV and 250–360 mA, respectively. The powder samples were held on the heating attachment under nitrogen atmosphere. X-ray absorption spectra were recorded in transmission mode using the ionization chamber detector. The measurement temperatures for the X-ray absorption spectra were selected carefully from the thermal analysis (the flat region of TG and DT curves) [Sudoh & Katagiri, 1991]. The EXAFS analyses were performed according to XANADU code described in the literature [Miyanaga & Sudoh, 1995 and Sakane *et al.*, 1993]. The EXAFS parameters of interatomic distance  $r$ , coordination number  $N$  and Debye-Waller factor  $\sigma$  are determined from the non-linear least square method for first nearest shell. The standard samples are Ln(thd)<sub>3</sub> complexes. The theoretical parameters calculated by Mckale *et al.* [Mckale *et al.*, 1988] were used. The  $k$ -range for fitting is 3.5–11.0 Å<sup>-1</sup> in which the Mckale's parameters are good. The  $r$ -range for filtering to remove the contribution from second nearest Ln-C distance is about 1.0 Å around the top of the first peak. The index of fit is a residual,  $f$ , calculated by

$$f = \sqrt{\frac{\sum k^6 (\chi - \chi_{cal})^2}{\sum k^6 \chi^2}}$$

where  $\chi$  is EXAFS signal and the summation is taken over all the data points in the  $k$ -range used for fitting. In the present study,  $f$  is approximately 5–10%.

### 3. Results and Discussion

Fourier transforms at the  $k$ -range 3–12 Å<sup>-1</sup> for Tb(III) chloranilate complex in which back scattering amplitude and phase shift were corrected by Mckale *et al.* [Mckale *et al.*, 1988] are shown in Fig. 1. We found that peaks shift shorter and the intensities become smaller as temperature increases.

The EXAFS parameters which are obtained from the least-square method are summarised in Table 1. The large values of  $\sigma$  may come from the large static disorder in these complexes. We found that the  $\sigma$  values increase with temperature monotonically quite generally. This fact indicates that the values of  $N$  and  $\sigma$  are successfully obtained in the present fitting method.

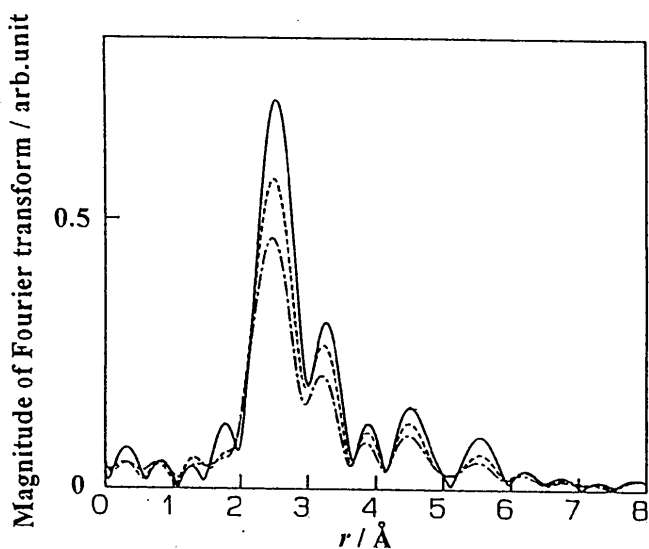
**Table 1.**

The structural parameters determined from curve-fitting method of EXAFS for  $\text{Ln}_2(\text{C}_6\text{O}_4\text{Cl}_2)_3 \cdot n\text{H}_2\text{O}$ .

Ln(III)	Temp. / °C	$r / \text{Å}$	$\sigma / \text{Å}$	$N$
Pr(III)	25	2.594	0.098	11.7
	145	2.587	0.105	9.1
	200	2.570	0.113	6.1
Nd(III)	25	2.499	0.090	10.2
	110	2.480	0.105	8.0
	140	2.476	0.108	7.1
	200	2.462	0.125	6.3
Tb(III)	25	2.439	0.080	7.7
	120	2.420	0.088	6.7
	200	2.400	0.097	5.8
Er(III)	25	2.340	0.084	7.2
	107	2.293	0.084	6.2
	150	2.288	0.095	5.4
	220	2.283	0.112	5.2

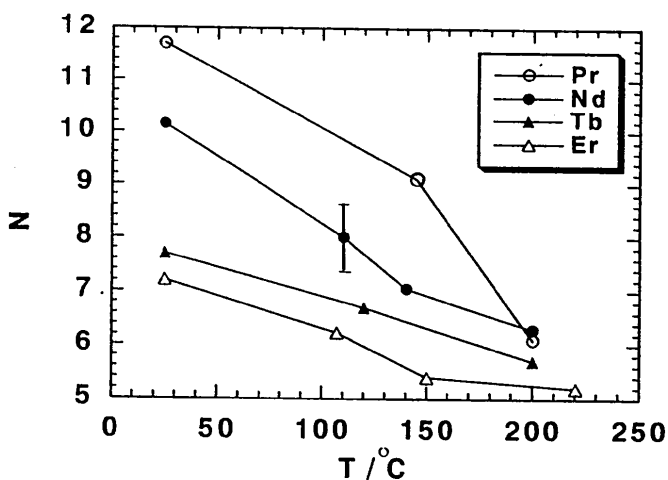
number due to the chloranilate ligand is 6 or three ligands are coordinated to central lanthanoid(III) ion. This result suggests that the  $\text{Ln}_2(\text{C}_6\text{O}_4\text{Cl}_2)_3 \cdot n\text{H}_2\text{O}$  have three-dimensional network structure, although  $\text{Cu}_2(\text{C}_6\text{O}_4\text{Cl}_2)_3$  has a one-dimensional ribbon structure [Verdaguer *et al.*, 1980]. On the other hand, for the complexes with the larger ionic radii, such as Pr(III) and Nd(III) complexes, the coordination numbers are 11.7 and 10.2, respectively, which are much larger than that for Tb(III) and Er(III). After heating the sample, the coordination number was reduced to 6 analogously to Tb(III) and Er(III). These results indicate that there are about 6 and 4 extra water molecules around Pr(III) and Nd(III) ions just after the preparation. Hydrated structures of lanthanoid(III) ions in aqueous solution have been studied by Yamaguchi *et al.* [Yamaguchi *et al.*, 1988] using EXAFS. It was reported that the average coordination number of the oxygen atoms in the first shell are 9.5 for Nd(III), 8.0 for Tb(III) and 7.5 for Er(III). Behaviour of decrease of the coordination number for chloranilate complexes with ionic radius of lanthanoid(III) ions at room temperature is approximately consistent with that in aqueous solutions.

The interatomic distance between central lanthanoid(III) ion and oxygen atoms become shorter with temperature as shown in Fig. 2 (b). It can be interpreted that local structure around the lanthanoid(III) ions complexed as extra water molecules are removed.

**Figure 1**

Fourier transforms of the phase and amplitude corrected EXAFS data at the  $k$ -range 3–12  $\text{Å}^{-1}$  for Tb(III) chloranilate complex of three different temperatures, 25°C (solid line), 120°C (dashed line) and 200°C (dot-dashed line).

Figure 2 shows the change of the coordination numbers (a) and interatomic distances (b) of oxygen atoms around central Ln(III) ions with temperature. The coordination numbers for Tb(III) (Er(III)) complexes decrease from 7.7 (7.2), 6.7 (6.2), 5.8 (5.2) stepwise as temperature increases. This result indicates that the complexes of Tb(III) and Er(III) include two extra coordinated water molecules after preparation and the water molecules are removed as heating to 200°C; that is, the net coordination

**Figure 2 (a)**

The variation of the coordination numbers of oxygen atoms around central Ln(III) ions with temperature. Ln=Pr (open circle), Nd (solid circle), Tb (solid triangle) and Er (open triangle). Lines are drawn as guides for eye.

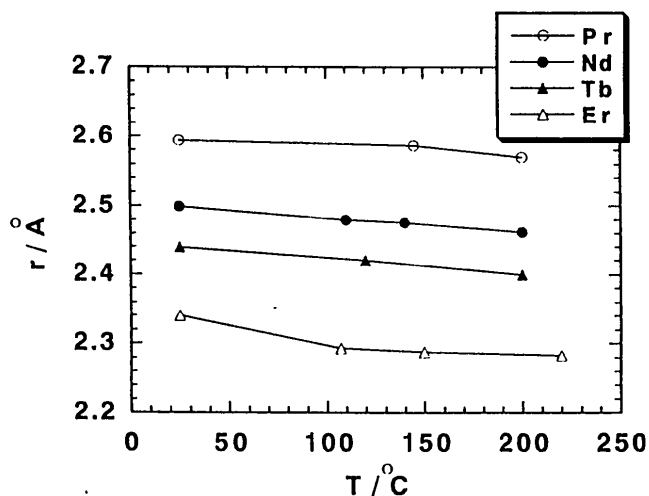


Figure 2 (b)

The variation of the interatomic distance of oxygen atoms around central Ln(III) ions with temperature. Ln=Pr (open circle), Nd (solid circle), Tb (solid triangle) and Er (open triangle). Lines are drawn as guides for eye.

We can evaluate the variations of coordination numbers,  $\Delta N$ , and atomic distances,  $\Delta r$ , in the present temperature range. We introduce the ratio,  $R = \Delta r / \Delta N$ , that means the variation of the atomic distance as one coordinated water molecule is removed. The  $R$  values are shown for various complexes in Fig. 3. It is interesting that the  $R$  value depends on the kind of central lanthanoid ion and has a good correlation with ionic radii of the central lanthanoid(III) ions: The larger  $R$  value, the smaller ionic radius. This result indicates that the coordinated water molecules are easily adhered to and removed from the larger radius lanthanoid(III) ion.

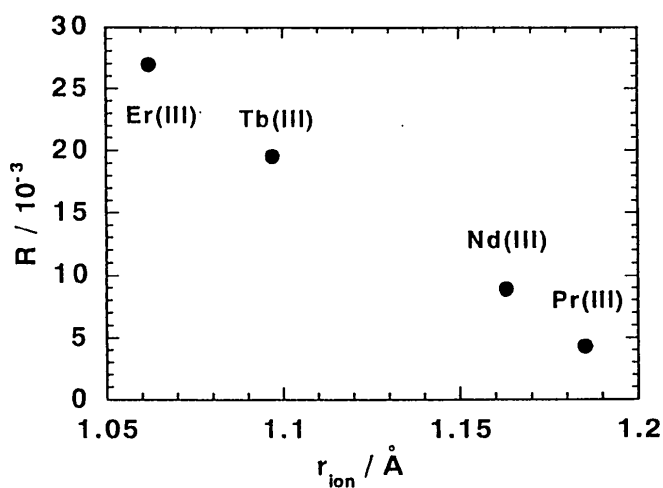


Figure 3

Variation of the parameter  $R (= \Delta r / \Delta N)$  with  $r_{ion}$  for various  $\text{Ln}_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot n\text{H}_2\text{O}$ .

#### 4. Conclusion

We discussed the temperature dependence of the local structures of lanthanoid(III) chloranilates by using EXAFS. The coordination number around central lanthanoid(III) ion was reduced stepwise as the dehydration proceeds. The linear relation between the change of interatomic distance,  $\Delta r$ , and that of the coordination number,  $\Delta N$ , during the dehydration process was found. The ratio of  $\Delta r / \Delta N$  has a good correlation with ionic radius of the lanthanoid(III) ion.

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