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Hydrated structures and dehydration processes of lanthanoid(III) chloranilates studied by EXAFS

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Abstract

The local structures of lanthanoid(III) chloranilate complexes of Pr(III), Nd(III), Tb(III) and Er(III) have been studied by EXAFS (extended X-ray absorption fine structure). Hydrated structures of the lanthanoid(III) ions in these complexes have been investigated with respect to their coordination numbers and interatomic distances. Six or four water molecules coordinate to the lanthanoid(III) ion of Pr(III) or Nd(III), respectively, just after preparation of the complexes. The temperature dependence of the first coordinated structures has been studied in order to reveal the behavior of the coordinated water molecules in dehydration process. The coordination number around the central lanthanoid(III) ion decreases stepwise as temperature increases, depending on the type of central lanthanoid(III) ion present. The interatomic distance between the central lanthanoid(III) ion and oxygen atoms in the first shell decreases, accompanying the decrease of the coordination numbers. A parameter representing proportion shows the reduction of interatomic distance as one coordinated water molecule removes from the central ion, depending on the type of lanthanoid(III) ions.

Keywords: EXAFS; Lanthanoid(III) chloranilate; Dehydration process

1. Introduction

It is well known that a good knowledge of the structure of complexes is needed to allow a thorough interpretation of the various physical and chemical properties, e.g. magnetic property, of polynuclear complexes. However, frequently these compounds are prepared as polycrystalline powders. EXAFS (extended X-ray absorption fine structure) is a powerful technique for structural study of such a polycrystalline powder and even for liquid state samples. The X-ray powder diffraction method is another useful technique to study the structures of metal complexes, however the interpretation of diffraction patterns was difficult in the present case. On the other hand, it is easy to obtain structural information about such complex systems, at least for the nearest neighbor shell, from EXAFS.

The chloranilate ligand has a molecular structure as represented schematically in Fig. 1. It is easily understood that the chloranilate ligand can connect two metal ions and these complexes have a chain-like or network structure, which is interesting from the viewpoint of structural

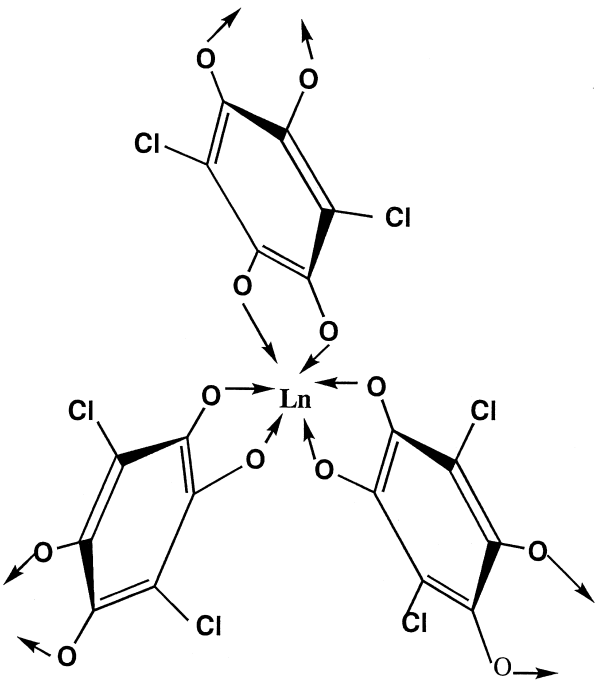

Fig. 1. The schematic molecular structure of chloranilate ligand and Ln(III).

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chemistry. These complexes are also prepared as polycrystalline compounds. Verdaguer et al. [1] have studied the local structure of copper chloranilate complex, $Cu(C_6O_4Cl_2)$, by EXAFS. They reported that the complex does not have a two-dimensional structure but a one-dimensional ribbon like structure.

We have studied the local structures of a series of the lanthanoid(III) chloranilate and bromanilate complexes by EXAFS spectroscopy [2,3], IR spectroscopy [4] and thermal analysis [5]. The existence of some coordinated or lattice water molecules was conformed by thermal analysis and diffuse reflectance IR spectra at various temperatures. To investigate the origins and behavior of these coordinated water molecules in the first coordination shell, temperature dependent EXAFS studies for Nd(III) and Er(III) chloranilate complexes have been performed [6–8]. It was reported that the coordination number of the oxygen atoms in a first shell changes stepwise as the temperature increases, for Nd(III) and Er(III) chloranilate and bromanilate complexes. In the present paper, we present further temperature dependent EXAFS data for the chloranilate complexes of Pr(III) and Tb(III), and discuss the coordination structure of the water molecules and the dehydration process more generally from the microscopic view-point. The present system under consideration is appropriate for EXAFS study because both the coordination number and the interatomic distance change concurrently with temperature.

Conventionally, dehydration processes have been studied by macroscopic techniques, e.g. the thermal analysis method. Recently, the dehydration process associated with chemical reactions in a MgO catalysis has been successfully studied by Yoshida et al., by using XAFS [9]. The formation process of Ag clusters in zeolite 4A by the dehydration process has been studied by EXAFS [10]. It was reported that the Ag–O distance decreases as dehydration proceeds and the Ag cluster forms. It is important to understand the dehydration process not only for the syntheses of organometallic compounds, but also the adsorption and desorption process in the molecules, the catalyses and the surfaces.

2. Experimental and data analysis

The chloranilic acid was prepared from chloranil($C_6Cl_4O_2$) by alkaline hydrolysis, and recrystallized from hot water. Lanthanoid(III) trichloride hydrates($LnCl_3 \cdot nH_2O$, Ln=Pr, Nd, Tb, Er) were prepared from the corresponding lanthanoid(III) oxides, i.e., dissolving the oxides into dilute HCl solution completely, concentrating the solution on a water bath and cooling it, the lanthanoid(III) trichloride hydrates were separated. All lanthanoid(III) trichloride hydrates were recrystallized from 2N-HCL solution. The lanthanoid(III) chloranilate complexes ($Ln_2(C_6O_4Cl_2)_3 \cdot nH_2O$, Ln=Pr, Nd, Tb, Er) were prepared from aqueous solutions of the chloranilic acid and the lanthanoid(III) trichloride hydrates in the molar ratio 3:1. The solution was kept hot for about 1 h. The precipitates were filtered, washed with hot water to remove unreacted chloranilic acid completely, and dried under vacuum. All the complexes synthesized are polycrystalline fine powders and are insoluble in almost all organic solvents.

L_{III}-edge X-ray absorption spectra were obtained at BL 7C of the Photon Factory in KEK (Tsukuba). A Si(111) double crystal monochromator was used. The energy and current of the storage ring were 2.5 GeV and 250–400 mA, respectively. About 100 mg sample was mixed with 700 mg BN powder and pressed into a uniform disk with 10 mm diameter and 1 mm thickness. Thickness was optimized to give edges for an X-ray absorption spectrum of about 1.5. The disk was held on the heating attachment and heated under nitrogen atmosphere. X-ray absorption spectra were recorded in transmission mode using ionization chamber detectors. The measurement temperatures for the X-ray absorption spectra were selected carefully from the thermal analysis (the flat region of TG and DT curves) as shown in Ref. [5]. Higher harmonics were rejected by inserting the mirror or by detuning of one of the monochromator crystals.

The EXAFS interference function, $\chi(k)$, was extracted from the absorption spectra and was Fourier Transformed using the program of XANADU code described elsewhere [11]. In order to obtain the structural parameters of interatomic distance and the coordination number, the EXAFS function was fitted by a non-linear least-square method to the theoretical function as:

$$\chi(k) = \frac{Bf(k, r)}{kr^2} \exp(-2r/\lambda) \exp(-2\sigma^2 k^2) \sin\left[2kr + \phi(k) + \frac{2}{3} C_3 k^3\right] \quad (1)$$

where r is the interatomic distance between X-ray absorbing and photoelectron scattering atoms, $f(k, r)$ and $\phi(k)$ are the backscattering amplitude and phase shift functions, which are calculated by McKale et al., using a curved-wave method [12]. λ is the electron mean free path being defined as $\lambda = k/0.5$ which is a typical value for inorganic compounds [13]. σ^2 is the mean square relative displacement and C_3 is third-order cumulant. The third-order cumulant can not be neglected in the analysis of temperature dependent EXAFS [14]. k is the wave number given by

$$k = \sqrt{\frac{2m}{\hbar}(E - E_0)}. \quad (2)$$

The edge energy E_0 was selected at the energy position of the half edge jump in the absorption spectra and the energy shift ΔE_0 was corrected using $Ln(thd)_3$ complexes as the standard sample [15]. $B = S_0^2 N$, where N is the coordination

number and S_0^2 is the reduction factor due to many body effect, was also determined from the standard sample of $Ln(thd)_3$ [16]. Fourier filtering was performed for the first main peak. The *k*-range for the curve-fitting method was around 4–10 $Å^{-1}$, in which *k*-range, the McKale's parameters are satisfactory. 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

$$f = \sqrt{\frac{\sum k^6(\chi - \chi_{cal})^2}{\sum k^6 \chi^2}} \quad (3)$$

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

IR diffused reflectance spectra of the lanthanoid(III) chloranilates were measured at various temperatures using a Bio–Rad fourier transform spectrometer FT–IR T30.

3. Results and discussions

The k^2-weighted EXAFS $\chi(k)$ spectra of Tb(III) chloranilate complexes at three different temperatures are given in Fig. 2 as an example. These spectra demonstrate the quality of the data. The corresponding Fourier transforms for the *k*-range from 3 to 12 $Å^{-1}$ in which backscattering amplitude and phase shift were corrected using the approach of McKale et al. [12] are shown in Fig. 3. The first peak around 2.5 Å corresponds to Tb–O in first coordinated shell and the second one around 3.2 Å corresponds to Tb–C. Clearly multiple scattering effect should be considered for the analysis of higher shell peaks. However, in the present study, our discussions focus on the analysis of the first coordination shell, so the multiple scattering can be neglected. McKale's parameters are suitable for the analysis of the first shell EXAFS. We found that the peak shifts decrease and the intensities become smaller as temperature increases. Structural parameters such as the interatomic distances and the coordination numbers for the first peak (Ln–O) can be determined by the curve-fitting method described in the previous section. Fig. 4 shows the curve-fitting result for $Nd_2(C_6O_4Cl_2)_3 \cdot nH_2O$ at 140°C as an example. The indices of fitting *f* are 5–10% for various lanthanoid(III) complexes. The structural parameters are summarized in Table 1. The large values of σ may come from the large static disorder or variation of *r* in the first shell, however multi-shell fittings could not give reasonable results. We found generally that the σ values monotonically increase with temperature.

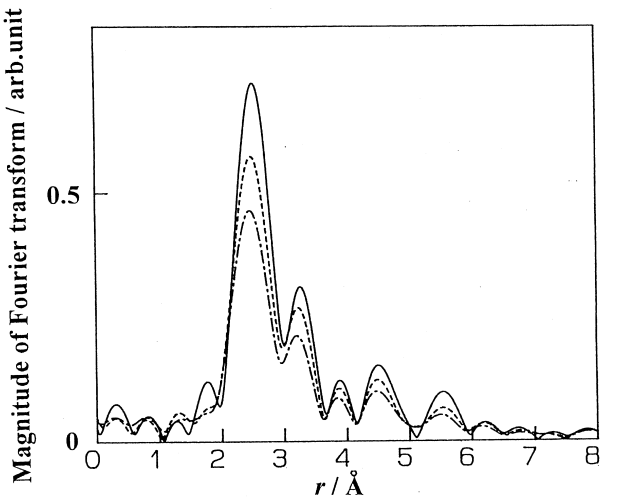

Fig. 3. Fourier transforms of EXAFS spectra for $Tb_2(C_6O_4Cl_2)_3 \cdot nH_2O$ at 25°C (solid line), 120°C (dashed line) and 200°C (dot-dashed line).

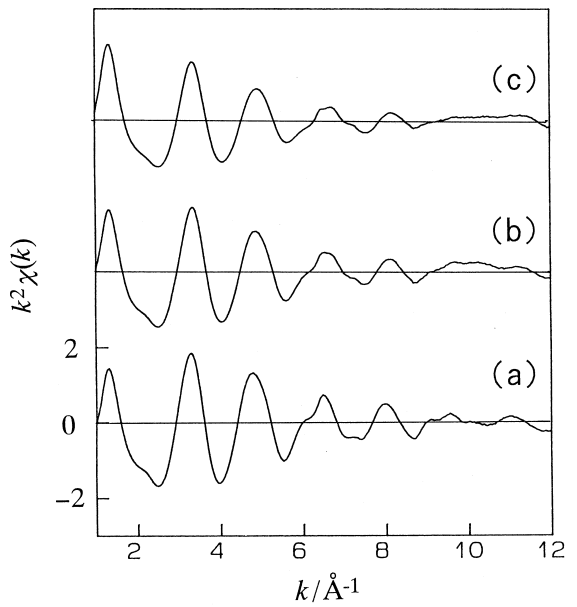

Fig. 2. $k^2\chi(k)$ EXAFS spectra for $Tb_2(C_6O_4Cl_2)_3 \cdot nH_2O$ at (a) 25°C, (b) 120°C and (c) 200°C.

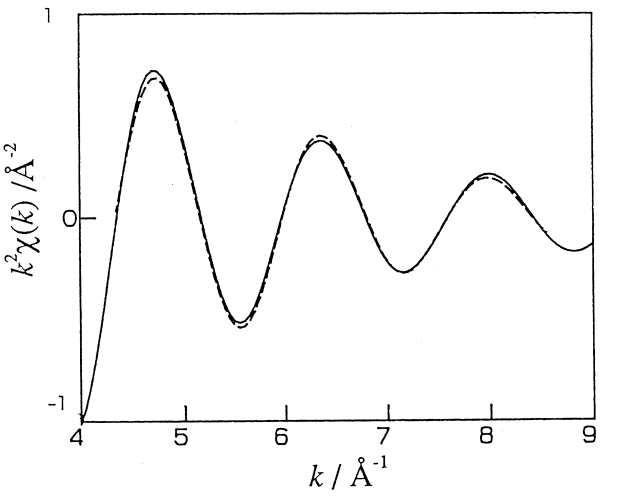

Fig. 4. The curve-fitting result for $Nd_2(C_6O_4Cl_2)_3 \cdot nH_2O$ at 140°C. Solid line represents the experimental data and dashed line is theoretical curve.

Table 1
The structural parameters determined from the curve-fitting method of EXAFS for $Ln_2(C_6O_4Cl_2)\cdot nH_2O$

Ln(III)	Temp./°C	r/Å ±0.001	σ/Å ±0.005	N ±0.8
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

This indicates that in the present fitting method values of N and σ can be successfully obtained. Temperature dependences of S_0^2 and C_3 can be negligible.

Fig. 5 shows the temperature dependence of the XANES (X-ray absorption near edge structure) for $Nd_2(C_6O_4Cl_2)_3\cdot nH_2O$ complexes as an example. Although XANES is only slightly temperature dependant, we can observe the change of the intensity of the white line A and the shoulder structure B. These results suggest that some structural changes occur with temperature increase.

Fig. 6 shows the change of coordination number of the central lanthanoid(III) ion with temperature for the

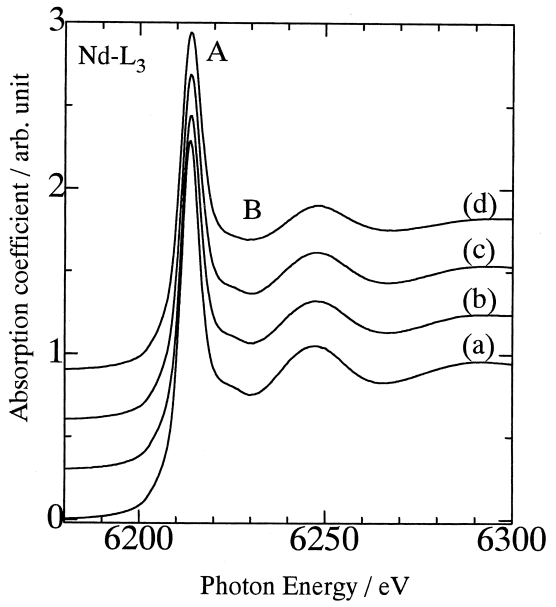

Fig. 5. Temperature dependence of XANES for $Nd_2(C_6O_4Cl_2)_3\cdot nH_2O$ complexes. (a) r.t., (b) 105°C, (c) 140°C, (d) 195°C.

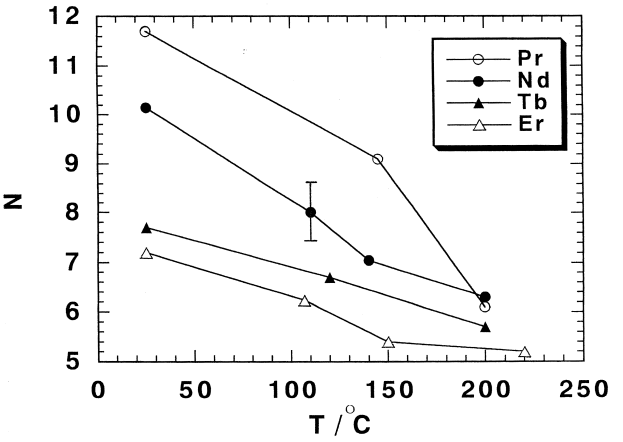

Fig. 6. The variation of Coordination number, N, with temperature for $Ln_2(C_6O_4Cl_2)_3\cdot nH_2O$. Ln = Pr (open circle), Nd (solid circle), Tb (solid triangle) and Er (open triangle).

chloranilate complexes. The coordination numbers for Tb(III) (Er(III)) complexes decrease 7.7 (7.2), 6.7 (6.3), 5.7 (5.2) stepwise as temperature increases. This result indicates that complexes of Tb(III) and Er(III) include approximately two extra coordinated water molecules after preparation and the water molecules are removed completely after heating at 200°C. This means that the net number of coordination oxygen atoms belonging to the chloranilate ligand is six, i.e. three chloranilate ligands are coordinated to the central lanthanoid(III) ion. This suggests that the $Ln_2(C_6O_4Cl_2)_3\cdot nH_2O$ complexes have a three-dimensional network structure as shown in Fig. 1, although $Cu(C_6O_4Cl_2)\cdot nH_2O$ has a one-dimensional ribbon like structure in which two chloranilate ligands are coordinated to Cu atom [1]. On the other hand, for complexes of lanthanoids 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 those of Tb(III) and Er(III) at room temperature. After heating the sample, the coordination number was reduced to six, similar to that of Tb(III) and Er(III). It is noted that there are about six and four extra water molecules, respectively, around Pr(III) and Nd(III) ions just after the preparation. It has been reported that the coordination numbers and the atomic distances for re-cooled samples are similar to the values obtained after heating at 200°C [6,7].

Hydrated structures of lanthanoid(III) ions in aqueous solution have been studied by Yamaguchi et al., using EXAFS [16]. It was reported that the average number of coordinating oxygen atoms in the first shell are 9.5 for Nd(III), 8.0 for Tb(III) and 7.5 for Er(III). The relation of coordination number to the ionic radius of lanthanoid(III) ions in aqueous solutions is similar to that for chloranilate complexes at room temperature. The interatomic distances between the central lanthanoid(III) ion and coordinated oxygen atoms in the chloranilate complexes are also shown

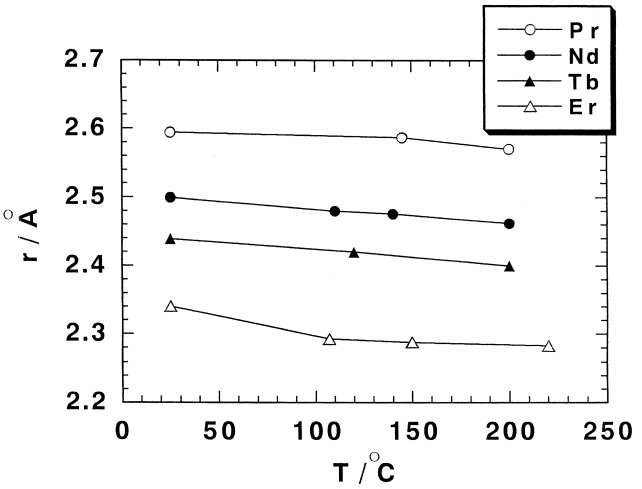

Fig. 7. Variation of interatomic distance, r, with the temperature for $Ln_2(C_6O_4Cl_2)_3 \cdot nH_2O$. Ln = Pr (open circle), Nd (solid circle), Tb (solid triangle) and Er (open triangle).

in Table 1. It has also been reported that the interatomic distances for aqueous solutions of Nd–O is 2.51 Å, that of Tb–O is 2.39 Å and that of Er–O is 2.34 Å [16]. These values are quite close to the results observed for lanthanoid(III) chloranilate complexes at room temperature (Table 1). We conclude that the local structure of lanthanoid(III) chloranilates at room temperature (or just after preparation) is similar to the hydrated structures of lanthanoid(III) ions in the aqueous solutions.

The interatomic distances between the central lanthanoid(III) ion and coordinated oxygen atoms for corresponding temperatures are shown in Fig. 7. As temperature increases, the interatomic distances decrease, i.e., the distance between central lanthanoid(III) ion and oxygen atoms in the ligand becomes shorter as coordinated water molecules are removed. An interpretation is that the local volume around the lanthanoid(III) ions becomes compressed as coordinated water molecules are removed. The linear relationships between the change in the interatomic distances, Δr, and that of the coordination numbers, ΔN, with temperature for these lanthanoid(III) complexes are plotted in Fig. 8.

Here we introduce the constant parameter, $R = \Delta r/\Delta N$, that indicates the variation of atomic distance as one coordinated water molecule is removed. In Fig. 9, the R values determined by linear fittings from Fig. 8, are plotted against the ionic radius (r_{ion}) of the central lanthanoid(III) ion [17]. It is interesting that the R value depends on the type of central lanthanoid(III) ion and has a good correlation with r_{ion}: the larger R value, the smaller r_{ion}. From these qualitative observations of the relationship between the R and r_{ion}, we may derive the relation

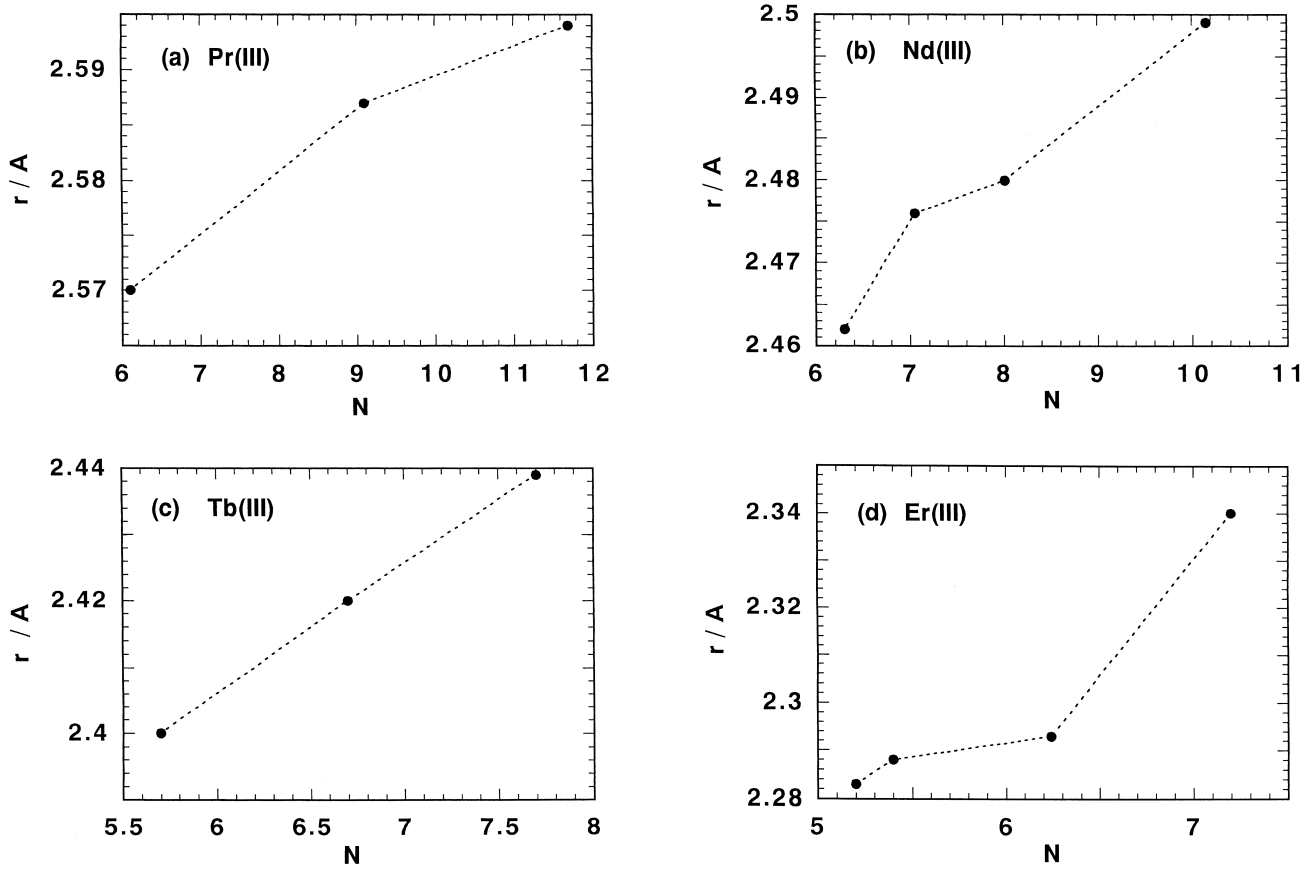

Fig. 8. The relation between r and N for $Ln_2(C_6O_4Cl_2)_3 \cdot nH_2O$. (a) Ln = Pr(III), (b) Nd(III), (c) Tb(III) and (d) Er(III).

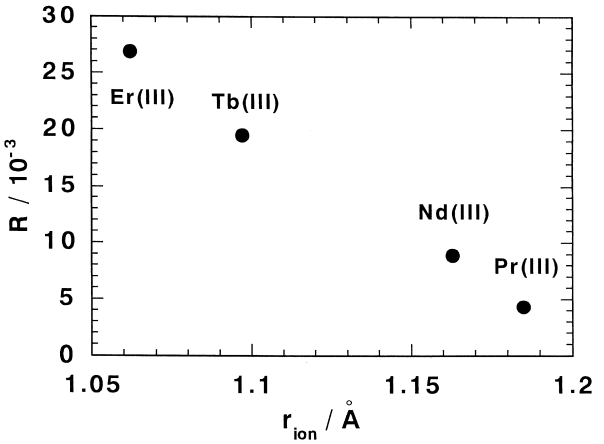

Fig. 9. Variation of the parameter $R(=\Delta r/\Delta N)$ with r_{ion} for various $Ln_2(C_6O_4Cl_2)_3 \cdot nH_2O$.

$$R = (\Delta r/\Delta N) \propto 1/(r_{ion} - r_0) \quad (4)$$

where r_0 is the characteristic ionic radius. Taking r_{ion} as the variable, Eq. (4) can be integrated as

$$\int (r_{ion} - r_0)\, dr_{ion} = c \int dN \quad (c \text{ is constant}) \quad (5)$$

and finally we obtained the simple relation

$$N \propto r^2 \quad (6)$$

at large value of r. The result represented by Eq. (6) is expected, i.e. the coordination number is proportional to the surface area of the central lanthanoid(III) ion sphere. From the present experimental data r_0 is optimized to be 1.01 Å, which can be considered as the minimum value of r for the coordination of water molecule to the lanthanoid(III) ion (or, at which only six oxygen atoms of the chloranilate ligand are coordinated).

Observations of the structural changes of the lanthanoid(III) complexes are supported by IR spectroscopy. Fig. 10 shows the diffuse reflectance spectra of $Tb_2(C_6O_4Cl_2)_3 \cdot nH_2O$, as an example, in the region from 400 cm^{-1} to 1100 cm^{-1} at different temperatures which were determined from TG curves [5]. These spectra are characterized by the of following three points: (1) There is a broad band from 400 cm^{-1} to 900 cm^{-1} due to lattice or coordinated water molecules in the complexes. (2) This broad band disappears when temperature increases. (3) The band at 450 cm^{-1} which is assigned to the Tb–O stretching vibration shifts to the higher wavenumbers with the increase of temperature i.e., 443.8, 444.9, 445.0 and 447.3 cm^{-1} for (a), (b), (c) and (d), respectively, as shown in Fig. 10. The second point above demonstrates the fact that dehydration took place in the complexes. These features of the diffuse reflection spectra are all common to other complexes [6,7]. Especially, the third point is in agreement with the analysis of the temperature dependence

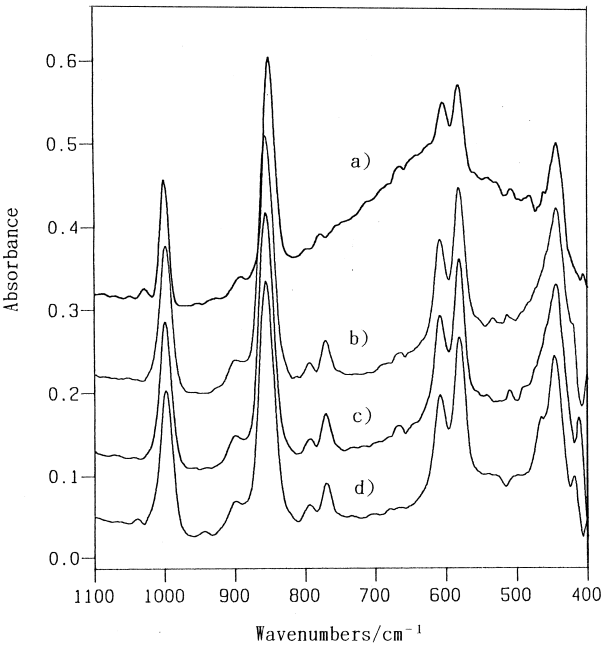

Fig. 10. IR diffused reflectance spectra of $Tb_2(C_6O_4Cl_2)_3 \cdot nH_2O$ at various temperatures; (a) 25°C, (b) 110°C, (c) 140°C, (d) 200°C.

of EXAFS spectra in which the Ln–O distance became shorter as the temperature increases.

4. Conclusion

The temperature dependence of the local structures of lanthanoid(III) chloranilates using EXAFS and IR spectroscopy has been discussed. The local structures of lanthanoid(III) chloranilates are similar to the hydrated structures of lanthanoid(III) ions in aqueous solution. The present EXAFS results indicate that a large number of water molecules, about six and four, coordinate in the first shell to the central lanthanoid(III) ions for Pr(III) and Nd(III), respectively. There is a linear relation between the change of interatomic distance, Δr, and that of the coordination number, ΔN, during the dehydration process. There is a good correlation of the parameter $R = \Delta r/\Delta N$ with ionic radius of the lanthanoid(III) ion. The coordination number is proportional to the surface area of the central lanthanoid(III) ion in the present prepared lanthanoid(III) complexes.

The results from the techniques of EXAFS and IR spectroscopy are consistent.

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