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A Study of Temperature Dependence of Local Structure of Erbium(III) Bromanilate Complex by EXAFS Spectroscopy

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The local structure of erbium(III) bromanilate complex was studied by the EXAFS (extended X-ray absorption fine structure) and IR spectra of some different temperatures. From the EXAFS analyses the coordination numbers and the distances between Er(III) and oxygen atoms were recognized to change as temperature changed. IR spectra showed that the frequency of Er(III)-oxygen stretching vibration was increased with temperature. The water molecules involved play important roles in the local structures of this complex.

In our previous papers we examined the local structures of lanthanoide(III) chloranilate and bromanilate complexes by EXAFS spectroscopy,[1, 2] IR spectra[3] and thermal analysis.[4] We determined the coordination number, N, and the distance, r, between lanthanoid(III) and the coordination atom. The thermal analysis gave the results that there are some coordinated or lattice water molecules in the lanthanoide(III) chloranilate and bromanilate complexes. And we also recognized the existence of the water molecules in the complexes from the reflectance IR spectra of various temperatures. In this letter, we report the temperature dependence of the local structure of the erbium(III) bromanilate. This is the first EXAFS experiment where the temperature dependence of the local structure of the Er(III) bromanilate complex is studied.

The complex $Er_2(C_6O_4Br_2)_3 \cdot nH_2O$ was prepared from aqueous solutions of bromanilic acid and erbium(III) trichloride hydrate in the molar ratio 3:1.

Er L_{III}-edge absorption spectra were obtained at BL-6B and 7C of the Photon Factory in the National Laboratory for the High Energy Physics (KEK) in Tsukuba. Si(111) double crystal

monochrometer was used. The sample was mixed with BN powder and the mixture was pressed as a disk. The sample disk was held on the heating attachment and heated under nitrogen atmosphere. The X-ray absorption spectra were measured at about one hour after the desired temperature was obtained. The measurement temperatures were selected carefully as room temperature, 100 °C, 150 °C and 210 °C from the thermal analysis (the flat region of TG and DTA curves).[4] The EXAFS data were analyzed by the procedure described in the previous paper.[2]

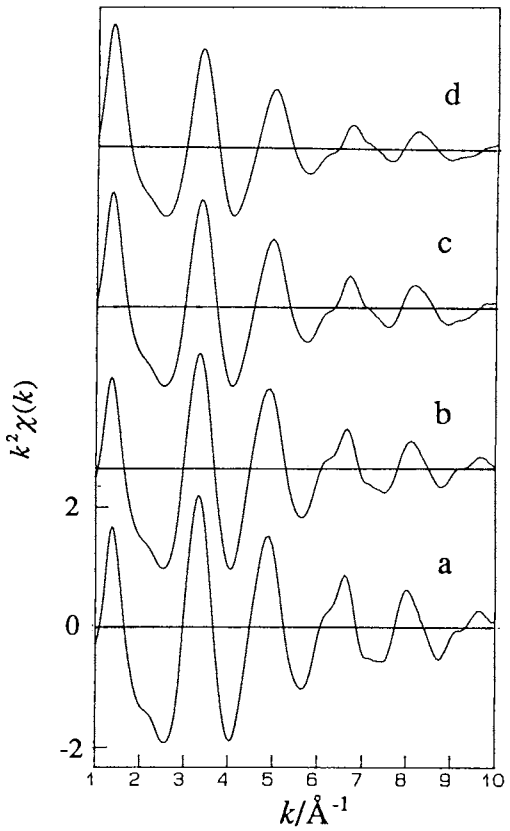

Fig. 1. $k^2\chi(k)$ spectra of L_{III} edge of $Er_2(C_6O_4Br_2)_3 \cdot nH_2O$ for a): r.t., b): 100 °C, c): 150 °C and d): 210 °C.

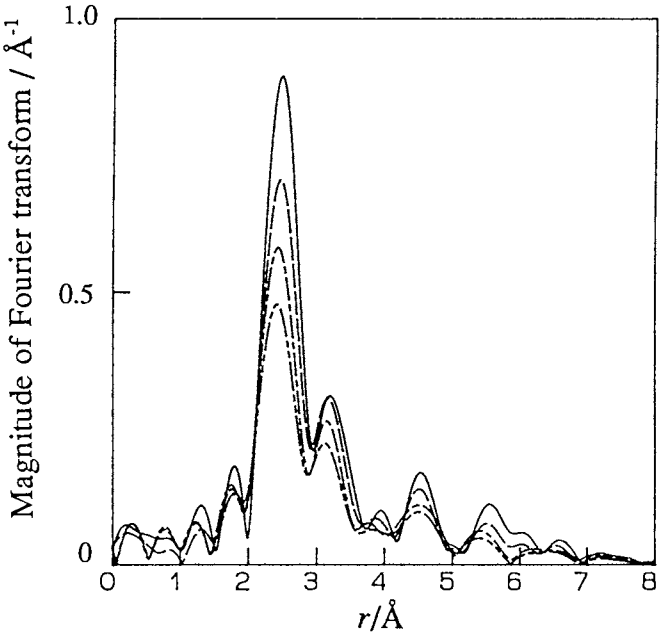

Fig. 2. Fourier transform of EXAFS of $Er_2(C_6O_4Br_2)_3 \cdot nH_2O$ for r.t. (——), 100 °C(– –), 150 °C (–·–) and 210 °C (–···–).

The k^2-weighted EXAFS spectra and the Fourier transforms of Er(III) bromanilate complex for the various temperatures are shown in Fig. 1 and Fig. 2, respectively. The first peak which is attributed to the scattering of the nearest coordinated oxygen atoms was observed at about 2.3 Å. The relative intensity of this peak changes smaller and peak position shifts shorter as temperature rises. It is not clear whether the change of the intensity of this peak comes from the reduction of the coordination number or thermal vibration effect to Debye-Waller factor. In order to reveal this result, one-shell curve-fitting procedure is performed, which is also described in Ref. 2).

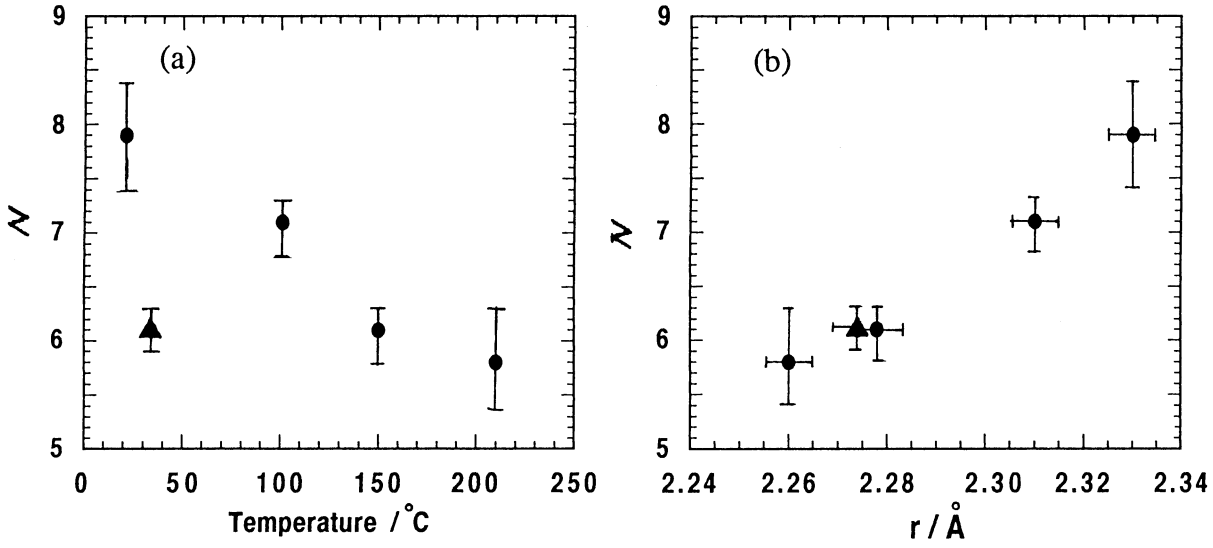

Fig. 3. (a) Temperature dependence of the coordination number of the first nearest atoms.
(b) Relation between N and r. Symbol ▲ represents the value re-cooled to 35 °C from 210 °C.

Figure 3 (a) shows the temperature dependence of the coordination number obtained from the curve-fitting. The coordination number is 8 at room temperature as reported previously.[2] It should be noted that the coordination number change from 8, 7 to 6 stepwise as temperature increases. This result indicates a process that the water molecule is released from the central Er(III) ion step by step and there is no water molecule in the first coordination sphere at 210 °C. It is expected that the bond distance shifts shorter as the coordination number is reduced. Figure 3 (b) shows the relation between the coordination number and the bond distance in the present temperature range. It is interesting that there is a linear correlation between them. At 210 °C, r=2.26 Å which is longer than r for $Er(thd)_3$ complex (r=2.21 Å for N=6).[5] We can find another interesting feature from Fig. 3. The point symbolized by solid triangle in Fig. 3 is the value measured when the sample was cooled again to 35 °C from 210 °C. The figure shows the structure of the complex re-cooled is similar to that at 150 °C.

The diffuse reflectance spectra of the complex are measured by using FT-IR T30 of Bio-Rad Laboratory Ltd. The measurement temperatures were set the same as EXAFS experiments. The IR spectra of $Er_2(C_6O_4Br_2)_3 \cdot nH_2O$ are shown in Fig. 4. The peak at 456 cm^{-1} at room temperature was assigned to Er(III)-O stretching vibrational frequency.[4] At 210 °C, the frequency of this mode shifts to 465 cm^{-1}. This agrees with the change of the distance obtained from EXAFS. About this

peak there was no further change by raising the measurement temperature (see Fig. 4, (e)).

We are now studying the local structures of other lanthanoid(III) complexes at various temperatures by the EXAFS along with thermal analysis.

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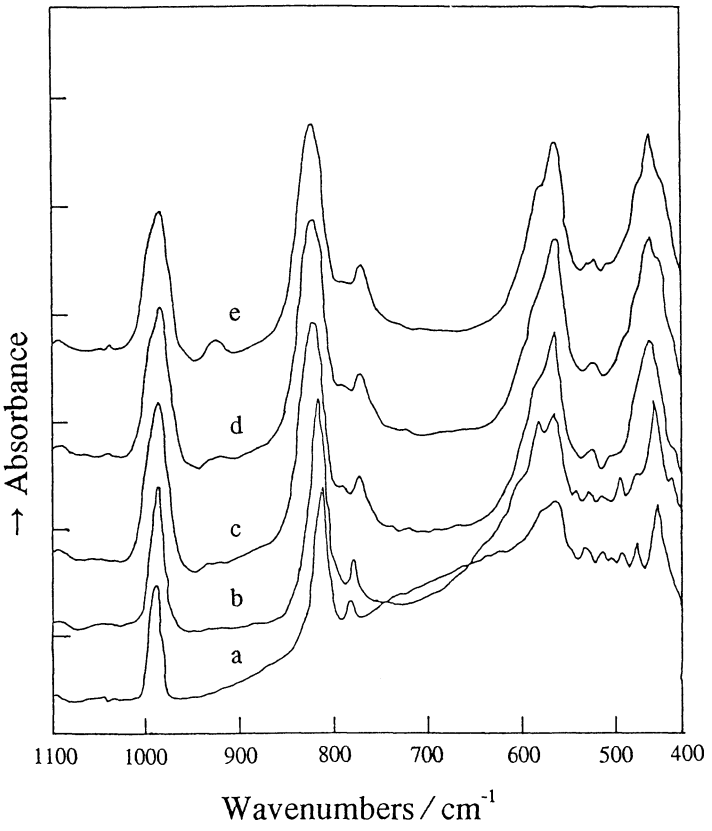

Fig. 4. The IR spectra of $Er_2(C_6O_4Br_2)_3 \cdot nH_2O$ at various temperatures in the region 400 cm^{-1}-1100 cm^{-1}, a): Room temperature, b): 100 °C, c): 150 °C, d): 210 °C, e): 240 °C.

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