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# EXAFS Study on Chloranilate Complexes of Lanthanoid(Ⅲ)

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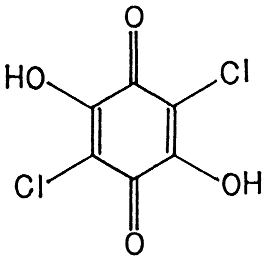
The local structures of lanthanoid(Ⅲ) chloranilate complexes have been studied by the extended X-ray absorption fine structure (EXAFS) spectroscopy. The Fourier transformed EXAFS spectra suggest that the complexes are rigid three dimensional network structures. The distances between a metal and coordinated atoms estimated from EXAFS spectra are correlated to the ionic radii of lanthanoid(Ⅲ) ions very well.

Though chloranilic acid (1) has been well known as an analytical reagent, the structural studies on chloranilate complexes of metals have not been performed so much due to the fact that these complexes are usually polycrystalline fine powders which are not suitable for the X-ray diffraction study.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Just a decade ago Verdaguer et al. applied the EXAFS technique to the chloranilate and bromanilate comolexes of copper(Ⅱ) and showed that these complexes have ribbon structures.1) However, any structural study of chloranilate complexes of lanthanoid(Ⅲ)

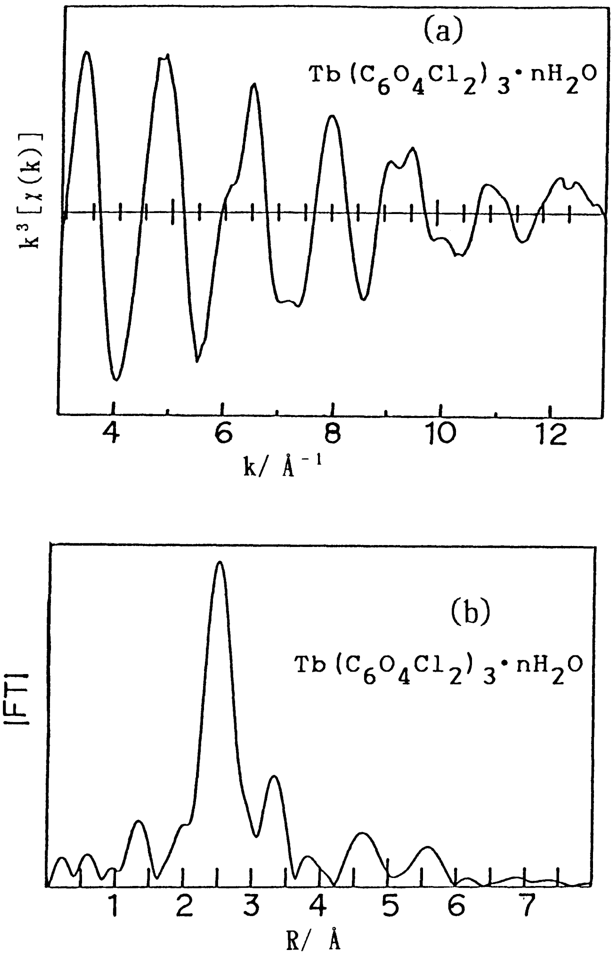

Fig. 1. k-Space spectra (a) and R-space spectra (b) of Tb(III) complex in arbitrary units.

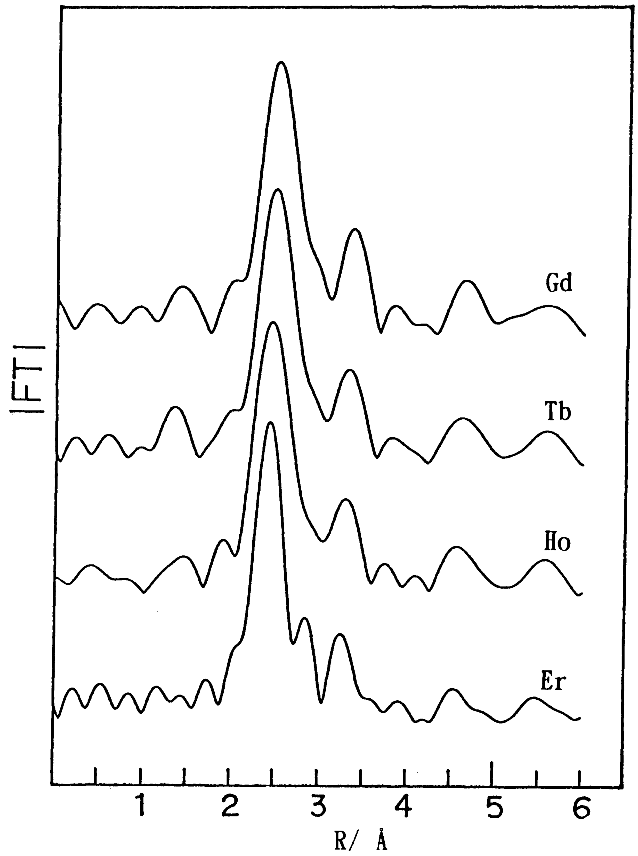

Fig. 2. R-Space spectra of Ln(III) complexes in arbitrary units.

has not been reported except that of Pr(III) chloranilate by Riley et al.[2)] Our report is somewhat preliminary but the first EXAFS study on the local structure of lanthanoid(III) chloranilate complexes.

We prepared lanthanoid(III) chloranilate complexes ($Ln_3(C_6O_4Cl_2)_3\cdot nH_2O$; Ln = La, Gd, Tb, Ho, Er) from aqueous solutions of the molar ratio 3:1 mixture of chloranilic acid and lanthanoid(III) trichloride hydrates. All Ln(III) chloranilate complexes were obtained as polycrystalline fine powders. The chemical analyses were not performed for all these complexes. The IR spectrum of La(III) chloranilate was measured by the KBr disk method. This resulted in almost the same spectrum as that in the literature.[3)] The IR spectra of other chloranilate complexes of Ln(III) also had striking resemblance to that of La(III) complex, so we recognized the complexes being prepared as desired ones.

Lanthanoid L-edge X-ray absorption spectra were obtained at BL-7C and BL-6B of the Photon Factory in the National Laboratory for High Energy Physics using the Si(111) double crystal monochromator. The measurement was done at room temperature. The Fourier transformation of EXAFS was performed by using the phase shift and scattering amplitude parameters by Teo and Lee (for the elements not tabulated, interpolated values were used).[4] A PC9801 (NEC) computer was used with a set of the programs written by Matsubayashi.[5]

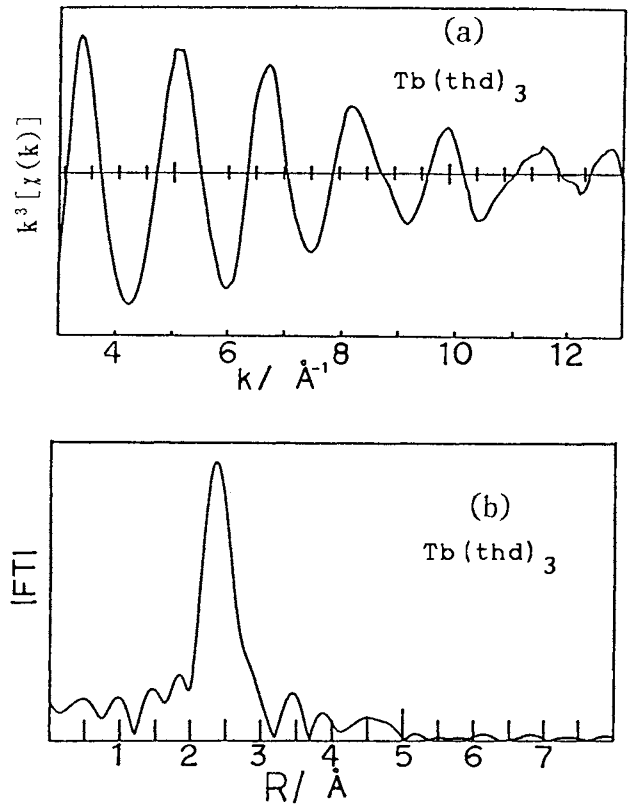

Fig. 3. k-Space spectra (a) and R-space spectra (b) of $Tb(thd)_3$ complex in arbitrary units.

The EXFAS results of Tb(III) chloranilate complex are shown in Fig. 1. We easily find three peaks at the R-space spectrum (Fig. 1(b)). The Fourier transformed spectra of other complexes are summarized in Fig. 2 along with that of Tb(III). All spectra are just alike, i.e. in addition to one intense peak, two other peaks are clearly observed. These types of spectra have been observed in the complexes which have a rigid ligand skelton.[1,6] So we can suppose that the chloranilate complexes of Ln(III) have also the rigid network structures. The peak positions in each spectra are given at Table 1. We assign these as follows; the first intense peak is due to the scattering from chloranilate oxygen, the second peak is due to carbon atom $C_1$, the third one to carbon $C_2$, respectively (see Fig. 4). The estimated bond distance between Ln and the coordinated oxygen atom in the complexes decreases gradually from La to Ho. This tendency is correlated to the change of ionic radius of the lanthanoid(III) ions very well (see Table 1).

Table 1. Peak Positions in Fourier Transforms of EXAFS and Ionic Radii[a] of Ln(Ⅲ) (Å)

| Ln | 1st | 2nd | 3rd | $R_{ion}$ |
|---|---|---|---|---|
| La | 2.77 | 3.47 | 4.59 | 1.216 |
| Gd | 2.51 | 3.36 | 4.65 | 1.107 |
| Tb | 2.49 | 3.33 | 4.62 | 1.095 |
| Ho | 2.44 | 3.28 | 4.57 | 1.072 |
| Er | 2.43 | 3.24 | 4.54 | 1.062 |

a) From Ref. 9.

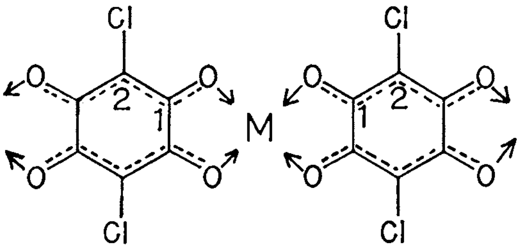

Fig. 4. Numbering on carbon atoms in the complex.

Figure 3 shows EXAFS spectra of $Tb(thd)_3$, thd = tetramethylheptanedione, which was prepared by the procedure given in the literature.7) It is interesting that only one intense peak at 2.36 Å was observed in this complex unlike the chloranilate ones. The ratio of the relative scattering intensities of $Tb(thd)_3$ and Tb(Ⅲ) chloranilate complexes is about 6:9 in the first intense peaks. This means that three coordinated water molecules are located in the Tb(Ⅲ) chloranilate. The existense of the coordinated water molecules was also suggested by our IR study.8)

Besides three peaks discussed above, we find one additional peak around at 5.5 Å (Fig. 2), which may correspond to the scattering from chlorine atoms. To clarify such an assumption we are now preparing the EXAFS study on the bromanilate complexes of lanthanoid(Ⅲ).

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