

Coordination Structure of PTA-Er complexes in Methanol

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Introduction

Recovery of minor actinides, e.g., Am, Cm, prior to geological disposal is one of the important subject to solve the problem regarding volume reduction of radioactive waste. Hence, this topic is taken up in development of a new separation ligand by many researchers. Up to date, the ligands having soft donor have been attracted and proposed. The N-donor type ligands, e.g., BTP, BTBP, TPEN, Benzimidazol (BIZ) are known to be a promising ligand. On the other hand, we recently proposed new type of ligand having both hard and soft donors, i.e., PTA (Phenanthroline amide) and PDA (Pyridine amide) ligands. In this study, the local structures of PTA-lanthanide complexes in solution were investigated by EXAFS.

Experimental

Sample Preparation

Sample solutions were prepared by following procedure. 50 mM Er and 100 ~ 400 mM PTA in methanol solutions were mixed to adjust to pH2 with HCl.

EXAFS measurements

Er-L_{III} EXAFS were measured in fluorescence modes at the BL-27B of Photon Factory (PF), KEK. The synchrotron radiation was monochromatized with double crystal Si(111). Solution samples were sealed in a polyethylene bag with a Teflon spacer for lanthanides. EXAFS data reduction and curve fitting were carried out by XAS data analysis package WinXAS ver.3.2 [1]. The theoretical phases and amplitude were calculated by FEFF8[2].

Results and Discussion

Figure 1 showed the radial structural functions (RSF) of Er-L_{III} EXAFS oscillations of 1:1 to 1:4 in metal to ligand ratio. The sharp peaks at 2 Å are allocated to Er-O, N interaction, based on the crystal data shown Fig.2, of which intensity decreased with an increase in ligand ratio, indicating that PTA surely coordinates to Er under pH2. This is noteworthy result, since most of N-donor ligands are generally influenced by protonation under this condition and thus these ligands do not work as an effective ligand. Consequently, an addition of oxygen to N-donor ligand would be effective for preventing from protonation. The second peaks at 3 Å arising from Er-C interaction does not change significantly on 1:1 to 1:3 of the samples, while that on 1:4 intensified. These peaks also show a coordination of PTA to Er. Therefore, change in the spectra suggests that two PTA would ligate

to Er at the ratio of 1:4. Figure 2 present the crystal structure of Er(NO₃)₃(PTA)₂ complex measured by X-ray diffraction. Both two PTA coordinated to Er with tridentate fashion, while one nitrate ion did not bind to Er directly. EXAFS spectra of this crystal were quite similar shape to Er-PTA complex except for nitrate feature.

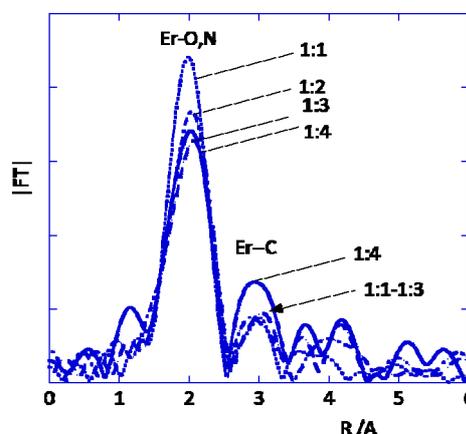


Figure 1 The radial distribution functions of Er-L_{III} EXAFS for Er-PTA complexes in methanol. *The ratio in the figure presents a metal to ligand ratio in each sample.

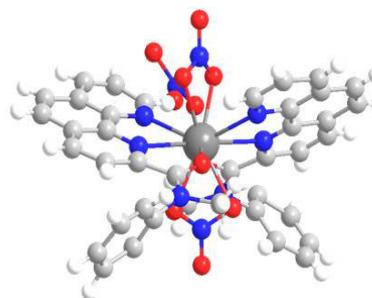


Figure 2 The structure of single crystal for Er-PTA complex. * Red: oxygen; Blue: nitrogen; Gray(small): carbon; Dark Gray(large): Er; White: hydrogen.

References

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