

Coordination Structure of Er-PTA complex in Ethanol Solution

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1 Introduction

Soft donor ligands are promising for separation of the minor actinides (MA), i.e., Am, Cm, from trivalent lanthanides in high level radioactive wastes (HLW)[1]. Since lanthanides in HLW, which are included 30 times as MA, show large neutron cross section, this separation process would be very important for improvement of transmutation efficiency toward MA. On these background, we developed a new type of soft donor ligand, *N*-methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (PTA) which coordinates to a trivalent lanthanide or actinide ion with two nitrogens and one oxygen, and showed the sufficient separation factor between Am and Eu from the acidic media less than pH 2 on biphasic extraction system. [2] In this study, coordination structure of PTA with lanthanide, in particular Er in this study, was studied as preliminary investigation of coordination structure of MA for elucidation of discrimination mechanism between lanthanide and actinides.

2 Experiment

Structural determinations were carried out by x-ray crystallography for solid state and synchrotron radiation based EXAFS for solution state, respectively. EXAFS spectrum was measured at BL27B in transmission mode. The sample for EXAFS was prepared by dissolution of 1:4 ratio mixture in metal to ligand ratio into methanol. EXAFS analysis was done by WinXAS ver.3.2 [3] software and FEFF8 [4].

3 Results and Discussion

The crystal structure of [Er(NO₃)₂(PTA)₂] complex, isolated from the unit cell, in Fig. 1 shows that two PTA and nitrates coordinates directly to Er. Especially, oxygen of PTA ligates more strongly than the other donor atoms due to evaluation from bond distances. The radial structural function based on the Fourier transformed EXAFS oscillation in Fig.2 dominantly consists of three peaks, and the first peak would probably include the three interactions with oxygen from carbonyl group of PTA, oxygen from nitrate ion, and nitrogen from PTA of phenanthroline (phen) moiety. Although EXAFS fitting for first shell should be carried out one or two shell model based on averaging, FEFF simulation spectrum estimated from the crystal coordinate really agreed with real spectrum, demonstrating that the coordination structure shows quite similar to the crystal. The bond distances by EXAFS fitting done by 3 shell model are 2.31(1) Å for carbonyl oxygen of PTA, 2.46(5) Å for nitrogen from phen moiety, 2.58(3) Å for oxygen of nitrate ion. Accordingly, PTA works as efficient ligand toward trivalent lanthanides and actinides with the same size of

erbium.

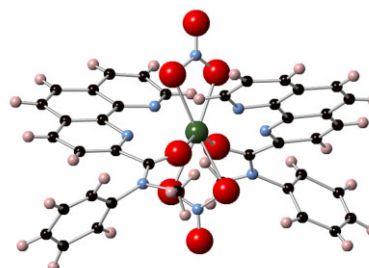


Fig. 1: The single crystal structure of [Er(NO₃)₂(PTA)₂] complex. *The symbols denote Green: erbium, Red: oxygen, Blue: nitrogen, Black: carbon, Pink: hydrogen. Space group: Cc, Crystal system: monoclinic, a=19.200(3), b=17.841(3), c=13.091(2), α=114.5650(14), β=γ=90.0000, Z=4.

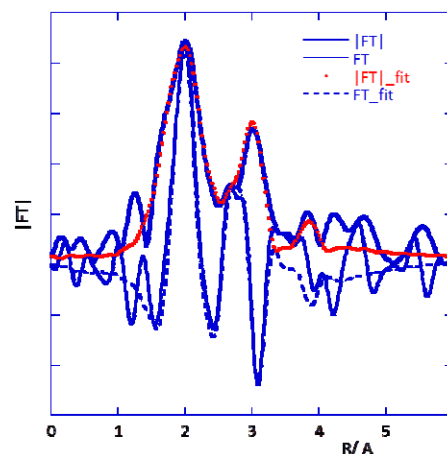


Fig. 2: The radial structural functions based on the Fourier transformed Er-L_{III} EXAFS oscillation of Er-PTA complex in ethanol. *This function consists of three dominant peaks arising from 1) O&N of PTA and O of nitrate ion, 2) C around donor atoms of PTA, 3) multiple scattering contribution of Er-N-O of nitrate ion. The phase shifts was not corrected.

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