

Substituent effect of the hybrid type PDA complexes

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Introduction

The ion recognition compounds which coordinate to a specific metal ion are used for many separation industries. Especially, the development of actinide ion recognition compound is a very important topic for treatment of radioactive wastes generated from nuclear fuel cycle. We developed the pyridinedicarboxamide (PDA) ligand which can recognize tri- and tetra-valent actinides efficiently [1].

For employing this type of ligand in an actual process, it is required that PDA is soluble in paraffinic solvent and has high separation ability for actinides. From the point of view, the relationship between structure of PDA and separation factor would possibly provide us key information for molecular design toward improvement of PDA derivatives. MePh-PDA ($R_1=R_2$ =Methyl group, $R_3=R_4=R_5=R_6=R_7=H$) was regarded as starting material and, then straight alkyl chain was introduced into the position of methyl group. As a result, the solubility to paraffinic solvent was increased by changing the length of side chain. In this study, the lanthanide complex structures with these PDA derivatives were determined by EXAFS methods in order to clarify recognition mechanism.

Experimental

Figure 1 shows the pyridinedicarboxamide (PDA) ligand. The PDA derivatives with each alkyl chain of which number of carbon is from 1 to 12 at R_1 and R_2 positions were synthesized. The lanthanide complexes were synthesized by mixing with PDA in methanol. Local structures around methanol were determined by EXAFS method.

The EXAFS measurements were performed at the BL-27B station in the Photon Factory, KEK, and the BL11XU in SPring-8[2]. The lanthanide L_{III} absorption edge spectra were measured in fluorescent mode by a 7 arrayed solid state detector, while lanthanide K absorption edge spectra were measured in transmission method at SPring-8.

Results and Discussions

The relationship between Gd-N distance and carbon number is shown in Fig. 2. The plot against carbon number shows a minimum value at about 5. This V-shape tendency might be arising from combined effects as following. Generally, a decreasing tendency in bond

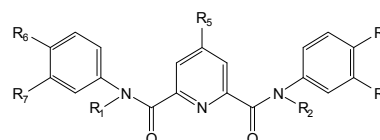


Fig.1 Structure of PDA.

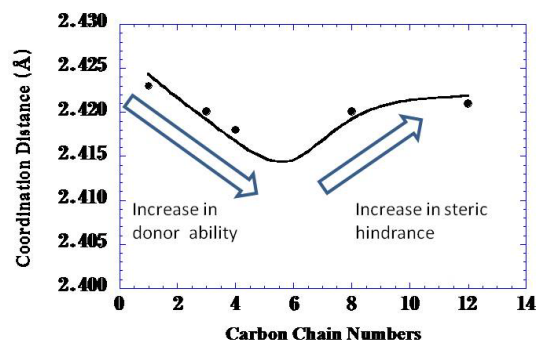


Fig.2 Relationship between coordination distance and Carbon chain numbers of substituent.

distance along carbon number indicates an improvement of donor ability on nitrogen with an increase in electron density by introduction of alkyl group. On the other hand, since bulky PDAs of which alkyl chain is longer interfere each other on formation of complex, so that the steric hindrance tendency might become larger. Consequently, V-shape in the relationship might be observed. Besides, an enhanced tendency was observed in heavier lanthanide complex, while was not in lanthanum complex.

These results suggest a suitable carbon number on formation of complex. Therefore, we can adjust carbon number in a chain also by considering solubility of a PDA molecule. This information will be helpful for improvement of molecular design technique.

References

- [1] T. Yaita, et al., Physica Scripta, T115, 302 (2005).
- [2] A part of XAFS measurement was performed under the approval of the SPring-8 Proposal No. 2007A3504, 2007B3504, 2008A3504 and 2008B3504.

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