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Study of Lanthanides/Actinides – Crown Ether Complex by DFT Calculation Aiming to Reveal the Mechanism of Solvent Extraction

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1. Introduction

Selective separation of minor actinides from high-level liquid waste which generated from reprocessing spent nuclear fuel is important for treating the waste safely. One of the promising separation methods is solvent extraction. Many types of ligand were investigated for separation, and their extraction property was compared each other. However, the framework was not considered in comparison. In the present study, we tried to reveal the difference in donor atom in the same framework. That is, oxygen donor ligand 18-crown-6 ether and its derivative which has nitrogen and sulfur atoms as donor atoms (Fig.1, X = O, S, NH) were used. The bonding character between those ligands and lanthanides or actinides was investigated using DFT.

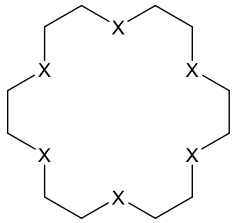

Fig.1 Structure of 18C6X

2. Method

Calculation program ORCA was used for all calculation process. BP86 and B2PLYP were applied as functional for structure optimization and single-point energy calculation, respectively. Calculation model was made by modifying the single crystal structure of $[Gd(18C6O)(H_2O)_3]^{3+}$ to $[M(18C6X)(H_2O)_3]^{3+}$ (M = Eu, Am, Cm, X = O, S, NH). Complexation Gibbs energy change (ΔG) upon complexation was calculated based on the equation (1).

$$[M(H_2O)_9]^{3+} + 18C6X \rightarrow [M(18C6X)(H_2O)_3]^{3+} + 6H_2O \quad (1)$$

3. Results and Discussion

Table 1 shows the comparison of ΔG upon complexation. It can easily be seen that the present ligands (18C6X) (X = O, S, NH) show actinide selectivity even in O-donor. This is different from the result of Cyanex-272[1)]. This is maybe due to that the 18C6O is a neutral ligand, while Cyanex-272 is an anionic ligand. We calculated metal- donor atom distances. The metal donor atom distance for Am and Cm are slightly shorter than that of Eu, albeit the ionic radii for Am and Cm are longer than that of Eu. This suggests the small contribution of covalent bond between M(= Am, Cm) and ligand atom (O, S, NH). This will become the reason of actinide selectivity of the present ligands.

Table 1 Comparison of ΔG

X	ΔG / kJ mol^{-1}		
	M=Eu	M=Am	M=Cm
O	–409	–426	–420
S	–323	–348	–340
NH	–459	–487	–471

4. Reference

1) M. Kaneko, S. Miyashita, and S. Nakashima, *Inorg. Chem.*, **54**, 7103-7109 (2015).