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Computational analysis of Eu(III) and Am(III) complexes with pnictogen atom (N, P, As, Sb) using DFT calculation

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The solvent extraction has been performed for partitioning minor actinide (MA) from lanthanide (Ln) in radioactive high-level liquid waste. N- and S-donor ligands have been used as soft-donor ligands for the MA separation. Recently, extraction of MA and Ln using P-donor ligands regarded as soft donor ligands was reported and P-donor ligands can separate them.^[1] The selectivity is closely related to the hardness or the softness of donor atoms. Therefore, we focused on bonding between metal ions and donor atoms and considered whether the other pnictogen atoms can extract MA and Ln ions or not.

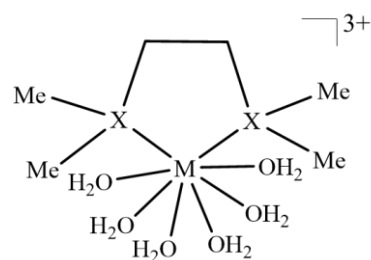


Fig.1 Calculated structure

In this study, we performed the density functional calculations to the complex such as Fig.1 (M = Eu, Am; X = N, P, As, Sb) in order to elucidate the correlation between Am/Eu selectivity and metal-pnictogen bonding property. As a result, the structure of Fig.1 formed square anti-prism and N-, P- and As-donor ligands indicated Am selectivity. In particular, P-donor ligand favors

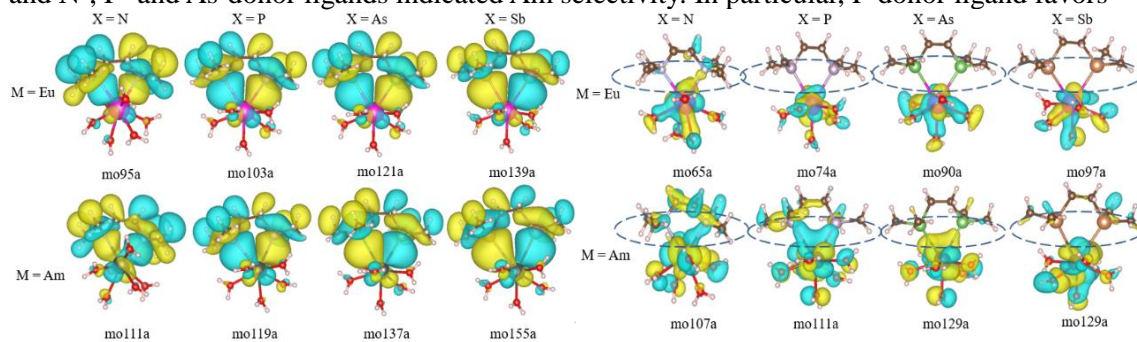


Fig.2 d-type molecular orbital surfaces

Fig.3 f-type molecular orbital surfaces

Am ions the most among pnictogen atoms. The tendency of Am selectivity is $N < P > As > Sb$ and this tendency is identical with soft acid classification in hard and soft acids and bases (HSAB) rule. The interactions between d-orbital of metal ions and donor atoms were almost the same in all complexes (Fig.2). On the other hands, in the case of f-orbital, the interactions between Am ions and P-donor atoms were stronger than other donors (Fig.3). Also, we performed the population analysis and the results indicated that the Am/Eu selectivity correlated with the interaction between f-orbital of the metal ions and pnictogen donor atoms.

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