

論文 / 著書情報  
Article / Book Information

題目(和文)	中性ジアミドを配位子とする硝酸ランタノイド(III)錯体の錯形成反応及び分子構造に関する研究
Title(English)	Studies on Complex Formation and Molecular Structures of Lanthanoid(III) Nitrate Complexes with Neutral Diamide Derivatives
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

専攻 : Department of	原子核工学	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	( 学術 )
学生氏名 : Student's Name	奥村 森		指導教員 (主) : Academic Advisor(main)	池田 泰久	
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

The selective complexation of trivalent actinides (An(III)) over trivalent lanthanide (Ln(III)) is the most challenging key issue for the developments of new efficient extractant because of their chemical similarities. Understanding fundamental properties of extracted species must be crucial for the development of more efficient extractant. In this thesis, the Ln(III) nitrates and two neutral diamide derivatives (N,N,N',N'-tetraalkyldiglycolamide; DGA and N,N,N',N'-tetraalkyl-3,6-dioxaoctanediamide; DOODA) were chosen as model cases, the structure of their complexes and complex formation behavior were investigated by single crystal X-ray diffraction, UV-visible, infrared (IR), and multi nuclear magnetic resonance (NMR) spectroscopy techniques. This study also focused on the relationship between the molecular structures and the selectivity of hard donor extractants through the systematical investigation across the Ln(III) series.

Chapter 1. As the background of this thesis, the potential importance of coordination chemistry of these elements in the reprocessing of spent nuclear fuels process was described. The oxygen bearing hard donor extractants are in interest because of less of knowledge of the factors for affecting selectivity for Ln(III) and An(III). From this point, objective of this thesis was described.

Chapter 2. The Ln(III) nitrate complexes with TEDGA,  $[Ln(TEDGA)_3](NO_3)_3$  (Ln = Tb-Lu) were synthesized and characterized in crystallographically and also confirmed by IR spectra.

Chapter 3. The differences in complexations, stabilities and structures of Ln(III) nitrate complexes with DGA in acetonitrile solutions were investigated by UV-vis and NMR spectroscopy. It was revealed that the 1:1 and 1:3 metal to ligand ratio complexes were formed. There are significant differences in stabilities and structures between the light and heavy Ln(III). The 1:3 complexes for heavy Ln(III) are highly stable than that of light Ln(III) in the acetonitrile solutions.

Chapter 4. The Ln(III) nitrate complexes with DOODAC2 were synthesized and characterized in crystallographically. The complexes are classified into three groups. The first two light Ln(III) form  $[Ln(DOODAC2)_2(EtOH)_2][Ln(NO_3)_6]$  (Ln = La-Ce) complexes, the next ten light to middle Ln(III) form  $[Ln(DOODAC2)(NO_3)_3]$  (Ln = Nd-Yb) complexes, and final one Ln(III), i.e. Lu, forms  $[Lu(DOODAC2)(NO_3)_2](NO_3)$  complex. The coordination modes of DOODA and nitrate ions were confirmed by infrared spectroscopy.

Chapter 5. The differences in complexations, stabilities and structures of the Ln(III) complexes with DOODAC2 in acetonitrile solutions were examined by UV-vis and NMR spectroscopy. It was revealed that the complexes with 1:1 and 1:2 metal to ligand ratio were formed. The isostructural series of 1:1 complex were examined by LIS plots. There are small differences in stabilities and structures between the light/middle and heavy Ln(III). The 1:2 complexes are relatively unstable especially for heavy Ln(III).

Chapter 6. The effects of the existence of nitrate ion on complexation of DGA and DOODA were investigated by UV-vis spectroscopy. According to the qualitative discussion of this result, the strength for interaction to Ln(III) ions are in the order of  $DGA > DOODA \geq$  nitrate ion. The number of nitrate ion coordinated to the Ln(III) was calculated by the chemical shift variations of  $^{15}N$  NMR spectra. The number of coordinated nitrate ion strongly supported that the reaction schemes obtained by UV-vis,  $^1H$  NMR and IR spectra, and successfully demonstrated the formation of inner- and outer-sphere complexes with nitrate ions.

These results are excellent agreement with the variations of distribution ratios shown in the solvent extraction. The relationship between the molecular structures and the selectivity of hard donor extractants through the systematical investigation across the Ln(III) series have provided valuable insight into both the coordination chemistry of Ln(III) and the knowledge of fundamental interaction properties between Ln(III) and hard donor extractants.

In Chapter 7, author summarized the research.

備考 : 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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