

## Structural studies on extracted species using diamide compounds as extractant for actinide/lanthanide separation

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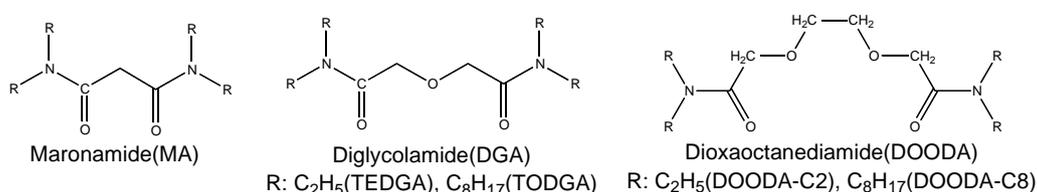
### Abstract

Complex formation and structural studies of trivalent lanthanide (Ln (III), Ln: La and Eu) with N,N,N',N'-Tetraalkyl-3,6-dioxaoctanediamide (DOODA) have been carried out. The complexes were synthesised and characterised by single-crystal X-ray diffraction. Complex formation between Ln (III) and DOODA was determined by multi nuclear NMR spectroscopy in CD<sub>3</sub>CN solutions. Stoichiometry was determined from <sup>1</sup>H NMR spectra by changing the concentration ratio of Ln (III) and DOODA ([Ln]/[DOODA]). The 1:1 and 1:2 metal to ligand complexes were found to be formed in the ratios [Ln (III)]/[DOODA] > 1 and [Ln(III)]/[DOODA] < 0.5, respectively. This study demonstrates that the structure analyses of the extracted species in the solution using NMR can well interpret solvent extraction mechanism of lanthanide (III) by diamide compounds as an extractant.

## Introduction

The separation of minor actinides (MA, trivalent actinides, An (III)) from high-level liquid waste (HLLW) has been widely studied for several decades. In particular, the separation of MA from trivalent lanthanides [Ln (III)] has been a challenging issue, because of their chemical similarities. Neutral diamide compounds (Figure 1) have been known as good extractants for solvent extraction. Malonamides and diglycolamide (DGA) are typical diamide compounds that have been widely studied for separation of MA and Ln(III) [1][2]. Recently, much attention has been paid to *N,N,N',N'*-Tetraalkyl-3,6-dioxaoctanediamide (DOODA) as a novel extractant [3]. Malonamide, DGA, and DOODA have 2, 3, and 4 donor oxygen atoms which can strongly co-ordinate to Ln(III) and An(III) ions, respectively. *N,N,N',N'*-Tetraoctyl-diglycolamide (TODGA) and *N,N,N',N'*-tetraoctyl-3,6-dioxaoctanediamide (DOODA-C8) have two octyl chains. They show an opposite tendency in the distribution ratios (*D*) for Ln(III) series, i.e. DOODA-C8 has higher *D* values for lighter Ln(III), whilst TODGA has those for heavier Ln(III) [4].

**Figure 1: Neutral amide compounds for separation of MA by solvent extraction**



In most extractions of metal ions from aqueous phase to organic phase, metal ions are extracted through the formation of uncharged complexes with the extractant and anions such as nitrate or perchlorates as expressed in Equation (1).



The number of extractant molecules or anions participating in the solvent extraction can become known by means of analyses of  $\log D$ - $\log[X]$  plots ( $[X]$ : the concentrations of the extractant or anions). The  $\log D$ - $\log [L]$  plots for TODGA and DOODA-C8 showed that approximately three TODGA, two DOODA-C8 molecules, and three nitrate ions participate in the extraction of Ln(III) from nitric acid solution to *n*-dodecane. A similar variation in stoichiometry has also been reported on the basis of the EXAFS study, which showed that 3 – 4 TODGA molecules are present around Ln (III) in non-polar diluents [5]. If they fully co-ordinate to the Ln(III), the co-ordination number exceeds more than 14, which is too high compared to that found in crystal structure. However, the structures in solutions which can satisfy the number of extractant molecules and anions participating in the extraction process have not been clarified. In order to understand the extraction mechanism and factors for controlling selectivity to metal ions, it is important to know accurate stoichiometry and the structure of the extracted species. In this study, complex formation of Ln (III)-nitrate (Ln: La and Eu) with DOODA and their structures were examined by multinuclear NMR and single-crystal X-ray diffraction.

## Experimental

Ln (III) nitrate salts, <sup>15</sup>N enriched sodium nitrate and acetonitrile-*d*<sub>3</sub> (CD<sub>3</sub>CN) were purchased from KANTO Chemical Co. Inc., Aldrich and ACROS, respectively. DOODA-C2 and -C8 were provided by JAEA (Japan Atomic Energy Agency). Other chemicals were of reagent grade and were used without further purification. NMR spectra were recorded on a JEOL ECX 400 spectrometer. Tetramethylsilane (TMS) was used as an internal standard

for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Sample solutions for NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) were prepared by dissolving Ln(III) complexes in  $\text{CD}_3\text{CN}$ , and their spectra were recorded in the range of  $-35$  to  $25^\circ\text{C}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals were assigned by DEPT,  $^1\text{H}$ - $^1\text{H}$  COSY and HMQC. The ligand exchange reactions based on NMR line-broadening method were analysed by using the WINDNMR computer programme. Single-crystal X-ray analyses were carried out at  $173\text{ K}$  using Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71075$ ). The structures of complexes were solved by Patterson and Fourier methods, and refined by full-matrix least-squares against  $F^2$  for all data using SHELXTL software. A summary of the crystallographic data and experiment details are listed in Table 1.

**Table 1: Summary of crystallographic data of Ln (III)-DOODA-C2 complexes**

	$[\text{La}(\text{DOODA-C2})_2(\text{CH}_3\text{OH})_2]^{3+} [\text{La}(\text{NO}_3)_6]^{3-}$	$[\text{Eu}(\text{DOODA-C2})(\text{NO}_3)_3]$
Empirical Formula	$\text{C}_{31}\text{H}_{68}\text{N}_{10}\text{O}_{29}\text{La}_2$	$\text{C}_{14}\text{H}_{30}\text{O}_{14}\text{N}_5\text{Eu}$
Formula weight	1322.74	644.38
Crystal Color, Habit	colorless, block	colorless, block
Crystal Dimensions (mm)	0.25 X 0.16 X 0.12	0.27 x 0.26 x 0.18
Crystal System	triclinic	monoclinic
Space Group	P-1 (#2)	$P2_1/c$ (#14)
a / Å	12.6343(6)	10.7678(8)
b / Å	14.7809(8)	16.3155(13)
c / Å	15.3798(7)	14.5781(9)
$\alpha/^\circ$	75.3929(14)	90
$\beta/^\circ$	77.0144(12)	104.3497(18)
$\gamma/^\circ$	83.5101(14)	90
Volume ( $\text{Å}^3$ )	2703.4(2)	2481.2(3)
Z	2	4

### Syntheses of Ln(III)-DOODA-C2 complexes (Ln = La and Eu)

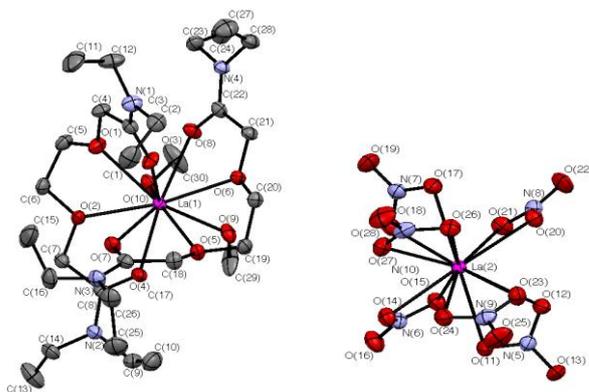
Ln(III) nitrate (1 mmol) was dissolved in 20 ml of ethyl acetate. This solution was added to ethyl acetate solution (20 ml) dissolved DOODA-C2 (3 mmol). The mixture was stirred for 2 h. Ethyl acetate was decanted off to obtain the oily complex. The complex was washed with hot ethyl acetate to remove unreacted ligand completely. The flask was connected to a vacuum pump (30 mmHg) to obtain the solid complex. The resulting complexes were further dried in a desiccator over  $\text{P}_2\text{O}_5$ . In a dram vial, approximately 15 mg of the complex was dissolved in methanol and recrystallised from a vapour diffusion method with diethyl ether as the poor solvent.

## Results and discussion

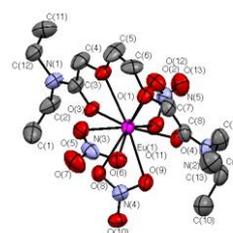
### Solid state structures

The crystal structures of La (III) and Eu (III) nitrate complexes with DOODA-C2 were characterised by single-crystal X-ray diffraction. Thermal ellipsoids drawing of their structures are shown in Figures 2 and 3. As seen from Figure 2, La(III) complex consists of  $[\text{La}(\text{NO}_3)_6]^{3-}$  anion and  $[\text{La}(\text{DOODA-C2})_2(\text{CH}_3\text{OH})_2]^{3+}$  cation, in which six nitrate ions co-ordinate to La(III) as bidentate ligand and two DOODA-C2 co-ordinate to Ln(III) as tetradentate ligand through four oxygen atoms. In contrast to the La(III)-DOODA-C2 complex, as seen from Figure 3, Eu(III) formed 10-co-ordinated complexes with one tetradentate DOODA-C2 and three bidentate nitrate ions. The co-ordination polyhedron of the complex is a distorted bicapped square antiprism. However, in each case of the crystal structures, the  $[\text{Ln}(\text{III})]/[\text{DOODA-C2}]$  ratios are 1.

**Figure 2: ORTEP view of  $[\text{La}(\text{DOODA-C2})_2(\text{CH}_3\text{OH})_2]^{3+}$  (left) and  $[\text{La}(\text{NO}_3)_6]^{3-}$  (right), probability: 50%**



**Figure 3: ORTEP view of  $[\text{Eu}(\text{DOODA-C2})(\text{NO}_3)_3]$ , probability: 50%**



### Complex formation with DOODA-C8

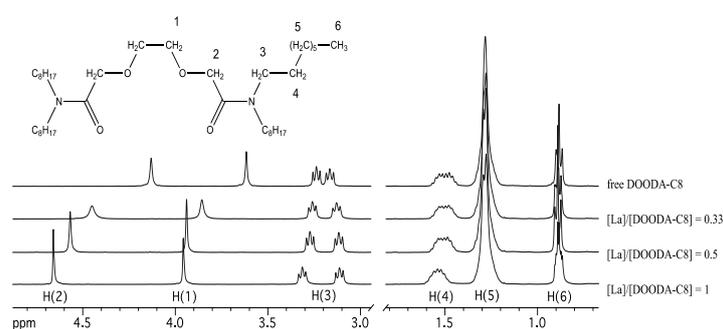
La(III) nitrate system: Complex formation between La(III) nitrate with DOODA-C8 in  $\text{CD}_3\text{CN}$  was examined by varying the ratio,  $[\text{La}]/[\text{DOODA-C8}]$ , from 2 to 0.1. Partial  $^1\text{H}$  NMR spectra of free DOODA-C8 and the sample of  $[\text{La}]/[\text{DOODA-C8}] = 1, 0.5$  and  $0.33$  are shown in Figure 4 with assignments. In free DOODA-C8,  $^1\text{H}$  NMR spectra showed 7 signals. Methylene protons in position H (1) and H (2) showed singlet signals. This indicates that the DOODA-C8 has a symmetric structure, and both H (1) and H (2) are equivalent in the  $\text{CD}_3\text{CN}$  solution.

In the  $[\text{La}]/[\text{DOODA-C8}] = 1$  and 2 system, the same number of sharp and shifted signals were observed. This suggests that DOODA-C8 co-ordinates with La(III) symmetrically and forms 1:1 metal to ligand complex. With increasing DOODA-C8 concentration (i.e. the  $[\text{La}]/[\text{DOODA-C8}]$  ratios decrease), methylene proton signals of H(1) and H(2) became broad and shifted to the up-field. The variations of the chemical shift of H(1) and H(2) are plotted in Figure 5. Only one average signal was observed, indicating that the exchange rate of the DOODA-C8 between the free and the co-ordinated site is fast on the NMR timescale. In general, one signal is observed at the weight average of the chemical shifts corresponding to two individual sites depending on their mole fractions (i.e. concentrations) of two exchanging sites. The observed chemical shift is described by the following equation:

$$\begin{aligned}\bar{\delta}_{\text{obs}} &= f_A \bar{\delta}_A + f_B \bar{\delta}_B \\ f_A + f_B &= 1\end{aligned}\quad (2)$$

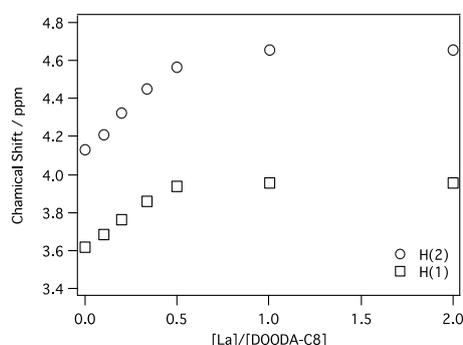
where  $f_A$  and  $f_B$  are the site populations (i.e. mole fractions) of two states,  $\bar{\delta}_A$  and  $\bar{\delta}_B$  are the chemical shift of the corresponding two sites. Calculated fractions of the individual states by Equation (2) are summarised in Table 2. The  $f_A$  and  $f_B$  represent the fractional population of free and co-ordinated DOODA-C8, respectively. The  $f_B^*$  represents a theoretical value, and  $f_{B(1:1)}^*$  and  $f_{B(1:2)}^*$  are calculated by the assumption of 1:1 and 1:2 complex formation, respectively. The  $f_B$  of H(1) and H(2) were in agreement with the theoretical value of  $f_{B(1:2)}^*$ . This result suggests the existence of 1:2 complex under the conditions,  $[\text{La}]/[\text{DOODA-C8}] < 0.5$ .

**Figure 4: Partial  $^1\text{H}$  NMR spectra of  $\text{CD}_3\text{CN}$  solutions containing La(III) nitrate and DOODA-C8 measured at 298 K with the signal assignments**



The  $[\text{La}]/[\text{DOODA-C8}]$  ratios from bottom to top are 1, 0.5, 0.33, 0 (only free DOODA-C8).  $[\text{La(III)}] = 10 \text{ mM}$ .

**Figure 5: Plots of chemical shifts of H(1) and H(2) signals vs. the  $[\text{La(III)}]/[\text{DOODA-C8}]$  ratios**



In the  $[\text{La}]/[\text{DOODA-C8}] = 0.33$  system, the signals of methylene proton, H(1) and H(2), were broadened, depending on the temperature (298 K – 238 K). This indicates that there is a fast exchange reaction with rates between the  $10^2 - 10^5 \text{ s}^{-1}$  order in this temperature range. To evaluate the pseudo first order rate constants of an exchange reaction, temperature dependence of H(1) and H(2) signals were analysed by lineshape analysis:

- the 1:2 complex forms in this system and the fraction of free DOODA is 33%;
- the exchange system is two site inter-molecular exchange between free and co-ordinated DOODA-C8.

The simulated spectra based on these assumptions were well fitted to the experimental result. The exchange rates are fast at 298 K ( $k = 1.7 \times 10^4 \text{ s}^{-1}$ ) and 238 K ( $k =$

$7.4 \times 10^2 \text{ s}^{-1}$ ). However, there is a possibility of existing intra-molecular exchange reaction in 1:2 complex, or both intra- and inter-molecular exchange.

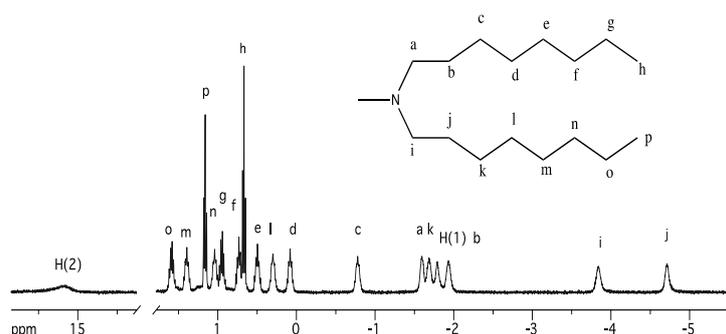
**Table 2: Calculated fractions of free and coordinated DOODA-C8**

[La]/[DOODA-C8]	Theoretical		H(1)	H(2)
	$f_{B(1:1)}^*$	$f_{B(1:2)}^*$	$f_B$	$f_B$
0.10	0.10	0.20	0.19	0.16
0.20	0.20	0.40	0.44	0.37
0.33	0.33	0.66	0.71	0.61
0.50	0.50	1	0.95	0.83
1	1		1.00	1.00

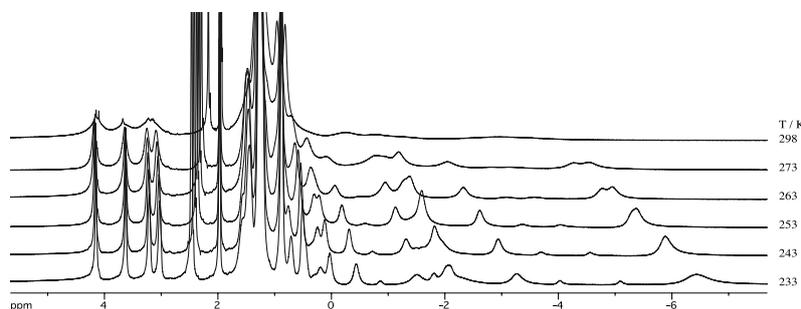
Eu(III) nitrate system: Complex formation between Eu(III) nitrate with DOODA-C8 in  $\text{CD}_3\text{CN}$  was examined by the same procedure as that in La(III) nitrate system. The  $^1\text{H}$  NMR spectra was measured by changing the ratio of  $[\text{Eu}]/[\text{DOODA-C8}]$  from 2 to 0.33.

In the  $[\text{Eu}]/[\text{DOODA-C8}] = 2$  and 1 system, 18 sharp signals were observed at 238 K as shown in Figure 6. All signals were shifted dramatically compared to free DOODA-C8. Thus, they can be assigned to co-ordinated DOODA-C8. The 16 numbers of sharp signals of the octyl chain on the amide group were observed from -5 to 1.7 ppm. Based on the analysis, it was found that one octyl chain (a-h) is located at the remote from Eu(III) and another one (i-p) is located close to the paramagnetic Eu(III) center. The signals at -1.8 and 15.2 ppm were assigned to H(1) and H(2), respectively. Only one signal corresponds to H(1) and H(2), indicating that the DOODA-C8 co-ordinate symmetrically to Eu(III). This result implies that a complex of 1:1 metal to ligand ratio is formed when the ratios are more than 1 ( $[\text{Eu}]/[\text{DOODA-C8}] > 1$ ).

**Figure 6: Partial  $^1\text{H}$  NMR spectrum of  $[\text{Eu}]/[\text{DOODA-C8}] = 1$  system at 238 K**



**Figure 7:  $^1\text{H}$  NMR spectra measured at various temperatures in the  $[\text{Eu}]/[\text{DOODA-C8}] = 0.33$  system in  $\text{CD}_3\text{CN}$**

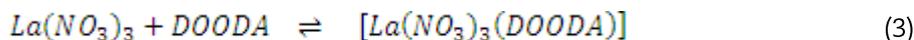


With increasing  $[\text{DOODA-C8}]$ , the signals assigned to H(1) and H(2) were extensively broadened and disappeared into the baseline, and the new signals appeared from around 2.5 to 5 ppm with increasing DOODA-C8 concentration. Other signals were broadened and finally coalesced due to the exchange between free and co-ordinated DOODA-C8. When the sample was cooled down to 238 K, the exchange reaction became slow enough and the signals could be observed separately. Figure 7 shows the temperature dependence of  $^1\text{H}$  NMR spectra of the  $[\text{Eu}]/[\text{DOODA-C8}] = 0.33$  system. The co-ordinated signals change the chemical shift with decreasing temperature because of the temperature dependency of LIS (lanthanide induced shift), while the free signals do not change their positions. Thus, the signals in the range from -6 to around 0 ppm were assigned to the signals of co-ordinated DOODA-C8, and the signals from around 1.5 to 5 ppm were assigned to free DOODA-C8. The signals in the range from 0 to 1.5 ppm could not be assigned because of overlapping.

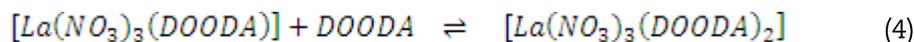
### Complex formation with DOODA-C2

La (III) nitrate system: La (III) nitrate with DOODA-C2 system showed similar phenomena to those in La (III) with DOODA-C8 system. Therefore, it was concluded that DOODA-C2 also co-ordinates to La (III) similar to DOODA-C8, and that the 1:1 and 1:2 complexes are formed under conditions  $[\text{La}]/[\text{DOODA-C2}] > 1$  and  $[\text{La}]/[\text{DOODA-C8}] < 0.5$ , respectively.  $^{15}\text{N}$  NMR spectra showed only one peak due to nitrates in any ratio and shifted downfield from the chemical shift of the free nitrate. This means that the nitrates do not dissociate from La(III).

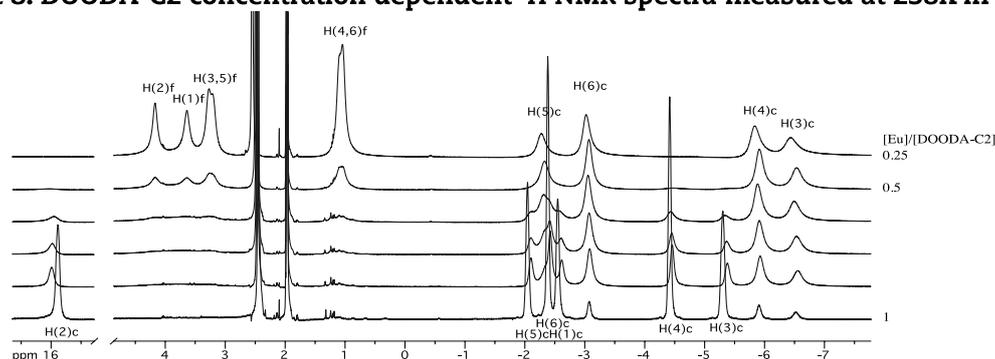
In  $[\text{La}]/[\text{DOODA}] > 1$



In  $[\text{La}]/[\text{DOODA}] < 0.5$



Eu(III) nitrate system: Figure 8 shows the concentration dependency of  $^1\text{H}$  NMR spectra of Eu(III) nitrate with DOODA-C2. Between the ratio 1 and 0.5, the signals changed drastically. In the  $[\text{Eu}]/[\text{DOODA-C2}] = 1$  system, 6 signals were observed and could be assigned to co-ordinated DOODA-C2.

**Figure 8: DOODA-C2 concentration dependent  $^1\text{H}$  NMR spectra measured at 238K in  $\text{CD}_3\text{CN}$** 

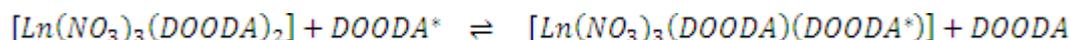
The ratios  $[\text{Eu}]/[\text{DOODA-C2}]$  from bottom to top are from 1 to 0.25.

In the  $[\text{Eu}]/[\text{DOODA-C2}] = 0.5$  system, 4 new signals appeared in the range from -7 ppm to -2 ppm, which were assigned to the ethyl chain on the amide group (i.e. H(3), H(4), H(5) and H(6)). The signals for H (1) and H (2) broadened and disappeared into baseline, and four other signals appeared from 0 ppm to 5 ppm, which were assigned to free DOODA-C2. The co-ordinated signals had total integral for approximately two DOODA-C2 molecules. The ratios of integrals of free and co-ordinated signals showed non-stoichiometric composition. This indicates that two DOODA-C2 molecules are not symmetrically co-ordinated (i.e. only by two or three oxygen atoms) due to the probably strong competition with the nitrate ions, and two DOODA-C2 molecules are in the symmetric position in the 1:2 complex.

In the  $[\text{Eu}]/[\text{DOODA-C2}] < 0.5$  system, the signals of co-ordinated H (1) and H (2) were missing. The integral of co-ordinated signals did not change, whereas that of free signals increased by increasing the  $[\text{DOODA-C2}]$ . Thus, it is clear that the 1:2 complex was formed in the condition of  $[\text{Eu}]/[\text{DOODA-C2}] < 0.5$ . EXSY spectra of the  $[\text{Eu}]/[\text{DOODA-C2}] = 0.33$  system showed the correlation at ethyl chains on the amide group between free and co-ordinated DOODA-C2. This indicates the existence of exchange between free and co-ordinated DOODA-C2.

In the Eu(III) nitrate system with DOODA-C2 showed that the DOODA-C2 is not symmetrically co-ordinated to Eu(III). To explain the structure of 1:2 complex, it is necessary to consider the co-ordination mode of DOODA by bidentate or tridentate. Three possible modes of complex formation of Ln (III) with the DOODA-C8 were considered. In case 1, DOODA associates with Ln (III) by two carbonyl oxygen to make an eleven-membered ring (bidentate). In case 2, it associates with one carbonyl oxygen and **one ether** oxygen to make one five-membered ring (bidentate). In case 3, it associates with carbonyl oxygen and two ether oxygen (tridentate) to form two five-membered rings. While in case 1 the eleven-membered ring is not stable, and in case 3 two five-membered rings cannot explain the spectra that DOODA molecule symmetrically co-ordinates to Ln(III), case 2 is the most likely species.

In the Eu(III) nitrate system with DOODA-C8 and -C2, EXSY spectra showed the correlation peak between free and co-ordinated  $^1\text{H}$  NMR signals alkyl chains on the amide group in the  $[\text{Eu}]/[\text{DOODA}] = 0.33$  system. This result suggests that the possibility of inter-molecular exchange between free and co-ordinated DOODA is represented by the following equation:



There is a possibility of intra-molecular exchange or both inter- and intra-molecular exchange occurring in the  $[Ln]/[DOODA] < 0.5$  systems. Unfortunately, in the temperature range of this study, the exchange system and pathway cannot be clarified.

## Conclusion

Based on this study it can be concluded that in the solid state, La(III)- and Eu(III)-nitrate complexes with DOODA-C2 have different structure. In  $CD_3CN$  solutions, Ln(III) (Ln: La and Eu) nitrate showed similar complex formation with DOODA-C8 and -C2. In the condition  $[Ln]/[DOODA] > 1$ , DOODA forms rigid 1:1 complex with Ln(III). In the 1:1 complex, DOODA symmetrically co-ordinates to Ln(III), thus it could be assumed that the structure of the 1:1 complex is similar to that of the crystal structure of  $[Eu(NO_3)_3(DOODA-C2)]$ . In the condition  $[Ln]/[DOODA] < 0.5$ , DOODA forms 1:2 complex with Ln(III). The structure of the 1:2 complex might have (a) one five-membered ring and (b) two DOODA molecules in the symmetric position.

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