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Study on Stabilization Effect of Neutral Soft Donor on Trivalent Lanthanide and Actinide Dicarboxylate Complexes by Time-Resolved Laser-Induced Fluorescence Spectroscopy

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Stability constants for trivalent *f*-elements of Eu, Am, and Cm with dicarboxylates containing neutral donors such as secondary amine and ether oxygen were determined by the solvent extraction method in 0.1 M $NaClO_4$ at 25 °C. Six carboxylic acids of suberic acid, 3,6-dioxaoctanedioic acid, ethylenediamine-N,N'-diacetic acid, glutaric acid, diglycolic acid, and iminodiacetic acid were examined for a systematic comparison. The hydration number of Eu^{3+} in the 1:2 complex was also determined by time resolved laser-induced fluorescence spectroscopy. The role of the softdonor atoms in the complex formation of *f*-elements and the impact of multiple softdonor atoms on An/Ln selectivity are discussed.

1. Introduction

In the separation chemistry of trivalent *f*-elements, it has been recognized that the most efficient group separation is accomplished through the agency of donor atoms softer than oxygen, and extensive efforts are being devoted to design more powerful and useful extractants having softdonor atoms. Efficient group separation is needed for the development of advanced nuclear fuel cycles that include recovery and transmutation of the minor actinides of Np, Am, and Cm from the fission products. A variety of new reagents and processes have been developed and/or are being developed around the world.[1–6] In the environment, on the other hand, the naturally-occurring humic substances contain neutral donor atoms that can coordinate heavy metal ions, and they can make highly stable water soluble complexes. However, the mechanism of the contribution of neutral atom donation to the stabilization of complex is still unclear due to the heterogeneous structures involved.

In the present study, the complex stabilization of trivalent An/Ln with simple dicarboxylates containing nitrogen as a softdonor was investigated on the basis of their stability constants and of the number of water molecules in the first coordination sphere of the central metal ion; these data were determined by solvent extraction and by time resolved laser-induced fluorescence spectroscopy, respectively.[7–8] Comparing these values suggested the possible structures of these complexes in the aqueous phase. The role of the donor atoms in the complex formation of *f*-elements and the impact of multiple donor atoms on An/Ln selectivity are also discussed.

2. Experimental

Solvent extraction for formation constants. For the solvent extraction to obtain the distribution ratio of metal ion D, an aqueous phase, containing 10^{-2} to 10^{-8} M carboxylic acid (see Figure 1) and ca. 0.1 kBq ^{241}Am and ^{242}Cm ions each, was adjusted to the desired pH with sodium hydroxide, perchloric acid and buffer reagents (a mixture of 5×10^{-3} M MES and MOPS (Dojindo)). The preparation method of the Am and Cm mixture was described previously in detail.[9] The six carboxylic acids used in this study are shown in Figure 1; suberic acid (C-2 as abbreviation), 3,6-dioxaoctanedioic acid (O-2), ethylenediamine-N,N'-diacetic acid (N-2), glutaric acid (C-1), diglycolic acid (O-1), and iminodiacetic acid (N-1). The ionic strength was adjusted to 0.1 M with $NaClO_4$. Organic solution, containing 1×10^{-3} M TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) as an extractant and TBP (tributyl phosphate) as a synergist in xylene, was pre-equilibrated with 5×10^{-3} M MES and MOPS and 0.1 M $NaClO_4$ aqueous solution. The aqueous (3.5 mL) and organic (2.5 mL) phases were brought into contact in a borosilicate glass vial with screw cap, and were shaken horizontally and gently with the aid of a mechanical shaker at 25 ± 1 °C. A shaking time of 6 hours was found to be long enough to attain the extraction equilibrium. For comparison, non-radioactive europium was extracted in the same procedure. The total recovery of these elements usually was more than 97%; no unexpected reactions such as precipitation were observed. After phase separation, the pH of the aqueous phase was measured and taken as the equilibrium pH. A combination glass electrode (D-50, Horiba) was used for pH measurement, and its reference electrode was filled with 3.6 M NaCl + 0.4 M $NaClO_4$ to avoid precipitation of $KClO_4$ at the junction of the electrode and the solution. The correction of the observed pH value to the pH_c (the negative logarithms of hydrogen ion concentrations) was made following the literature.[10] The alpha radioactivity of Am and Cm in both phases was measured by α-ray spectrometry, using an alpha spectrometer (SOLOIST, EG&G ORTEC) with a silicon surface detector, after stripping from the organic phase with 0.1 M HNO_3 solution and coprecipitation with SmF_3.[11] The concentration of Eu was determined by ICP-AES (ICPS-5000,

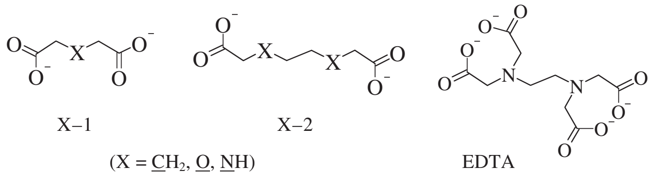

Figure 1. Scheme of chemical structures of six carboxylic acids as anion forms: C-2, O-2, N-2, C-1, O-1, and N-1, and EDTA for comparison.

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Shimadzu). All reagents were of analytical grade and used without further purification.

The extraction equilibrium constant, K_{ex}, of a trivalent metal ion, M, can be described as

$$K_{ex} = \frac{[MT_3B_l]_o[H^+]^3}{[M][HT]_o^3[B]_o^l} \tag{1}$$

where the square brackets denote the concentration, and o, T and B denote the species in the organic phase, TTA, and TBP, respectively. When the complex formation of M by TTA is negligible in the aqueous phase, the distribution ratio of M, D_0, in the absence of a complexation ligand can be expressed simply by

$$D_0 = [M]_o / [M] \tag{2}$$

On the other hand, the distribution ratio, D, in the presence of a complexation ligand (L) is expressed by

$$D = [M]_o / ([M] + [ML] + [ML_2] + \dots), \tag{3}$$

where [ML] and $[ML_2]$ are the concentrations of metal complexes in the aqueous phase. The formation constant of 1 : n complex ML_n can be expressed by

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \tag{4}$$

where n is the number of ligand molecules in the complex. When it is unlikely that more than three molecules coordinate to one metal ion, n is considered to be equal to one and two. Therefore, eq 5 can be described from eqs 2–4. From the plots of log D *vs.* log [L] in eq 6, the free parameters of β_1, β_2, and D_0 can be obtained by a least-square fitting analysis.[12]

$$\frac{D_0}{D} = 1 + [L]\beta_1 + [L]^2\beta_2 \tag{5}$$

$$\log D = \log D_0 - \log (1 + [L]\beta_1 + [L]^2\beta_2) \tag{6}$$

Time-resolved laser-induced fluorescence spectroscopy (TRLFS). The Eu^{3+} in the solution was excited to the $^5L_6$ state by a pulsed laser beam at 394 nm, and the emission from the $^5D_0$ state to the ground state ^7F manifold ($^7F_1$), 592 nm, was measured. A 394 nm pulsed laser beam was obtained with a pulsed 308 nm output of a Lambda Physik COMpex 201 XeCl excimer laser pumping PBBO (Lambda Physik) in a dioxane solution in a Lambda Physik SCANmate 2 dye laser head. The pulse power was typically 3–5 mJ for 394 nm and the pulse width was about 15 ns. The solution sample was taken in a standard 1 cm fluorimetric cell for luminescence measurement. The emission light was collected at 90° in an Oriel 77257 monochromator and detected by a Hamamatsu R928 photomultiplier tube. The whole emission wavelength range was observed. The signal was fed into a digitizing oscilloscope, which was connected to a computer through a GP-IB interface. All of the luminescence decays observed in this work were analyzed by single-exponential curves.

The apparent and average hydration number of Eu^{3+} (N_{H_2O}) can be determined from the decay constants (k'_{obs}) of the luminescent excited state of Eu^{3+} using eq 7.[7]

$$N_{H_2O} = 1.05 \times 10^{-3}\, k'_{obs} - 0.44. \tag{7}$$

The $N_{H_2O,1:2}$ (for 1:2 complex) was determined at a given pH_c by taking into account the fractional abundances of Eu species Eu^{3+}, EuL^+, and EuL_2^{2-} (L = dicarboxylate), which were calculated from the stability constants of the complexes and the acid dissociation constants of the ligands.

The contribution from the ligands for C-1, C-2, O-1 and O-2–namely, that from the oxygen donors of carboxyl groups and ether–to the de-excitation of the excited luminescence is negligible.[7] In the case of N-1 and N-2 complexes, the ligands contain amino groups capable of coordination with the Eu^{3+} ion. The N-H oscillators in the ligand have vibronic frequencies closely similar to those of water O-H oscillators, and they contribute to nonradiative deactivators of the excited Eu(III). Lis and Choppin estimated that the deactivating frequency of a bound N-H oscillator was about 1.5 times higher than that of a bound water O-H oscillator for Eu by using dicarboxylate-containing imino groups.[13] Thus, special consideration of the effect of Eu-N-H bonding on the deexcitation process is required.

3. Results and Discussion

The log β_1 and log β_2 values for six ligands containing N and O donors were obtained, as summarized in Table 1. Here, the distribution coefficient to obtain the β did not change significantly by the addition of pH buffers containing a sulfonic acid group. The stability constants increased in the order of C-1 < O-1 < N-1 and C-2 < O-2 < N-2 for each metal ion. This general tendency depends on the additional neutral donors oxygen and nitrogen, which can donate to the metal ion when the terminal carboxylates are bound to that ion. In particular, the lone pair electrons on the secondary amines show a highly nucleophilic and basic character due to their high electron density, while those on the ether oxygen show a weaker basicity in the Brønsted sense. The variation in the electric charge on terminal carboxylate groups due to the electron-withdrawing effect by N and O donors can be ignored, since the alkyl chains are present between them. Thus, it was concluded that the increase of β was caused by the additional coordination of neutral donors to the central metal ion.

TABLE 1: Summary of Stability Constants of Dicarboxylate Complex (X-1 and -2), $N_{H_2O,1:2}$, and R at 25 °C and I = 0.1 M ($NaClO_4$)

		C-1	O-1	N-1	C-2	O-2	N-2	EDTA[16]
Eu	log β_1	3.24 ± 0.04	5.57 ± 0.02	7.02 ± 0.09	2.96 ± 0.05	5.18 ± 0.13	9.78 ± 0.10	17.29
	log β_2	4.76 ± 0.11	9.42 ± 0.03	12.6 ± 0.13	4.47 ± 0.16	8.90 ± 0.08	17.9 ± 0.05	
	pH_c	5.30	5.35	5.55	5.30	5.30	5.55	
	$N_{H_2O,1:2}$	2.8	2.0	2.2		2.0	0.5	
	R	3.1	3.5	3.4		3.5	4.2	
Am	log β_1		6.07 ± 0.11	7.04 ± 0.04	2.92 ± 0.12	5.39 ± 0.12	10.21 ± 0.58	17.8
	log β_2		10.23 ± 0.14	12.42 ± 0.05	4.49 ± 0.27	8.59 ± 0.18	19.59 ± 0.23	18.1
Cm	log β_1		6.08 ± 0.13	7.12 ± 0.05	3.00 ± 0.08	5.55 ± 0.12	10.76 ± 0.71	
	log β_2		10.62 ± 0.12	12.58 ± 0.06	4.66 ± 0.14	8.90 ± 0.57	20.09 ± 0.38	
	pH_c		5.40	5.60	5.35	5.50	5.60	

Tetradentate for N-2 and O-2, tridentate for N-1 and O-1, and bidentate for C-1 (and C-2) at its full coordination

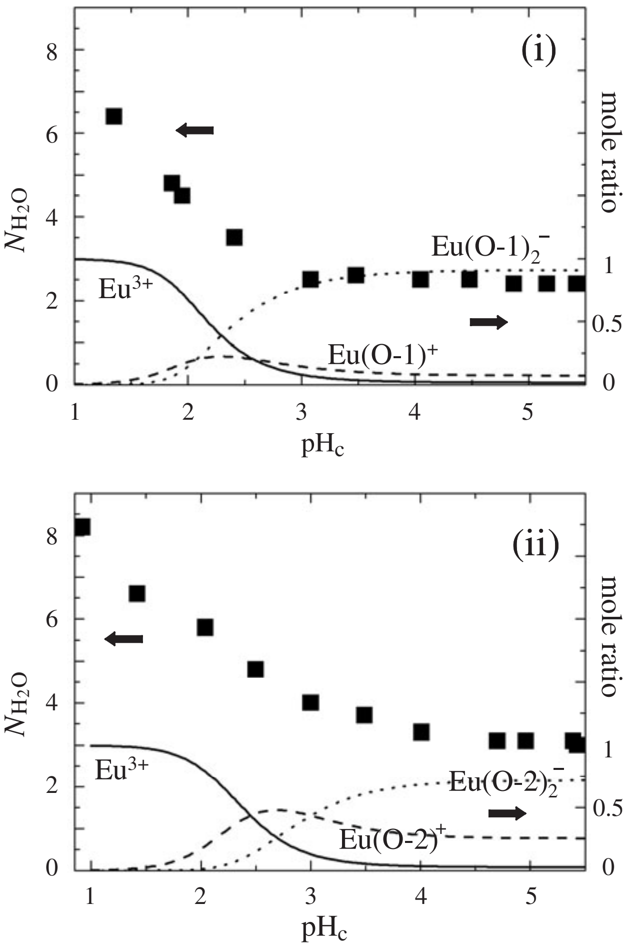

Figure 2. Fractional abundances of (i) Eu/O-1 and (ii) Eu/O-2 and the N_{H_2O} measured by TRLFS, as a function of pH$_c$. The pH$_c$ for the determination of $N_{H_2O,1:2}$ is the same as that for the solvent extraction.

Figure 2 shows the N_{H_2O} and fractional abundance of Eu/O-1 and /O-2 species as a function of pH$_c$. The N_{H_2O} obtained in acidic pH was 9.0 ± 0.5, which agreed with the literature value for the hydrated Eu^{3+} ion in H$_2$O.[7] The apparent hydration number N_{H_2O} decreases with an increase of the ratio of higher order complexes.

The summary of $N_{H_2O,1:2}$ for 1:2 complexes, which are calculated on the basis of the fractional abundance, is shown in **Table 1**. From the extremely high log β values for ligands containing N donors, it is suggested that the secondary amine groups may coordinate directly to the Eu ion. Then, in the calculation of N_{H_2O} for N-ligands, the contribution of a bound N-H oscillator to the luminescence deactivation is assumed to be as high as 1.3 times that for the O-H oscillator by taking into account the literature values.[13, 14]

The number of dehydrated water molecules R in the coordination of one ligand is defined as follows:

$$N_{H_2O,1:2} + 2R \equiv N_{H_2O,1:1} + R = 9.0, \qquad (8)$$

where it is assumed that R is independent of the order of the complex. R values are listed in Table 1. From the $N_{H_2O,1:2}$ of 0.5 for N-2, the R is calculated to be 4.2, and this is reasonable for a tetradentate ligand. Also, the values of log β_1 and log β_2 for this complex are the highest in this work, supporting the high stabilization by the two amino groups. By considering the present results of β and R, a snapshot of the possible structures of the europium carboxylate complexes is postulated and illustrated in Figure 3.

In the case of N-2, the stabilization by nitrogen donors is more significant in the trivalent actinides than in the lanthanides as shown in Table 1: namely, Eu(N-2)$^+$ < Am(N-2)$^+$ < Cm(N-2)$^+$ and Eu(N-2)$_2^-$ < Am(N-6)$_2^-$ < Cm(N-2)$_2^-$. The log β_1s for Am and Cm are 3 and 10 times higher than that for Eu, in spite of their similar ionic radii.[15] It is interesting to compare the present result for N-2 with the result for EDTA (ethylenediaminetetraacetic acid), which is known as a hexadentate nitrogen-containing ligand consisting of two tertiary amines and four carboxyl groups. The structural frame of EDTA can be considered as the frame of N-2 (Figure 1) with the addition of two extra carboxyl groups. The literature values of log β_1 for EDTA are 17.29 (Eu), 17.8 (Am), and 18.1 (Cm),[16] much larger than that for N-2. Thus, the selectivity of Am/Eu for EDTA, defined as Δlog β_1 (= log $\beta_{1,Am}$ − log $\beta_{1,Eu}$), is obtained to be 0.51. This value agrees well with the present finding of 0.43. In the cases except for N-2, however, the selectivity between Eu and Am/Cm is not significantly observed.

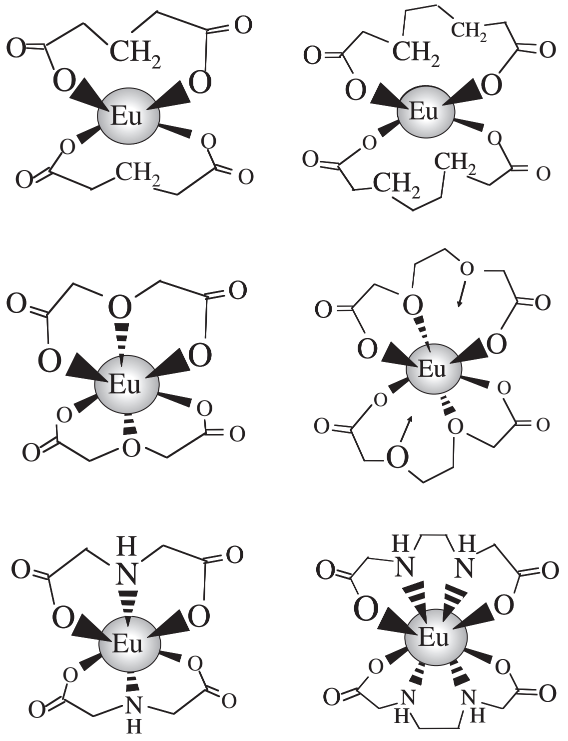

Figure 3. Snapshot of possible structures for 1:2 complexes expected from the values of $N_{H_2O,1:2}$ and log β_2. The solid and broken triangles denote an ion-ion and ion-dipole interaction, respectively. The display of water molecules was omitted.

The values of R for N-1 and O-1 are obtained as 3.4 and 3.5, respectively. They may be consistent with the chemical structure in which each ligand can coordinate as a tridentate. On the other hand, the R for C-1 is 3.1, which is rather higher than expected from its bidentate structure. When the C-1 coordinates to Eu^{3+} in the most stable chemical formation, an alkyl chain may needed to exclude the hydrated water molecules. In other words, this extra dehydration needs some energy, as reflected in the low value of β.

In Figure 4, the logarithms of β_1 and β_2 for C-1 (m = 3) and C-2 (m = 6) complexes are plotted in comparison with the reference data of dicarboxylic acids containing a different alkyl length (m = 0, 1 for Eu, and 2, 4 for Gd).[16, 17] Although some reference data are not for Eu but for Gd, it is found that the values change continuously over all alkyl chain lengths as shown by the broken curves. The values decrease significantly at the shorter lengths with the increase of alkyl length. From the result in Figure 4 at the shorter length and from the R for the bidentate C-1, the decrease of the βs is caused by the additional energies for the change of the ligand conformation and for the dehydration by an approach of neutral alkyl chain. At the longer length, the log β_1 and log β_2 fall into almost constant values 3 and 4.5, respectively. Thus, the additional energies for the coordination reaction seem constant at the longer

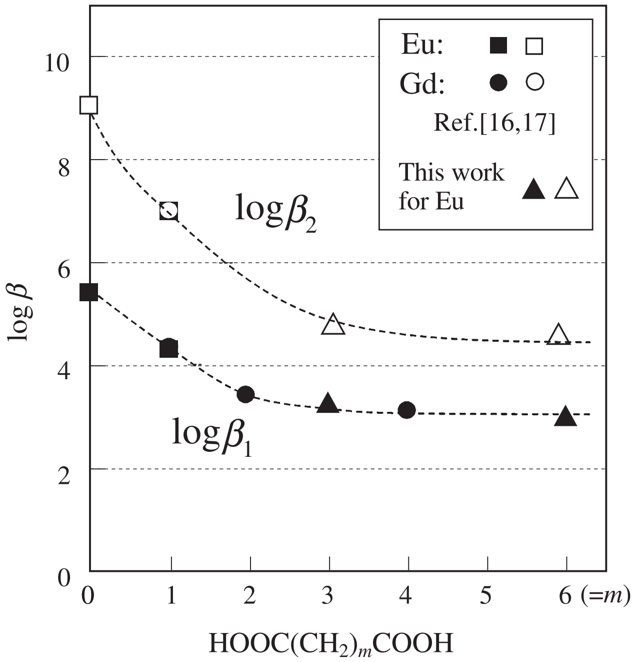

Figure 4. Dependence of alkyl chain length (m) in dicarboxylic acids on the stability constants of Eu- and Gd-complexes[16,17] and the present data for Eu.

length. The R for other ligands with different alkyl chain lengths is now under investigation for confirmation.

The R for O-2 (3.5) is as same as that for O-1. This means that three water molecules are excluded by one O-2 ligand, as in the case of O-1. By comparing the log β of O-1 and O-2, it is found that these values are close to each other, in spite of the higher number of coordination sites for O-2. As indicated in Figure 3, the two neutral ether oxygens in O-2 may not coordinate strongly to the Eu^{3+} ion, since the donating power of ether oxygen to the Eu^{3+} ion is relatively low compared with that of amine. The additional energy stability mentioned above may also contribute to the destabilization of the O-2 complex.

4. Conclusions

For a systematic comparison, the log β_1 and log β_2 values of trivalent f-elements for six dicarboxylates containing N and O donors were obtained in the present study. By taking into consideration the study of TRLFS, it was shown that the neutral donors in these dicarboxylates enhance the stabilization of the metal complexes by the presence of negatively charged oxygen donors in terminal carboxyl groups and cause a higher selectivity between lanthanides and actinides. Especially, softdonor atoms such as secondary-amine-group nitrogens, which can coordinate covalently to $5f$-elements, show a higher selectivity of $5f$ elements over $4f$ elements than the harder oxygen atom. Further study should be performed to understand the selectivity and stabilization mechanisms of organic ligands with neutral donors such as nitrogen, oxygen and sulfur, in different chemical frames such as alkyl chains and aromatic rings.

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