Several Factors Influencing the Stability of Extracted Species in Synergistic Extraction of Lanthanide(III) with Pivaloyltrifluoroacetone and 2,2'-Bipyridyl

Tadahisa SAITO, Kazuaki SATO, Mitsunobu MIRATSU, Izuru MATSUBAYASHI, Masayuki INOUE, and Yuko HASEGAWA[†]

Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

The stability constants and the hydration number of a complex between tris(pivaloyltrifluoroacetato)lanthanide(III) (LnA₃) and 2,2'-bipyridyl (B), LnA₃B, and the complexation heat were determined across the Ln series by a solvent-extraction technique, Karl Fischer coulometry, and calorimetry, successively. The number of water molecules released from LnA₃ upon the complexation with B as well as the values of the stability constant increased along with increasing Ln atomic number to around Dy(III); *via* a maximum, it decreased. It is concluded that the largest stability constant of the complex of Ho(III) or this vicinity is derived from the strongest bond energy, due to the fitness between LnA₃ and B. This conclusion was supported by the trend of the variation of the entropy change as well as that of the hydration number across the Ln series.

(Received August 7, 2010; Accepted October 18, 2010; Published November 10, 2010)

Introduction

It is generally accepted that the extraction of lanthanides(III) (Lns(III)) is synergistically enhanced with most β -diketones (HA) and Lewis bases (B), due to complexation between tris(β -diketonato)Ln(III) (LnA₃) and B.¹⁻¹¹ The synergistic effectiveness is related to two process; the extraction of Ln(III) as LnA₃ from the aqueous phase into the organic phase and complexation between LnA₃ and B in the organic phase. Accordingly, the synergistic extraction constant, $K_{\text{ex}31} = [\text{LnA}_3\text{B}]_{\text{o}}[\text{H}^+]^3[\text{Ln}^{3+}]^{-1}[\text{HA}]_{\text{o}}^{-3}[\text{B}]_{\text{o}}^{-1} = K_{\text{ex}30} \times \beta_1$, where $K_{\text{ex}30}$ is the extraction constant of LnA₃ ($K_{\text{ex}30} = [\text{LnA}_3]_{\text{o}}[\text{H}^+]^3[\text{Ln}^{3+}]^{-1}[\text{HA}]_{\text{o}}^{-3}$) and $\beta_1 (= [\text{LnA}_3\text{B}]_{\text{o}}[\text{LnA}_3]_{\text{o}}^{-1}[\text{B}]_{\text{o}}^{-1})$, where the subscript "o" indicates the species in the organic phase; the lack of a subscript indicates the species in the aqueous phase. There are many reports that in synergistic extraction with HA and monodentate B, such as tributylphosphate^{1,2} and carboxylic acids,³⁻⁶ the extractability does not change much across the Ln series, although extraction with β -diketone alone increases along with increasing Ln atomic number. On the other hand, there are several reports that in extraction with HA and bidentate B, such as 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy), the extractability increases along with increasing Ln atomic number,⁷⁻¹¹ because of the formation of a more stable complex for heavier Ln(III), even if the same β -diketone is used in the extraction with both Lewis bases. The difference has been explained in terms of the variation pattern of the stability of the complexes formed between monodentate and bidentate Lewis bases across the Ln series; the former forms a less-stable

complex, and the latter forms a more stable complex with LnA₃ along with increasing Ln atomic number. To obtain some information about the different variation patterns of the extractability with monodentate and bidentate Lewis bases across the Ln series, the complexation heats of the extracted species, LnA₃B, as well as the stability constants of Ln(tta)₃ (Htta = 2-thenoyltrifluoroacetone) adducts with phen (B)¹⁰ in CHCl₃ across the Ln series have been measured. The complexation heat varied from endothermic to exothermic along with increasing Ln atomic number. This suggests that phen forms a stronger bond with the heavier Lns(III). Besides from the variation of the entropy change across the Ln series, the involvement of water molecules coordinated to Ln(III) upon the extraction with β -diketone was suggested, and later it was proved by measuring the hydration number of LnA₃B.¹¹⁻¹³ Decreasing stability constants of the Ln(tta)₃ complex with a weak Lewis base was explained in relation to the released water molecules.⁶ Complexation of Ln(III) is strongly influenced by water molecules, either in aqueous solutions or in organic solvents, because Ln(III) is a typical hard Lewis acid, and has strong affinity to O donor atoms. When the relation of water molecules coordinating to LnA₃ and the strength of Lewis basicity of ligands to the complexation of LnA₃ is elucidated, it would offer effective information to separate a proper Ln(III) among all Lns(III) selectively. Thus, in the present work, pivaloyltrifluoroacetone (Hpta) and bpy have been selected as HA and B, respectively, and the complexation between LnA₃ and B in CHCl₃ has been studied systematically by measuring the stability constants, the hydration number of LnA₃B, and also the complexation heats across the Ln series.

[†] To whom correspondence should be addressed.
E-mail: yhasegaw@rs.kagu.tus.ac.jp

Experimental

Reagents and chemicals

All reagents were of analytical grade. Hpta and bpy were purchased from Dojin Laboratories, and Nacalai Tesque, Inc., respectively. Lanthanide(III) oxides (purity >99.9%) were purchased from the following companies: from Shin-Etsu Chemical Co. (La and Gd), Nacalai Tesque (Nd), Inc. and Mitsuwa Chemicals (other Lns). The Ln(III) aqueous solutions were prepared by dissolving the respective oxide in a little excess of perchloric acid. The exact concentration of Ln(III) was determined by titration with an EDTA solution at pH 5 using Xylenol Orange as an indicator. Chloroform was washed with deionized water just before use. Other reagents were used without purification.

Procedure

Most experiments were performed in a thermostatted room at 298 ± 1 K. The total ionic concentration was adjusted to 0.1 M ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) with sodium perchlorate.

Extraction of Ln(III) with Hpta and/or bpy. Six milliliters of aqueous solution containing Ln(III) ($2 \times 10^{-5} - 4 \times 10^{-3} \text{ M}$) were vigorously shaken with an identical volume of a chloroform solution containing Hpta (0.02 – 0.1 M) and/or bpy (0 – 0.03 M) for 1 h. Then, two phases were centrifuged. Lanthanide(III) remaining in chloroform was back-extracted into 0.1 M perchloric acid, and Ln(III) transferred into aqueous phases was diluted with 0.1 M HClO_4 by a factor of 10 to protect it from any influence of the Na ion. Then, the concentration was measured by ICP-OES (Hitachi P-4000). The distribution ratio, D , was denoted as the total concentration ratio of Ln(III) between both phases. The hydrogen ion concentration ($\text{pC}_\text{H} = -\log[\text{H}^+]$) at equilibrium was measured potentiometrically using a solution containing $1.00 \times 10^{-2} \text{ M}$ perchloric acid at 0.1 M (H, Na) ClO_4 as the standard $\text{pC}_\text{H} = 2.00$ (Corning, Model 445).

Hydration number of Ln(III) with Hpta and/or bpy. The procedure was performed in a similar way as described elsewhere.^{11–13} Lanthanide(III) was extracted from 6.0 mL of a 0.030 M Ln(III) perchlorate solution at $\text{pC}_\text{H} = 4$ to 6 (for the lighter Ln(III), e.g., La(III) and Pr(III), higher pC_H 5.6 – 5.7, for the heavier ones, e.g., Yb(III) and Lu(III), lower pC_H 4.4 – 4.7) into an equal volume of CHCl_3 containing 0.06 or 0.08 M Hpta and/or 0.02 M bpy. The exact concentration of Ln(III) extracted into CHCl_3 was determined by ICP/OES. The water content in CHCl_3 was measured by Coulometric Karl Fischer titration (Hiranuma Sangyo Co., Ltd., Model AQ-7).

Calorimetric titration of Ln(III) with Hpta and/or bpy. Eight milliliters of an aqueous solution containing Ln(III) (0.02 M) at pC_H 5 – 6 were shaken with an identical volume of CHCl_3 containing Hpta (0.03 M) for 1 h. After centrifuging, a portion of the organic phase was diluted as much as 5 or 10 times with CHCl_3 , and it was then used as a sample solution. Into a sample solution of 3.00 mL placed in a glass vessels, $3.00 \times 10^{-2} \text{ M}$ bpy solution of 10.0 μL was injected ten times. The heat change at each injection was measured by an isothermal titration microcalorimeter (TAM 2277; Thermometric AB, Sweden) controlled by Digitam 4.1 software.

Results and Discussion

Before studying the extraction of Ln(III), the dissociation and distribution constants of bpy (= B) were determined; A chloroform solution containing a constant concentration of B

was shaken with 0.1 M NaClO_4 at different pC_H values until they attained at extraction equilibrium. The concentration of B remained in CHCl_3 , and that transferred into aqueous phase were determined by measuring the absorbance of the CHCl_3 directly and after being adjusted pC_H to basic and reextracted into CHCl_3 at 283.4 nm (the molar absorptivity, 1.44×10^4), respectively. At the same time pC_H was also measured. When B distributes between organic and aqueous phases, the distribution ratio of B can be represented as

$$D = \frac{[\text{B}]_0}{[\text{B}] + [\text{HB}^+]}. \quad (1)$$

Introducing the dissociation constant ($K'_\text{a} = [\text{H}^+][\text{B}][\text{HB}^+]^{-1}$) and the distribution constant ($K'_\text{d} = [\text{B}]_0[\text{B}]^{-1}$) into Eq. (1),

$$\log D = \log K'_\text{d} - \log(1 + [\text{H}^+]K'_\text{a}^{-1}) \quad (2)$$

is obtained. The value of $\text{p}K'_\text{a}$ was also determined by analyzing the data based on the mass balance of B and H^+ when a B/ CHCl_3 solution was shaken with 0.1 M NaClO_4 at various pC_H values. The $\text{p}K'_\text{a}$ values determined by both methods agreed well. As $\log K'_\text{d}$, 2.66 ± 0.03 and as $\text{p}K'_\text{a}$, 4.31 ± 0.01 were obtained, respectively.

Extraction of Ln(III) with Hpta and/or bpy

Plots of $\log D$, the distribution ratio of Ln(III), against the Hpta (HA) concentration at a constant pC_H as well as that against pC_H at a constant HA concentration (0.10 or 0.20 M) showed straight lines having a slope of +3. It was confirmed that three molecules of proton as well as HA participated for the extraction of Ln(III); $\log D$ changes linearly to 3pC_H , and also to $3\log[\text{HA}]_0$. Accordingly the extraction of LnA_3 and the extraction constant, K_ex , described in "Introduction" can be represented as follows:

$$K_\text{ex} = D[\text{H}^+]^3[\text{HA}]_0^{-3}, \quad (4)$$

i.e., $\log K_\text{ex} = \log D - 3(\text{pC}_\text{H} + \log[\text{HA}]_0)$. The concentration of HA in the organic phase can be calculated from the mass balance of the β -diketone as follows:

$$A_\text{T} = [\text{HA}] + [\text{HA}]_0 + [\text{A}^-] + 3[\text{LnA}_3]_0, \quad (5)$$

$$[\text{HA}]_0 = \frac{A_\text{T} - 3[\text{LnA}_3]_0}{K'_\text{d}^{-1}(1 + K'_\text{a}/[\text{H}^+]) + 1}, \quad (6)$$

where K_d ($\log K_\text{d} = 2.51$) and K_a ($\text{p}K_\text{a} = 7.01$) are the distribution constant ($K_\text{d} = [\text{HA}]_0/[\text{HA}]$) and the dissociation constant of Hpta ($K_\text{a} = [\text{H}^+][\text{A}^-][\text{HA}]^{-1}$), respectively.¹⁴ The extraction constants of LnA_3 obtained in the present study are listed in Table 1 together with the standard deviation. The constant increases along with increasing Ln atomic number.

When Ln(III) was extracted with HA and B, the extractability was remarkably enhanced. Figure 1 shows several examples of the correlation between the distribution ratio and the concentration of B at equilibrium, where the concentration of the protons and HA was normalized. Since the slope of the plot of $\log(D[\text{H}^+]^3[\text{HA}]_0^{-3})$ vs. $\log[\text{B}]_0$ was unity for all Lns(III) studied, and the distribution ratio was much higher in the extraction with HA and B at a same pC_H and $[\text{HA}]_0$ than that with HA alone, the first stability constant of the LnA_3 adduct with B, β_1 , can be obtained from the following equation by

Table 1 Extraction constant (K_{ex}) of $\text{Ln}(\text{pta})_3$ and stability constants, hydration number of LnA_3B $n\text{H}_2\text{O}$, and the number of water molecules released from LnA_3 upon complexation

$\text{Ln}(\text{III})$	$\log K_{\text{ex}}^a \pm \sigma$	$\log \bar{\beta}_1^b \pm \sigma$	$n \pm \sigma$	$n - n_0$
La	-13.05 ± 0.06	4.5 ± 0.1	0.30 ± 0.03	1.90
Pr	-11.78 ± 0.08	5.19 ± 0.08	0.17 ± 0.03	1.97
Nd	-11.42 ± 0.05	5.27 ± 0.08	0.20 ± 0.03	1.99
Sm	-10.61 ± 0.05	5.61 ± 0.05	— ^c	—
Eu	-10.48 ± 0.05	5.76 ± 0.06	0.15 ± 0.04	2.15
Gd	-10.58 ± 0.08	5.8 ± 0.1	0.17 ± 0.01	2.39
Tb	-10.12 ± 0.09	5.9 ± 0.1	0.14 ± 0.02	2.35
Dy	-10.04 ± 0.08	6.05 ± 0.09	—	—
Ho	-9.92 ± 0.06	6.03 ± 0.07	0.11 ± 0.03	2.29
Er	-9.64 ± 0.02	5.97 ± 0.04	—	—
Tm	-9.34 ± 0.04	5.89 ± 0.05	0.12 ± 0.02	2.06
Yb	-9.07 ± 0.03	5.79 ± 0.05	0.12 ± 0.02	1.86
Lu	-9.17 ± 0.06	5.75 ± 0.05	0.10 ± 0.02	1.96

a. $K_{\text{ex}} = [\text{LnA}_3]_0[\text{H}^+]^3[\text{Ln}^{3+}]^{-1}[\text{HA}]_0^{-3}$.

b. $\bar{\beta}_1 = [\text{LnA}_3\text{B}]_0([\text{LnA}_3]_0[\text{B}]_0)^{-1}$.

c. No data.

Fig. 1 Extraction enhancement of $\text{Ln}(\text{III})$ with Hpta in the presence of bipyridyl. ○, Pr; ●, Nd; △, Sm; ▲, Tb; □, Ho; ■, Yb.

assuming the dominant extracted species being as only LnA_3B :

$$D = \frac{K_{\text{ex}} \bar{\beta}_1 [\text{B}]_0 [\text{HA}]_0^3}{[\text{H}^+]^3}. \quad (7)$$

Here, $[\text{B}]_0$ can be calculated from the mass balance of the corresponding species as

$$B_T = [\text{HB}^+] + [\text{B}] + [\text{B}]_0 + [\text{LnA}_3\text{B}]_0, \quad (8)$$

$$[\text{B}]_0 = \frac{B_T - [\text{LnA}_3\text{B}]_0}{K_d'^{-1} \left(1 + \frac{[\text{H}^+]}{K_a'} \right) + 1}. \quad (9)$$

The stability constants of the complex formed between LnA_3 and B are also listed in Table 1. The constants increase with increasing atomic number from light to the middle of the Ln

Table 2 Water content in CHCl_3 containing the $\text{Ho}(\text{pta})_3$ adduct with bpy prepared by solvent extraction and the hydration number of $\text{Ho}(\text{pta})_3$ obtained

Extraction condition				Concentration at equilibrium			
$[\text{Ho}(\text{ClO}_4)_3]_T / \text{mM}$	pC_H	$[\text{HA}]_T / \text{mM}$	$[\text{B}]_T / \text{mM}$	$[\text{Ho}(\text{III})]_0 / \text{mM}$	$[\text{H}_2\text{O}]_0 / \text{mM}$	$[\text{H}_2\text{O}]_{\text{CHCl}_3} / \text{mM}$	n
31.1	5.5	80.0	26.0	25.9	73.1	71.4	0.07
31.1	4.9	80.0	26.0	25.8	74.5	71.6	0.11
31.1	4.9	80.0	26.0	25.3	75.3	71.7	0.14
31.1	5.0	80.0	26.0	25.8	75.2	71.4	0.15
31.6	5.2	60.0	19.5	19.5	72.9	71.4	0.08
31.6	4.9	60.0	19.5	18.9	73.6	71.6	0.11
31.6	5.1	60.0	19.5	19.3	74.0	71.6	0.12
31.6	5.0	60.0	19.5	18.9	74.1	71.7	0.13

series, although in a more detailed observation, the constant had a maximum in the middle of the Ln series and then they gradually decreased. This point, in other words, the increase of the stability constants along with increasing Ln atomic number, is quite different from the variation of the constant of the monodentate Lewis base complex, because they generally decrease. When the reason why the stability constant increases along with increasing Ln atomic number and also the constant gives a maximum in a vicinity of $\text{Ho}(\text{III})$ is elucidated, the selective extraction of a certain $\text{Ln}(\text{III})$ might be possible. Then, as the next step, the residual hydration number of LnA_3B and the complexation heat were measured.

Effect of water molecules coordinated to $\text{Lns}(\text{III})$ on complexation between $\text{Ln}(\text{pta})_3$ and bpy

When an aqueous solution containing 0.03 M $\text{Ln}(\text{III})$ at pC_H 5 was shaken with a CHCl_3 solution consisting of 8×10^{-2} M HA and 2.6×10^{-2} M B, almost 2.5×10^{-2} M $\text{Ln}(\text{III})$ was extracted. The residual hydration number was calculated from dividing concentration of water coordinated to $\text{Ln}(\text{III})$, with the concentration of $\text{Ln}(\text{III})$ extracted into the CHCl_3 , i.e.,

$$n = \frac{[\text{H}_2\text{O}]_{0,\text{total}} - [\text{H}_2\text{O}]_{\text{CHCl}_3}}{[\text{Ln}(\text{III})]_0}, \quad (10)$$

where $[\text{H}_2\text{O}]_{0,\text{total}}$ is the water concentration in CHCl_3 extracted $\text{Ln}(\text{III})$ and $[\text{H}_2\text{O}]_{\text{CHCl}_3}$ is the background, i.e., saturated water solubility in CHCl_3 . A typical example of the experimental data to obtain the hydration number of LnA_3B is given in Table 2. The residual hydration numbers of LnA_3B , n , across the Ln series are also listed in Table 1. Similar to the hydration number of $\text{Ln}(\text{tta})_3\text{phen}^{13}$ and $\text{Ln}(\text{pta})_3\text{bpy}^{11}$ where $\text{Ln}(\text{III})$ is La(III) and Lu(III), almost all water molecules coordinated to $\text{Ln}(\text{pta})_3$ are removed from $\text{Ln}(\text{pta})_3$ upon complexation with bpy. In the last column in Table 1, the number of water molecules released from LnA_3 upon complexation between LnA_3 and B is given. The hydration number, n_0 , is the number of water molecules accompanied by $\text{Ln}(\text{pta})_3$.¹² The number of water molecules released, which is obtained as a balance of the hydration number between $\text{Ln}(\text{pta})_3$ and $\text{Ln}(\text{pta})_3\text{bpy}$, increases gradually among light $\text{Lns}(\text{III})$, via the maximum among the middle of the series, it then decreases. The variation in the number of water molecules released would be related to the variation in the charge density, the size and coordination number of $\text{Ln}(\text{III})$. As can be seen from Table 1, the trend of the change in number of the water molecules released is similar to that in the stability constants of LnA_3B . The variation of the stability constants

Table 3 Example of calorimetric titration data

Total titrant/mL	Q/mJ	$m_{\text{Yb(pta)}_3}/\mu\text{mol}$	$-\Delta H/\text{kJ mol}^{-1}$
0.0099	5.49	0.298	18.4
0.0199	11.6	0.596	20.6
0.0298	17.9	0.894	21.1
0.0398	24.0	1.19	20.5
0.0497	30.4	1.49	21.6
0.0597	36.5	1.78	21.0
0.0696	41.8	2.04	19.9
0.0796	44.1	2.21	14.0
0.0895	44.5	2.24	12.7

Initial conditions: cup contents, $[\text{Yb(pta)}_3] = 0.756 \text{ mM}$; volume, 3.00 mL; titrant, 30.1 mM bpy/ CHCl_3 .

across the Ln series can be qualitatively explained in terms of the entropy change derived from the number of released water molecules. Since the stability constants, or the free energy change, $-\Delta G$, are consisted of the enthalpy change and the entropy change, $-\Delta G = -\Delta H + T\Delta S$, at the next stage, the complexation heats of LnA_3 with B are measured.

Calorimetric titration of Ln(pta)_3 with bpy

In advance to measure the complexation heat, it was tried to measure the background heat change; titration with CHCl_3 to a CHCl_3 solution containing Hpta or bpy was performed, *i.e.*, CHCl_3 was injected into CHCl_3 , bpy/ CHCl_3 , and Hpta/ CHCl_3 . Further, the titration was carried out along with the injection of bpy/ CHCl_3 into CHCl_3 or Hpta/ CHCl_3 . Some heat was involved when each 10 μL of the CHCl_3 solution was dropped 10 times into 3.0 mL of the CHCl_3 solution in the reaction vessel at 0.5 $\mu\text{L/s}$. As the average, heat of 0.2 mJ at each drop was involved into all of the injections measured. This means that the heat is generated by mechanical mixing, and the heat involving the interaction between bpy and Hpta or by the dilution of bpy is much smaller.

Table 3 gives the titration data when a 0.030 M bpy solution was injected at 0.5 $\mu\text{L/s}$ into a 0.756 mM Yb(pta)_3 chelate chloroform solution of 3.00 mL. The calorimetric titration was repeated several times for each Ln(III). Titration data for several Lns(III) are shown in Fig. 2; the heat emitted was plotted as a function of the substance amounts of the complex in the solution. The heat varied from endothermic to exothermic along with increasing Ln atomic number. The emitted heat changed linearly in the substance amounts of the complex in the solution, except for the highest region. The slope should be the complexation heat or the enthalpy change:

$$Q = -\Delta H \times m, \quad (11)$$

where m is the total number moles of the first adduct in the solution. The value m was calculated as follows:

$$M_T = [\text{LnA}_3]_0 + [\text{LnA}_3\text{B}]_0 = [\text{LnA}_3\text{B}]_0(1 + \bar{\beta}_1^{-1}[\text{B}]_0^{-1}), \quad (12)$$

$$B_T = [\text{B}]_0 + [\text{LnA}_3\text{B}]_0. \quad (13)$$

Then, the bpy concentration at equilibrium can be represented as

$$[\text{B}]_0 = \frac{(B_T - M_T)\bar{\beta}_1 - 1 + \sqrt{(1 - (B_T - M_T)\bar{\beta}_1)^2 + 4\bar{\beta}_1 B_T}}{2\bar{\beta}_1}. \quad (14)$$

Fig. 2 Total heat emitted in the injection of bpy into a $\text{Ln(pta)}_3/\text{CHCl}_3$ solution (Q) as a function of the number of moles of the complex formed between Ln(pta)_3 and bpy ($m_{\text{LnA}_3\text{B}}$). The solid lines were calculated by using $-\Delta H$ in Table 4, according to $Q = -\Delta H \times m$. $\circ$, Nd; $\bullet$, Gd; $\triangle$, Dy; $\blacktriangle$, Er; $\square$, Lu.

Table 4 Thermodynamic parameters in forming the Ln(pta)_3 adduct with bpy in CHCl_3

Ln(III)	$-\Delta G \pm \sigma / \text{kJ mol}^{-1}$	$-\Delta H \pm \sigma / \text{kJ mol}^{-1}$	$T\Delta S \pm \sigma / \text{kJ mol}^{-1}$
La	25.7 ± 0.6	-11.3 ± 0.7	36.9 ± 0.9
Pr	29.6 ± 0.5	-5.6 ± 0.6	35.2 ± 0.8
Nd	30.1 ± 0.5	-5.5 ± 0.8	35.5 ± 0.9
Sm	32.1 ± 0.3	-3.8 ± 0.9	35.9 ± 0.9
Eu	32.9 ± 0.3	-0.8 ± 1.0	33.7 ± 1.0
Gd	33.3 ± 0.6	0.4 ± 1.0	32.8 ± 1.1
Tb	33.8 ± 0.6	2.0 ± 0.3	31.8 ± 0.7
Dy	34.6 ± 0.5	8.2 ± 0.7	26.4 ± 0.9
Ho	34.4 ± 0.3	11.0 ± 0.9	23.4 ± 0.9
Er	34.1 ± 0.2	16.0 ± 0.9	18.1 ± 0.9
Tm	33.6 ± 0.3	19.0 ± 0.9	14.6 ± 0.9
Yb	33.0 ± 0.3	21.3 ± 0.8	11.8 ± 0.9
Lu	32.8 ± 0.5	22.4 ± 0.7	10.4 ± 0.8

The moles of the LnA_3 adduct formed with bpy, m , should be

$$\left. \begin{aligned} m &= (B_T - [\text{B}]_0)(3.00 + \nu)10^{-3} \\ B_T &= [\text{B}]_{\text{initial}} \times \nu / (3.00 + \nu) \end{aligned} \right\} \quad (15)$$

and

$$M_T = [\text{Ln(III)}]_{\text{initial}} \times 3.00 / (3.00 + \nu),$$

where ν is the volume (mL) of the bpy solution added into the solution in the reaction vessel. The solid line for each plot in Fig. 2 was calculated from Eq. (11) using the obtained $-\Delta H$. All of the thermodynamic parameters obtained in the present work are listed in Table 4. The change in the Gibbs free energy ($-\Delta G$) was calculated according to $-\Delta G = RT \ln \bar{\beta}_1$ where R is the gas constant, $8.313 \text{ J K}^{-1} \text{ mol}^{-1}$.

As can be seen from Table 4, the enthalpy change increases along with increasing Ln atomic number. Compared to the

variation of the enthalpy change, that of the entropy change is small until around Tb. The entropy change should decrease with turning a more rigid structure due to the formation of a chelate and increase with the release of water molecules. Due to the balance between the increase and the decrease, the entropy change is almost constant among light Lns, but around post Gd the ordering of the complex structure becomes dominant; that is, the size of Ln(III) is going to match to the distance between N and N in bpy. This idea is supported by the trend in the variation of the enthalpy change; the enthalpy change consists of the heat involving the dehydration (endothermic) and the bond formation between LnA_3 and B (exothermic). Among light lanthanides, since the energy to dehydrate may be more dominant than that to form a new bond, $-\Delta H$ should be endothermic and the degree of the change is not large. In the middle of the series, the coordination number turns from 9 to 8, so that change in the charge density and the size is much larger than that estimated from the uniform coordination number. Due to the fitness of the size of Ln(III) to the distance between N and N in bpy, heavier Lns(III) are more favorable for $-\Delta H$. In the heaviest ones, since the fitness between Ln(III) and bpy becomes worse, the increment should become smaller, although the charge density still gradually increases with increasing Ln atomic number. The smaller number of the released water molecules among the heaviest Lns(III) also functions unfavorably for an entropy change. This should be a reason why the stability constant of LnA_3B is the largest for around Ho(III) among the Ln series.

Conclusions

From measurement of $-\Delta G$, $-\Delta H$, and $T\Delta S$ upon complexation between $\text{Ln}(\text{pta})_3$ and bpy, and also the number of dehydrated water molecules across Ln series, it was found that the stability of the $\text{Ln}(\text{pta})_3$ bpy complex is mostly influenced by the fitness

between the size of Ln(III) and the distance between N and N in bpy as well as the number of released water molecules upon complexation between $\text{Ln}(\text{pta})_3$ and bpy.

References

1. T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **1967**, 29, 1481.
2. L. Farbu, J. Alstad, and J. H. Augustson, *J. Inorg. Nucl. Chem.*, **1974**, 36, 2091.
3. T. Shigematsu, M. Tabushi, M. Matsui, and T. Honjo, *Bull. Chem. Soc. Jpn.*, **1967**, 40, 2807.
4. Y. Hasegawa, T. Yamada, and K. Nagata, *Solvent Extr. Ion Exch.*, **1996**, 14, 89.
5. Y. Hasegawa, T. Ohyama, and S. Katsuta, *Bull. Chem. Soc. Jpn.*, **1995**, 68, 3091.
6. I. Matsubayashi, E. Ishiwata, T. Shionoya, and Y. Hasegawa, *Talanta*, **2004**, 63, 625.
7. A. S. Kertes and E. E. Kassierer, *Inorg. Chem.*, **1972**, 11, 2108.
8. S. Nakamura and N. Suzuki, *Inorg. Chim. Acta*, **1986**, 114, 101.
9. S. Nakamura and N. Suzuki, *Polyhedron*, **1988**, 7, 155.
10. S. Yajima and Y. Hasegawa, *Bull. Chem. Soc. Jpn.*, **1998**, 71, 2825.
11. T. Ito and Y. Hasegawa, *Solvent Extr. Res. Dev., Jpn.*, **2001**, 8, 47.
12. Y. Hasegawa, M. Miratsu, and T. Kondo, *Inorg. Chim. Acta*, **2000**, 303, 291.
13. Y. Hasegawa, M. Miratsu, and G. R. Choppin, *Anal. Chim. Acta*, **2001**, 428, 149.
14. T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **1973**, 35, 3968.