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Effect of substituent of β-diketones on the synergistic extraction of lanthanoids with linear polyether

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ABSTRACT

The synergistic extraction of 14 trivalent lanthanoids (Ln^{3+}) into 1,2-dichloroethane with a linear polyether (DEO6), $HO(C_2H_4O)_6C_{12}H_{25}$, and β-diketones (HA) having different substituents was investigated at 25.0 °C. The HAs used were trifluoroacetylacetone (Htfa), thenoyltrifluoroacetone (Htta), benzoyltrifluoroacetone (Hbta), naphthoyltrifluoroacetone (Hnta), and pivaloyltrifluoroacetone (Hpta). By the extraction of Ln^{3+} with β-diketone alone, the extraction constants of the neutral LnA_3 complex, $K_{ex} = [LnA_3]_{org}[H^+]^3_{aq}/[Ln^{3+}]_{aq}[HA]^3_{org}$, were determined. The intrinsic extraction constants, $K^*_{ex} = [LnA_3]_{org}/[Ln^{3+}]_{aq}[A^-]^3_{aq}$, were evaluated by employing the regular solution theory. Results indicate that the extractability of LnA_3 is dependent on the lipophilicity of the ligand, and the planar aromatic rings do not cause steric hindrance in the formation of the binary complex. Addition of DEO6 significantly enhanced the extraction of Ln^{3+} by the formation of $LnA_3(DEO6)$. The ternary complex formation constants, β_{add}, were determined for all the Ln^{3+} and HA. The β_{add} of bta^- and nta^- complexes is similar with those of tfa^- complexes, indicating that planar aromatic rings do not sterically hinder even the formation of the ternary complex. The higher values of β_{add} for the complexes of tta^-, which has a slightly dipolar thenoyl moiety, can be accounted for the presence of ligand–ligand interaction. The formation constants of the ternary complexes of pta^- were lower compared to complexes of other β-diketones because of steric hindrance due to the bulky *t*-butyl moiety. The detailed structures of the ternary complexes in solution were elucidated by NMR spectroscopy. Estimated structures sufficiently explain the variation in stability constants of $LnA_3(DEO6)$ among HAs and across the series of Ln^{3+}. The structures thus obtained were ascertained by the molecular models created by MM2 calculation.

1. Introduction

Coordination complexes of lanthanoid ions (Ln^{3+}) have been extensively studied in the recent decades due to their increasing applications as functional materials [1]. Because of their luminescence and magnetic property, Ln^{3+} ions are suitable as contrast agents [2–4], biomolecular markers [5], and molecular magnet component [6]. Also, one concern of lanthanoid coordination chemistry is the safe, long-term treatment and management of nuclear wastes associated with nuclear energy production. One step for a successful nuclear reprocessing is the separation of trivalent lanthanoids from transmutable actinoids [7–9]. Thus, the great demand for high purity lanthanoid compounds in high technology optics and sensors, and the need for efficient techniques in the safe isolation of nuclear waste have prompted many analytical chemists to better understand the extraction of rare-earth ions.

β-Diketones (HA) have been widely used as an effective extractant for rare-earth ions. One of the β-diketones that has been a subject of steady interest in the extraction and separation of Ln^{3+} is 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione (Htta) [10–14]. We have previously reported the extraction of the whole series of Ln^{3+} with tta^- forming the $Ln(tta)_3$ binary complex in 1,2-dichloroethane [15]. The $Ln(tta)_3$ complex extracted into an organic phase has a strong tendency to form a more lipophilic adduct complex with electrically neutral ligands or Lewis bases. This adduct formation tends to significantly enhance the extraction of Ln^{3+} from the aqueous phase into the organic phase through the displacement of residual water molecules coordinated to the Ln^{3+}–β-diketone complex [16]. Such synergistic effect on Htta extraction of Ln^{3+} ions has been extensively studied for monodentate and polydentate ligands such as phosphoric esters [17], phosphine oxides [18], 1,10-phenanthroline [12,19,20] and crown ethers [15,21–25].

Polyethers (POE), which consist of repeating units of ethylene oxide (EO), are known to form cationic complex with alkali and alkaline earth metal ions [26,27]. Just like their cyclic counterparts, linear polyethers form complexes with metal ions such as

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potassium ion by assuming a pseudo-helical configuration [28–33]. Because of their flexible structures, linear polyethers are less selective than crown ethers thus they are very useful for the group extraction of metal ions. In a previous paper, we have reported the extraction of tta$^-$ complexes for the whole series of lanthanoid ions with various linear polyethers from nitrate medium [34]. The synergistic extraction proceeds by the formation of a 1:1 adduct of the Ln(tta)$_3$ complex with POE in the organic phase, that is, Ln(tta)$_3$(POE). Moreover, we have elucidated the structures of these complexes in solution by NMR spectroscopy [35]. In the ternary complex, two or three oxygen atoms in the ethylene oxide chain of linear POE are bonded to the central metal ion to saturate the coordination sites of the metal ion.

In this paper, the synergistic extraction of 14 lanthanoid ions with a linear polyether (DEO6), HO(C$_2$H$_4$O)$_6$C$_{12}$H$_{25}$, and various β-diketones having different substituents but with similar acid-dissociation constants is reported. The β-diketones used in this study are 1,1,1-trifluoro-2,4-pentadione (trifluoroacetylacetone or Htfa), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione (thenoyltrifluoroacetone or Htta), 4,4,4-trifluoro-1-phenyl-1,3-butadione (benzoyltrifluoroacetone or Hbta), 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butadione (naphthoyltrifluoroacetone or Hnta) and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexadione (pivaloyltrifluoroacetone or Hpta). The structural formula of these β-diketones is depicted in Scheme 1. The effect of substituent of these β-diketones on the formation and extraction of the binary Ln(tta)$_3$ and ternary Ln(tta)$_3$(POE) complexes was investigated. The detailed structures of the ternary complexes in organic solution were determined by means of NMR spectroscopy.

2. Experimental

2.1. Reagents

Stock solutions of lanthanoid nitrates were prepared from their metal oxides by weighing appropriate amounts of each Ln$_2$O$_3$ [Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu] (Shinetsu), dissolving it with 6 M HNO$_3$, evaporating the solution to dryness, and redissolving the residue with distilled water. Htfa (Tokyo Kasei), and Htta, Hbta, Hnta and Hpta (Acros Organics) were used as received. The monodispersed dodecyl polyether DEO6 (Nikko Chemicals) was used without further purification. 1,2-Dichloroethane (Nacalai Tesque, AR grade) and dichloromethane (Wako, AR grade) were washed twice with distilled water prior to use. Deuterated dichloromethane (DCM-d_2, Aldrich) was used as solvent for NMR analysis. All other reagents used were of analytical reagent grade.

2.2. Extraction procedure

The extraction of 14 lanthanoid ions from an aqueous phase into 1,2-dichloroethane solution containing one of the HAs with or without DEO6 were done in similar manner as that described in our previous paper [15,34]. An aqueous solution containing a mixture of Ln^{3+} and an equivolume solution of 1,2-dichloroethane containing the extractants were mixed in a centrifuge tube. The ionic strength of the aqueous phase was maintained at 0.1 M (M = mol dm^{-3}) with potassium nitrate, and the pH was adjusted to the desired value (3.5–5.5) with acetic acid–potassium acetate buffer. The mixture was shaken for 30 min at 25.0 ± 0.1 °C in a mechanical shaker equipped with a thermostat. After phase separation through centrifugation, the pH of the aqueous phase was measured by a pH meter (DKK PHL-40). The concentrations of Ln^{3+} remaining in the aqueous phase were determined with an ICP-MS (HP4500 Yokogawa Agilent). The Ln^{3+} in the organic phase was back-extracted into 0.1 M HNO$_3$ prior to concentration determination. It was confirmed that potassium ion was not extracted at the present experimental conditions.

The distribution coefficient, K_d, of HAs between 1,2-dichloroethane and water was determined by the following procedure. A 10 cm^3 aliquot of 1,2-dichloroethane solution containing an appropriate amount of HA was mixed with an equivolume of aqueous solution containing 0.1 M potassium nitrate at pH 2.0. After shaking for 30 min, the amounts of HA in each phase were determined by UV–vis spectrophotometry (Shimadzu UV-1600).

2.3. NMR measurements

Sample preparation for NMR measurement is described in details in our previous paper [35]. An aqueous solution containing La^{3+} or Lu^{3+} and an equivolume solution of dichloromethane (DCM) containing HA and DEO6 were mixed and shaken for 30 min at 25.0 ± 0.1 °C. The pH of the aqueous phase was adjusted to around 5 with acetic acid–potassium acetate buffer. Aliquots of the organic phase were mixed with appropriate amounts of fresh DEO6 in DCM to prepare sample solutions with varying metal complex-to-DEO6 ratio, x_{comp}. The sample solutions (1 cm^3) were dried under reduced pressure and then reconstituted with 1 cm^3 of DCM-d_2. ^{1}H NMR spectra were measured at 25 °C with a Varian Unity-500 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. All NMR spectral data were analyzed by NUTS program [36]. The concentration of metal complexes in the sample solutions was determined by ICP-MS after back-extraction of Ln^{3+} from the organic phase into 0.1 M HNO$_3$. This is used to confirm the x_{comp} values of the samples.

3. Results

3.1. Ln^{3+}–β-diketonato complex

The whole series of Ln^{3+} is extracted with β-diketones into an organic phase as the neutral LnA$_3$ complex [15]. The extraction equilibrium and the corresponding extraction constant of LnA$_3$ are described as follows

$$\text{Ln}^{3+}_{\text{aq}} + 3\text{HA}_{\text{org}} \overset{K_{\text{ex}}}{\rightleftharpoons} \text{LnA}_{3,\text{org}} + 3\text{H}^{+}_{\text{aq}}, \tag{1}$$

$$K_{\text{ex}} = \frac{[\text{LnA}_3]_{\text{org}}[\text{H}^+]^3_{\text{aq}}}{[\text{Ln}^{3+}]_{\text{aq}}[\text{HA}]^3_{\text{org}}}. \tag{2}$$

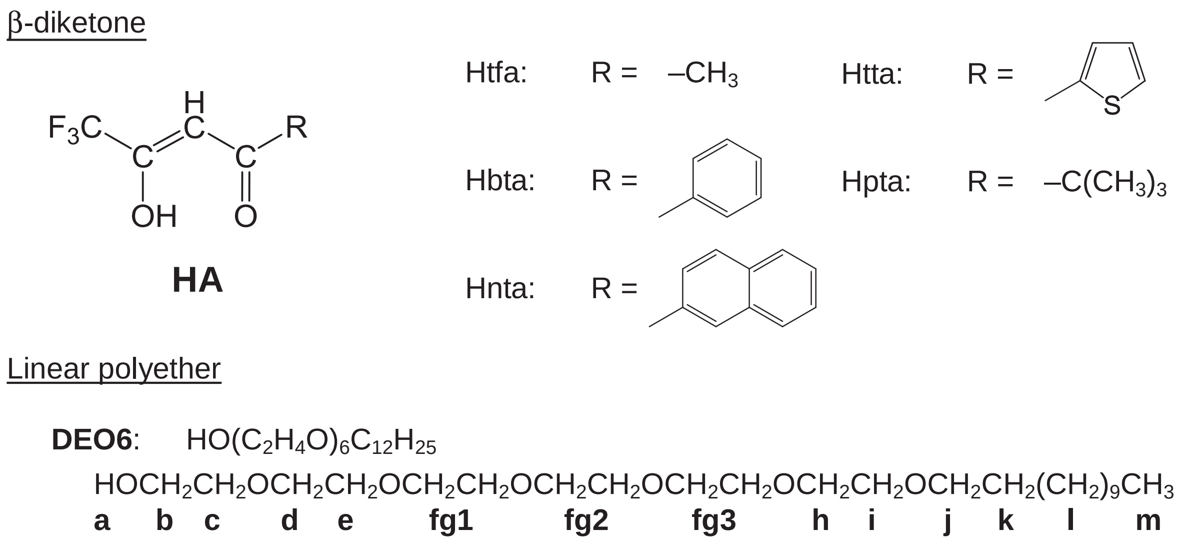
The distribution ratio (D_0), which is defined as the distribution of Ln^{3+} between the organic and aqueous phases, is given as

$$D_0 = \frac{C_{\text{Ln, org}}}{C_{\text{Ln, aq}}}, \tag{3}$$

where $C_{\text{Ln,org}}$ and $C_{\text{Ln,aq}}$ are the total concentrations of Ln^{3+} in the organic and aqueous phases, respectively.

As reported previously for the extraction of lanthanoids with Htta [15,23], the predominant species extracted into the organic phase is Ln(tta)$_3$. It can be assumed that LnA$_3$ complex is extracted for any kind of β-diketone. Thus, the total concentration of Ln^{3+} in the organic phase is equal to the concentration of the LnA$_3$, that is, $C_{\text{Ln,org}} = [\text{LnA}_3]_{\text{org}}$. The formation of LnA$_n$$^{(3-n)+}$ and Ln(OH)$_n$$^{(3-n)+}$ complexes in the aqueous phase can also be neglected under the present experimental conditions. Thus, the total concentration of Ln^{3+} in the aqueous phase is equal to the free Ln^{3+} ions, that is, $C_{\text{Ln,aq}} = [\text{Ln}^{3+}]_{\text{aq}}$. The distribution ratio becomes

$$D_0 = \frac{[\text{LnA}_3]_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}}}. \tag{4}$$



Scheme 1. Structural formula of β-diketones and linear polyether.

Substitution of Eq. (2) into Eq. (4) results to

$$D_0 = \frac{K_{ex}[\mathrm{HA}]^3_{org}}{[\mathrm{H}^+]^3_{aq}}. \quad (5)$$

Taking the logarithm of Eq. (5) gives

$$\log D_0 = \log K_{ex} + 3\log[\mathrm{HA}]_{org} + 3\mathrm{pH}. \quad (6)$$

Experimentally determined log D_0 is plotted as a function of pH in Fig. 1 for some representative Ln^{3+}. The slope of the plots for each Ln^{3+} and for all β-diketones is three, which confirms that Ln^{3+} are extracted into 1,2-dichloroethane as LnA_3 complex. The log K_{ex} obtained from these plots is summarized in Table 1.

3.2. Synergistic extraction of Ln^{3+} with linear polyether

By the addition of DEO6, the extractability of Ln^{3+} into the organic phase is significantly enhanced. This can be explained by the formation of a more hydrophobic ternary complex in the organic phase [16]. In the extraction of Ln^{3+} with a synergistic mixture of tta^- and DEO6, it was found out that one molecule of the polyether forms an adduct with $Ln(tta)_3$ to produce $Ln(tta)_3(DEO6)$ [34]. Thus, the over-all extraction equilibrium is given by

$$\mathrm{Ln}^{3+}_{aq} + 3\mathrm{HA}_{org} + \mathrm{DEO6}_{org} \rightleftharpoons \mathrm{LnA_3(DEO_6)}_{org} + 3\mathrm{H}^+_{aq}. \quad (7)$$

From Eqs. (1) and (7), the ternary complex formation in the organic phase can be described as follows

$$\mathrm{LnA}_{3,org} + \mathrm{DEO6}_{org} \overset{\beta_{add}}{\rightleftharpoons} \mathrm{LnA_3(DEO6)}_{org}. \quad (8)$$

The corresponding ternary complex formation constant, β_{add}, is defined as

$$\beta_{add} = \frac{[\mathrm{LnA_3(DEO6)}]_{org}}{[\mathrm{LnA_3}]_{org}[\mathrm{DEO6}]_{org}}. \quad (9)$$

As the total concentration of each Ln^{3+} ion in the organic phase is the sum of the concentrations of LnA_3 and $LnA_3(DEO6)$, the distribution ratio of Ln^{3+}, D, in the extraction with HA and DEO6 is

$$D = \frac{[\mathrm{LnA_3}]_{org} + [\mathrm{LnA_3(DEO6)}]_{org}}{[\mathrm{Ln}^{3+}]_{aq}}. \quad (10)$$

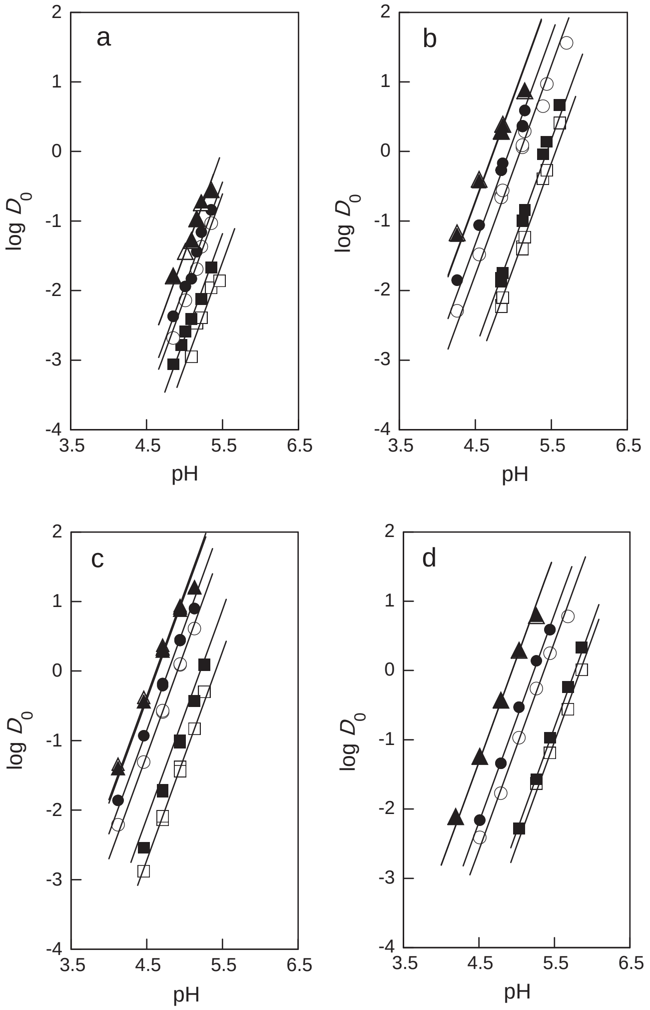


Fig. 1. Plots of log D_0 vs. pH in the extraction of Ln^{3+} with 1.0×10^{-2} M HA. HA: (a) Htfa, (b) Hbta, (c) Hnta and (d) Hpta. Representative Ln^{3+}: □ = Ce^{3+}, ■ = Pr^{3+}, ○ = Gd^{3+}, ● = Tb^{3+}, △ = Yb^{3+} and ▲ = Lu^{3+}. The slope of solid lines is 3.

Table 1
Extraction constants of LnA_3, K_{ex}, into 1,2-dichloroethane for various β-diketones for the whole lanthanoid series.

Ln^{3+}	Atomic no.	$\log K_{ex}$				
		tfa^-	tta^-	bta^-	nta^-	pta^-
La^{3+}	57	[a]	−10.33	−11.55	−11.20	−12.78
Ce^{3+}	58	−11.31	−9.58	−10.65	−10.21	−11.52
Pr^{3+}	59	−10.90	−9.27	−10.32	−9.83	−11.31
Nd^{3+}	60	−10.80	−9.09	−10.09	−9.61	−11.10
Sm^{3+}	62	−10.38	−8.42	−9.42	−8.90	−10.32
Eu^{3+}	63	−10.26	−8.25	−9.21	−8.72	−10.10
Gd^{3+}	64	−10.32	−8.32	−9.26	−8.70	−10.08
Tb^{3+}	65	−10.16	−7.94	−8.82	−8.34	−9.67
Dy^{3+}	66	−10.09	−7.80	−8.68	−8.21	−9.49
Ho^{3+}	67	−10.07	−7.77	−8.64	−8.18	−9.41
Er^{3+}	68	−10.00	−7.71	−8.56	−8.10	−9.29
Tm^{3+}	69	−9.85	−7.55	−8.42	−7.96	−9.08
Yb^{3+}	70	−9.68	−7.44	−8.20	−7.85	−8.80
Lu^{3+}	71	−9.69	−7.48	−8.22	−7.90	−8.81

[a] Cannot be determined.

Substitution of Eqs. (2) and (9) into Eq. (10) gives

$$D = \frac{K_{ex}[HA]^3_{org}(1+\beta_{add}[DEO6]_{org})}{[H^+]^3_{aq}}. \tag{11}$$

Taking the logarithm of Eq. (11) and with subsequent rearrangement results to

$$\log D = \log K_{ex} + 3\log[HA]_{org} + 3pH + \log(1+\beta_{add}[DEO6]_{org}). \tag{12}$$

The number of HA molecules involved in the formation of the ternary complex was confirmed by the determination of D at various pH under constant concentrations of HA and DEO6. The plots of $\log D$ vs. pH are shown in Fig. 2 for some representative Ln^{3+} for each HA. The plots show straight lines with a slope of three for all Ln^{3+}. The same results were obtained for the tta^- system [34]. Thus, it is confirmed that three A^- are present in the extracted ternary complex, that is, $LnA_3(DEO6)$.

Substitution of Eq. (5) into Eq. (12) gives

$$\log D = \log D_0 + \log(1+\beta_{add}[DEO6]_{org}), \tag{13}$$

where $\log D_0 = \log K_{ex} + 3\log[HA]_{org} + 3$ pH. At fixed $[HA]_{org}$ and pH, the value of D_0 is constant. Since the distribution coefficient of DEO6 between 1,2-dichloroethane and water is larger than 10^3 [30,31] and the total concentration of DEO6 is much higher than the total concentration of metal ions, then the concentration of free DEO6 in organic phase can be approximated to be equal to the total concentration of DEO6, that is, $[DEO6]_{org} = C_{DEO6}$. The number of DEO6 molecule forming a ternary complex with LnA_3 is confirmed by the analysis of D at varying concentrations of DEO6 and at constant pH and HA concentration. Plots of $\log D$ as a function of $\log [DEO6]_{org}$ are shown in Fig. 3 for some representative Ln^{3+}. The slopes of these plots approach unity at higher $[DEO6]_{org}$ region irrespective of the kind of HA. Any other lanthanoids not depicted in Fig. 3 also show the same results. These results confirm that one molecule of DEO6 forms an adduct with LnA_3 complex as described in Eq. (8).

The β_{add} values were calculated by applying least-squares method to the plots of Fig. 3 using Eq. (13). The calculated regression curves are depicted by solid lines in Fig. 3, which are in good agreement with the experimental results. The horizontal part of the curves is equal to the $\log D_0$ values obtained for each metal ion in the extraction using only HA at pH = 4.90 (pH = 5.24 for Hpta). The logarithmic values of ternary complex formation constants, $\log \beta_{add}$, are summarized in Table 2.

3.3. NMR measurement

In order to fully understand the formation of ternary complexes during synergistic extraction, their structures in solution were estimated by means of ^1H NMR spectrometry. The ethylene oxide region of the NMR spectrum of DEO6 is shown in Fig. 4a with proton

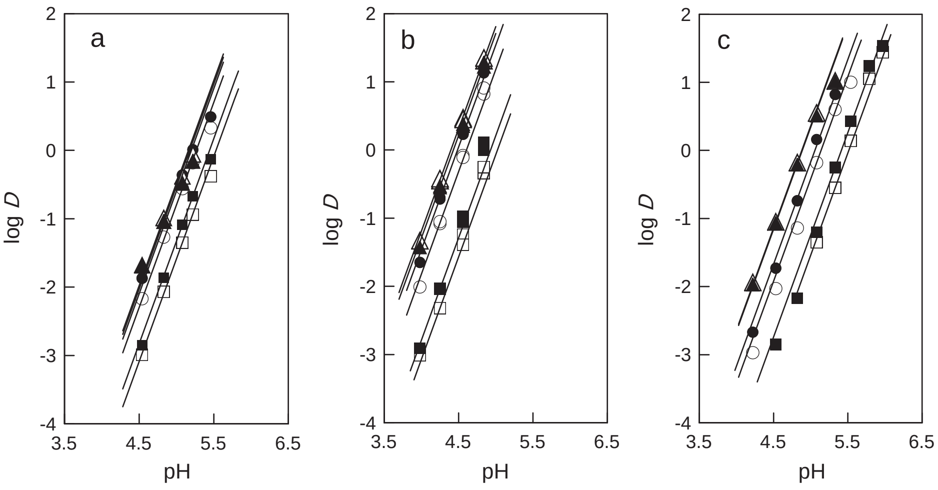


Fig. 2. Plots of $\log D$ vs. pH in the extraction of Ln^{3+} with 1.0×10^{-2} M HA and 1.0×10^{-3} M DEO6. HA: (a) Htfa, (b) Hbta and (c) Hpta. Representative Ln^{3+}: □ = Ce^{3+}, ■ = Pr^{3+}, ○ = Gd^{3+}, ● = Tb^{3+}, △ = Yb^{3+} and ▲ = Lu^{3+}. The slope of solid lines is 3.

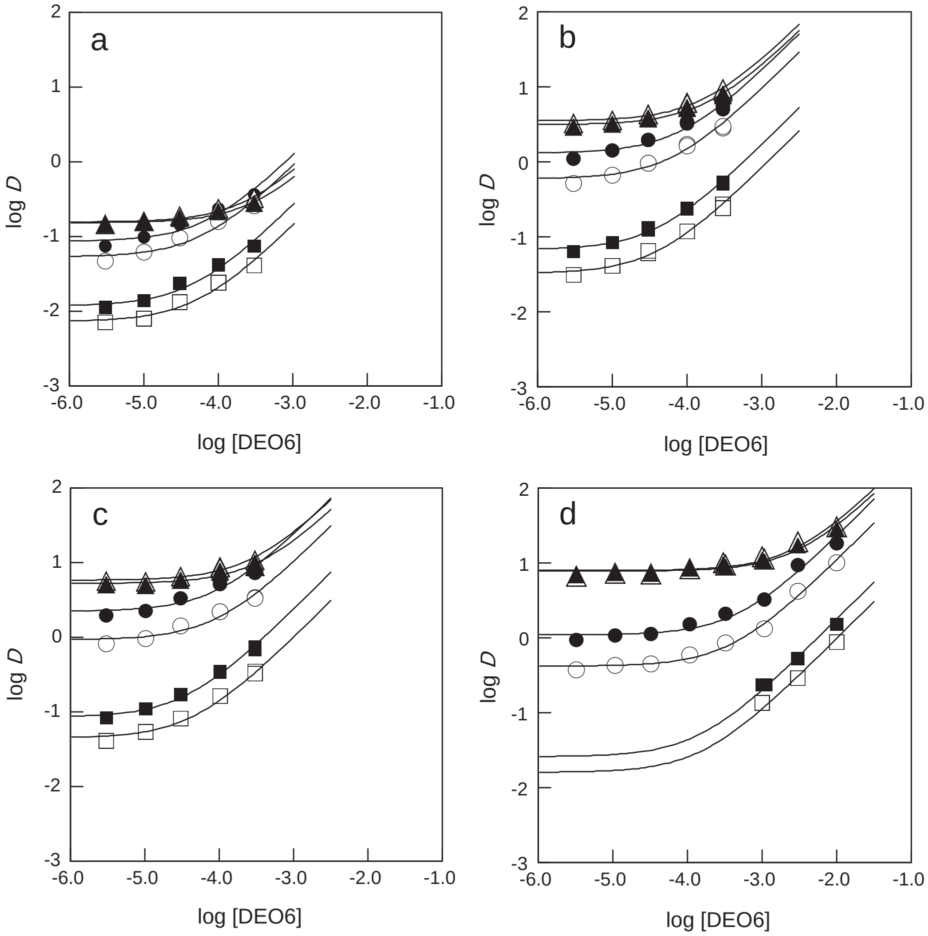


Fig. 3. Plots of log D vs. log $[DEO6]_{org}$ in the extraction of Ln^{3+} with 1.0×10^{-2} M HA at pH = 4.90 (pH = 5.24 for Hpta). HA: (a) Htfa, (b) Hbta, (c) Hnta and (d) Hpta. Representative Ln^{3+}: □ = Ce^{3+}, ■ = Pr^{3+}, ○ = Gd^{3+}, ● = Tb^{3+}, △ = Yb^{3+} and ▲ = Lu^{3+}. Solid lines are calculated curves; see text.

labels corresponding to that illustrated in Scheme 1. By the addition of LaA_3 complex to a solution of DEO6, the signals of the protons in close proximity to the oxygen atoms of DEO6 coordinating to Ln^{3+} are shifted downfield as depicted in Fig. 4b.

Since the concentration of Ln^{3+} is much lower than the total concentration of DEO6 under the present experimental conditions, then the concentration of the ternary complex, $LnA_3(DEO6)$, can be assumed to be equal to the total concentration of Ln^{3+} in the organic phase, C_{Ln}. Here, we define the mole ratio, x_{comp}, of the concentration of $LnA_3(DEO6)$ to the total concentration of DEO6, C_{DEO6}, as

$$x_{comp} = \frac{[LnA_3(DEO6)]}{[DEO6] + [LnA_3(DEO6)]} = \frac{C_{Ln}}{C_{DEO6}}. \tag{14}$$

The x_{comp} values of the samples were determined from the molar peak area ratio of the β-diketone protons of the ternary complex to methylene protons of DEO6. These x_{comp} values were in close agreement with those calculated using C_{Ln} and C_{DEO6}.

By the addition of LnA_3 to DEO6 solution, a new set of signals for the formed ternary complex was not observed, but some of the pro-

Table 2
Formation constant of $LnA_3(DEO6)$ ternary complex, β_{add}, in 1,2-dichloroethane.

Ln^{3+}	Ionic radius/Å	log β_{add}				
		tfa^-	tta^{-a}	bta^-	nta^-	pta^-
La^{3+}	1.22	4.07	5.11	4.44	4.39	4.07
Ce^{3+}	1.20	4.27	5.09	4.40	4.33	3.78
Pr^{3+}	1.18	4.34	4.95	4.39	4.43	3.83
Nd^{3+}	1.16	4.34	4.91	4.41	4.41	3.78
Sm^{3+}	1.13	4.27	4.89	4.23	4.24	3.50
Eu^{3+}	1.12	4.22	4.81	4.19	4.16	3.43
Gd^{3+}	1.11	4.20	4.70	4.18	4.01	3.41
Tb^{3+}	1.10	4.13	4.60	4.08	4.00	3.30
Dy^{3+}	1.08	4.07	4.50	4.02	3.89	3.27
Ho^{3+}	1.07	4.02	4.48	4.02	3.89	3.15
Er^{3+}	1.06	3.95	4.39	3.97	3.82	3.04
Tm^{3+}	1.05	3.73	4.25	3.89	3.64	2.85
Yb^{3+}	1.04	3.60	4.07	3.76	3.53	2.55
Lu^{3+}	1.03	3.48	3.91	3.73	3.44	2.50

[a] [35].

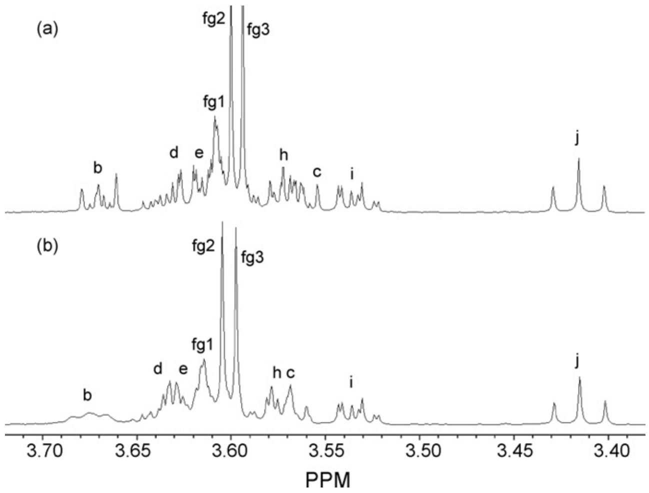


Fig. 4. ^{1}H NMR spectra showing the ethylene oxide moiety of DEO6 in DCM-d_2. (a) free DEO6, (b) DEO6 in the presence of La(pta)$_3$(DEO6) (x_{comp} = 0.048).

ton signals are shifted downfield. This suggests that the exchange of DEO6 between the coordinated and free states is fast with respect to the NMR timescale. The observed chemical shift (δ_{obs}) at various x_{comp} values is thus given by the weighted average of the chemical shifts of methylene protons of free DEO6 (δ_{DEO6}) and coordinated DEO6 (δ_{comp}) which is given as follows

$$\delta_{obs} = (1 - x_{comp})\delta_{DEO6} + x_{comp}\delta_{comp}. \qquad (15)$$

Rearrangement of Eq. (15) gives

$$\Delta\delta_{obs} = \Delta\delta_{comp}x_{comp}, \qquad (16)$$

where $\Delta\delta_{obs}$ is the change in observed chemical shifts of DEO6 by the addition of LnA$_3$(DEO6) complex, $\Delta\delta_{obs} = \delta_{obs} - \delta_{DEO6}$; and, $\Delta\delta_{comp}$ is the change in chemical shift caused by the complex formation, $\Delta\delta_{comp} = \delta_{comp} - \delta_{DEO6}$. The $\Delta\delta_{obs}$ of methylene protons b–m of DEO6 for La(pta)$_3$(DEO6) complex are plotted against x_{comp} in Fig. 5 as an example. The plot shows a linear correlation of $\Delta\delta_{obs}$ with x_{comp} for any methylene protons. This was also observed for the complexes of Lu^{3+} and Y^{3+}. The values of $\Delta\delta_{comp}$ for each proton are obtained from the slope of these plots, and are summarized in Table 3.

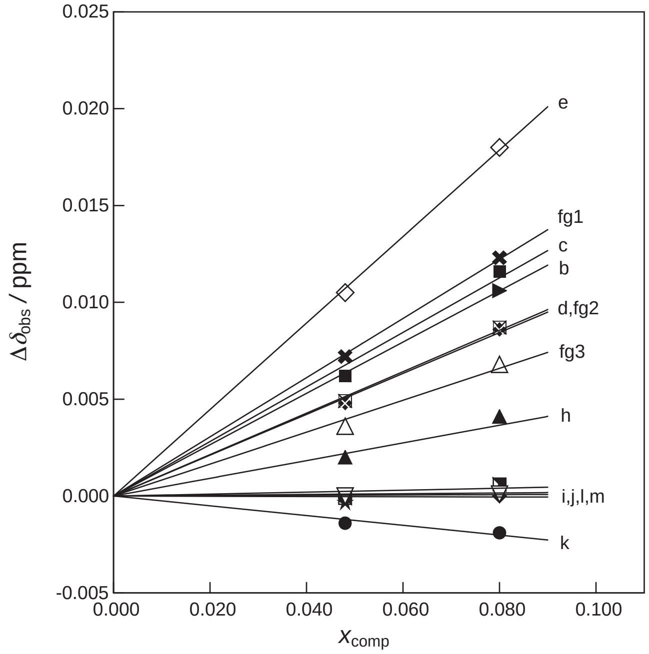


Fig. 5. Change in chemical shift of each methylene proton, $\Delta\delta_{obs}$, as a function of mole ratio of La(pta)$_3$(DEO6) with respect to the total concentration of DEO6, x_{comp}.

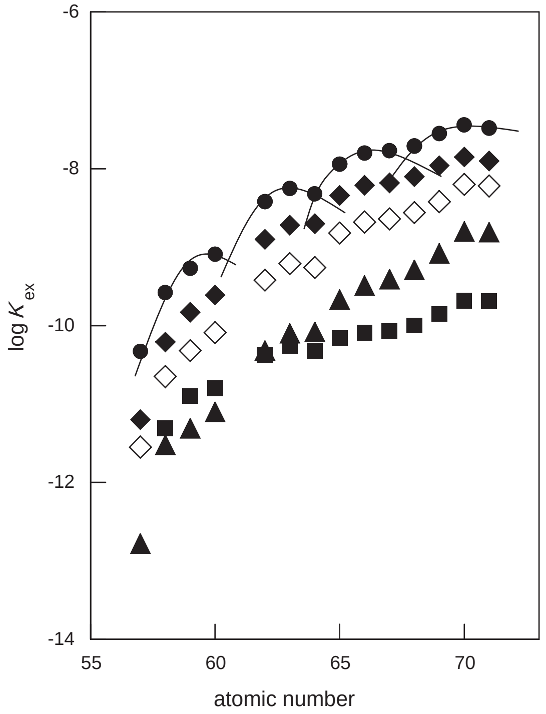


Fig. 6. Comparison of extraction constants, K_{ex}, among HAs for the whole Ln^{3+} series. ■ = Htfa, ● = Htta, ◇ = Hbta, ◆ = Hnta, ▲ = Hpta. See text for description of curves.

4. Discussion

4.1. *Extraction of LnA$_3$*

The logarithm of extraction constants, log K_{ex}, of LnA$_3$ binary complexes are plotted as a function of atomic number in Fig. 6. This plot illustrates the division of the series of Ln^{3+} into four smooth curves for all the β-diketones. This phenomenon, known as the tetrad effect, was described by Peppard et al. where the Gd point is common to the second and the third tetrads, and the extended smooth curves of the first and second tetrads, and the third and fourth tetrads intersect at the atomic number 60–61 and 67–68 regions, respectively [38]. The tetrad effect exhibited in the extraction of binary complexes of tta$^-$ as an example is depicted by the solid curves in Fig. 6.

In order to systematically compare the extractability of Ln^{3+} among various β-diketones, their difference in partition coefficients, K_d, and acid-dissociation constants, K_a, must be taken into consideration. To account for these differences, the following extraction equilibrium must be used

$$\mathrm{Ln}^{3+}_{aq} + 3\mathrm{A}^-_{aq} \overset{K^*_{ex}}{\rightleftharpoons} \mathrm{LnA}_{3,org}. \qquad (17)$$

The intrinsic extraction constant, K^*_{ex}, is

$$K^*_{ex} = \frac{[\mathrm{LnA}_3]_{org}}{[\mathrm{Ln}^{3+}]_{aq}[\mathrm{A}^-]^3_{aq}}. \qquad (18)$$

Substituting Eq. (2) to Eq. (18) yields

$$K^*_{ex} = K_{ex}\left(\frac{K_d}{K_a}\right)^3, \qquad (19)$$

Table 3
Changes in chemical shifts of DEO6 protons ($\Delta\delta_{\mathrm{comp}}$/ppm) upon formation of $\mathrm{LnA_3(DEO6)}$ complexes in deuterated dichloromethane.

Complex	b	c	d	e	fg1	fg2	fg3	h	i	j	k	l	m
$\mathrm{La(tta)_3(DEO6)}$[a]	0.176	0.166	0.129	0.210	0.178	0.115	0.071	0.063	0.029	−0.007	−0.051	−0.010	0.000
$\mathrm{La(pta)_3(DEO6)}$	0.133	0.141	0.107	0.223	0.153	0.106	0.082	0.046	0.005	0.002	−0.025	−0.001	0.001
$\mathrm{Y(tta)_3(DEO6)}$[a]	0.266	0.229	0.185	0.049	−0.005	−0.025	−0.007	0.012	−0.048	−0.019	−0.063	−0.004	0.003
$\mathrm{Y(pta)_3(DEO6)}$	0.165	0.182	0.130	0.039	0.005	0.017	0.020	0.031	−0.002	0.007	−0.003	−0.012	−0.008
$\mathrm{Lu(tta)_3(DEO6)}$[a]	0.218	0.207	0.136	0.036	−0.012	−0.012	−0.003	0.011	−0.012	−0.004	−0.025	−0.002	0.003
$\mathrm{Lu(pta)_3(DEO6)}$	0.177	0.111	0.054	0.017	0.009	−0.004	0.014	0.020	−0.006	0.000	−0.015	−0.005	−0.004

[a] [35].

where $K_{\mathrm{d}} = [\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{aq}}$, and $K_{\mathrm{a}} = [\mathrm{H^+}]_{\mathrm{aq}} \times [\mathrm{A^-}]_{\mathrm{aq}}/[\mathrm{HA}]_{\mathrm{aq}}$. The values of $\mathrm{p}K_{\mathrm{a}}$ and $\log K_{\mathrm{d}}$ listed in Table 4 were used to calculate $\log K^*_{\mathrm{ex}}$, which are also summarized in the same table.

The extraction process in Eq. (17) can be dissected into two hypothetical steps. First is the formation of neutral $\mathrm{LnA_3}$ complex in the aqueous phase

$$\mathrm{Ln^{3+}_{aq}} + 3\mathrm{A^-_{aq}} \overset{\beta_{\mathrm{LnA_3}}}{\rightleftharpoons} \mathrm{LnA_{3,aq}}. \tag{20}$$

This is followed by the partition of the complex into the organic phase

$$\mathrm{LnA_{3,aq}} \overset{K_{\mathrm{d,LaA_3}}}{\rightleftharpoons} \mathrm{LnA_{3,org}}. \tag{21}$$

The intrinsic extraction constant is given by

$$K^*_{\mathrm{ex}} = \beta_{\mathrm{LnA_3}} K_{\mathrm{d,LnA_3}}, \tag{22}$$

where β_{LnA3} is the formation constant of $\mathrm{LnA_3}$ in the aqueous phase and $K_{\mathrm{d,LnA_3}}$ is the distribution coefficient of this complex into the organic phase. In the present study, the $\mathrm{p}K_{\mathrm{a}}$ values of the β-diketones are close to each other, that is, the basicity of these HAs is similar. Consequently, the β_{LnA3} values can be assumed to be constant among HAs for a given $\mathrm{Ln^{3+}}$. As such, the variation in K^*_{ex} is thus mainly attributed to the difference in $K_{\mathrm{d,LnA_3}}$.

Regular solution theory has been successful in explaining the partition of organic ligands and chelates in various solvents [39,40]. The distribution coefficient of the complex is related to its molar volume, $V_{\mathrm{m,LnA_3}}$, as shown by the following equation

$$\log K_{\mathrm{d,LnA_3}} = \frac{V_{\mathrm{m,LnA_3}}}{2.30RT}(\delta_{\mathrm{aq}} + \delta'_{\mathrm{org}} - 2\delta_{\mathrm{LnA_3}})(\delta_{\mathrm{aq}} - \delta_{\mathrm{org}}), \tag{23}$$

where δ is the solubility parameter, and the subscripts “org” and “aq” refer to organic solvent and water, respectively. The term δ'_{org} is defined as

$$\delta'_{\mathrm{org}} = \delta_{\mathrm{org}} - \frac{RT}{\delta_{\mathrm{aq}} - \delta_{\mathrm{org}}}\left(\frac{1}{V_{\mathrm{aq}}} - \frac{1}{V_{\mathrm{org}}}\right), \tag{24}$$

where V is the molar volume of the solvents.

Correspondingly, the distribution coefficient of the free ligand is given by

$$\log K_{\mathrm{d,HA}} = \frac{V_{\mathrm{m,HA}}}{2.30RT}(\delta_{\mathrm{aq}} + \delta'_{\mathrm{org}} - 2\delta_{\mathrm{HA}})(\delta_{\mathrm{aq}} - \delta_{\mathrm{org}}). \tag{25}$$

Since it can be assumed that the metal-bound β-diketones interact with the solvents similarly with the free β-diketones, then $\delta_{\mathrm{LnA_3}} = \delta_{\mathrm{HA}}$. Thus, combination of Eqs. (23) and (25) yields

$$\log K_{\mathrm{d,LnA_3}} = \frac{V_{\mathrm{m,LnA_3}}}{V_{\mathrm{m,HA}}} \log K_{\mathrm{d,HA}}. \tag{26}$$

As the volume of the ligand is much greater than that of $\mathrm{Ln^{3+}}$, the molar volume of $\mathrm{LnA_3}$ can be approximated to be three-fold that of the free ligand, that is $V_{\mathrm{m,LnA_3}} = 3V_{\mathrm{m,HA}}$. The logarithmic form of Eq. (22) then becomes

$$\log K^*_{\mathrm{ex}} = 3\log K_{\mathrm{d,HA}} + \log \beta_{\mathrm{LnA_3}}. \tag{27}$$

The $\log K^*_{\mathrm{ex}}$ values are plotted as a function of $\log K_{\mathrm{d,HA}}$ for some representative $\mathrm{Ln^{3+}}$ in Fig. 7. As shown in this figure, $\log K^*_{\mathrm{ex}}$ values for the complex are linearly correlated to $\log K_{\mathrm{d}}$ of the corresponding free β-diketone with a slope of three, excluding the data for $\mathrm{pta^-}$ complexes. This clearly confirms that the intrinsic extraction constant simply varies with lipophilicity of the ligand, and the assumption that $\beta_{\mathrm{LnA_3}}$ for a given $\mathrm{Ln^{3+}}$ is constant among HAs having similar $\mathrm{p}K_{\mathrm{a}}$ is reasonable. If a ligand poses steric hindrance in

Table 4
Intrinsic extraction constants of $\mathrm{LnA_3}$, K^*_{ex}, into 1,2-dichloroethane for various β-diketones for the whole lanthanoid series.

		Htfa	Htta	Hbta	Hnta	Hpta
$\mathrm{p}K_{\mathrm{a}}$ [a]		6.4	6.2	6.3	6.3	7.0
$\log K_{\mathrm{d}}$		0.08[c]	1.68[b]	3.57[c]	5.28[c]	3.03[c]
$\mathrm{Ln^{3+}}$	Atomic no.	$\log K^*_{\mathrm{ex}}$				
$\mathrm{La^{3+}}$	57	[d]	13.40	18.07	23.55	17.35
$\mathrm{Ce^{3+}}$	58	8.14	14.15	18.96	24.54	18.61
$\mathrm{Pr^{3+}}$	59	8.56	14.46	19.30	24.92	18.82
$\mathrm{Nd^{3+}}$	60	8.65	14.64	19.53	25.14	19.03
$\mathrm{Sm^{3+}}$	62	9.07	15.31	20.20	25.85	19.81
$\mathrm{Eu^{3+}}$	63	9.19	15.48	20.41	26.03	20.03
$\mathrm{Gd^{3+}}$	64	9.13	15.41	20.36	26.05	20.05
$\mathrm{Tb^{3+}}$	65	9.30	15.79	20.80	26.41	20.45
$\mathrm{Dy^{3+}}$	66	9.37	15.93	20.94	26.54	20.64
$\mathrm{Ho^{3+}}$	67	9.38	15.96	20.98	26.57	20.71
$\mathrm{Er^{3+}}$	68	9.45	16.02	21.06	26.65	20.84
$\mathrm{Tm^{3+}}$	69	9.60	16.18	21.20	26.79	21.05
$\mathrm{Yb^{3+}}$	70	9.77	16.29	21.41	26.90	21.32
$\mathrm{Lu^{3+}}$	71	9.77	16.25	21.39	26.85	21.32

[a] [22,37].
[b] [23].
[c] This work.
[d] Cannot be determined.

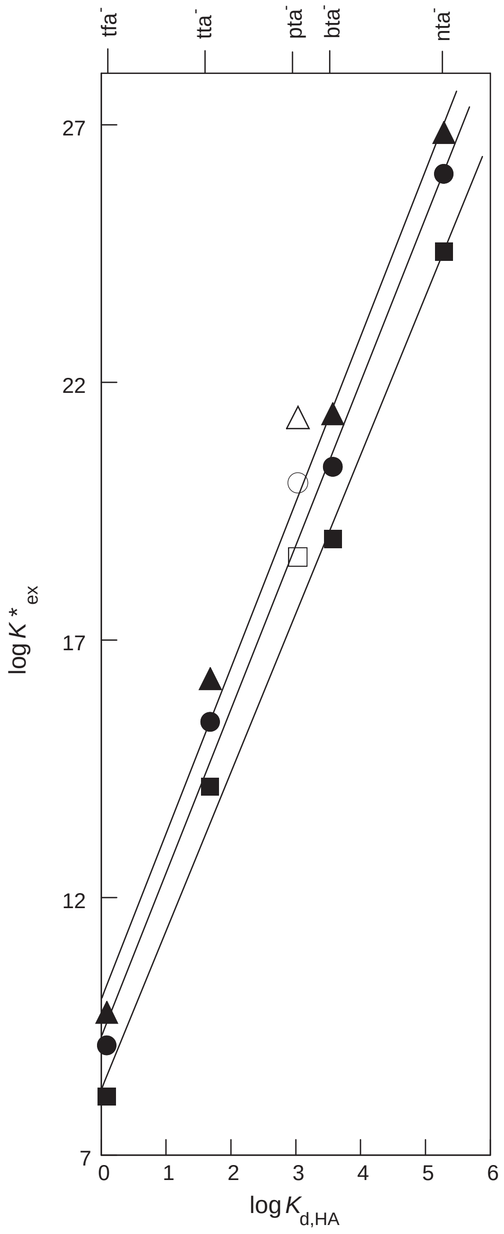


Fig. 7. Relationship between intrinsic extraction constant, K^*_{ex}, and partition coefficient of β-diketones, $K_{d,HA}$. Representative Ln^{3+}: ■ = Ce^{3+}, ● = Gd^{3+} and ▲ = Lu^{3+}; open symbols are for pta^- complexes. The slope of solid lines is 3.

complex formation, then β_{LnA_3} decreases thus affecting K^*_{ex}. Since the present result showed that K^*_{ex} varies only with $K_{d,HA}$, then it can be implied that the aromatic benzoyl and bulky *t*-butyl moieties do not sterically affect the formation of the binary complex. Even the naphthoyl substituent, which has a large molar volume, does not have any steric contribution in the formation of $Ln(nta)_3$ since it is oriented outward of the complex as depicted by the estimated structure shown in Fig. 8. The molecular models were optimized by MM2 calculation using MMFF94 force field and default atomic parameters of Spartan software [41].

Among the β-diketones, nta^- has the highest lipophilicity, thus it has the highest K^*_{ex} value. Similar observation was reported in the extraction of alkali metal ions with β-diketones [42]. The log K^*_{ex} for the pta^- complexes positively deviated from the linear curves of log K^*_{ex} vs. log $K_{d,HA}$ plots. This can be accounted for by the slightly higher basicity of pta^- which has a positive contribution on the log β_{LnA_3} term in Eq. (27).

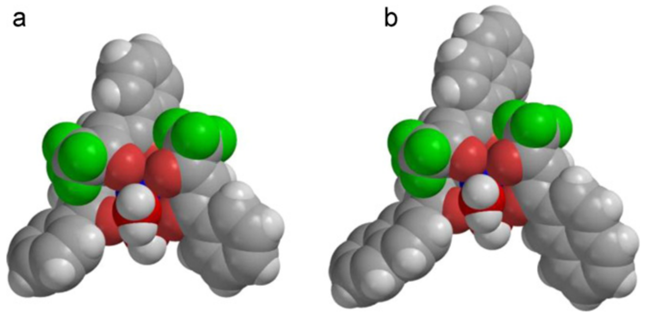


Fig. 8. Molecular structures of the binary complexes in solution optimized by MM2 calculation: (a) $La(bta)_3$ and (b) $La(nta)_3$. O = red spheres; C = gray spheres; and F = green spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

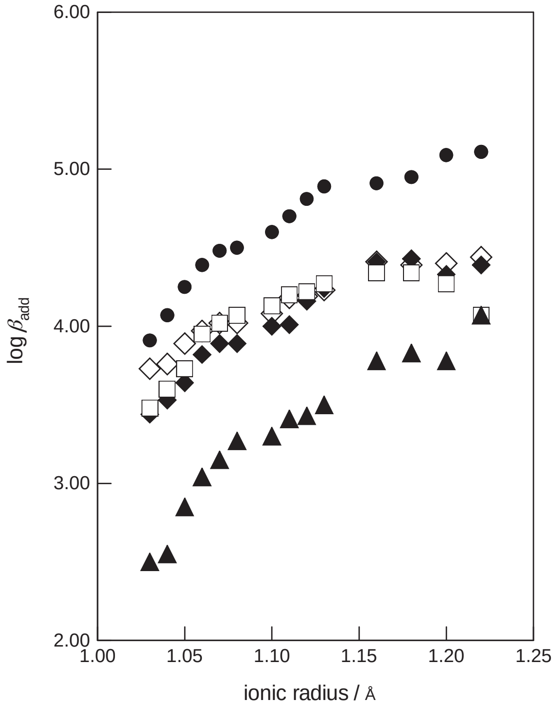


Fig. 9. Comparison of logarithmic formation constants of ternary complex, log β_{add}, as a function of radii of Ln^{3+}. HA: □ = Htfa, ● = Htta, ◇ = Hbta, ◆ = Hnta, ▲ = Hpta.

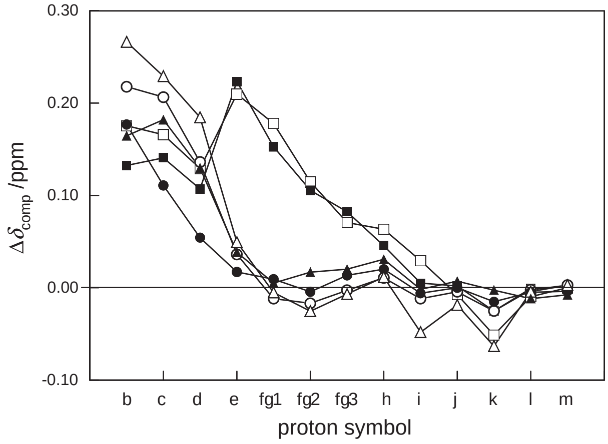


Fig. 10. Change in chemical shift of methylene protons of DEO6, $\Delta\delta_{comp}$, upon formation of ternary complexes: □ = $La(tta)_3(DEO6)$, ■ = $La(pta)_3(DEO6)$, ○ = $Lu(tta)_3(DEO6)$ and ● = $Lu(pta)_3(DEO6)$, △ = $Y(tta)_3(DEO6)$ and ▲ = $Y(pta)_3(DEO6)$.

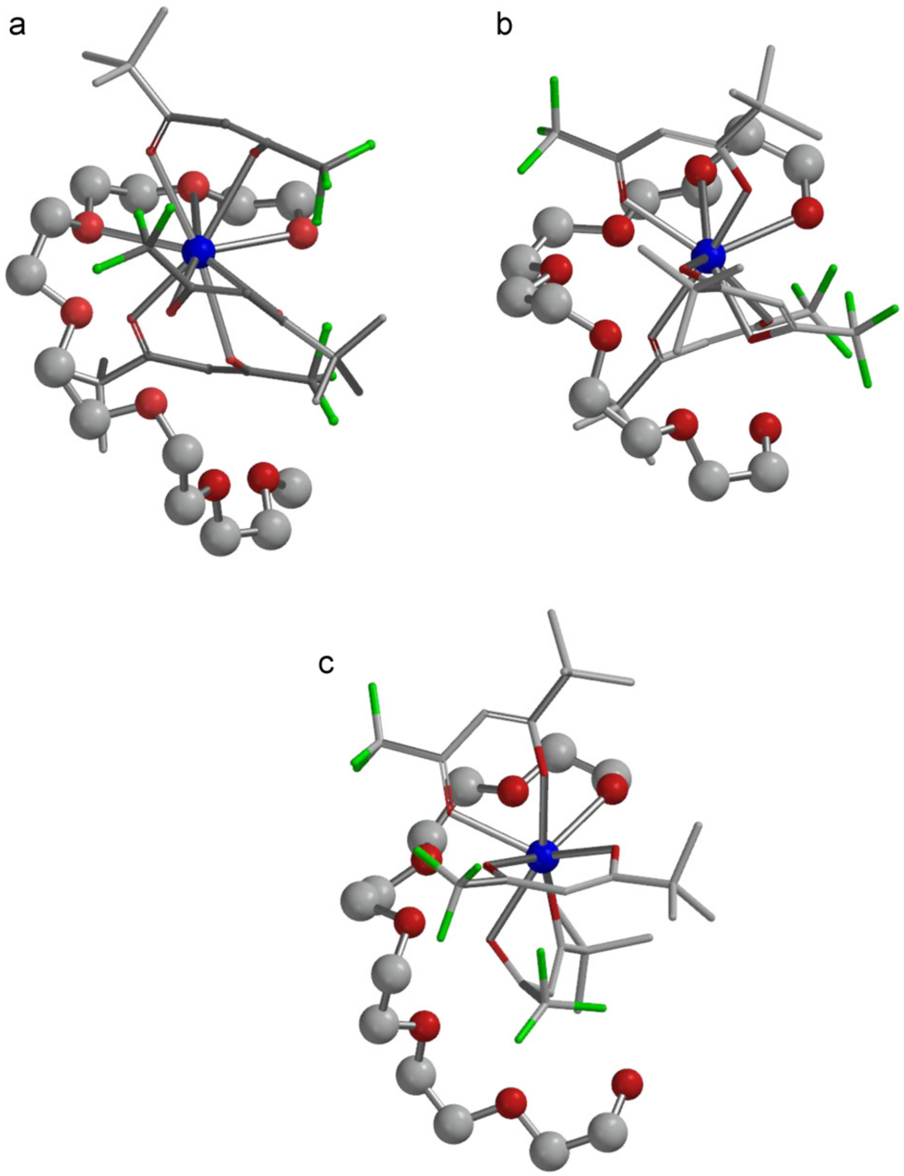


Fig. 11. Molecular structures of the ternary complexes in solution optimized by MM2 calculation: (a) $La(pta)_3(DEO6)$, (b) $Y(pta)_3(DEO6)$ and (c) $Lu(pta)_3(DEO6)$. O = red spheres; C = gray spheres; H atoms are omitted for simplicity; pta^- ligands are depicted as stick frames. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4.2. Structures of $LnA_3(DEO6)$ ternary complex

The logarithm of ternary complex formation constant, log β_{add}, is plotted as a function of lanthanoid ionic radius [43] in Fig. 9. In the extraction with β-diketone alone, Ln^{3+} are extracted into the organic phase as the hydrated complex $LnA_3 \cdot nH_2O$, where $n = 2$ or 3 [44]. The extractability of the metal complex considerably increases by the replacement of these water molecules by the lipophilic DEO6. Because of its weak basicity and flexibility, the linear polyethers do not displace the β-diketonate from the primary coordination sphere, that is, all three bidentate A^- are directly coordinated to the central Ln^{3+} [35]. As a consequence, the remaining two or three coordination sites for the eight- or nine-coordinate Ln^{3+} are occupied by the donor oxygen atoms of DEO6.

As shown in Fig. 9, the magnitude of β_{add} for HAs containing the aromatic benzoyl and naphthoyl rings are similar to those of the complexes of tfa^-, which has the least steric contribution. This clearly indicates that the planar benzoyl and naphthoyl rings do not have any steric effect in the formation of $LnA_3(DEO6)$ ternary complex.

The log β_{add} values of tta^- complexes are higher than those of bta^- complexes, although the thenoyl substituent in tta^- is similar in shape and volume to that of the benzoyl moiety in bta^-. This may indicate ligand–ligand interaction between the non-coordinating oxygen atoms of DEO6 and the slightly dipolar thenoyl moiety of tta^-. This interaction is absent in tfa^- or bta^- complexes because of the nonpolar character of the methyl or benzoyl substituents.

On the other hand, the log β_{add} values of pta^- complexes are generally lower than those of the tfa^- complexes especially for the smaller Ln^{3+}. This could be attributed to steric hindrance brought about by the bulky *t*-butyl moiety in pta^-. In particular, the steric effect becomes severe with decreasing ion size of Ln^{3+} as a consequence of decreasing coordination space around the central metal ion.

To confirm if indeed pta^- sterically affects the formation of the ternary complex, the structures of $LnA_3(DEO6)$ complexes in solution were investigated by NMR spectroscopy. The changes in chemical shift caused by the complex formation, $\Delta\delta_{\mathrm{comp}}$, for the methylene protons of DEO6 in $\mathrm{Ln(pta)_3(DEO6)}$ are depicted in Fig. 10 by filled symbols. Those previously reported for $\mathrm{Ln(tta)_3(DEO6)}$ [35] are shown in open symbols for comparison. In the case of $\mathrm{La(pta)_3(DEO6)}$ complex, methylene protons b–fg1 show large downfield shifts compared to other polyether protons. The $\Delta\delta_{\mathrm{comp}}$ values for the DEO6 protons in the $\mathrm{pta^-}$ complex are similar to that reported for the $\mathrm{tta^-}$ complex. In both $\mathrm{La(pta)_3(DEO6)}$ and $\mathrm{La(tta)_3(DEO6)}$, the first three oxygen atoms from the hydroxyl end of DEO6 directly coordinate to $\mathrm{La^{3+}}$ ion. This similarity in structures explains the similar magnitude of β_{add} for the complexes of larger $\mathrm{La^{3+}}$ among the β-diketones (Fig. 6), although the β_{add} values for the complexes of $\mathrm{tta^-}$ are higher because of additional interaction as described above. The estimated structure of $\mathrm{La(pta)_3(DEO6)}$ complex optimized by MM2 calculation is shown in Fig. 11a.

In the case of $\mathrm{tta^-}$ complex of the smaller $\mathrm{Y^{3+}}$ and $\mathrm{Lu^{3+}}$, only two oxygen atoms from the hydroxyl terminal of the polyether directly coordinate to the central metal ion as shown by the significant downfield shift of methylene protons b–d in Fig. 10. This decrease in number of coordinated oxygen atoms of DEO6 is explained by the decreasing coordination number across the lanthanoid series. The usual coordination number of heavier $\mathrm{Ln^{3+}}$ ($\mathrm{Tb^{3+}}$–$\mathrm{Lu^{3+}}$) is eight, whereas that of lighter $\mathrm{Ln^{3+}}$ ($\mathrm{La^{3+}}$–$\mathrm{Sm^{3+}}$) is nine [45]. In the case of the $\mathrm{pta^-}$ complex of $\mathrm{Y^{3+}}$ (similar ionic size with $\mathrm{Dy^{3+}}$ and $\mathrm{Ho^{3+}}$), methylene protons b–d are also significantly shifted downfield. This means that the coordination mode of DEO6 in the $\mathrm{pta^-}$ complex is the same as that for the $\mathrm{tta^-}$ complex, that is, two oxygen atoms of the polyether coordinate to the central $\mathrm{Y^{3+}}$ ion. As the ease of complex formation is affected by the steric constraints imposed by the bulky *t*-butyl of $\mathrm{pta^-}$, the β_{add} values for the $\mathrm{pta^-}$ complexes of mid-sized $\mathrm{Ln^{3+}}$ are slightly lower compared to other β-diketones. The estimated structure of $\mathrm{Y(pta)_3(DEO6)}$ complex is shown in Fig. 11b.

As the ionic size further decreases such as that in $\mathrm{Lu(pta)_3(DEO6)}$ complex, only methylene proton b is significantly shifted downfield. This means that only the hydroxyl oxygen atom of DEO6 is directly coordinated to $\mathrm{Lu^{3+}}$. Molecular model for $\mathrm{Lu(pta)_3(DEO6)}$ is depicted in Fig. 11c. The bulky *t*-butyl moiety of the $\mathrm{pta^-}$ ligand does not allow the direct coordination of two oxygen atoms of DEO6 for very small $\mathrm{Lu^{3+}}$. The estimated structures corroborate with the significant decrease of stability for $\mathrm{pta^-}$ complexes around $\mathrm{Lu^{3+}}$.

5. Conclusion

The effect of substituent of β-diketone on the extraction of $\mathrm{Ln^{3+}}$ with or without the DEO6 synergistic agent was systematically investigated. Results showed that (1) the extractability of $\mathrm{LnA_3}$ binary complex is proportional to the hydrophobicity of the free ligand, (2) no steric effect of the substituent was observed in the formation of $\mathrm{LnA_3}$ complexes, (3) the planar benzoyl, naphthoyl, and thenoyl substituents do not pose any steric hindrance even in the formation of $\mathrm{LnA_3(DEO6)}$ ternary complex, (4) the mode of coordination of DEO6 for the $\mathrm{pta^-}$ complexes of large and mid-sized $\mathrm{Ln^{3+}}$ is the same as that of the complexes of other β-diketones, and (5) steric effect is significantly predominant for the $\mathrm{pta^-}$ complex of very small $\mathrm{Lu^{3+}}$ such that the number of coordinating oxygen atom of DEO6 decreased.

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