



# Effect of substituent of $\beta$ -diketones on the synergistic extraction of lanthanoids with linear polyether

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## ABSTRACT

The synergistic extraction of 14 trivalent lanthanoids ( $\text{Ln}^{3+}$ ) into 1,2-dichloroethane with a linear polyether (DEO6),  $\text{HO}(\text{C}_2\text{H}_4\text{O})_6\text{C}_{12}\text{H}_{25}$ , and  $\beta$ -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 (Hpata). By the extraction of  $\text{Ln}^{3+}$  with  $\beta$ -diketone alone, the extraction constants of the neutral  $\text{LnA}_3$  complex,  $K_{\text{ex}} = [\text{LnA}_3]_{\text{org}}[\text{H}^+]_{\text{aq}}^3/[\text{Ln}^{3+}]_{\text{aq}}[\text{HA}]_{\text{org}}^3$ , were determined. The intrinsic extraction constants,  $K_{\text{ex}}^* = [\text{LnA}_3]_{\text{org}}/[\text{Ln}^{3+}]_{\text{aq}}[\text{A}^-]_{\text{aq}}^3$ , were evaluated by employing the regular solution theory. Results indicate that the extractability of  $\text{LnA}_3$  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  $\text{Ln}^{3+}$  by the formation of  $\text{LnA}_3(\text{DEO6})$ . The ternary complex formation constants,  $\beta_{\text{add}}$ , were determined for all the  $\text{Ln}^{3+}$  and HA. The  $\beta_{\text{add}}$  of  $\text{bta}^-$  and  $\text{nta}^-$  complexes is similar with those of  $\text{tfa}^-$  complexes, indicating that planar aromatic rings do not sterically hinder even the formation of the ternary complex. The higher values of  $\beta_{\text{add}}$  for the complexes of  $\text{tta}^-$ , 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  $\text{pta}^-$  were lower compared to complexes of other  $\beta$ -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  $\text{LnA}_3(\text{DEO6})$  among HAs and across the series of  $\text{Ln}^{3+}$ . The structures thus obtained were ascertained by the molecular models created by MM2 calculation.

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## 1. Introduction

Coordination complexes of lanthanoid ions ( $\text{Ln}^{3+}$ ) have been extensively studied in the recent decades due to their increasing applications as functional materials [1]. Because of their luminescence and magnetic property,  $\text{Ln}^{3+}$  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.

$\beta$ -Diketones (HA) have been widely used as an effective extractant for rare-earth ions. One of the  $\beta$ -diketones that has been a subject of steady interest in the extraction and separation of  $\text{Ln}^{3+}$  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  $\text{Ln}^{3+}$  with  $\text{tta}^-$  forming the  $\text{Ln}(\text{tta})_3$  binary complex in 1,2-dichloroethane [15]. The  $\text{Ln}(\text{tta})_3$  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  $\text{Ln}^{3+}$  from the aqueous phase into the organic phase through the displacement of residual water molecules coordinated to the  $\text{Ln}^{3+}$ – $\beta$ -diketone complex [16]. Such synergistic effect on Htta extraction of  $\text{Ln}^{3+}$  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  $\text{tta}^-$  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  $\text{Ln}(\text{tta})_3$  complex with POE in the organic phase, that is,  $\text{Ln}(\text{tta})_3(\text{POE})$ . 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),  $\text{HO}(\text{C}_2\text{H}_4\text{O})_6\text{C}_{12}\text{H}_{25}$ , and various  $\beta$ -diketones having different substituents but with similar acid-dissociation constants is reported. The  $\beta$ -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  $\beta$ -diketones is depicted in Scheme 1. The effect of substituent of these  $\beta$ -diketones on the formation and extraction of the binary  $\text{Ln}(\text{tta})_3$  and ternary  $\text{Ln}(\text{tta})_3(\text{POE})$  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  $\text{Ln}_2\text{O}_3$  [ $\text{Ln}=\text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ ] (Shinetsu), dissolving it with 6 M  $\text{HNO}_3$ , 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 ( $\text{DCM-d}_2$ , 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  $\text{Ln}^{3+}$  and an equimolar 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 ( $\text{M}=\text{mol dm}^{-3}$ ) 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  $25.0 \pm 0.1^\circ\text{C}$  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  $\text{Ln}^{3+}$  remaining in the aqueous phase were determined with an ICP-MS (HP4500 Yokogawa Agilent). The  $\text{Ln}^{3+}$  in the organic phase was

back-extracted into 0.1 M  $\text{HNO}_3$  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  $10\text{ cm}^3$  aliquot of 1,2-dichloroethane solution containing an appropriate amount of HA was mixed with an equivalent volume 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).

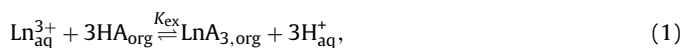
### 2.3. NMR measurements

Sample preparation for NMR measurement is described in details in our previous paper [35]. An aqueous solution containing  $\text{La}^{3+}$  or  $\text{Lu}^{3+}$  and an equivalent volume solution of dichloromethane (DCM) containing HA and DEO6 were mixed and shaken for 30 min at  $25.0 \pm 0.1^\circ\text{C}$ . 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,  $\chi_{\text{comp}}$ . The sample solutions ( $1\text{ cm}^3$ ) were dried under reduced pressure and then reconstituted with  $1\text{ cm}^3$  of  $\text{DCM-d}_2$ .  $^1\text{H}$  NMR spectra were measured at  $25^\circ\text{C}$  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  $\text{Ln}^{3+}$  from the organic phase into 0.1 M  $\text{HNO}_3$ . This is used to confirm the  $\chi_{\text{comp}}$  values of the samples.

## 3. Results

### 3.1. $\text{Ln}^{3+}$ – $\beta$ -diketonato complex

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



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

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

$$D_0 = \frac{C_{\text{Ln,org}}}{C_{\text{Ln,aq}}}, \quad (3)$$

where  $C_{\text{Ln,org}}$  and  $C_{\text{Ln,aq}}$  are the total concentrations of  $\text{Ln}^{3+}$  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  $\text{Ln}(\text{tta})_3$ . It can be assumed that  $\text{LnA}_3$  complex is extracted for any kind of  $\beta$ -diketone. Thus, the total concentration of  $\text{Ln}^{3+}$  in the organic phase is equal to the concentration of the  $\text{LnA}_3$ , that is,  $C_{\text{Ln,org}} = [\text{LnA}_3]_{\text{org}}$ . The formation of  $\text{LnA}_n^{(3-n)+}$  and  $\text{Ln}(\text{OH})_n^{(3-n)+}$  complexes in the aqueous phase can also be neglected under the present experimental conditions. Thus, the total concentration of  $\text{Ln}^{3+}$  in the aqueous phase is equal to the free  $\text{Ln}^{3+}$  ions, that is,  $C_{\text{Ln,aq}} = [\text{Ln}^{3+}]_{\text{aq}}$ . The distribution ratio becomes

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

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