



Selective separation of samarium(III) by synergistic extraction with β -diketone and methylphenylphenanthroline carboxamide

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ABSTRACT

Synergistic extraction of trivalent lanthanides (Lns(III)) with pivaloyltrifluoroacetone (HA) and *N*-methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) was evaluated across the Ln series. The distribution ratio (*D*) of Sm(III) under an identical condition was the largest among all Lns(III). The separation factor (SF) between Sm(III) and Nd(III) ($SF = D_{Sm}/D_{Nd}$) was 2.0 and SF between Sm(III) and Eu(III), (D_{Sm}/D_{Eu}) was 1.4. Upon analyzing the extraction data in detail on the basis of mass balance, it was found that the dominant extracted species of light Lns(III) was a stable ternary complex consisting of Ln(III), HA, and MePhPTA (B), namely, LnA_3B , while the dominant extracted species of heavy Lns(III) was the ion pair, $[LnA_2B]^+ClO_4^-$.

The complex for Pr(III) was very stable (the stability constant, $\bar{\beta}$, denoted as $[LnA_3B]_o[LnA_3]_o^{-1}[B]_o^{-1}$, was $10^{8.3}$). It suggests that LnA_3 can form two 5-membered rings with MePhPTA, and the size of Pr(III) matches to the distance between the donor atoms in MePhPTA. Although the stability constant decreased with increasing Ln atomic number, the synergistic extraction constant ($K_{ex31} = [LnA_3B]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3}[B]_o^{-1}$) was the largest for Sm(III). Since the constant, K_{ex31} , is given by $K_{ex31} = K_{ex30} \times \bar{\beta}$ where $K_{ex30} = [LnA_3]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3}$, the largest K_{ex31} of Sm(III) is attributable to the difference of the degree of the variation of K_{ex30} between the light and the heavy Lns(III); the increment of extraction constant of LnA_3 ($\log K_{ex30}$) for light Lns is larger than the decrement of the stability constant of LnA_3B ($\log \bar{\beta}$), while the increment of $\log K_{ex30}$ of post-Sm lessens than the decrement of $\log \bar{\beta}$. From these results, it is concluded that selective separation of a particular Ln(III) among all Lns(III) is possible using synergistic extraction with a suitable combination of a multidentate β -diketone and a Lewis base.

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1. Introduction

In these days, rare earths or lanthanides are extensively used in functional materials. Each trivalent lanthanide (Ln(III)) has unique functions; for example, europium(III) and terbium(III) show specific fluorescence, and neodymium, samarium and dysprosium are important materials in permanent magnets. Hence the development of a selective separation method of a necessary Ln(III) should be desirable. However, in general, since the properties of Lns(III) are very similar, the mutual separation is very difficult. Further, since in the detailed observation, the properties change gradually across the Ln series, e.g., the ionic size and the coordination number decrease while the surface charge density increases, a selective separation of a particular Ln(III) among the Ln series seems to be impossible,

except for the first and the last Ln(III), i.e., La(III) [1,2] and Lu(III) [3], or Eu(III) [4]. It was also reported that Y(III) was separated from heavy Lns(III) using different stability constants of aminopolycarboxylic acids [5,6].

In the present study, it was attempted to separate a particular Ln(III) by using extraction with β -diketone (HA) and Lewis base (B). When Ln(III) is extracted with HA and B, it is well-known that the extraction of Ln(III) is remarkably improved due to the extraction of the ternary complex. The advantage in using the synergistic extraction to selective separation is that the different properties of two extractants (HA and B) can be utilized to extract Ln(III). Even if the difference is small for each Ln(III), the total difference should be larger. The extraction of the ternary complex can be separated into two steps. The first step is the extraction of β -diketonato chelate as LnA_3 , and the second step is the formation of the complex between LnA_3 and B in the organic phase. Actually when the synergistic extraction data of Lns(III) with pivaloyltrifluoroacetone

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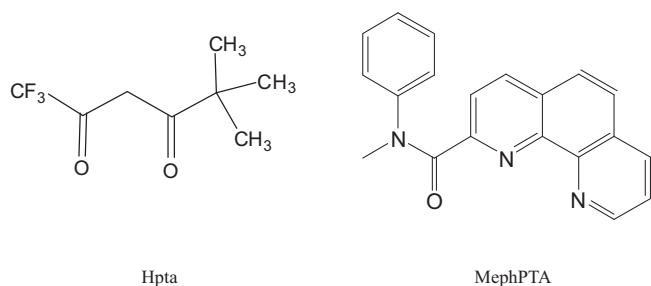


Fig. 1. Structure of pivaloyltrifluoroacetone and MePhPTA.

(Hpta) as β -diketone (HA) and 2,2'-bipyridyl (B) were carefully analyzed, it was found that the dominant extracted species was LnA_3B , and that the stability constant increased with increasing Ln atomic number, reached a maximum at Dy(III) or Ho(III), and decreased thereafter [7]. However, the synergistic extraction constant simply increased along with increasing Ln atomic number. With these findings borne in mind, we postulated that if a much stronger Lewis base is used, with which a Ln(III) can form a much more stable complex, the extraction constant should give a maximum for the Ln(III). *N*-Methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA), which is capable of forming three 5-membered rings, should be promising Lewis base for achieving good extraction of Lns(III) and selective separation of a particular Ln(III).

In the present work, the synergistic extraction of Lns(III) with Hpta and MePhPTA was evaluated across the Ln series.

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Pivaloyltrifluoroacetone (Hpta) was purchased from Dojin Laboratories. The Lewis base, MePhPTA, was prepared as follows; 1,10-phenanthroline-2-carboxylic acid (0.2 g, 0.89 mmol) was refluxed in thionyl chloride (3.18 g, 26.7 mmol) for 8 h, and then residual thionyl chloride was removed by rotary evaporation. Without isolation and purification, the resulting 1,10-phenanthroline-2-carbonyl chloride was used in the subsequent step. The crude product was dissolved in DMF (1.5 mL) at room temperature, and *N*-methylaniline (0.95 g, 8.9 mmol) was added. The mixture was stirred for 18 h at room temperature. The reaction mixture was concentrated by rotary evaporation and poured into chloroform (30 mL). The chloroform solution was washed with an aqueous solution of 1 M ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) NaOH ($3 \times 30 \text{ mL}$) and water ($3 \times 30 \text{ mL}$), and the product was purified by column chromatography (silica gel, ethyl acetate/ $\text{CHCl}_3 = 1:1$). $^1\text{H NMR}$ (CDCl_3) data of MePhPTA are as follows: δ 9.2 (br, 1H), 8.2 (br d, 1H), 8.1 (br d, 1H), 7.8 (br d, 1H), 7.7–7.5 (br m, 3H), 7.2 (br, 2H), 7.1 (br, 2H), 7.0 (br, 1H), 3.7 (s, 3H) [8]. The chemical structure of MePhPTA (B) is depicted in Fig. 1 together with Hpta. Lanthanide(III) oxides (purity > 99.9%) were purchased from the following companies: Shin-Etsu Chemical Co. (La and Gd), Nacalai Tesque Inc. (Nd), and Mitsuwa Chemicals (other Lns). Aqueous solutions of Ln(III) were prepared by dissolving the respective oxide with perchloric acid, of which concentration was stoichiometrically equivalent to the amount of substance of Ln(III), and was used after filtration. Chloroform was washed with deionized water three times just before use. Other reagents were used without purification.

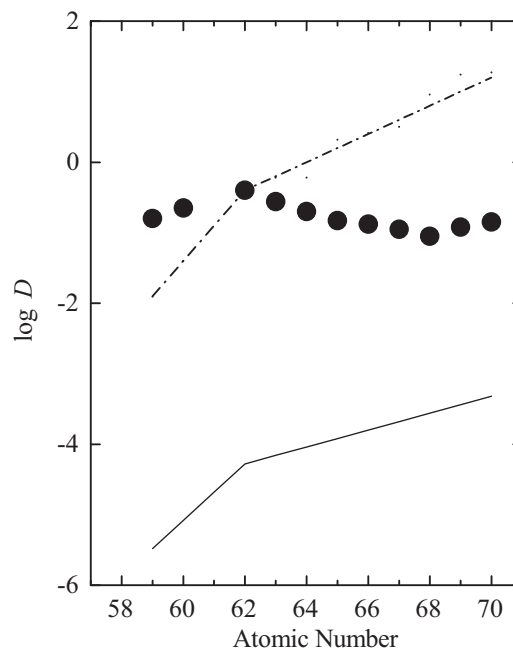


Fig. 2. Variation of $\log D$ across the lanthanide series under identical experimental conditions. Aqueous phase: 0.10 M NaClO_4 , $\text{pC}_\text{H} = 3.5$, organic phase: ● CHCl_3 containing 0.04 M Hpta and 2×10^{-4} M MePhPTA, --- CHCl_3 containing 0.04 M Hpta and 2×10^{-4} M phen, — CHCl_3 containing 0.04 M Hpta.

2.2. Procedure

Most experiments were performed in a thermostatted room at $298 \pm 1 \text{ K}$. The total ionic concentration was adjusted to 0.1 M with sodium perchlorate. The procedure used was similar to that described elsewhere [7,9]. Eight milliliters of aqueous solution containing Ln(III) ($1 \times 10^{-4} \text{ M}$) was vigorously shaken with an identical volume of chloroform solution containing Hpta and/or MePhPTA for 15 min and then, the two phases were centrifuged. The aqueous phase in which lanthanide(III) remained was diluted with 0.1 M perchloric acid by a factor of 10 to exclude the effect of the Na ion, and Ln(III) transferred into chloroform phase was back-extracted into 0.1 M HClO_4 . The concentration was then measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Horiba Ultima 2000). The distribution ratio 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 of $\text{pC}_\text{H} = 2.00$ (Corning, Mode1 445).

3. Results and discussion

3.1. Variation pattern of extraction of Lns(III) with Hpta and MePhPTA across the Ln series

First the trend of the difference of the extraction across the Ln series under a same experimental condition was compared. Fig. 2 shows the variation of the distribution ratio (D) of Ln(III) across the Ln series (●) when each Ln(III) was extracted at $\text{pC}_\text{H} = 3.5$ with 0.04 M Hpta and $2 \times 10^{-4} \text{ M}$ MePhPTA into CHCl_3 . The variation of $\log D$ under the identical experimental condition except for the absence of MePhPTA is also shown by solid line. The distribution ratio was calculated using the extraction constant of LnA_3 , $K_{\text{ex}30}$ [7]. As seen in Fig. 2, in the extraction with Hpta and MePhPTA, a greater synergistic effect was clearly observed for the lighter Lns(III) than for the heavier ones. The value of $\log D$ for Sm(III) was the largest among

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