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Novel synergism by complex ligands in solvent extraction of rare earth metals(III) with β-diketones

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Abstract

The extraction of rare earth metals(III) (RE) with hexafluoroacetylacetone (Hhfa) and 2-thenoyltrifluoroacetone (Htta) was studied in the presence of some cobalt(III) chelates such as tris(acetylacetonato)cobalt(III), tris(4-isopropyltropolonato)cobalt(III), tris(8-quinolinolato)cobalt(III), tris(8-quinolinethiolato)cobalt(III), and tris(diethyldithiocarbamato)cobalt(III) in benzene or toluene. The synergistic enhancement of the extraction of RE, especially of lanthanum(III) was found in all the systems. Therefore, those cobalt(III) chelates act as synergists or complex ligands. The equilibrium analysis and IR spectroscopic study were performed to evaluate the present synergistic mechanism. It was found that the RE–β-diketone chelates form 1:1 adducts, i.e., binuclear complexes, with the cobalt(III) chelates in the organic phase. The formation constants ($\beta_{s,1}$) were determined and compared with those reported previously. The spectroscopic studies demonstrated that adducts have two different structures with inner- and outer-sphere coordination. In the former the cobalt(III) chelate directly coordinated to the RE ion and displaced the coordinated water molecules. In the latter the hydrogen-bonding was formed between the coordinating oxygen or sulfur atoms of cobalt(III) chelate and hydrogen atoms of the coordinated water molecules in the RE–β-diketone chelate. The types of the adducts are mainly due to the steric factors of the RE–β-diketone chelates and the cobalt(III) chelates.

Keywords: Interfaces; Chemical synthesis; Ligand fields; Light absorption

1. Introduction

The synergistic extraction of rare earth metals(III) (RE) has been extensively studied using various β-diketones and neutral organic ligands such as phosphates, phosphine oxides, sulfoxides, pyridines, and quinolines. The synergism is caused by the formation of adducts of RE, which has been considered to be due to the displacement of residual coordinated water of the RE chelate by the additional ligand in the organic phase. Recently, we have found that some metal chelates act as a neutral ligand and bring about the synergistic effect in the extraction of RE with β-diketones. RE chelates with 2-thenoyltrifluoroacetone (Htta) were synergistically extracted with tris(acetylacetonato)cobalt(III) ($Co(acac)_3$) [1,2], tris(4-isopropyltropolonato)cobalt(III) ($Co(ipt)_3$) [3], tris(8-quinolinolato)cobalt(III) ($Co(q)_3$) [4], and tris(acetylacetonato)chromium(III) [5]. This phenomenon was explained by the adduct formation between $RE(tta)_3$ as a Lewis acid and the cobalt(III) chelates as a Lewis base or a complex ligand in the organic phase. Further study on the synergism with other β-diketones and complex ligands is necessary to clarify the mechanism and characteristic.

In the present paper, the effect of several cobalt(III) chelates as a complex ligand on the extraction of RE including Y with hexafluoroacetylacetone (Hhfa) and Htta in toluene was studied. The extraction constant and adduct formation constant were determined and discussed, compared with those reported previously. Furthermore, a spectrochemical study of the adduct formation was performed by electronic absorption and IR spectroscopy to clarify the role of coordinated water molecules of the RE chelates in the adduct formation.

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2. Experimental

2.1. Reagents and apparatus

Hhfa (Aldrich, 98%) was further purified by distillation in the presence of P_4O_{10}. Ligand solutions for synthesis of cobalt(III) chelates were appropriately prepared from 4-isopropyltropolone (Wako, biochemical grade), 8-quinolinethiol hydrochloride (Dojindo), and sodium diethyldithiocarbamate trihydrate (Wako, GR). $Co(ipt)_3$, tris(8-quinolinethiolato)cobalt(III) ($Co(qt)_3$), and tris(diethyldithiocarbamato)cobalt(III) ($Co(ddtc)_3$) were synthesized using the respective ligands and tris(carbonato)cobalt(III), which was prepared by the usual method [6]. Purification of the cobalt(III) chelates was thoroughly done by solvent extraction (phase washing with NaOH and HCl), column chromatography (silica gel and alumina), and recrystallization. The identification was done by the ^{1}H NMR and the elemental analysis: Found: C, 65.57; H, 6.11%. Calcd: C, 65.69; H, 6.06% for $Co(ipt)_3$. Found: C, 61.98; H, 3.73; N, 7.23. Calcd: C, 60.10; H, 3.36; N, 7.79 for $Co(qt)_3$. Found: C, 35.80; H, 5.59; N, 8.02. Calcd: C, 35.77; H, 6.00; N, 8.34 for $Co(ddtc)_3$. The purity was examined by HPLC with an ODS column and a multichannel UV/vis detector. $Co(ipt)_3$ and $Co(ddtc)_3$ were of high purity at least more than 99.5%. $Co(qt)_3$ contained geometric isomers, mer and fac, and the purity was 90.4%. RE stock solutions, Htta, $Co(acac)_3$, and other reagents were the same as those used previously [1,2].

To obtain reproducible results of the extraction of RE with Hhfa, glasswares such as centrifuge tubes were used after silanization with 2–5% dimethyldichlorosilane in toluene.

2.2. Extraction procedure

An aqueous solution of $(1.0\text{–}10) \times 10^{-5}$ M (1 M = 1 mol dm^{-3}) RE was shaken with an equal volume of an organic solution of $(7.8\text{–}55) \times 10^{-3}$ M β-diketone in the presence or absence of 2.3×10^{-5} to 1.1×10^{-2} M cobalt(III) chelate for 1 h at 298 K. After centrifugation, RE in the aqueous phase was determined by ICP-AES (Nippon Jarrell Ash ICAP-575). An aliquot of the organic phase was shaken with 0.1 M perchloric acid for 1 h to strip RE into the aqueous solution, which was subjected to the ICP-AES determination. The distribution ratio of RE was calculated from the concentrations in the organic and the aqueous phase. The equilibrium pH was measured just after phase separation with a Radiometer PHM93 pH meter with a combination glass electrode. The ionic strength of the aqueous phase was maintained at 0.10 M with sodium perchlorate.

2.3. Spectroscopic measurements

A sample solution containing RE chelate and cobalt(III) chelate for the measurement of electronic absorption was prepared by mixing the cobalt(III) chelate solution with the RE–β-diketone chelate solution prepared by the solvent extraction of 1×10^{-2} M RE with $(1\text{–}2) \times 10^{-1}$ M Hhfa in toluene at pH 4.5–4.7. Electronic absorption spectra of $(1.5\text{–}3.0) \times 10^{-3}$ M $Co(ipt)_3$ were measured in the presence of varying concentration of $RE(tta)_3$ (RE: Sm and Lu) at 500–700 nm with a JASCO V-560 UV/vis spectrophotometer at 298 K.

A sample solution for the IR measurement was prepared by the same manner except that 2.0×10^{-2} M Hhfa was used for $(8\text{–}10) \times 10^{-3}$ M RE because of the suppression of an excess of Hhfa in the sample solution. IR spectra of free water and the coordinated water of $(3\text{–}4) \times 10^{-3}$ M $RE(hfa)_3$ (Ln: Sm and Lu) in toluene were measured in the presence of varying concentration of $Co(ipt)_3$ at 3000–4000 cm^{-1} with a Shimadzu-8200A FT-IR spectrophotometer at 298 K. A demountable liquid cell with calcium fluoride windows was used and the path length was adjusted to 1 mm.

3. Results and discussion

3.1. Extraction of RE with Hhfa

The extraction of RE with β-diketone (HA) in an organic phase (org) is expressed as:

$$\mathrm{RE}^{3+} + 3\mathrm{HA}_{\mathrm{org}} \rightleftharpoons \mathrm{RE(A)}_{3,\mathrm{org}} + 3\mathrm{H}^+$$

$$K_{\mathrm{ex}} = \frac{[\mathrm{RE(A)}_3]_{\mathrm{org}}[\mathrm{H}^+]^3}{[\mathrm{RE}^{3+}][\mathrm{HA}]^3_{\mathrm{org}}} \tag{1}$$

where K_{ex} is the extraction constant. The distribution ratio of RE is given by:

$$D_0 = \frac{[\mathrm{RE(A)}_3]_{\mathrm{org}}}{[\mathrm{RE}^{3+}] + \sum \left[\mathrm{RE(A)}_n^{(3-n)+}\right]} \tag{2}$$

and can be rewritten using distribution constant ($K_{\mathrm{D,HA}}$) and acid-dissociation constant (K_{HA}) of HA, formation constant (β_n) of $\mathrm{RE(A)}_n$ in the aqueous phase, and K_{ex}:

$$D_0 = \frac{K^3_{\mathrm{D,HA}} K_{\mathrm{ex}} [\mathrm{A}^-]^3}{K^3_{\mathrm{HA}}(1 + \Sigma\beta_n[\mathrm{A}^-]^n)} \tag{3}$$

The equilibrium concentration of A^- in the aqueous phase was calculated from the total concentration (C_{HA}) of HA and pH as follows:

$$[\mathrm{A}^-] = \frac{C_{\mathrm{HA}}}{1 + ((1 + K_{\mathrm{D,HA}})[\mathrm{H}^+])/K_{\mathrm{HA}}} \tag{4}$$

$K_{\mathrm{D,HA}}$ of Hhfa between the toluene and the aqueous phase was determined to be $10^{-1.95}$ by spectrophotometry in this work.

The extraction of Y, La, Pr, Sm, Gd, Er, and Lu with different concentrations of Hhfa in toluene was carried out at varying pH. The K_{ex} and β_n values were determined by applying a nonlinear least-squares method based on Eq. (3) to

Table 1
Equilibrium constants in the RE(III)–Hhfa–toluene system

RE	$\log([\mathrm{hfa}^-]/\mathrm{M})$	$\log \beta_1$	$\log K_{\mathrm{ex}}$
Y	−2.95 to −2.48	2.26 ± 0.31	−1.53 ± 0.08
La	−2.58 to −1.87	–[a]	−2.88 ± 0.02
Pr	−2.62 to −1.98	2.20 ± 0.12	−2.28 ± 0.06
Sm	−3.00 to −2.09	2.47 ± 0.07	−1.54 ± 0.03
Gd	−3.11 to −2.43	3.08 ± 0.36	−1.34 ± 0.25
Er	−2.98 to −2.42	–[a]	−1.76 ± 0.02
Lu	−3.10 to −2.23	2.21 ± 0.22	−1.11 ± 0.06

[a] Not determined.

the plots of the $\log D_0$ against logarithmic concentration of hfa^- in the aqueous phase. Table 1 shows these equilibrium constants obtained. The β_1 values of La and Er were not determined because of the limited concentration range of hfa^- under the given conditions. The β_1 values of Sm and Lu were reasonably consistent with those in the Hhfa-benzene system [7]. The K_{ex} and β_1 values of Y are close to those of Sm as expected from the literature in which the position of Y in the lanthanide (Ln) series is investigated to be on the light to middle Ln with respect to the complex formation with relatively weak ligands as acetate [8].

Since the D_0 values calculated by Eq. (3) using K_{ex} and β_1 determined were in good agreement with the experimental plots, these equilibrium constants can be used for the calculation of D/D_0 as shown below.

3.2. *Effect of cobalt(III) chelates on the extraction of RE with Hhfa*

Fig. 1 shows the significant enhancement of the distribution ratio of RE by the addition of 3.0×10^{-3} M $\mathrm{Co(ipt)_3}$. The D values of Y, La, Sm, and Lu increased by a factor of 40, 2500, 630, and 30, respectively. This enhancement can be ascribed to the formation of adduct of $\mathrm{RE(hfa)_3}$ with $\mathrm{Co(ipt)_3}$ in the organic phase. Therefore, the distribution ratio of RE is expressed as follows:

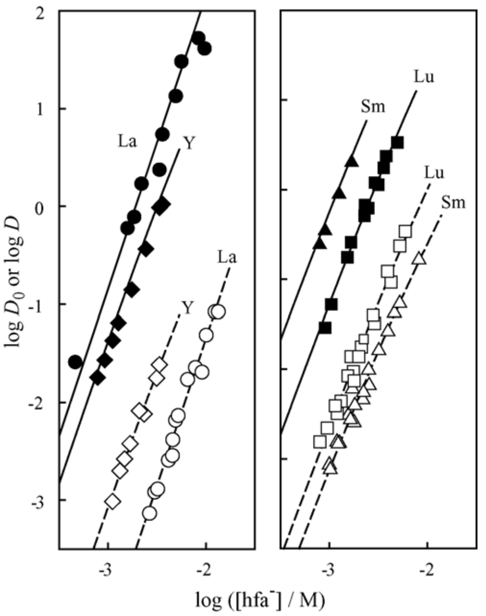

Fig. 1. Distribution ratio of RE in the presence (solid lines) or absence (broken lines) of 3.0×10^{-3} M $\mathrm{Co(ipt)_3}$ as a function of the hfa^- concentration in the aqueous phase: $C_{\mathrm{Hhfa}} = (0.78\text{–}5.5) \times 10^{-2}$ M.

$$D = \frac{[\mathrm{RE(A)_3}]_{\mathrm{org}} + \sum [\mathrm{RE(A)_3(Co(L)_3)}_m]_{\mathrm{org}}}{[\mathrm{RE}^{3+}] + \sum [\mathrm{RE(A)}_n^{(3-n)+}]} \quad (5)$$

The adduct formation reaction in the organic phase is expressed as:

$$\mathrm{RE(A)}_{3,\mathrm{org}} + m\mathrm{Co(L)}_{3,\mathrm{org}} \rightleftharpoons \mathrm{RE(A)_3(Co(L)_3)}_{m,\mathrm{org}} \quad (6)$$

$$\beta_{\mathrm{s},m} = \frac{[\mathrm{RE(A)_3(Co(L)_3)}_m]_{\mathrm{org}}}{[\mathrm{RE(A)_3}]_{\mathrm{org}}[\mathrm{Co(L)_3}]_{\mathrm{org}}^m} \quad (7)$$

where $\beta_{\mathrm{s},m}$ is the adduct formation constant. The following relationship can be derived from Eqs. (3), (5) and (7):

$$\frac{D}{D_0} = 1 + \Sigma\beta_{\mathrm{s},m}[\mathrm{Co(L)_3}]_{\mathrm{org}}^m \quad (8)$$

Fig. 2 shows the relationship between $\log(D/D_0)$ and $\log[\mathrm{Co(ipt)_3}]_{\mathrm{org}}$. Since the plots of every RE indicate straight lines with a slope of unity, a 1:1 adduct of $\mathrm{RE(hfa)_3}$ and $\mathrm{Co(ipt)_3}$ is formed in the organic phase. The log–log plots of Eq. (8) for Y, La, Sm, and Lu in the Hhfa-$\mathrm{Co(acac)_3}$ system also gave the straight lines with a slope unity in the higher concentration region of $\mathrm{Co(acac)_3}$. These results indicate the formation of a binuclear complex in the organic phase and are consistent with our previous results using Htta [1–3]. The $\beta_{\mathrm{s},1}$ values were determined by a nonlinear least-squares method for those plots based on Eq. (8), and are listed in Table 2.

3.3. *Other cobalt(III) complex ligand systems*

The extraction of La and Eu with 1.0×10^{-2} M Htta in toluene was investigated in the presence of 2.0×10^{-4} M

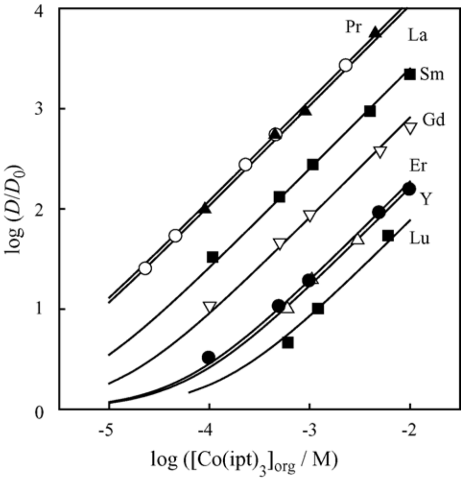

Fig. 2. $\log(D/D_0)$ of RE as a function of the $\mathrm{Co(ipt)_3}$ concentration in toluene: $C_{\mathrm{Hhfa}} = 3.0 \times 10^{-2}$ M, pH 3.1–3.6.

Table 2
Summary of adduct formation constants (log $\beta_{s,1}$) in the RE–β-diketone-complex ligand systems

	Hhfa $Co(acac)_3$ toluene	Hhfa $Co(ipt)_3$ toluene	Htta $Co(qt)_3$ toluene	Htta $Co(ddtc)_3$ toluene	Htta [2] $Co(acac)_3$ benzene	Htta [3] $Co(ipt)_3$ benzene	Htta [4] $Co(q)_3$ benzene	Hacac [14] $Co(acac)_3$ benzene
La	5.04	6.03	3.67	<2.0	4.64	5.05	4.96	2.59
Ce					4.6	4.97		
Pr		6.08			4.59	4.6		
Nd					4.53	4.02		
Sm	4.72	5.4			3.34	3.75		
Eu			3.29	<1.6	2.95	3.59	4.56	
Gd		4.91			2.87	2.98		
Tb					2.5	2.78		
Dy					2.35			
Ho					2.31			
Er		4.27			2.09	2.59		
Tm					2.05			
Yb					2.07			
Lu	3.03	3.88			2.07	2.58	3.97	1.70
Y	3.41	4.21						

$Co(qt)_3$ or 2.0×10^{-3} M $Co(ddtc)_3$. The enhancement effect of $Co(qt)_3$ on the distribution ratio of La was observed and was larger than that of Eu. The $\beta_{s,1}$ values were determined by assuming the formation of the 1:1 adduct and using Eq. (8). The values in Hhfa-$Co(ddtc)_3$ were also estimated in the same manner, and these data are summarized in Table 2.

The $\beta_{s,1}$ values in Hhfa-$Co(ipt)_3$, especially those of La and Pr, are as high as more than 10^6, which is higher than $\beta_{s,1}$ of La in the Hhfa-2,2′-bipyridine (bpy)-benzene system, $10^{5.61}$ [9]. Also the value of La in Htta-$Co(ipt)_3$ is close to that in Htta-bpy, $10^{5.36}$ [10]. Thus the adducts or binuclear complexes are very stable and the complexation ability or Lewis-basicity of $Co(ipt)_3$ is comparable to the bidentate ligand like bpy. To understand the adduct formation in the hfa system, spectroscopic studies using electronic and IR absorption were carried out.

3.4. *Spectrochemical studies of adduct formation*

Electronic absorption spectra of 1.5×10^{-3} M $Co(ipt)_3$ were measured in the presence of 4.4×10^{-4} to 4.2×10^{-3} M $Sm(hfa)_3$. An absorption band of the d–d transition with a maximum absorbance at 620 nm is gradually shifted to the shorter wavelength with increase in the concentration of $Sm(hfa)_3$. Fig. 3 shows the relationship between the wavelength of the d–d transition band and the molar ratio of $Sm(hfa)_3$ to $Co(ipt)_3$ in toluene. The plot indicates two straight lines with a clear intersection at the molar ratio of unity, which corresponds to the formation of a 1:1 adduct as expected from the extraction equilibrium analysis. Consequently, the shift of the d–d transition band is induced by the adduct formation and related to the change in the ligand field stabilization energy or the structural deformation of $Co(ipt)_3$ [3]. Therefore, the direct coordination of the oxygen atoms of $Co(ipt)_3$ toward the Sm ion in $Sm(hfa)_3$ is expected. On the other hand, no shift of the d–d transition band of $Co(ipt)_3$ was observed in $Lu(hfa)_3$ although the adduct was formed in the solution. This suggests the weaker bonding between $Lu(hfa)_3$ and the oxygen atoms of $Co(ipt)_3$.

It is known that RE–β-diketonate chelates have two or three coordinated water molecules in the organic phase, e.g., $Eu(tta)_3(H_2O)_3$ in benzene [5]. Hence, some water molecules can be displaced by the additional ligand in the inner sphere of RE. On the other hand, when the adduct formation is caused in the outer sphere of RE, water molecules are not displaced by the ligand. Such behavior of coordinated water molecules was studied by IR.

Fig. 4 shows IR absorption spectrum of 4.0×10^{-3} M hydrated $Sm(hfa)_3$ chelate extracted into toluene (dotted line) and the mixture with 5.7×10^{-3} M of $Co(ipt)_3$ (solid line). The dotted line shows the strong absorption peaks of excess free water at 3595 and 3680 cm^{-1} which are due to the symmetric and asymmetric O–H stretching vibration of H_2O as well as the shoulders at 3550 and 3640 cm^{-1} and broad band at 3300 cm^{-1}, which are due to the coordinated water molecules in $Sm(hfa)_3(H_2O)_n$ [2,3,5]. When $Co(ipt)_3$ was added to the $Sm(hfa)_3(H_2O)_n$ solution, IR absorption due to the coordinated water molecules decreases with

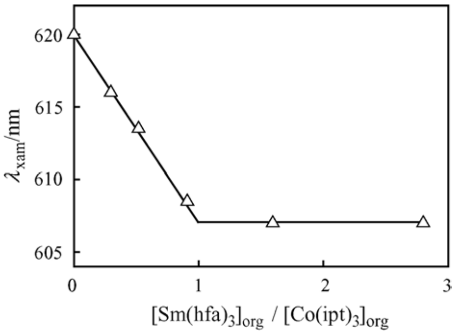

Fig. 3. Relationship between the wavelength at the absorption maximum of $Co(ipt)_3$ and the molar ratio of $RE(hfa)_3$ to $Co(ipt)_3$: $[Co(ipt)_3] = 1.5 \times 10^{-3}$ M; $[Sm(hfa)_3] = (0–4.2) \times 10^{-3}$ M.

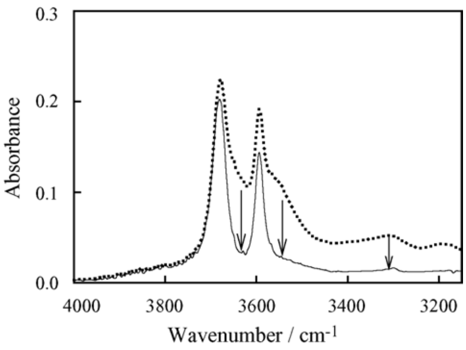

Fig. 4. IR spectra of hydrated Sm(hfa)$_3$ in the presence or absence of Co(ipt)$_3$ in toluene. [Sm(hfa)$_3$] = 4.0×10^{-3} M. Dotted line, without Co(ipt)$_3$; solid line, 5.7×10^{-3} M Co(ipt)$_3$.

increase in the Co(ipt)$_3$ concentration and almost disappears at the mole ratio of Sm(hfa)$_3$ to Co(ipt)$_3$ of 1.4. This spectral change demonstrates that the coordinated water molecules of Sm(hfa)$_3$ are displaced by Co(ipt)$_3$. Therefore, Co(ipt)$_3$ directly coordinates to the central Sm ion through the coordinating oxygen atoms of the ipt ligands.

Fig. 5 shows the IR spectra of the hydrated Lu(hfa)$_3$ chelate in the presence or absence of Co(ipt)$_3$. Absorption corresponding to the coordinated water molecules and an excess of free water are observed. The variation of the spectra of Lu by the addition of Co(ipt)$_3$ is obviously different from that of Sm. The absorbance of the two shoulders for the coordinated water molecules decreases, but that of the broad band increases with increase in the Co(ipt)$_3$ concentration. This suggests the formation or enhancement of hydrogen bond of the coordinated water molecules with Co(ipt)$_3$. Therefore, the adduct should be formed by hydrogen bonding between the hydrogen atoms of coordinated water molecules and the oxygen atoms of Co(ipt)$_3$.

3.5. Comparison of the adduct formation constants

The variation of $\beta_{s,1}$ in various β-diketone-cobalt(III) complex ligand systems is summarized in Fig. 6. The $\beta_{s,1}$ values are plotted against the ionic radius of RE at the coordination number of 8. The plots of Y in the Hhfa-CoL$_3$ are positioned on the heavy RE as expected from its ionic radius. This result contrasts with that for K_{ex} in Table 1 and means the importance of the steric factors in the adduct formation with the complex ligand.

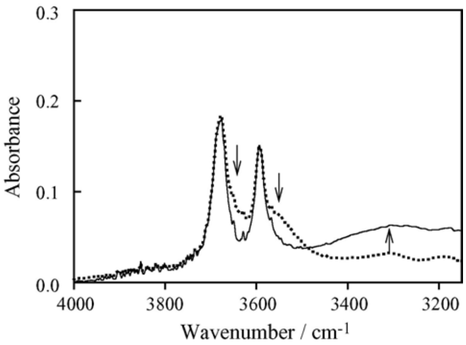

Fig. 5. IR spectra of hydrated Lu(hfa)$_3$ in the presence or absence of Co(ipt)$_3$ in toluene. [Lu(hfa)$_3$] = 2.8×10^{-3} M. Dotted line, without Co(ipt)$_3$; solid line, 7.2×10^{-3} M Co(ipt)$_3$.

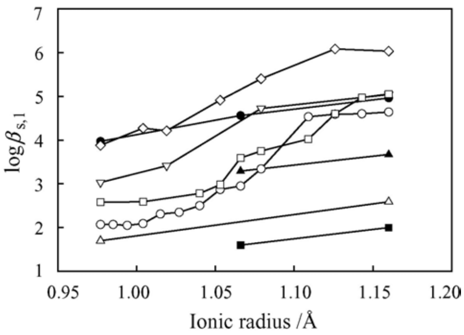

Fig. 6. Variation of the adduct formation constants vs. ionic radius of RE at the coordination number of 8. (◇) hfa-Co(ipt)$_3$; (▽) hfa-Co(acac)$_3$; (●) tta-Co(q)$_3$; (□) tta-Co(ipt)$_3$; (○) tta-Co(acac)$_3$; (▲) tta-Co(qt)$_3$; (△) acac-Co(acac)$_3$; (■) tta-Co(ddtc)$_3$.

The $\beta_{s,1}$ values increase with increasing the ionic radius of RE, but there are significant differences between the small and the large RE ion in the Hhfa and Htta systems with Co(ipt)$_3$ and Co(acac)$_3$. In the middle to large RE of which the coordination number is usually nine, the CoL$_3$ may act as a terdentate ligand with three coordinating oxygen atoms of the CoL$_3$ and directly coordinate to the central RE. As the result, the stable adducts are formed. On the other hand, in the small RE ion, which has the coordination number of 8, an outer sphere complex is formed because the CoL$_3$ cannot enter the inner sphere of the RE–β-diketone chelates. These mechanisms of adduct formation are supported by the results of the electronic and IR absorption spectroscopy.

The $\beta_{s,1}$ values are strongly influenced by β-diketones. The Hhfa systems with Co(ipt)$_3$ and Co(acac)$_3$ as a synergist have higher $\beta_{s,1}$ values than other β-diketone systems. The similar trend is usually observed in the synergistic extraction with β-diketones and neutral ligands, e.g., trioctylphosphine oxide for metal(II) [11] and bpy for RE [9]. This can be explained by the higher Lewis acidity of the RE–hfa chelates, which is derived from the very low basicity of hfa. The present $\beta_{s,1}$ values of Lu-β-diketone chelates should give the relative acidity or the hydrogen-bond donating power of coordinated water molecules because the adduct formation with the complex ligand is due to the outer sphere hydrogen-bond and is free from the steric effect.

In the Htta system, the $\beta_{s,1}$ values of Lu are in the following order, Co(q)$_3$ > Co(ipt)$_3$ > Co(acac)$_3$, which is consistent with the order of hydrogen-bond accepting power (basicity) of the complex ligands [12,13]. In the La case, however, the $\beta_{s,1}$ values decrease in the order of Co(ipt)$_3$ ≥ Co(q)$_3$ > Co(acac)$_3$. This suggests the steric effect of bidentate mer-Co(q)$_3$ [4] as a complex ligand on the adduct formation owing to the inner sphere coordination.

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