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Effect of Tris(acetylacetonato)chromium(III) as a Complex Ligand on the Extraction of Lanthanoid(III) with 2-Thenoyltrifluoroacetone

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Enhancement of the extraction of lanthanoid(III) (Ln) with 2-thenoyltrifluoroacetone (Htta) in cyclohexane or benzene has been observed by the addition of tris(acetylacetonato)chromium(III) (Cr(acac)$_3$). The equilibrium analysis suggested that the effect of Cr(acac)$_3$ could be ascribed to the formation of a 1 : 1 adduct of Ln(tta)$_3$ with Cr(acac)$_3$, i.e., a binuclear complex, in the organic phase. The formation constants ($\beta_{s,1}$) of the adducts were determined across the Ln series. The $\beta_{s,1}$ values decreased with decrease in the ionic radii of Ln in the light Ln, and were constant in the heavy Ln. Spectroscopic studies such as electronic absorption, IR, and ^{1}H NMR were performed to explain the difference between the light and heavy Ln. The adduct of light Ln is mainly an inner sphere complex in which Cr(acac)$_3$ displaces the coordinated water of the Ln chelate and directly coordinates to the Ln ion. On the other hand, the adduct of heavy Ln is an outer sphere complex formed by the hydrogen bonding between Cr(acac)$_3$ and the coordinated water of the Ln chelate. Abilities of Cr(acac)$_3$ as a complex ligand, i.e., the basicity and the steric factor, were evaluated by comparing with Co(acac)$_3$ reported previously.

Tris(β-diketonato)lanthanoid(III) extracted into an organic phase has a strong tendency to form adduct complexes with electrically neutral ligands or Lewis bases. The adduct formation has been considered to be due to the displacement of residual coordinated water molecules of the lanthanoid(III) (Ln) chelate by the neutral ligands in the organic phase. This causes significant enhancement of the extraction of Ln, that is, a synergistic effect of the β-diketone and the neutral ligand. On the other hand, coordinately saturated chelates such as tris(acetylacetonato)metals(III) of aluminum(III),[1] scandium(III),[2] chromium(III),[3] iron(III),[4] cobalt(III),[5] gallium(III),[6] and indium(III)[6] have been found to form stable association complexes with proton donors such as chlorophenol derivatives in the organic phase. This phenomenon has been ascribed to the hydrogen-bond formation between coordinating oxygen atoms of the chelate and hydroxy hydrogen of the chlorophenol. This shows that these coordinately saturated chelates act as hydrogen-bond accepters or Lewis bases. Therefore, some interaction is expected between coordinately unsaturated Ln chelates and the coordinately saturated metal(III) chelates described above.

More recently, in fact, we have found binuclear complexation between tris(thenoyltrifluoroacetonato)lanthanoid(III) (Ln(tta)$_3$) and tris(acetylacetonato)cobalt(III) (Co(acac)$_3$) in water-saturated benzene.[7,8] The formation constants of the binuclear complex showed the large difference between light Ln and heavy Ln. Various spectroscopic studies suggested that the behavior of the coordinated water and the structure of the binuclear complex were quite different between light and heavy Ln.

In the present research, the effect of tris(acetylacetonato)chromium(III) (Cr(acac)$_3$) on the extraction of Ln with thenoyltrifluoroacetone (Htta) in benzene and cyclohexane is studied to clarify the adduct formation between Ln(tta)$_3$ and Cr(acac)$_3$. Furthermore, spectrochemical studies of the adduct formation are performed by electronic absorption, IR, and ^{1}H NMR, especially to clarify the role of coordinated water molecules of the Ln chelates in the adduct formation. The ability of Cr(acac)$_3$ as a Lewis base or a complex ligand is evaluated and discussed by comparing with that of Co(acac)$_3$.

Experimental

Reagents and Apparatus. Cr(acac)$_3$ (Dojindo) was recrystallized from benzene–hexane and dried in vacuo. The purity was confirmed to be high enough by high performance liquid chromatography (HPLC). Benzene and cyclohexane were of HPLC grade and were used without further purification. Ln stock solutions were prepared by dissolving each high purity Ln oxide in nitric acid, evaporating to dryness, and redissolving in perchloric acid. Htta and other reagents were the same as those used previously.[7]

Eu(tta)$_3$(H$_2$O)$_3$ was synthesized according to the literature[9] and stored in a vacuum desiccator. Yield 53%. Mp 132–140 °C. Found: C, 33.31; H, 2.10%. Calcd. for $C_{24}H_{18}EuF_9S_3O_9$: C, 33.15; H, 2.17%.

Ln ions were determined with a Nippon Jarrell Ash ICAP-575 inductively coupled plasma atomic emission spectrophotometer (ICP-AES). Electronic absorption spectra were measured with a JASCO V-560 UV/vis spectrophotometer with a 10-mm cuvette at 25 °C. IR spectra were measured with a Shimadzu-8200A FT-IR spectorophotometer at 25 °C. A demountable liquid cell with calcium fluoride windows was used and the path length was adjusted to 1 mm. Proton-NMR was recorded on a JEOL GSX-400 NMR spectrometer. TMS was used as an internal standard for chemical shifts.

Determination of Distribution Constant of Cr(acac)$_3$. A cyclohexane solution of 1.0×10^{-3} M (1 M = 1 mol dm^{-3}) Cr(acac)$_3$ was shaken with an equal volume of an aqueous phase

(0.10 M (H, Na)ClO$_4$) for 5–60 min at 25 °C. The absorbance of Cr(acac)$_3$ in the organic phase before ($A_{\rm i,org}$) and after ($A_{\rm org}$) shaking was measured at 390 nm, and the distribution constant ($K_{\rm D,Cr}$) was calculated as follows:

$$K_{\rm D,Cr} = A_{\rm org}/(A_{\rm i,org} - A_{\rm org}). \quad (1)$$

The distribution constant was determined to be 1.04 ± 0.02 from 5 measurements. This value was used to calculate the Cr(acac)$_3$ concentration in the organic phase after equilibration with the aqueous phase.

Procedure of Extraction of Ln Ions. An aqueous solution of 1.0×10^{-6} –1.0×10^{-5} M Ln at pH 3.4–5.5 was shaken with an equal volume of benzene or cyclohexane containing 5.0×10^{-3} –5.0×10^{-2} M Htta in the presence or absence of Cr(acac)$_3$ (5.0×10^{-4} –5.0×10^{-2} M) for 1 h at 25 °C. After phase separation, Ln in the aqueous phase was determined with an ICP-AES, and that in the organic phase was determined in the same manner after stripping Ln into 0.1 M perchloric acid. The distribution ratio (D) of Ln was calculated from the Ln concentrations in both phases. The equilibrium pH was measured using a Radiometer PHM93 REFERENCE pH meter with a combination glass electrode calibrated by the usual pH standard solutions just after phase separation. The ionic strength of the aqueous phase was maintained at 0.10 M with sodium perchlorate.

Sample Preparation for Spectroscopic Measurements. Sample solutions for the measurement of electronic absorption spectra of an adduct were prepared by mixing a benzene solution of Cr(acac)$_3$ and a Ln(tta)$_3$ solution prepared by the solvent extraction of 1.0×10^{-2} M Ln with 1.0×10^{-1} M Htta in benzene at pH 5.7–6.3. The sample solutions for the ^{1}H NMR and IR measurements were prepared in the same manner except that 3.0×10^{-2} M Htta equivalent to the total concentration of Ln was used because of the suppression of an excess of Htta in the sample solution. The concentration of the free Htta in the organic phase was less than 9×10^{-4} M. The water content in the sample solutions was kept constant at 2.0×10^{-2} M using benzene saturated with water and anhydrous benzene. In the IR experiment, an anhydrous benzene solution of Eu(tta)$_3$(H$_2$O)$_3$ was also used.

Theoretical

The distribution ratio (D_0) of Ln with Htta can be written as follows:

$$D_0 = \frac{[\mathrm{Ln(tta)_3}]_{\rm org}}{[\mathrm{Ln^{3+}}] + \sum[\mathrm{Ln(tta)}_n{}^{(3-n)+}]}, \quad (2)$$

where the subscript, org, denotes the organic phase. When Ln(tta)$_n{}^{(3-n)+}$ chelates in the aqueous phase can be neglected, the extraction equilibrium of Ln is given as

$$\mathrm{Ln^{3+}} + 3\mathrm{Htta_{org}} \rightleftharpoons \mathrm{Ln(tta)_{3,org}} + 3\mathrm{H^+}. \quad (3)$$

The extraction constant ($K_{\rm ex}$) for Eq. 3 is written as follows:

$$K_{\rm ex} = \frac{[\mathrm{Ln(tta)_3}]_{\rm org}[\mathrm{H^+}]^3}{[\mathrm{Ln^{3+}}][\mathrm{Htta}]_{\rm org}{}^3} = \frac{K_{\rm HA}{}^3 D_0}{K_{\rm D,HA}{}^3[\mathrm{tta^-}]^3}, \quad (4)$$

where $K_{\rm HA}$ and $K_{\rm D,HA}$ denote the acid-dissociation constant and the distribution constant of Htta, respectively.

Supposing that Cr(acac)$_3$ acts as a complex ligand, the distribution ratio of Ln can be written as

$$D = \frac{[\mathrm{Ln(tta)_3}]_{\rm org} + \sum[\mathrm{Ln(tta)_3(Cr(acac)_3)}_m]_{\rm org}}{[\mathrm{Ln^{3+}}] + \sum[\mathrm{Ln(tta)}_n{}^{(3-n)+}]}. \quad (5)$$

When tta chelates in the aqueous phase can be neglected, Eq. 5 is rewritten using $K_{\rm ex}$ as follows:

$$D = \frac{K_{\rm ex}K_{\rm D,HA}{}^3[\mathrm{tta^-}]^3(1 + \sum\beta_{\rm s,m}[\mathrm{Cr(acac)_3}]_{\rm org}{}^m)}{K_{\rm HA}{}^3}, \quad (6)$$

where $\beta_{{\rm s},m}$ is the adduct formation constant in the organic phase corresponding to the following equilibrium:

$$\mathrm{Ln(tta)_{3,org}} + m\mathrm{Cr(acac)_{3,org}} \rightleftharpoons \mathrm{Ln(tta)_3(Cr(acac)_3)}_{m,\rm org}. \quad (7)$$

$$\beta_{{\rm s},m} = \frac{[\mathrm{Ln(tta)_3(Cr(acac)_3)}_m]_{\rm org}}{[\mathrm{Ln(tta)_3}]_{\rm org}\,[\mathrm{Cr(acac)_3}]_{\rm org}{}^m}. \quad (8)$$

From Eqs. 4 and 6, the following equation is derived:

$$D/D_0 = 1 + \Sigma\beta_{\rm s,m}[\mathrm{Cr(acac)_3}]_{\rm org}{}^m. \quad (9)$$

The enhancement of the distribution ratio of Ln is expressed as a function of the Cr(acac)$_3$ concentration in the organic phase.

Results and Discussion

Enhancement of Extraction with Cr(acac)$_3$. The extraction of Ln with different concentrations of Htta was carried out in the presence or absence of a constant concentration of Cr(acac)$_3$ in benzene. Since Cr(acac)$_3$ is quite inert, it is not necessary to consider the dissociation or decomposition of the chelate under the given conditions. In fact, it was ascertained that the distribution ratio of Ln in the presence of 5.0×10^{-2} M Cr(acac)$_3$ did not vary during the shaking for 0.5–3 h. Figure 1a shows plots of the logarithms of the distribution ratio of Ln against the logarithms of the tta$^-$ concentration in the aqueous phase. The tta$^-$ concentration was calculated from the total concentration of Htta ($C_{\rm HA}$) and pH as follows:

$$[\mathrm{tta^-}] = \frac{C_{\rm HA}}{1 + (K_{\rm D,HA} + 1)[\mathrm{H^+}]/K_{\rm HA}}. \quad (10)$$

The literature values, $\log K_{\rm D,HA} = 1.62$[10] and $\log K_{\rm HA} = -6.23$,[11] were adopted in this paper. Remarkable enhancement of the distribution ratio, especially of La, is observed by the addition of 5.0×10^{-2} M Cr(acac)$_3$; the values of La, Eu, and Lu increase by a factor of 120, 6, and 4 respectively. All the plots give straight lines with a slope of 3, as expected from Eqs. 4 and 6. Therefore, three molecules of tta$^-$ participate in the extraction of Ln irrespective of the presence of Cr(acac)$_3$. The $K_{\rm ex}$ values were also determined by using the D_0 plots in Fig. 1 and are summarized in Table 1. As shown in Fig. 1b, similar results were obtained in cyclohexane, where $\log K_{\rm D,HA} = 0.56$[12] was used. The D values of La, Eu, and Lu increased by a factor of 60, 3, and 1.2 respectively by the addition of Cr(acac)$_3$ even in a concentration as low as 1.0×10^{-3} M.

Plots of log (D/D_0) toward log [Cr(acac)$_3$]$_{\rm org}$ in the extraction of various Ln metals with Htta and Cr(acac)$_3$ in cyclohexane are shown in Fig. 2. The equilibrium concentration of Cr(acac)$_3$ in the organic phase was calculated using the distribution constant, 1.04 in cyclohexane and 338[13] in benzene. The D/D_0 values of respective Ln metals increase with increase

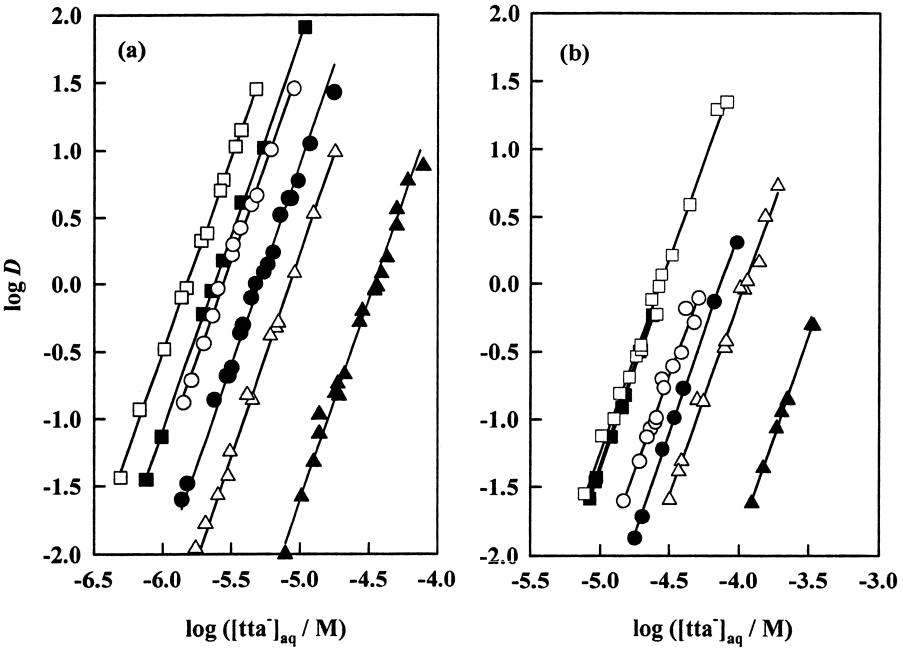

Fig. 1. Enhancement of the extraction of Ln with 5.0×10^{-3}–5.0×10^{-2} M Htta in benzene (a) or cyclohexane (b) by the addition of $Cr(acac)_3$ at pH 3.4–5.5.
(a) Open symbols, with 5.0×10^{-2} M $Cr(acac)_3$; solid symbols, without $Cr(acac)_3$ (Ref. 7); △▲, La; ○●, Eu; □■, Lu.
(b) Open symbols, with 1.0×10^{-3} M $Cr(acac)_3$; solid symbols, without $Cr(acac)_3$; △▲, La; ○●, Eu; □■, Lu.

Table 1. Extraction Constants (K_{ex}) and Adduct Formation Constants ($\beta_{s,1}$) in the Ln(III)–Htta–$Cr(acac)_3$ System

Ln	Cyclohexane		Benzene		
	log K_{ex}	log $\beta_{s,1}$	log K_{ex}	log $\beta_{s,1}$	log $\beta_{s,1}$ a)
La	−10.25 ± 0.01	5.08 ± 0.02	−10.14 ± 0.01	3.37 ± 0.02	3.41 ± 0.27
Ce			−9.19 ± 0.01	3.25 ± 0.02	
Pr	−9.53 ± 0.01	4.80 ± 0.03	−8.99 ± 0.01	3.10 ± 0.02	3.19 ± 0.15
Nd	−8.95 ± 0.01	4.22 ± 0.02	−8.52 ± 0.01	2.49 ± 0.01	2.52 ± 0.16
Sm	−8.13 ± 0.01	3.85 ± 0.01	−7.70 ± 0.01	2.14 ± 0.01	2.30 ± 0.18
Eu	−7.95 ± 0.01	3.65 ± 0.01	−7.64 ± 0.01	1.97 ± 0.02	2.34 ± 0.19
Gd	−8.03 ± 0.01	3.44 ± 0.02	−7.62 ± 0.01	1.83 ± 0.01	2.27 ± 0.20
Tb			−7.21 ± 0.01	1.83 ± 0.02	2.24 ± 0.20
Er	−7.45 ± 0.01	3.43 ± 0.01	−6.89 ± 0.01	1.82 ± 0.01	2.14 ± 0.19
Lu	−7.11 ± 0.01	3.48 ± 0.01	−6.66 ± 0.01	1.82 ± 0.01	2.12 ± 0.21

Numerical values after ± show the standard errors.
a) Spectrophotometry.

in the $Cr(acac)_3$ concentration. The plots for La and Pr give straight lines with a slope of 1.0 over a wide concentration range of $Cr(acac)_3$. Also, in the Nd to Lu case, the plots approach to straight lines with a slope of unity. Similar results were also obtained in the benzene system. These results indicate the formation of a 1:1 adduct such as $Ln(tta)_3(Cr(acac)_3)$, i.e., a binuclear complex, in the organic phase. The $\beta_{s,1}$ values were determined by applying a nonlinear least-squares method to those plots based on Eq. 9, the values are listed in Table 1. It is obvious that the $\beta_{s,1}$ values for cyclohexane are much larger than those in benzene. This result agrees with that observed in the adduct formation between $Ln(tta)_3$ and various neutral ligands such as trioctylphosphine oxide[14] and phenanthroline.[15] The solvent effect has been explained by change in the activity of the solutes with the aid of the regular solution theory.

Figure 3 shows the variation of the $\beta_{s,1}$ values across the Ln series. The $\beta_{s,1}$ values of benzene and cyclohexane, on a parallel, decrease with increase in the atomic number of Ln, and show a steep decrease between Pr and Nd, and the constant values from Gd to Lu. As a result, there is a large difference in $\beta_{s,1}$ between the light and the heavy Ln. This decreasing tendency was obviously different from $Co(acac)_3$ reported previously,[8] in which there was a steep decrease between Nd and Sm, and there were constant values from Er to Lu. Moreover, the $\beta_{s,1}$ values of $Cr(acac)_3$ in benzene were lower than those of $Co(acac)_3$ in the same solvent for each of the Ln metals. This result agrees with the order of the hydrogen-bond accepting power or the basicity of both acetylacetonato chelates, i.e., $Cr(acac)_3 < Co(acac)_3$,[3] which will be described later in detail.

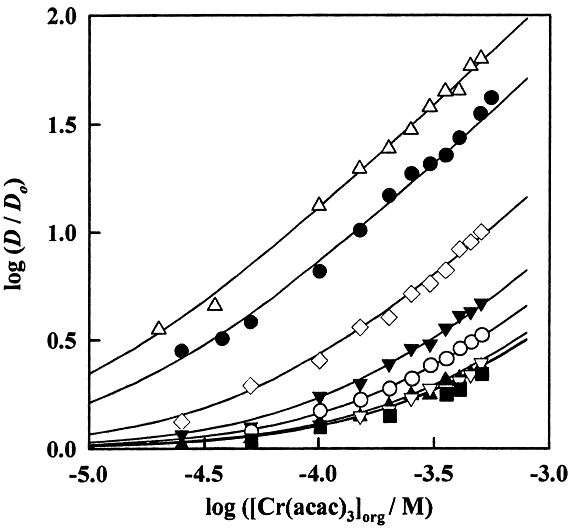

Fig. 2. Effect of the Cr(acac)$_3$ concentration in cyclohexane on the extraction of Ln with 1.0×10^{-2} M Htta at pH 4.1–5.2.
△, La; ●, Pr; ◇, Nd; ▼, Sm; ○, Eu; ▲, Gd; ▽, Er; ■, Lu.

Determination of $\beta_{s,1}$ by Spectrophotometry. Absorption spectra for the d–d transition of 2.0×10^{-3} M Cr(acac)$_3$ were measured in the presence of different concentrations (5.0×10^{-4} –8.0×10^{-3} M) of hydrated Ln(tta)$_3$ (Ln:La, Pr, Nd, Sm, Eu, Gd, Tb, Er, and Lu) in benzene. An absorption band with a maximum absorbance at 559 nm ($^4T_{2g} \leftarrow {}^4A_{2g}$) showed the hypsochromic shift in the presence of a light Ln chelate such as La(tta)$_3$ (554 nm) and Pr(tta)$_3$ (557 nm), while no shift occurred in the heavy Ln. The observed shifts of the absorption maximum suggest that the octahedral structure of Cr(acac)$_3$ is slightly distorted by the adduct formation with La(tta)$_3$ or Pr(tta)$_3$.

In addition, molar absorptivity of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition of Cr(acac)$_3$ was found to increase in the presence of every Ln(tta)$_3$. Figure 4 shows the relationship between the apparent molar absorptivity of Cr(acac)$_3$ and the molar ratio of Ln(tta)$_3$ to Cr(acac)$_3$. The plot of each Ln well fits with two straight lines having an intersection at [Ln(tta)$_3$]$_{total}$/[Cr(acac)$_3$]$_{total}$ = 1, which corresponds to a 1:1 stoichiometry, as expected from the result of the extraction. Therefore, the increase in the molar absorptivity observed is caused by the adduct formation. To determine $\beta_{s,1}$ as well as the molar absorptivity (ε_{BNC}) of Cr(acac)$_3$ in the adduct by spectrophotometry, the following equation was derived with respect to the apparent absorbance (A_{app}) of Cr(acac)$_3$ at 559 nm:

$$\begin{aligned}A_{app} &= \varepsilon_{BNC}[\mathrm{Ln(tta)_3(Cr(acac)_3)}]_{org} + \varepsilon_{Cr}[\mathrm{Cr(acac)_3}]_{org}\\ &= (\varepsilon_{BNC} - \varepsilon_{Cr}) \times\\ &\quad \frac{(\beta_{s,1}C_{Ln} + \beta_{s,1}C_{Cr} + 1) - \sqrt{(\beta_{s,1}C_{Ln} + \beta_{s,1}C_{Cr} + 1)^2 - 4\beta_{s,1}{}^2C_{Ln}C_{Cr}}}{2\beta_{s,1}}\\ &\quad + \varepsilon_{Cr}C_{Cr}, \end{aligned} \tag{11}$$

where ε_{Cr} denotes the molar absorptivity of free Cr(acac)$_3$, and C_{Cr} and C_{Ln}, the total concentration of Cr(acac)$_3$ and Ln(tta)$_3$ respectively. The $\beta_{s,1}$ and ε_{BNC} values were calculated by the least-squares fitting for the plots shown in Fig. 4 on the basis of Eq. 11. The $\beta_{s,1}$ values are listed in Table 1 along with those obtained by the extraction.

The values determined by both methods are reasonably consistent with each other although the values obtained by spectrophotometry contain larger errors and are slightly higher than those by the extraction. Such little differences of $\beta_{s,1}$ are probably due to the difference of the water content in the benzene solution in both methods, i.e., 2.0×10^{-2} M H_2O in the spectrophotometry toward 3.1×10^{-2} M in the extraction method. The increase in water content promotes the hydration of Ln(tta)$_3$ as well as Cr(acac)$_3$ which is a hydrogen-bond accepter. The adduct formation should compete with the hydration of the chelates.

The molar absorptivity (ε_{BNC}) of complexed Cr(acac)$_3$ in the adduct is plotted against the atomic number of Ln in Fig. 3. The ε_{BNC} decreases with increase of the atomic number of Ln along with the $\beta_{s,1}$ values. There is a good relationship between the ε_{BNC} and the $\beta_{s,1}$. Since the enhancement of the molar absorptivity is caused by the vibrational distortion or the slight change in symmetry of the Cr(acac)$_3$ molecule on the adduct formation as discussed in Co(acac)$_3$,[7] the large difference

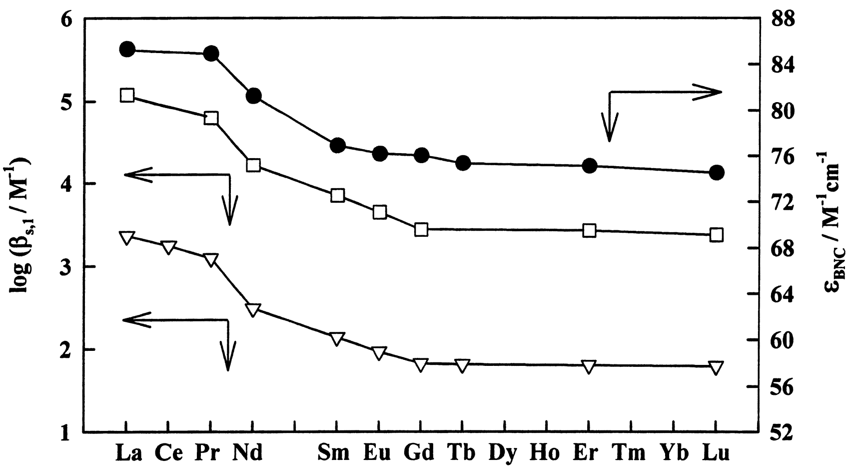

Fig. 3. Variation of the adduct formation constant and the molar absorptivity of complexed Cr(acac)$_3$ across the lanthanoid series.
□, log $\beta_{s,1}$ in cyclohexane; ▽, log $\beta_{s,1}$ in benzene; ●, ε_{BNC} in benzene.

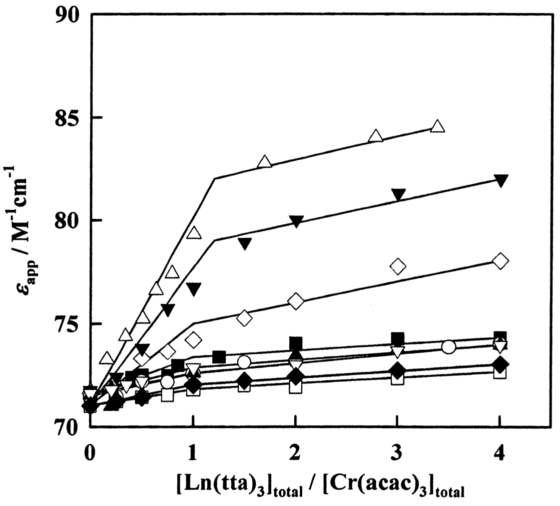

Fig. 4. Relationship between the apparent molar absorptivity of $Cr(acac)_3$ at 559 nm and the molar ratio of $Ln(tta)_3$ to $Cr(acac)_3$. $[Cr(acac)_3]_{total} = 2.0 \times 10^{-3}$ M.
△, La; ▼, Pr; ◇, Nd; ■, Sm; ○, Eu; ▲, Gd; ▽, Tb; ◆, Er; □, Lu.

of the ε_{BNC} observed between light Ln of La to Pr and heavy Ln of Gd to Lu suggests that the structure or the bonding of the adduct for the light Ln is different from those for the heavy Ln.

Spectroscopic Studies of the Adduct Formation. If $Cr(acac)_3$ directly coordinates to a Ln ion in the Ln-tta chelate, some water molecules must be displaced in the inner coordination sphere of Ln, because the Ln-tta chelate has coordinated water molecules even in the organic phase. To understand the behavior of the coordinated water molecules on the adduct formation, IR and ^{1}H NMR spectroscopy were applied to the particular Ln chelates.

IR. In an IR absorption spectrum of water in benzene, two intense peaks were observed at 3600 cm^{-1} and 3680 cm^{-1} which are assigned to the symmetric and asymmetric O–H stretching vibration of free water respectively. Figure 5 shows IR absorption spectra of 6.0×10^{-3} M $Eu(tta)_3(H_2O)_3$ in anhydrous benzene (a) as well as those in the presence of various concentrations (3.0×10^{-3} –2.3×10^{-2} M) of $Cr(acac)_3$ (b-d). The hydrated Eu chelate indicates two narrow absorption bands at 3552 and 3649 cm^{-1} and a broad band at 3335cm^{-1}, which are significantly different from those of free water. These three absorption bands disappeared by the formation of 1 : 1 as well as 1 : 2 adducts with trioctylphosphine oxide (TOPO), i.e., $Eu(tta)_3(TOPO)$ and $Eu(tta)_3(TOPO)_2$ respectively, and alternately the intense peaks corresponding to free water appeared. Therefore, the two narrow bands are assigned to the O–H stretching vibration of the coordinated water molecule, and the broad band at the lower wavenumber region is ascribed to the coordinated water hydrogen-bonded with the oxygen atoms of the ligand (tta) in $Eu(tta)_3$. This kind of hydrogen bond of the coordinated water molecule has been observed by IR spectra of tris(acetylacetonato)lanthanoid(III) monohydrate in solid state.[16]

In Fig. 5, the absorbance of the two narrow bands decreases with increase in the $Cr(acac)_3$ concentration, while the broad band gradually increases. Unlike TOPO as described above,

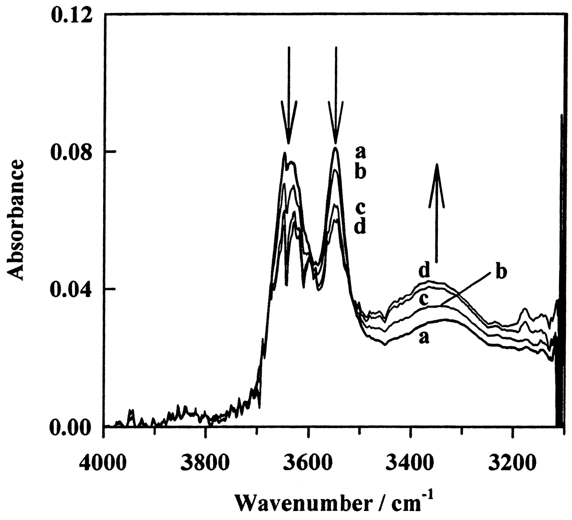

Fig. 5. IR spectra of 6.0×10^{-3} M $Eu(tta)_3(H_2O)_3$ in the presence or absence of 3.0×10^{-3} –2.3×10^{-2} M $Cr(acac)_3$ in benzene.
(a) $Eu(tta)_3(H_2O)_3$; (b) $[Cr(acac)_3]_{total}/[Eu(tta)_3(H_2O)_3]_{total} = 0.5$; (c) $[Cr(acac)_3]_{total}/[Eu(tta)_3(H_2O)_3]_{total} = 1.0$; (d) $[Cr(acac)_3]_{total}/[Eu(tta)_3(H_2O)_3]_{total} = 3.8$.

the peaks corresponding to the free water did not appear. These spectral changes suggest that the coordinated water molecules were not removed from $Eu(tta)_3(H_2O)_3$ on the adduct formation with $Cr(acac)_3$, and formed additional hydrogen bonding between the coordinated water and $Cr(acac)_3$. Namely, the adduct is an outer sphere complex with the formation of hydrogen bond between the hydrogen atom of the coordinated water and the ligand oxygen atoms of $Cr(acac)_3$. However, the increase in the absorbance of the broad band was smaller than that in the Gd, Er, and Lu case, as will be shown later.

Figures 6 and 7 show the IR spectra of hydrated Nd and Lu chelates in the presence or absence of $Cr(acac)_3$. In these spectra, not only the coordinated water but also an excess of free water (0.02 M) are found. The variation of the spectra in Nd is obviously different from that in Eu. The absorbance of the two narrow bands and the broad band for the coordinated water decreased, and the absorbance of the free water band increased. This is an indication of the inner sphere (direct) coordination of $Cr(acac)_3$ to the central metal of $Nd(tta)_3$. However, these absorption bands of the coordinated water, especially the broad band, can be observed even after most of the Nd chelate had formed the adduct with $Cr(acac)_3$. Hence, the coordinated water is not completely removed from the inner sphere of Nd, and the outer sphere complex formed by hydrogen bonding should coexist.

On the other hand, the variation of the spectra in the Lu case was similar to that for Eu (Fig. 7). The increase in the broad band was observed, but the absorption band of free water increases very little. These results show that the adducts are formed by the hydrogen bonding between $Cr(acac)_3$ and the coordinated water molecules of $Lu(tta)_3$.

The difference between the absorbance at 3320 cm^{-1} of hydrated $Ln(tta)_3$ and that of the adduct, ΔAbs, was calculated using the corresponding adduct formation constants. Figure 8 shows the plots of ΔAbs vs the atomic number of Ln in the

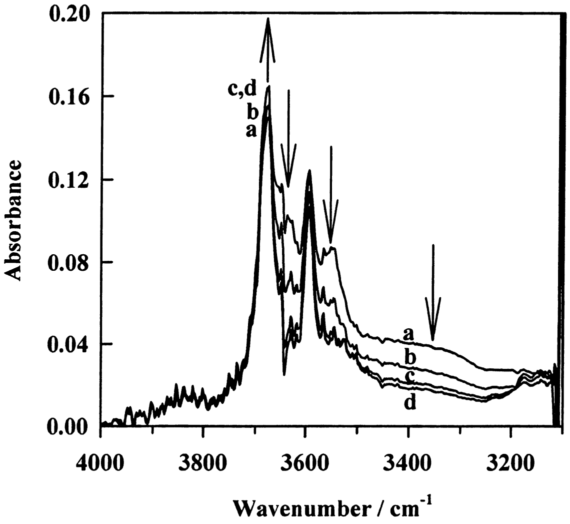

Fig. 6. IR spectra of 6.0×10^{-3} M hydrated Nd(tta)$_3$ in the presence or absence of 2.4×10^{-3} –2.0×10^{-2} M Cr(acac)$_3$ in benzene.
(a) hydrated Nd(tta)$_3$ in the presence of 2.0×10^{-2} M H_2O;
(b) $[Cr(acac)_3]_{total}/[Nd(tta)_3(H_2O)_n]_{total} = 0.5$;
(c) $[Cr(acac)_3]_{total}/[Nd(tta)_3(H_2O)_n]_{total} = 1.0$;
(d) $[Cr(acac)_3]_{total}/[Nd(tta)_3(H_2O)_n]_{total} = 3.3$.

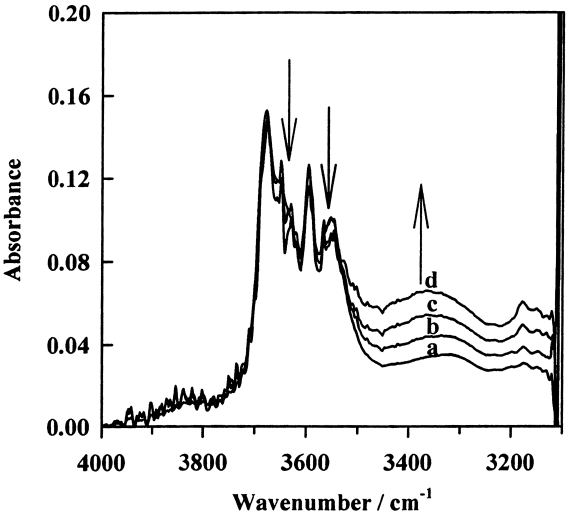

Fig. 7. IR spectra of 6.0×10^{-3} M hydrated Lu(tta)$_3$ in the presence or absence of 2.4×10^{-3} –2.0×10^{-2} M Cr(acac)$_3$ in benzene.
(a) hydrated Lu(tta)$_3$ in the presence of 2.0×10^{-2} M H_2O;
(b) $[Cr(acac)_3]_{total}/[Lu(tta)_3(H_2O)_n]_{total} = 0.5$;
(c) $[Cr(acac)_3]_{total}/[Lu(tta)_3(H_2O)_n]_{total} = 1.0$;
(d) $[Cr(acac)_3]_{total}/[Lu(tta)_3(H_2O)_n]_{total} = 3.3$.

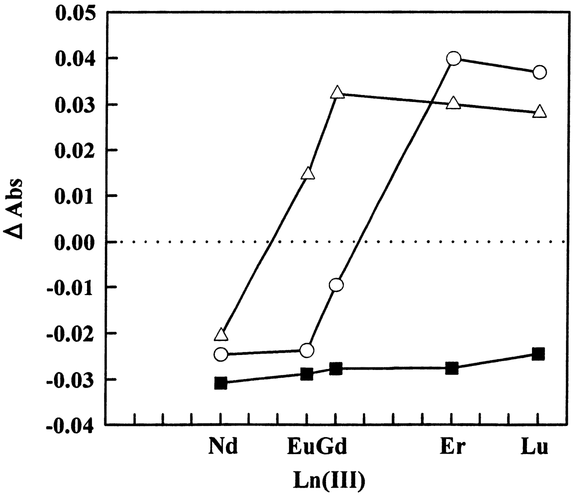

Fig. 8. Variation of the absorbance at 3320 cm^{-1} for the coordinated water of hydrated Ln(tta)$_3$ on the adduct formation with Cr(acac)$_3$ (△), Co(acac)$_3$ (○), and TOPO (■) in benzene.

Cr(acac)$_3$ system, together with those in the Co(acac)$_3$ and TOPO system. The negative ΔAbs means the release (displacement) of the coordinated water, or the direct coordination of the neutral ligand to the central metal of Ln(tta)$_3$. TOPO shows the largest negative ΔAbs values for all the Ln, as expected. The ΔAbs of the Nd(tta)$_3$(Cr(acac)$_3$) also indicates a negative value, but the magnitude is not as large as that of Nd-TOPO. Therefore, Nd(tta)$_3$(Cr(acac)$_3$) includes not only the inner sphere but also the outer sphere complex in the organic phase. The negative ΔAbs value of the Nd(tta)$_3$(Cr(acac)$_3$) is slightly smaller than that of the Nd(tta)$_3$(Co(acac)$_3$), which suggests that the fraction of the inner sphere complex of the former is less than that of the latter.

The large positive values of ΔAbs observed at Gd, Er, and Lu in Cr(acac)$_3$ show the formation of an additional hydrogen bond, or the formation of the outer sphere complex. Eu(tta)$_3$(Cr(acac)$_3$) showing the relatively small ΔAbs probably includes both inner and outer sphere complexes.

^{1}H NMR. To support the result of IR, ^{1}H NMR study of the hydrated Lu(tta)$_3$ was carried out in C_6D_6. A chemical shift of free H_2O in C_6D_6 was observed at 0.41 ppm, while that of coordinated H_2O of 6.0×10^{-3} M hydrated Lu chelate was observed at 1.40 ppm as an averaged position by the chemical exchange between free and coordinated H_2O. Therefore, if Cr(acac)$_3$ displaces the coordinated H_2O and binds to the central metal of the Lu chelate, the averaged peak is expected to shift to the higher magnetic field by the increase in free H_2O. After the addition of the equivalent quantity of Cr(acac)$_3$ to the Lu chelate, however, the H_2O peak disappeared. This phenomenon can be understood as follows. Since Cr(acac)$_3$ is a paramagnetic metal chelate, the chemical shift and the line width for the proton of the coordinated H_2O hydrogen-bonded with Cr(acac)$_3$ are strongly influenced by the pseudo-contact shift arising from the unpaired electron of Cr^{III}. The peak of the free H_2O in C_6D_6 containing only 1.8×10^{-2} M Cr(acac)$_3$ slightly shifts to the lower magnetic field (0.41 → 0.46 ppm) with expanding of the line width. These spectral differences also suggest that Cr(acac)$_3$ forms a stronger hydrogen bonding with the coordinated H_2O of the Lu chelate than with free H_2O, and the proton donor property of the coordinated H_2O may be stronger than that of free H_2O.

Comparison between Cr(acac)$_3$ and Co(acac)$_3$ as a Complex Ligand. To evaluate the complexing ability of Cr(acac)$_3$, the adduct formation constants ($\beta_{s,1}$(Cr)) of hydrated Ln(tta)$_3$ with Cr(acac)$_3$ were compared with those ($\beta_{s,1}$(Co))

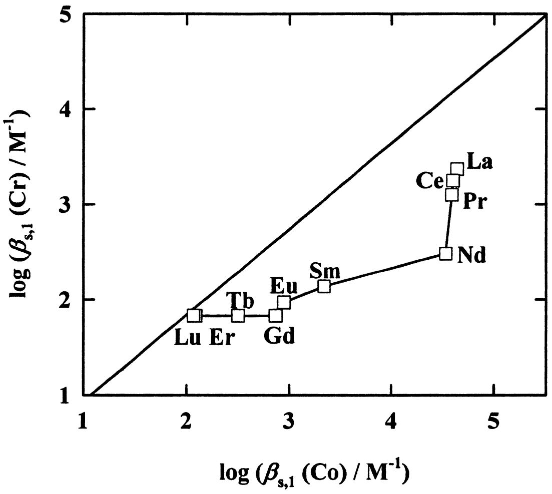

Fig. 9. Relationship between the adduct formation constants ($\beta_{s,1}$(Cr)) of hydrated Ln(tta)$_3$ with Cr(acac)$_3$ and those ($\beta_{s,1}$(Co)) with Co(acac)$_3$ in benzene. The solid line is given by the equation of log ($\beta_{ass,1}$(Cr)) = 0.90 log ($\beta_{ass,1}$(Co)) + 0.04, where $\beta_{ass,1}$(Cr) and $\beta_{ass,1}$(Co) are the formation constants of 1:1 hydrogen-bond complexes of chlorinated phenols with Cr(acac)$_3$ and Co(acac)$_3$ respectively (Ref. 3).

with Co(acac)$_3$ reported previously.[8] The relationship between $\beta_{s,1}$(Cr) and $\beta_{s,1}$(Co) is shown in Fig. 9. The solid line shows a linear free energy relationship between the formation constants of 1:1 hydrogen-bond complexes of Cr(acac)$_3$ with the various phenols and those of Co(acac)$_3$ with the corresponding phenols, and demonstrates a difference of the hydrogen-bond accepting ability between Cr(acac)$_3$ and Co(acac)$_3$. The hydrogen-bond accepting ability or basicity of Cr(acac)$_3$ is a little inferior to that of Co(acac)$_3$, and has been reported to depend on the difference of the oxygen–oxygen nonbonded (O–O) distance on the octahedral face of those chelates.[6]

The plots of Er and Lu are on the solid line. This is quite reasonable because Cr(acac)$_3$ and Co(acac)$_3$ form hydrogen-bond complexes with the hydrated Er(tta)$_3$ and Lu(tta)$_3$, as described in the IR study. It is clearly shown that the hydrogen-bond accepting ability of Cr(acac)$_3$ toward the coordinated water of those Ln chelates is also inferior to that of Co(acac)$_3$.

The plots for the other Ln metals deviated from the solid line. The influence of the steric factor must be considered when Cr(acac)$_3$ and Co(acac)$_3$ form the inner sphere complexes with those Ln chelates. Cr(acac)$_3$ and Co(acac)$_3$, which probably act as terdentate ligands, coordinate to the light Ln through the three oxygen atoms on an open octahedral face, since the coordination number (CN) of light Ln having a large ionic radius is most often 9 in solutions. The increase in the crowding of ligands (tta) around the Ln ion with decrease in the ionic radius of Ln produced the result that Cr(acac)$_3$ and Co(acac)$_3$ can enter the inner-coordination sphere of Ln(tta)$_3$ only with difficulty. According to the X-ray crystallographic data of Cr(acac)$_3$[17] and Co(acac)$_3$,[18] the oxygen-oxygen nonbonded (O–O) distances between the oxygen atoms on the octahedral face were different; Cr(acac)$_3$ has the O–O distance (av. 2.751 Å) longer than that of Co(acac)$_3$ (av. 2.629 Å), and a wider octahedral face. Therefore, it is expected that the steric repulsion between Cr(acac)$_3$ and Ln(tta)$_3$ is stronger than that between Co(acac)$_3$ and Ln(tta)$_3$. The increase in the deviation from the solid line observed at La to Nd in Fig. 9 was caused by the increase in the steric repulsion between Cr(acac)$_3$ and Ln(tta)$_3$ along with the decrease in the ionic radii of Ln.

The middle Ln also deviated from the solid line. As shown in Fig. 8, the adducts of the middle Ln with Cr(acac)$_3$ are mainly the outer sphere complexes, while those with Co(acac)$_3$ are mostly the inner sphere complexes. The deviation observed at middle Ln is ascribed to the greater contribution of the inner sphere complex of Co(acac)$_3$.

The difference of the O–O distance on the open octahedral face between Cr(acac)$_3$ and Co(acac)$_3$ influences not only the basicity but also the steric hindrance against Ln(tta)$_3$. Consequently, $\beta_{s,1}$ of Cr(acac)$_3$ is smaller than that of Co(acac)$_3$ across the Ln series. Moreover, Cr(acac)$_3$ has a tendency to form the outer sphere complex since Cr(acac)$_3$ having the wide octahedral face can not easily enter the inner-coordination sphere of Ln(tta)$_3$.

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