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Variation of Formation Constants of Adducts of Lanthanoid(III) Chelates with Benzoic and Phenylacetic Acids across the Series

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The extraction behavior of lanthanoids(III) with 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (TTA) and benzoic or phenylacetic acid from 0.1 M sodium perchlorate media into chloroform has been examined at 298 K. The extraction curves are interpreted by the extraction of the adducts of the TTA chelates accompanied with two molecules of the carboxylic acids at maximum as well as the extraction of the TTA chelate. The adduct formation constants decrease generally with the atomic number, but in the middle of the series, they change only slightly, then decrease more rapidly for the heavy elements. Such a trend indicates a change of the coordination number in the middle of the series.

The thermodynamic parameters in lanthanoid(III) complexation with benzoic and phenylacetic acids in aqueous solutions showed[1)] that the enthalpy change in the complexation of the heavier lanthanoids(III) is larger than that for the lighter ones(III), reflecting the stronger dehydration of the former. They also showed that the difference in the enthalpy change of the complexation with benzoate ion between the lighter and the heavier lanthanoids(III) is smaller than that with phenylacetate ion. This result may be related to the resonance which occurs between carboxyl group and benzene ring in benzoic acid, in which the phenyl group combines directly with carboxyl group, as well as the more inductive effect of a benzene ring less shielded than in phenylacetic acid.

The change of the coordination number in the middle of the series and the difference of the character of the carboxylic acids should be connected with stabilities in the complexation of lanthanoids(III) with these carboxylic acids in organic solvents. When several lanthanoids(III) were extracted with 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (hereafter abbreviated as TTA) and benzoic or phenylacetic acid,[2)] we have observed that the extraction with benzoic acid is better than with phenylacetic acid.

In order to examine in more detail the difference of the lanthanoid(III) complexation with these carboxylic acids in organic solvents in which the hydration is not significant, the adduct formation of lanthanoid(III)–TTA chelates with benzoic and phenylacetic acids across the lanthanoid family has been studied in the present work.

Experimental

Materials. All reagents were of analytical grade. 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione, benzoic acid, and phenylacetic acid were obtained from Dojindo Laboratories, Merck (Germany), and Aldrich (USA), respectively. Lanthanoid(III) oxides (purities>99.9%) were obtained from Shin-Etsu Chemical Co. or Mitsuwa Chemicals. Chloroform was washed three times with deionized water prior to use.

Procedures. Most procedures were similar to those described elsewhere.[2)] The procedures were carried out in a thermostatted room at 298 K. The total anion concentration was adjusted to 0.1 M (1 M=1 mol dm^{-3}) with sodium perchlorate. The hydrogen ion concentration at equilibrium was measured potentiometrically, using 1.00×10^{-2} M perchloric acid solution in 0.1 M (H, Na)ClO$_4$ as a standard of $-\log[\mathrm{H}^+]=2.00$ (hereafter $-\log[\mathrm{H}^+]$ is abbreviated as pC$_\mathrm{H}$). Eight milliliters of chloroform containing 0.1 M TTA and/or various amounts of carboxylic acid and 8 mL of aqueous solution containing 6.3×10^{-4} M lanthanoid(III) were shaken for an hour, which had been shown to be sufficient to attain equilibrium. The pC$_\mathrm{H}$ was adjusted to 2.9—4.0 and was higher for the lighter lanthanoids(III) and lower for the heavier ones. The lanthanoids(III) extracted into the chloroform phase were back-extracted into 0.1 M perchloric acid; the concentration in this stripping solution was measured by ICP-AES (SEIKO Instruments SPS 7000A). The concentration of lanthanoid(III) remaining in the aqueous phase was obtained as the balance between the initial concentration and the concentration in the organic phase. The concentration ratio between the two phases was defined as the distribution ratio of lanthanoid(III).

Results and Discussion

When lanthanoid(III) (Ln) is extracted from 0.1 M sodium perchlorate medium into chloroform containing

TTA (HA) and a carboxylic acid (HB), the distribution ratio (D) can be represented as follows:

$$\begin{aligned} D &= \frac{[\mathrm{LnA_3}]_\mathrm{o} + [\mathrm{LnA_3HB}]_\mathrm{o} + \cdots}{[\mathrm{Ln}^{3+}] + [\mathrm{LnB}^{2+}] + [\mathrm{LnB_2}^{+}]} \\ &= \frac{K_\mathrm{ex}[\mathrm{A}^-]^3(1+\overline{\beta}_1[\mathrm{HB}]_\mathrm{o}+\overline{\beta}_2[\mathrm{HB}]_\mathrm{o}{}^2+\cdots)}{1+\beta_1[\mathrm{B}^-]+\beta_2[\mathrm{B}^-]^2}, \end{aligned} \tag{1}$$

where the organic phase is denoted by the subscript "o", $K_\mathrm{ex}(=[\mathrm{LnA_3}]_\mathrm{o}/[\mathrm{Ln}^{3+}][\mathrm{A}^-]^3)$ is the extraction constant of the TTA chelate, $\overline{\beta}_m(=[\mathrm{LnA_3}\cdot m\mathrm{HB}]_\mathrm{o}/[\mathrm{LnA_3}]_\mathrm{o}[\mathrm{HB}]_\mathrm{o}{}^m)$ is the m-th adduct formation constant, and $\beta_n(=[\mathrm{LnB}_n{}^{3-n}]/[\mathrm{Ln}^{3+}][\mathrm{B}^-]^n)$ is the n-th stability constant of the aqueous complexes with these carboxylic acids, which were reported before.[1,3] The carboxylic acids form dimers in chloroform and dissociate in aqueous solutions. The equilibrium constants of the carboxylic acids reported[2] are listed in Table 1. From the mass balance of these acids, the concentrations of the monomer in chloroform and the dissociated acid, B^-, in Eq. 1 were calculated using these equilibrium constants, as follows:

$$[\mathrm{HB}]_\mathrm{o} = \frac{-\left(1+K_\mathrm{d}+\frac{K_\mathrm{a}}{[\mathrm{H}^+]}\right)+\sqrt{\left(1+K_\mathrm{d}+\frac{K_\mathrm{a}}{[\mathrm{H}^+]}\right)^2+8K_\mathrm{dim}K_\mathrm{d}{}^2B_\mathrm{T}}}{4K_\mathrm{dim}K_\mathrm{d}}$$

where B_T is the total concentration of the carboxylic acid added.

$$[\mathrm{B}^-] = \frac{K_\mathrm{a}[\mathrm{HB}]_\mathrm{o}}{K_\mathrm{d}[\mathrm{H}^+]}.$$

The extraction constants, K_ex, for all lanthanoids determined in this work are listed in Table 2.

Figure 1 shows several typical extraction data used to determine the formation constants of the adducts. As seen in Fig. 1, the extraction of lanthanoids(III) is enhanced with the increase in the monomer concentration of the carboxylic acid in the organic phase. The data were analyzed by assuming the formation of the adducts involved two molecules of the carboxylic acids as well as one molecule, similar to earlier reports.[2] The adduct formation constants obtained are listed in Table 3 with the standard deviations. The solid curves in Fig. 1 are drawn using these constants.

Table 1. Equilibrium Constants[a] (aq phase: 0.1 mol dm^{-3} sodium perchlorate, organic phase: chloroform), and Atomic Charge on Oxygen Atom in Carbonyl and Hydroxyl Groups of Carboxylic Acids

				Atomic charge on oxygen	
Acid	pK_a	log K_dim	log K_d	$\rangle$C=O	–OH
Benzoic	3.99	2.22	0.44	−0.364	−0.317
Phenylacetic	4.00	1.81	0.43	−0.359	−0.327

a) The values are taken from Ref. 2. $K_\mathrm{dim}=\frac{[(\mathrm{HB})_2]_\mathrm{o}}{[\mathrm{HB}]_\mathrm{o}{}^2}$, $K_\mathrm{d}=\frac{[\mathrm{HB}]_\mathrm{o}}{[\mathrm{HB}]}$.

Table 2. The Extraction Constants[a] of Lanthanoids(III) with TTA
Aq phase: 0.1 M $\mathrm{NaClO_4}$. Org. phase: $\mathrm{CHCl_3}$.

Ln^{3+}	log $K_\mathrm{ex}\pm\sigma$	Ln^{3+}	log $K_\mathrm{ex}\pm\sigma$
La	(13.67±0.04)[b]	Dy	16.67±0.07
Pr	15.03±0.01	Ho	16.79±0.02
Nd	15.29±0.05	Er	16.90±0.02
Sm	16.07±0.02	Tm	17.14±0.01
Eu	16.26±0.03	Yb	(17.34±0.02)*
Gd	16.10±0.02	Lu	17.30±0.03
Tb	16.53±0.04		

a) $K_\mathrm{ex}=[\mathrm{Ln(TTA)_3}]_\mathrm{o}/[\mathrm{Ln}^{3+}][\mathrm{TTA}^-]^3$. b) The values are taken from Ref. 4.

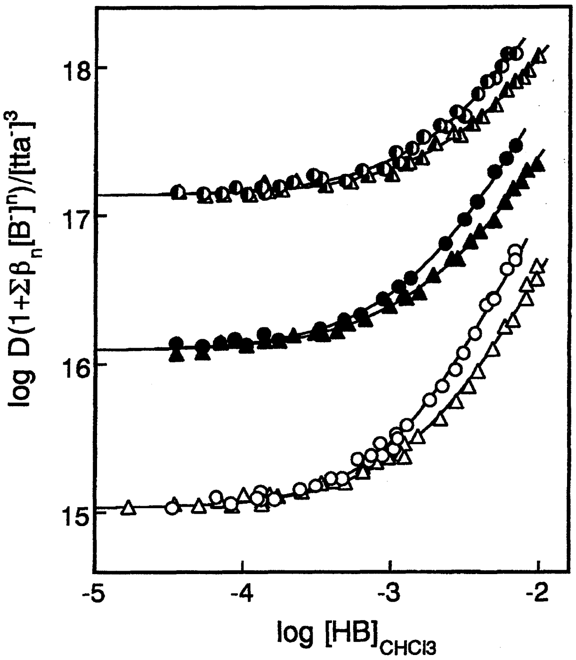

Fig. 1. Enhancement of the extraction of praseodymium(III) (open symbols), gadolinium(III) (closed symbols), and thulium(III) (semiclosed symbols) with TTA and benzoic (circles) or phenylacetic (triangles) acid as a function of the concentration of the carboxylic monomer in chloroform.

As seen from Table 3, the values of the first and the second formation constants of the adducts with benzoic acid as well as of those with phenylacetic acid seem to be smaller with increasing atomic number, as previously observed in the stabilities with both the acids. However, the adduct formation constants do not monotonically decrease across the lanthanoid series. There are three groups: The first and the second groups consist of the light (Pr-Sm) and the heavy (Ho-Lu) lanthanoids, respectively, in which the constants decrease with increasing atomic number. The third group contains the lanthanoids(III) in the middle of the series (Eu-Dy) which show little decrease with increasing atomic number.

A similar trend is observed in the adduct formation constants with naphthalenecarboxylic and naphthaleneacetic acids.[4] Such a pattern of the variation of the con-

Table 3. The Adduct Formation Constants of Lanthanoid(III)–TTA Chelates with Benzoic and Phenylacetic Acids in Chloroform at 298 K

$\mathrm{Ln}^{\mathrm{III}}$	Benzoic acid		Phenylacetic acid	
	$\log\overline{\beta}_1\pm\sigma$	$\log\overline{\beta}_2\pm\sigma$	$\log\overline{\beta}_1\pm\sigma$	$\log\overline{\beta}_2\pm\sigma$
La[a]	(3.10)	(5.84)	(3.04)	(5.72)
Pr	2.97±0.04	5.93±0.02	2.96±0.03	5.47±0.02
Nd	2.98±0.03	5.82±0.02	2.97±0.03	5.33±0.04
Sm	3.01±0.02	5.64±0.02	2.91±0.01	5.18±0.02
Eu	2.97±0.03	5.53±0.03	2.91±0.02	5.12±0.03
Gd	3.02±0.02	5.54±0.02	2.94±0.02	5.03±0.03
Tb	2.98±0.03	5.46±0.03	2.87±0.02	5.02±0.03
Dy	2.93±0.03	5.42±0.03	2.93±0.02	4.83±0.04
Ho	2.80±0.02	5.31±0.02	2.72±0.02	4.79±0.03
Er	2.86±0.05	5.27±0.06	2.63±0.04	4.75±0.05
Tm	2.82±0.03	4.93±0.06	2.69±0.02	4.46±0.08
Yb[a]	(2.85)	(4.74)	(2.64)	(4.32)
Lu	2.71±0.02	4.60±0.05	2.62±0.03	3.81±0.29

a) The numbers in parentheses are taken from Ref. 2.

stants against atomic number seems to be particular to the formation constants of the adducts of lanthanoid(III) chelates with carboxylic acids. The constants with tributyl phosphate scarcely change from the light to the middle series, and then they decrease;[5] the constants with phenylpyridines seem somewhat to increase from the light to the middle of the series;[6] those with bipyridyls[7] or 1,10-phenanthroline[8] increase with increasing atomic number.

The discontinuity between the light and the heavy lanthanoids has also been observed in the complexation heat in aqueous solutions previously reported.[1] Thus the variation of the adduct formation constants across the series also would be related to the change in the coordination number of lanthanoids(III) in the middle of the series. It is generally accepted that the coordination number of the lighter lanthanoids(III) is nine, and that of the heavier ones is eight,[9] with an equilibrium mixture of 8 and 9 in the middle of the series.

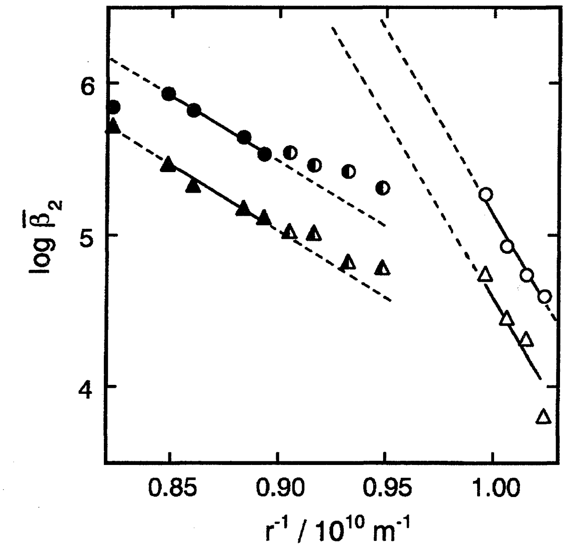

Fig. 2. Formation constants of the second adducts of $\mathrm{Ln}^{\mathrm{III}}$–TTA chelates with benzoic (circles) or phenylacetic acid (triangles) as a function of ionic radii (CN=9 (closed symbols), CN=8 (open symbols), and the mixture between 8 and 9 (semiclosed symbols)).

Figure 2 shows the correlation between the reciprocal of the ionic radii and the formation constants of the second adducts ($\mathrm{LnA}_3\cdot2\mathrm{HB}$) with benzoic and phenylacetic acids. The effective ionic radii cited in Ref. 9 are originally calculated by Shannon.[10] For the closed symbols, the values of ionic radii for the coordination number (CN) of 9 are used; for the open sysmbols, the radii of CN=8 are employed. The plot given with the closed symbols (La-Sm) and the open symbols (Er-Lu) shows straight lines with negative slopes, although in the middle of the series, the lines have much smaller negative slopes. It would be reasonable to assume that the coordination number of the lanthanoid(III) in the middle of the series is a mixture of 8 and 9. Using the formation constants estimated from the extension of the two lines for the adducts with benzoic acid and the experimental constants, the proportion of the species having coordination number of 8 in $\mathrm{Ln(TTA)}_3$ was calculated. For example, the extrapolated value of $\log\overline{\beta}_2$ for dysprosium(III)–TTA adduct with benzoic acid is 5.27 for CN=9 and 5.60 for CN=8, which are represented as $\overline{\beta}_{2(8\text{ or }9)}=[\mathrm{LnA}_{3(8\text{ or }9)}\cdot2\mathrm{HB}]_\mathrm{o}/[\mathrm{LnA}_{3(8\text{ or }9)}]_\mathrm{o}[\mathrm{HB}]_\mathrm{o}{}^2$. When the proportion of the species of CN = 8 to the total $\mathrm{LnA}_3([\mathrm{LnA}_{3(8)}]_\mathrm{o}/([\mathrm{LnA}_{3(8)}]_\mathrm{o}+[\mathrm{LnA}_{3(9)}]_\mathrm{o}))$ is represented as x, $\overline{\beta}_{2(8)}=[\mathrm{LnA}_{3(8)}\cdot2\mathrm{HB}]_\mathrm{o}/(([\mathrm{LnA}_{3(8)}]_\mathrm{o}+[\mathrm{LnA}_{3(9)}]_\mathrm{o})\cdot x\cdot[\mathrm{HB}]_\mathrm{o}{}^2)$, $\overline{\beta}_{2(9)}=[\mathrm{LnA}_{3(9)}\cdot2\mathrm{HB}]_\mathrm{o}/(([\mathrm{LnA}_{3(8)}]_\mathrm{o}+[\mathrm{LnA}_{3(9)}]_\mathrm{o})(1-x)\cdot[\mathrm{HB}]_\mathrm{o}{}^2)$, and $\overline{\beta}_{2(\mathrm{obs})}=([\mathrm{LnA}_{3(8)}\cdot2\mathrm{HB}]_\mathrm{o}+[\mathrm{LnA}_{3(9)}\cdot2\mathrm{HB}]_\mathrm{o})/(([\mathrm{LnA}_{3(8)}]_\mathrm{o}+[\mathrm{LnA}_{3(9)}]_\mathrm{o})[\mathrm{HB}]_\mathrm{o}{}^2)$. Accordingly, $\overline{\beta}_{2(\mathrm{obs})}=\overline{\beta}_{2(8)}x+\overline{\beta}_{2(9)}(1-x)$. Then, x equals 0.36, i.e., 36% of the species is estimated to have CN=8, because the experimental value, $\log\overline{\beta}_{2(\mathrm{obs})}$, is 5.42. By a similar calculation, in the case of $\mathrm{Tb(TTA)}_3$ adduct with benzoic acid, the proportion of CN=8 is 13%, but the proportions in the lighter lanthanoids(III) were less than 10%. The semiclosed symbols in Fig. 2 show the plot of the observed constants as a function of the radii calculated from the coordination number estimated from the adduct formation constants with benzoic acid. Using the ionic radii estimated by the calculation for the adduct formation constants with benzoic acid, the constants with phenylacetic acid are plotted in Fig. 2.

Generally, the metal(III) chelates which extract better form less stable adducts. Actually in each group, the constants decrease along with increasing atomic number or $1/r$. However, since the charge density of the lanthanoids(III) with coordination number 8 is higher than those with CN=9, the heavier lanthanoid(III) chelates would more strongly accept the Lewis base than the lighter ones do.

As described in the introduction, the present work started at the different observation of the differences of the complexation heats between the light and the heavy lanthanoids(III) with benzoate ion from those with phenylacetate ions. However, as seen in Fig. 2, the pattern of the variation of the adduct formation constants with these two acids along with the atomic number across the series is very similar. It seems that these carboxylic acids function lanthanoid(III) chelates in a similar way in chloroform, where the hydration of the metal(III) is not significant. Thus the function of these carboxylic acids to lanthanoids(III) which combine with three molecules of the chelating agent in the organic phase may be different from that the carboxylate ions to the hydrated lanthanoid ions in aqueous solutions.

As seen from Table 3 and Fig. 2, the formation constants of $\mathrm{Ln(TTA)_3}$ adducts with benzoic acid are a little larger than those with phenylacetic acid, although the values of $\mathrm{p}K_\mathrm{a}$ are similar, as already reported.[2)] The dimerization constant of benzoic acid is also somewhat larger than that of phenylacetic acid. This may indicate that the electron density on carbonyl oxygen atom in benzoic acid is higher than that in phenylacetic acid. We attempted to calculate the atomic charge on the oxygen atoms using the semi-empirical molecular orbital method (AM1 method in MOPAC Program[11)]), where geometry optimizations were set to be terminated when the change in energy on successive iterations was less than 10^{-9} kcal mol^{-1} and the change in gradient norm was less than 10^{-4}. The calculated values for benzoic and phenylacetic acids are also listed in Table 1. The electron density on the oxygen atom in the carbonyl group of phenylacetic acid is slightly less than that of benzoic acid, although the difference is very small, and qualitatively the difference of the electron density seems to interpret the sequence of a little larger stabilities with benzoic acid than with phenylacetic acids.

The formation constants would be influenced by many factors such as coordination number, the basicity of the donor atom, and structure of the ligands. In the complexation of lanthanoid(III)–TTA chelates with carboxylic acids in chloroform, the change in the coordination number would be assigned as the most significant factor.

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