Bull. Chem. Soc. Jpn., ***71***, *2825—2829 (1998)*

Variation of Thermodynamic Parameters in the Adduct Formation of *β*-Diketonato Chelates with 1,10-Phenanthroline across the Lanthanoid Series

Setsuko Yajima and Yuko Hasegawa*

Department of Chemistry, Faculty of Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162-8601

(Received May 7, 1998)

The enthalpy change in the adduct formation of tris[1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionato]lanthanoids (LnA_3) with 1,10-phenanthroline (phen) as well as the formation constant of the adduct has been determined in chloroform across the lanthanoid series at 298 K by calorimetric titration and solvent-extraction techniques. The enthalpy change in the first adduct formation changes remarkably from light lanthanoids (endothermic) to heavy ones (exothermic), while the entropy change decreases largely from the middle to the heavy lanthanoids along with a small change from light to the middle of the series. Such a trend has been explained on the basis of the difference in the dehydration from lanthanoid(III) chelates and in the strength of the new bonding of chelates formed between tris(*β*-diketonato) lanthanoid(III) and phen across the lanthanoid series.

There have been several reports that the formation constants of the adducts of tris[1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionato]lanthanoids (this *β*-diketone is usually called as 2-thenoyltrifluoroacetone, or TTA) with 1,10-phenanthroline (phen)[1,2] or with 2,2′-dipyridyl[1,3,4] increase along with an increase in the atomic number in the lanthanoid series. However, a similar trend can not always be observed with other *β*-diketones;[5] also, the formation constants of the second adduct of TTA chelates with monodentate ligands, corresponding to those with bidentate ones, generally decrease along with the atomic number, e.g., the second adduct formation constants of TTA-chelate with triphenylphosphine oxide[6] and carboxylic acids[7,8] decrease across the series.

To learn why the behavior of phen is different from that of most monodentate adduct-forming ligands, in the present study the thermodynamic parameters in the adduct formation in chloroform with phen were determined across the lanthanoid series by using calorimetry as well as solvent-extraction technique.

Experimental

Reagents. All of the reagents used were of analytical grade, and were used without purification, except for chloroform. Chloroform was washed three times with deionized water prior to use. 1,10-Phenanthroline as one hydrate and TTA were purchased from Kanto Chemicals and Dojindo Laboratories, respectively. The lanthanoid(III) stock solutions were prepared by dissolving the weighted oxides (mostly, from Mitsuwa Chemicals, Tokyo; purities $\geq 99.99\%$) into a perchloric acid solution and adjusting the total ionic concentration at 0.1 M ($1\ M = 1\ mol\,dm^{-3}$) using a sodium perchlorate solution. The concentration of lanthanoid(III) in the stock solution was determined by EDTA titration using Xylenol Orange as an indicator.

Procedures. All of the procedures were carried out in a thermostated room at 25 °C. The proton concentration was determined potentiometrically as a standard of $-\log[H^+] = 2.00$ (hereafter $-\log[H^+]$ is abbreviated as pC_H) using a mixed solution consisting of 0.0100 M perchloric acid and 0.09 M sodium perchlorate.

Determination of the Acid Dissociation Constant and the Distribution Constant of phen between 0.1 M $NaClO_4$ and $CHCl_3$. A five milliliter chloroform solution of phen at 5×10^{-4} M and 10 ml of 0.1 M (H, Na) ClO_4 were placed in stoppered glass tubes. After one hour of shaking, the absorbance of the organic phase was measured at 265.4 nm where the spectra of phen showed a maximum peak ($\varepsilon = 3.08_4\times10^4\ M^{-1}\,cm^{-1}$). The absorbance of the organic phase was usually measured after being diluted by a factor of 20 to 200. The concentration of phen in the aqueous phase was determined as follows: into 5 ml taken from the aqueous phase, a 1 ml sodium hydroxide solution of 1×10^{-3} M was added and the phen was reextracted into 5 ml chloroform. From the absorbance of the measured chloroform solution, the concentration of phen in the aqueous phases was determined. The concentration ratio between both phases was defined as the distribution ratio of phen (*D*).

Adduct Formation Constants of Ln^{III}–TTA Chelate with phen. A sodium perchlorate solution of 0.1 M containing a lanthanoid(III) of 6×10^{-5} M and an equal volume of chloroform containing TTA and/or phen placed in stoppered glass tubes were shaken mechanically for one hour. Then, lanthanoid(III) transferred into chloroform phase was back-extracted with 0.1 M perchloric acid, and the concentration was determined by inductively coupled plasma-emission spectrometry (ICP/AES). The concentration of Ln^{III} remaining in the aqueous phase was evaluated as the balance between the initial concentration and the concentration of the organic phase at equilibrium. The concentration ratio of Ln^{III} between both phases was defined as the distribution ratio of lanthanoid(III)) (*D*).

Calorimetric Titration of LnA_3 with phen. A stock solution of TTA-chelate (LnA_3) was prepared by extracting lanthanoid(III) with 0.05 M TTA into chloroform at pC_H 4—4.7. The stock solution ($[Ln^{III}]$) = ca. 0.01 M) was diluted with chloroform so as to adjust the LnA_3 concentration to around 2×10^{-3} M. To measure the heat change emitted during adduct formation, an isoperibol calorimeter with a motorized burette (Tronac Model 450, USA) was employed. Fifty milliliters of the working solution were placed in the reaction vessel. After it had attained thermal equilibria, a 1.5×10^{-2} M phen solution was constantly injected from the burette into the vessel for about 6 min at a rate of 1.3×10^{-2} $cm^3\,s^{-1}$. The temperature in the vessel was detected by a thermistor and recorded as a function of time. The temperature change may have been produced by dilution of the titrates or the titrants, and also by stirring or heat leaks caused by radiation and evaporation as well as adduct formation. The temperature change caused by all factors, except for adduct formation, was corrected. In order to turn the temperature change to a heat change, a heat capacity in the reaction solution before and after the titration was detected by adding a known amount of energy into the reaction vessel.

Results

Determination of the Acid-Dissociation Constant and the Distribution Ratio of phen. Figure 1 shows a plot of $\log D$ of phen against pC_H. This plot seems to show a straight line having a slope of plus unity below $pC_H = 4$ and a flat line to the X-axis at $pC_H > 6$. The distribution ratio (phen is represented as B in equations) can be represented as:

$$D = \frac{[B]_o}{[B]+[HB^+]} = \frac{K_d}{1+\frac{[H^+]}{K_a}}, \qquad (1)$$

where K_d is the distribution constant of phen as $K_d = [B]_o/[B]$ and $K_a = [H^+][B]/[HB^+]$. By a data analysis, 4.77±0.02 and 2.72±0.02 were obtained as pK_a and $\log K_d$, respectively. The pK_a value seems to be slightly smaller than that employed in Ref. 5, because 5.04 was used there.

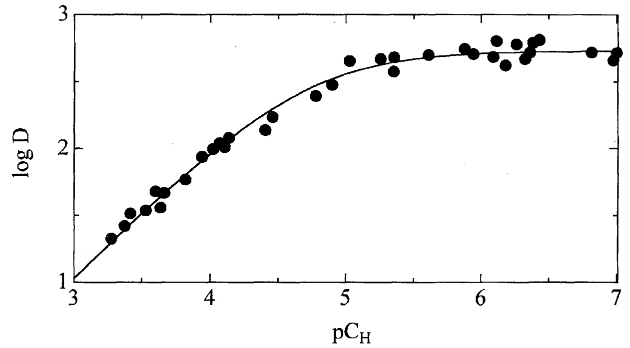

Fig. 1. Distribution ratio of phen between 0.1 M (H, Na) ClO_4 and $CHCl_3$ as a function of pC_H at 298 K. The total concentration of phen is 5.0×10^{-4} M.

Adduct-Formation Constants of TTA Chelates with phen and the Trend in the Variation across the Lanthanoid Series. Figure 2a shows the extraction enhancement of several lanthanoids(III) with adduct formation as a function of the phen concentration at equilibrium. The limiting slope of the plot of $\log D$ vs. $\log [B]_o$ seems to be unity for all lanthanoids.

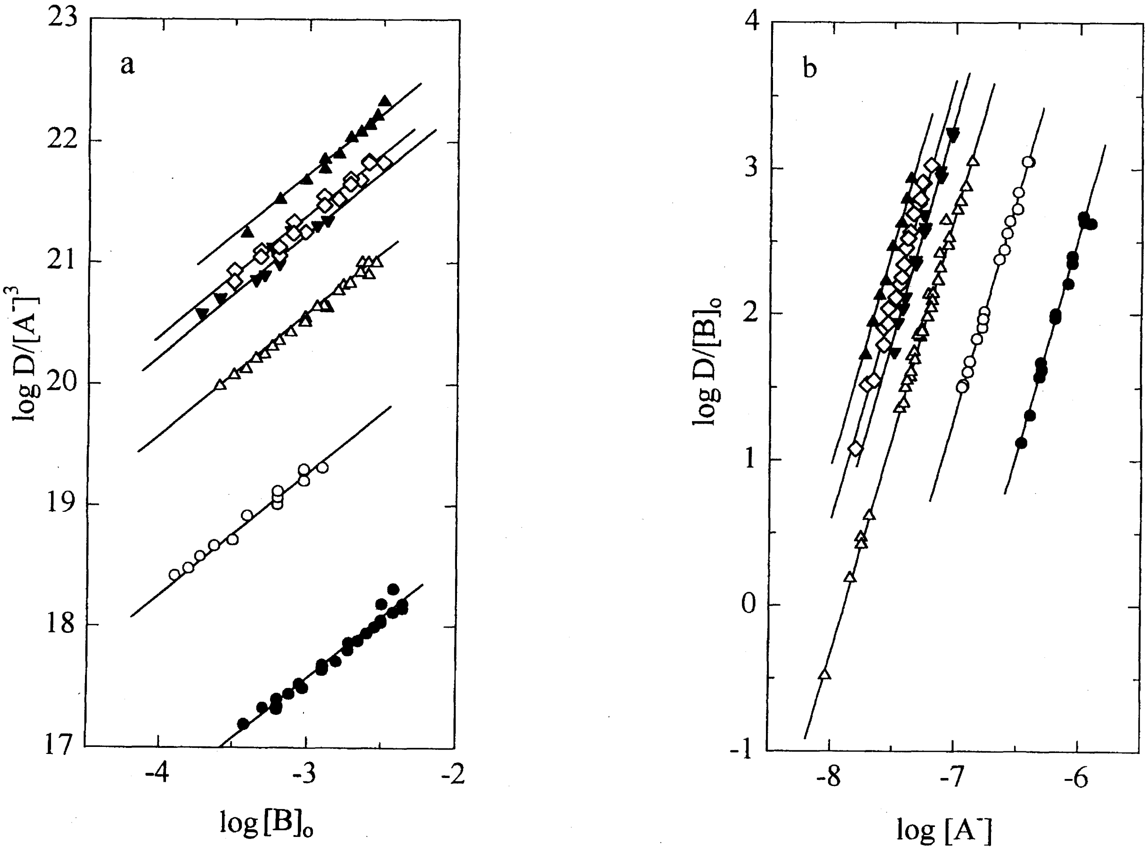

Fig. 2. Distribution ratio of several lanthanoids(III) between 0.1 M $NaClO_4$ and $CHCl_3$ containing TTA and phen as a function of phen concentration added (a) and TTA anion concentration (b) at equilibrium. ●, La; ○, Pr; △, Sm; ▼, Tb; ◇, Ho; ▲; Lu.

Figure 2b shows the dependence of the distribution ratio of Ln^{III} on the TTA anion concentration in the presence of phen at a constant concentration in chloroform. The plot shows a straight line having a slope of +3.

Accordingly, the distribution ratio of Ln^{III} can be represented as

$$D = \frac{[LnA_3]_o + [LnA_3\cdot B]_o}{[Ln^{3+}]} = K_{ex}[A^-]^3(1+\beta_1[B]_o)$$
$$\risingdotseq K_{ex}\beta_1[A^-]^3[B]_o, \qquad (2)$$

where K_{ex} is the extraction constant of Ln^{III} with the TTA anion defined as $K_{ex} = [LnA_3]_o[Ln^{3+}]^{-1}[A^-]^{-3}$, and β_1 is the first adduct formation constants of LnA_3 with phen ($\beta_1 = [LnA_3B]_o/[LnA_3]_o[B]_o$). The concentration of phen at equilibrium ($[B]_o$) is related to the total phen concentration (B_T) as $[B]_o = B_T\left(1+\frac{1}{K_d}(1+\frac{[H^+]}{K_a})\right)^{-1}$ when B_T is in a large excess of the extracted lanthanoid(III) concentration. The concentration of the TTA anion was calculated by introducing the total concentration (A_T), pC_H, the values[9] of K_d ($\log K_d = 1.85$) and pK_a (= 6.33) into the equation, $[A^-] = A_T\left(1+\frac{[H^+]}{K_a}(1+K_d)\right)^{-1}$. The data were also analyzed according to Eq. 2.

The obtained formation constants of the adducts are listed in Table 1. The solid lines in Fig. 2 were calculated on the basis of Eq. 2 using the formation constants of the adducts. Since the lines fit well to all of the experimental points, the values of the thus-obtained constants should reasonably well explain the relation of Eq. 2.

The constants increase with increasing the atomic number from light to the middle of the series, and among the heavy lanthanoids the constants do not change very much. The trend is similar to that with phen and 2,2′-dipyridyl, as reported before.[1—3]

Enthalpy Change in Adduct Formation across the Lanthanoid Series. Several points were arbitralily chosen from the titration curve, which was obtained as a function of the heat emitted (Q) against the volume of phen solution when phen solution was added into a lanthanoid(III)–TTA chelate solution. The values of each point were analyzed according to

$$Q = m_1\Delta H_1, \qquad (3)$$

where m_1 is the mole of the first adduct formed up to the titration point. The values of the moles were calculated from the following equations:

$$M_T = [LnA_3]_o + [LnA_3B]_o = [LnA_3B]_o(1+\beta_1{}^{-1}[B]_o{}^{-1}), \qquad (4)$$

$$B_T = [B]_o + [LnA_3B]_o. \qquad (5)$$

From Eqs. 4 and 5, the following equation can be derived:

$$[B]_o = \{(B_T - M_T)\beta_1 - 1 + [\{1-(B_T-M_T)\beta_1\}^2 + 4\beta_1 B_T]^{1/2}\}/(2\beta_1). \qquad (6)$$

Accordingly, $m_1 = (B_T - [B]_o)(50+v)/1000$ mol, where v is the volume (ml) of phen solution added into the lanthanoid(III) solution in the reaction vessel. To check the reaction heat between TTA and phen, including the dehydration heat of phen, the heat change was measured by injecting phen solution into a TTA chloroform solution. However, the heat change was not essentially different from the background. Accordingly, under the present experimental condition, the reaction heat between TTA and phen as well as the dehydration heat of phen can be neglected.

Table 2 shows the data at several points in a run when 1.50×10^{-2} M phen solution was injected to 1.00×10^{-3} M thulium–TTA chelate chloroform solution of 50 ml at 1.3×10^{-2} ml s^{-1}.

Figure 3 shows the correlation between the heat emitted and the total volume of phen solution added into the cup for several lanthanoids(III). The heat emitted is endothermic for light lanthanoids, while it turns to be exothermic for heavy lanthanoids. The emission of heat was substantially over when the concentration of phen was equivalent to that of the metal ion in the cup. This suggests that lanthanoid(III) chelates form only the first adduct with phen, and that the reaction is essentially quantitative. The data were analyzed to determine the enthalpy change upon adduct formation.

All of the thermodynamic parameters obtained in the present work are listed in Table 3. The solid curves in Fig. 3 were calculated from Eq. 3 using the thermodynamic parameters given in Table 3. Since the calculated curves fit well to the data, the parameters given in Table 3 would reasonably well explain the data.

Table 1. Adduct Formation Constants (β_1) of LnA_3 with phen in $CHCl_3$ at 298 K

Ln^{III}	$\log\beta_1 \pm \sigma$	Ln^{III}	$\log\beta_1 \pm \sigma$
La	6.90±0.06	Dy	7.85±0.03
Pr	7.27±0.04	Ho	7.82±0.06
Nd	7.42±0.04	Er	8.00±0.06
Sm	7.62±0.06	Tm	7.98±0.05
Eu	7.66±0.04	Yb	7.74±0.04
Gd	7.76±0.05	Lu	7.69±0.04
Tb	7.84±0.07		

Table 2. Calorimetric Titration Data in the Adduct Formation of Thulium–TTA Chelate with phen in $CHCl_3$

Titrant ml	Q(obs)[a] J	Q(cal)[a] J	Tm $(TTA)_3\cdot B$ 10^{-2} mmol
0.326	0.062	0.058	0.49
0.718	0.136	0.129	1.08
1.110	0.206	0.198	1.66
1.503	0.279	0.268	2.25
1.895	0.345	0.338	2.84
2.288	0.415	0.408	3.43
2.680	0.439	0.432	3.63

a) Q(obs) and Q(cal) are the observed heat and the heat calculated according to $Q = \Delta H_1\cdot m_{Tm(TTA)3\cdot B}$, respectively.

b) Initial condition
in the cup : 7.24×10^{-4} M Tm $(TTA)_3$, 50.0 ml.
in the burette : 1.50×10^{-2} M phen.

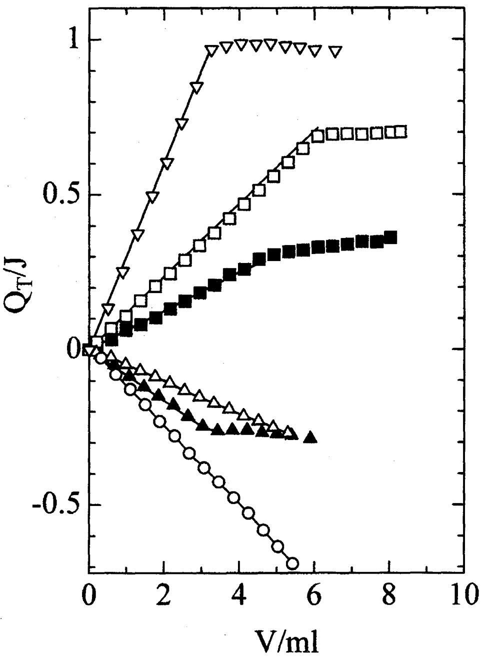

Fig. 3. Heat emitted on the adduct formation of LnA_3 with phen as a function of the volume of phen solution (1.5×10^{-2} M) added into 50.0 ml LnA_3 solution in the reaction cup. (○ ($[SmA_3]_i = 1.58\times10^{-3}$ M), ▲ ($[EuA_3]_i = 9.67\times10^{-4}$ M), △ ($[TbA_3]_i = 1.61\times10^{-3}$ M), ■ ($[HoA_3]_i = 9.08\times10^{-4}$ M), □ ($[ErA_3]_i = 1.81\times10^{-3}$ M), and ▽ ($[LuA_3]_i = 1.00\times10^{-3}$ M).

Table 3. Thermodynamic Parameters in the Adduct Formation of LnA_3 in $CHCl_3$ with phen

	$-\Delta G_1$	$-\Delta H_1$	$T\Delta S_1$
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
La	39.4±0.4	−13±1	52
Pr	41.5±0.2	−7±1	49
Nd	42.4±0.3	−7±1	49
Sm	43.5±0.3	−9±1	53
Eu	43.7±0.3	−5.5±0.9	49.2
Gd	44.3±0.3	−5.2±0.6	49.5
Tb	44.7±0.5	−3.6±0.4	48.3
Dy	44.8±0.2	−3.3±0.2	48.1
Ho	44.6±0.4	6.1±0.3	38.5
Er	45.7±0.4	8±1	38
Tm	45.5±0.3	11.9±0.4	33.6
Yb	44.2±0.2	17±1	27
Lu	43.9±0.2	20±2	24

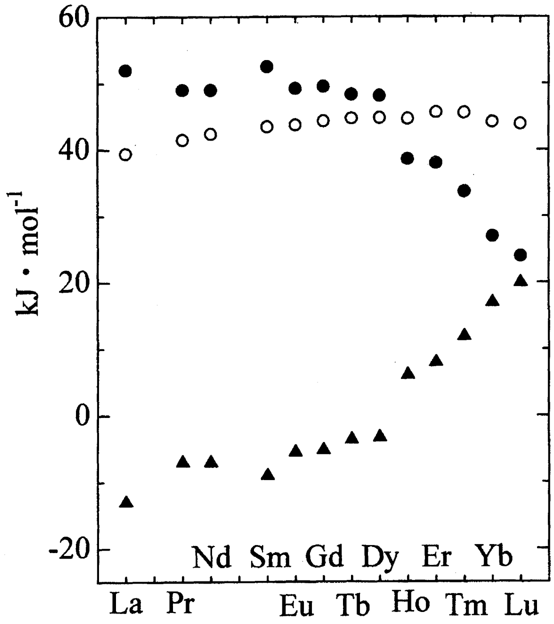

Fig. 4. Variation of thermodynamic parameters on the adduct formation of LnA_3 with phen in $CHCl_3$ across lanthanoid series. ○ $-\Delta G_1$, ▲ $-\Delta H_1$, ● $T\Delta S_1$.

Discussion

Figure 4 shows the variation in the thermodynamic parameters across the lanthanoid series. The enthalpy change ($-\Delta H$) increases with the atomic number, and inversely the entropy change decreases. Accordingly, the free energy does not change much across the lanthanoid series. The variation of the ΔH values in magnitude across the series ($-\Delta H_1$: -10 kJ mol^{-1} for LaA_3·phen and 20 kJ mol^{-1} for LuA_3·phen) is much larger than that of ΔG ($-\Delta G_1$: 40 kJ mol^{-1} in the formation of LaA_3·phen and 45 kJ mol^{-1} in that of LuA_3·phen). The difference may be explained as being related to the degree of dehydration from LnA_3 and the degree of the bond strength. Namely, the formation of a new bonding due to the formation of the chelate with phen should be exothermic, while the dehydration should be endothermic. 1,10-Phenanthroline would combine more strongly with heavier lanthanoid(III)–TTA chelates to form chelating adducts, although water molecules may also combine more strongly with the heavier ones. The larger $-\Delta H$ for heavier lanthanoids(III) may suggest that the energy emitted due to the formation of the new bond may largely overcome the dehydration energy.

We obtained data that in chloroform the TTA chelates of light-to-middle lanthanoids(III) keep around 3 hydrated molecules, while the hydration number in heavy lanthanoid(III) chelates with TTA decreases to 2.$^{10)}$ If all hydrated molecules are released from lanthanoid chelates upon the adduct formation, because phen is a very strong Lewis base, the larger entropy change in lighter lanthanoids than in heavier ones seen in Fig. 4 should be reasonable.

As mentioned above, upon adduct formation, due to a canceling out between the increase of $-\Delta H$ and the decrease of $T\Delta S$, the change in the formation constants of the adducts may be small.

In greater detail, it is considered that since the charge density increases from light to middle of the lanthanoid series, $-\Delta H$ increases in the series; however, since the hydration number of the TTA chelates from the light to middle lanthanoids(III) does not change, the $T\Delta S$ would be similar. Accordingly, the formation constants would increase slightly from light to middle of the lanthanoid series.

However, a detailed discussion would be accomplished after the hydration number of the adducts is accurately determined across the lanthanoid series.

The authors are grateful to R. Hibasami, K. Takeuchi, and A. Hirasawa of Science University of Tokyo for their experimental aid. The present work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 08220261 from the Ministry of Education, Science, Sports and Culture.

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