

## The thermodynamics of lanthanide complexing by bis(5,6-diphenyl-1,2,4-triazine-3-ylhydrazinocarbonyl) (DPTHC)

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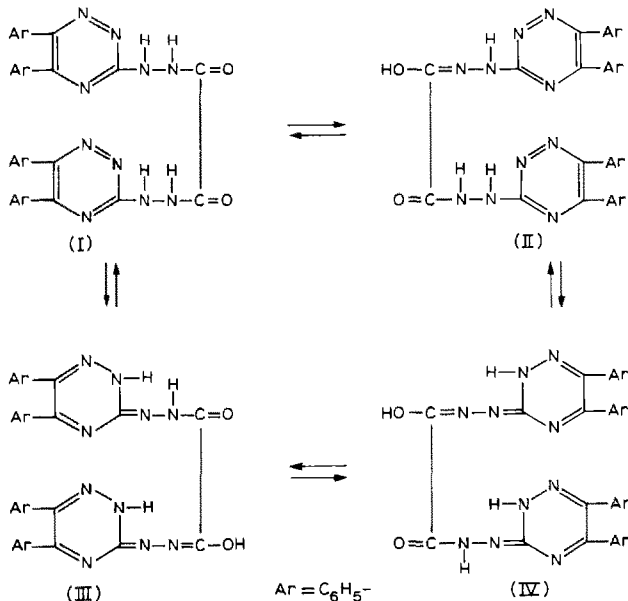
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### Abstract

The free energies, enthalpies and entropies of complexation of lanthanide ions by bis(5,6-diphenyl-1,2,4-triazine-3-ylhydrazinocarbonyl) (DPTHC) have been determined by potentiometry in 75% (v/v) dioxane–water and 0.10 M KNO<sub>3</sub> ionic strength. The data obtained support the interpretation of an expanded solvation sphere through the lanthanide series. Relatively large values of entropy of formation for chelation process ( $\Delta S_1$  and  $\Delta S_2$ ) imply an increase in the hydration number from lanthanum to lutetium and also the possibility of dioxane coordination in the solvent sphere. Probable structures of the metal chelates are inferred from IR examination of the solid copper, neodymium and ytterbium complexes.

### INTRODUCTION

The rare earth metals are readily oxidized to tri-positive ions that differ significantly from each other in the number of electrons in the 4f arrangement and in the crystal radius. These ions should provide therefore, a particularly interesting series in which to evaluate the effect of the progressive changes in electronic arrangement and size on complex ion formation. The comparative weakness of the cations as acids in the Lewis sense, as demonstrated by their ease of formation, their comparatively large size and by their behaviour in a variety of experimental conditions [1], suggest, however, that the formation of complex species is much less a characteristic of rare earth metal cations than it is of d-type transition metal cations. Indeed, only ligands with strongly chelating properties yield complex ions of significant stabilities. The absence of extensive covalent bonding in such complexes is dictated both by the electronic configurations of the cations and by their large size. Therefore it has been generally concluded that the ligands are held to the lanthanide cations by electrostatic or ionic interaction. Accordingly, the logarithm of the stabilities of the lanthanide complexes should be expected to vary linearly with ionic potential,  $Z^2/r$ , or more generally with  $1/r$ , where  $r$  is the cationic radius. Recent investigations [2–6] on various organic-solvent–water mixtures have revealed that the thermodynamic quantities accompanying the chemical reactions are in-



fluenced to a greater extent by the solute–solvent interaction than by the electrostatic interactions. Accordingly, the relationship between the  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  values and the dielectric constant of the medium cannot always be explained by the simple electrostatic theory [7].

In the present report, the thermodynamics of the lanthanide complexes with bis(5,6-diphenyl-1,2,4-triazine-3-ylhydrazinocarbonyl) (DPTHC) (**I**) have been measured.

## EXPERIMENTAL

### *Preparation of the solid ligand*

DPTHC was prepared by the reaction of 3-hydrazino-5,6-diphenyl-1,2,4-triazine (**I**) with oxalyl chloride. Oxalyl chloride (0.01 mol) was added to a well stirred ethanolic solution of **I** (0.02 mol) in dimethylformamide (DMF) (100 ml). The mixture was stirred for 1 h and then refluxed for another 1 h. The solvent was removed and the reaction mixture was poured onto crushed ice. The solid obtained was filtered, washed with cold water and crystallized from ethanol to give DPTHC. The elemental analysis results for C, H and N are shown in Table 1.

### *Preparation of solid complexes*

A mixture of equimolar amounts of ligand and copper nitrate in 75% (v/v) dioxane–water was refluxed for 30 min. After a while, the solid

complex separated as a red solid. This was filtered, washed several times with aqueous dioxane and dried under vacuum. In case of Nd and Yb, an excess of ammonia was first added to 50 ml of 0.01 M neodymium or ytterbium nitrate in order to obtain complete precipitation of the metal hydroxide. To this solution, 50 ml of 0.01 M ligand solution in dioxane was added dropwise with continuous stirring. The mixture was refluxed for 1 h, and then concentrated to eliminate excess ammonia. The brownish solid obtained was filtered, washed several times with aqueous dioxane and dried under vacuum. The elemental analysis results for C, H and N are given in Table 1. The total metal content was determined by decomposition of the solid by repeated treatment with concentrated nitric acid; the solution obtained was then titrated against standard ethylenediaminetetraacetic acid (EDTA) solution using a suitable indicator.

#### *Determination of stability constants*

Reagent grade metal nitrates were used for making stock solutions, which were standardized with EDTA [8]. Carbon dioxide-free potassium hydroxide solution was prepared and standardized as recommended [9]. The dioxane was purified by refluxing it with Na/LiAlH<sub>4</sub> for 8–10 h, followed by distillation. The procedure was repeated twice to ensure the disappearance of any acetals.

Solutions of metal nitrates and DPTHC in 75% (v/v) dioxane–water medium were titrated potentiometrically with standard potassium hydroxide (using a WTW digital pH-meter fitted with a combined glass–calomel electrode). The correction for pH values in 75% (v/v) dioxane–water was taken as 0.28 [10]. The temperature was maintained constant by use of cells jacketed with water circulated from a constant-temperature bath. Purified nitrogen was passed through the solution during the measurements. The ionic strength of the medium was kept virtually constant at 0.10 M with potassium nitrate as background electrolyte. In all cases, the metal-to-ligand ratio was kept at 1 : 3 with the metal concentration being 10<sup>-3</sup> M.

All the titrations were repeated at least twice and the titration curves agreed within  $\pm 0.02$  pH units.

The conductance of a  $1 \times 10^{-3}$  M solution of the solid complex in DMF was measured using a WTW D-812 Weilheium conductivity meter, Model LBR, fitted with cell model LTA 100.

The IR spectra (potassium bromide discs) were recorded on a Perkin–Elmer 437 spectrometer (4000–200 cm<sup>-1</sup>).

## RESULTS

The pH-metric curves for free and complexed DPTHC are shown in Fig. 1. Between  $a = 0$  and  $a = 1$ , where  $a$  is the number of moles of base added

TABLE 1  
Elemental analysis and molar conductance data of DPTHC and its chelates

Species and formula	C (%)		H (%)		N (%)		M (%)		Conductance <sup>b</sup> (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
C <sub>32</sub> H <sub>24</sub> N <sub>10</sub> O <sub>2</sub> (DPTHC) <sup>a</sup>	66.21	65.81	4.14	4.04	24.14	24.34			
[Cu(C <sub>32</sub> H <sub>23</sub> N <sub>10</sub> O <sub>2</sub> ) (H <sub>2</sub> O) <sub>4</sub> ][NO <sub>3</sub> ]	49.45	49.10	4.12	4.08	19.83	19.60	8.18	8.08	81.5
[Nd(C <sub>32</sub> H <sub>22</sub> N <sub>10</sub> O <sub>2</sub> ) (H <sub>2</sub> O) <sub>6</sub> ][NO <sub>3</sub> ]	43.04	43.15	3.92	3.89	17.26	17.11	16.17	16.00	69.7
[Yb(C <sub>32</sub> H <sub>22</sub> N <sub>10</sub> O <sub>2</sub> ) (H <sub>2</sub> O) <sub>6</sub> ][NO <sub>3</sub> ]	41.69	41.86	3.69	3.83	16.72	16.62	18.79	18.67	70.4

<sup>a</sup> Melting point, 120° C.

<sup>b</sup> 10<sup>-3</sup> M complex in DMF.

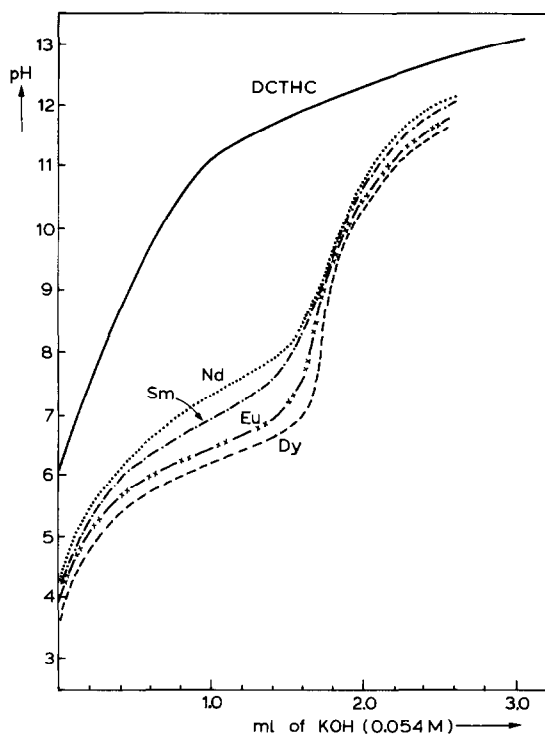


Fig. 1. Potentiometric titration curves of 30 ml DPTHCH (0.003 M) in absence and presence of 0.001 M lanthanide ion:  $t = 30^\circ\text{C}$ ; 75% dioxane-water;  $\mu = 0.10$ .

per mole of ligand present, and in the presence of different metal ions, only one proton dissociates. This suggests that under these conditions the ligand behaves as a monoprotic species, with the dissociation of either the hydrazo or enolic OH-group proton. The acid dissociation constant  $K^{\text{H}}$  was calculated as described previously [11] and is given in Table 2. The value of  $\log K^{\text{H}}$  obtained (11.31 in 75% dioxane-water) is close to that reported for enolic OH [12]. In contrast, ligands containing the grouping  $\text{Ar-NH-N=C-R}_2$  are normally ionized in moderately alkaline media, and have  $\text{p}K^{\text{H}}$  values ranging between 6 and 9 [13,14]. This suggests that in the ligand it is the enolic OH group that loses a proton. In order to confirm this, the IR spectra of the ligand and of some of the solid complexes were recorded.

The titration curves obtained in the presence of metal ions showed an inflection at  $m = 3$  (where  $m$  is the number of moles of base added per mole of metal) corresponding to formation of 1:3 metal-to-ligand complexes, represented by the equilibrium



TABLE 2

Stability constants <sup>a</sup> of metal chelates of DPTHC at different temperatures:  $\mu = 0.10$ ; 75% dioxane–water

M <sup>3+</sup>	15 °C			30 °C			40 °C		
	log K <sub>1</sub>	log K <sub>2</sub>	log K <sub>3</sub>	log k <sub>1</sub>	log K <sub>2</sub>	log K <sub>3</sub>	log K <sub>1</sub>	log K <sub>2</sub>	log K <sub>3</sub>
H <sup>+</sup>	11.68			11.31			11.05		
	±0.03			±0.04			±0.06		
La	7.49	6.56	5.51	7.36	6.41	5.00	7.22	6.30	4.82
Ce	7.71	6.72	5.89	7.54	6.56	5.28	7.43	6.43	5.02
Pr	7.99	6.93	6.24	7.81	6.72	5.54	7.68	6.62	5.36
Nd	8.10	7.06	6.61	7.90	6.88	6.01	7.78	6.73	5.66
Sm	8.37	7.34	7.12	8.16	7.14	6.44	8.03	7.00	6.15
Eu	8.44	7.36	7.22	8.24	7.16	6.56	8.12	7.03	6.34
Gd	8.37	7.20	7.18	8.19	7.04	6.62	8.08	6.96	6.42
Tb	8.32	7.21	6.98	8.14	7.04	6.67	8.02	6.95	6.36
Dy	8.29	7.40	7.01	8.12	7.23	6.65	7.98	7.12	6.40
Ho	8.43	7.54	7.13	8.21	7.38	6.78	8.17	7.24	6.50
Er	8.51	7.70	7.31	8.31	7.53	6.94	8.20	7.38	6.65
Tm	8.62	7.78	7.43	8.41	7.60	7.12	8.30	7.46	6.78
Yb	8.64	7.83	7.61	8.48	7.64	7.22	8.31	7.50	6.96
Lu	8.58	7.76	7.42	8.40	7.58	6.98	8.28	7.45	6.86

<sup>a</sup> ±(0.01–0.03) for log K<sub>1</sub>; ±(0.02–0.04) for log K<sub>2</sub>; ±(0.05–0.07) for log K<sub>3</sub>.

The calculation of the overall equilibrium constants for the following complexation reactions



were carried out using standard procedures based on the calculations of the average number of ligands bound per metal ion,  $\bar{n}_L$ , and the free ligand concentrations, [L]. The values of the logarithms of the formation constants were refined using the least-squares method. The error limits were calculated after subjecting the data to least-squares analysis and represent the standard deviation of an individual run. The potentiometric titrations were carried out at 15, 30 and 40 °C at a constant ionic strength of 0.10. The overall changes in free energy  $\Delta G$ , enthalpy,  $\Delta H$ , and entropy,  $\Delta S$ , shown in Fig. 2, were calculated using the temperature coefficient and the Gibbs–Helmholtz equation. The values of  $\Delta H$  were calculated in each case by a least-squares analysis of the data according to the relationship  $\log K = -(\Delta H/2.303RT) + \text{constant}$ . A least-squares analysis was also used to calculate the probable errors in  $\Delta H$  terms.

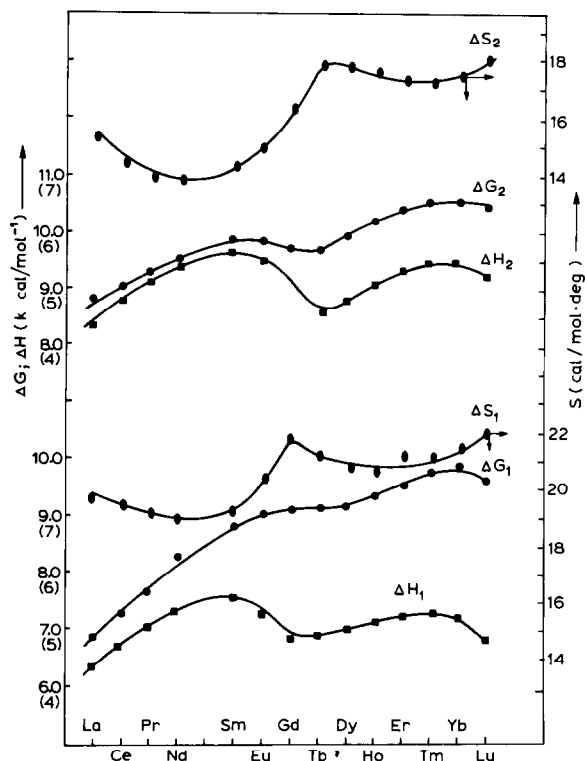


Fig. 2. Variation of the thermodynamic parameters for DPTHC chelates (scale between parentheses is for  $\Delta H$ ).

TABLE 3

Selected band groups in the IR spectra and their tentative assignments ( $\text{cm}^{-1}$ )<sup>a</sup>

DPTHC	Cu-DPTHC	Nd-DPTHC	Yb-DPTHC	Assignment
	3400 b	3400 b	3400 b	$\nu(\text{HOH})$
3460 b	—	—	—	$\nu(\text{OH, enolic})$
3200 b	3200 b	3200 b	3200 b	$\nu(\text{N-H})$
1720 s	1730 s	—	—	$\nu(\text{C=O})$
1680 sh	1650 b	1610 sh	1610 sh	
1500 b	1530 b	1520 b	1530 b	$\nu(\text{C=C}); \nu(\text{C=N})$
1480 m	—	—	—	
1440 m	—	1440 w	1440 w	
1390 b	1380 s	1380 s	1380 s	$\nu(\text{C-O})$
1370 m	—	—	—	
1300 w	1300 b	1300 w	1300 w	
1275 b	—	—	—	$\nu(\text{OH})$
1220 w	—	1220 w	1220 w	$\nu(\text{C-N}); \text{C-H in-plane def.}$
1185 b	1180 b	1180 w	1180 w	
1060 s	1070 b	1070 b	1080 b	
	480 w	480 w	480 w	$\nu(\text{M-O})$
	465 w	460 w	465 w	

<sup>a</sup> s, strong; b, broad; w, weak; sh, shoulder; m, medium.

## DISCUSSION

Of the various tautomeric forms (I–IV) of DPTHC, tautomer II accords well with potentiometric results. Further evidence for this assignment is provided by the IR spectra. The presence of a broad band at  $3460\text{ cm}^{-1}$  in the spectrum of the ligand (Table 3) can be assigned to  $\nu(\text{OH, enolic})$ . The broad band at  $3200\text{ cm}^{-1}$  in the spectrum of the free ligand may be assigned to  $\nu(\text{NH})$ ; this band is still apparent in the spectra of the complexes, which indicates that the  $-\text{NH}$  groups did not participate in chelate formation. The enol form of DPTHC (structure II) is confirmed by the presence of the OH-group stretching frequency. By comparing the IR spectra of the ligand and its chelates, we can try to distinguish between the OH and CO vibrations. The ligand has a strong band at  $1275\text{ cm}^{-1}$  which disappears following chelation and may be fairly confidently attributed to a vibration mainly involving the OH group. The bands at  $1390$  or  $1370\text{ cm}^{-1}$  may then be attributed to the C–O vibration; of these we tentatively select the second value because it is sensitive to chelation and also because it falls in the expected range. The participation of the carbonyl group in chelate formation is indicated by the shift or disappearance of the band at  $1720\text{ cm}^{-1}$  (C=O stretch) in the spectra of the complexes (Table 3). The appearance of the new bands at  $480$  and  $460\text{ cm}^{-1}$  in the spectra of the complexes, which could be assigned to  $\nu(\text{M–O, enolic})$  and  $\nu(\text{M–O, carbonyl})$ , strengthens the hypothesis that the enol form of DPTHC (structure II) is the dominant one.

From the values of the stability constants (Table 2) it is clear that the stepwise and overall stability constants decrease with a rise in temperature, indicating that the formation equilibria are exothermic in nature. This is also borne out by the fact that  $\Delta G$  and  $\Delta H$  are both negative. The higher  $\Delta H$  values could be explained by the increase in solvent basicity [15], which causes the transfer of metal ion from aqueous state to dioxane solvent to be exothermic. The enthalpy change ( $\Delta H_{\text{trans}}$ ) for the transfer of processes represented by eqns. (1)–(3), from water to organic solvent mixture, is made up of the partial transfer enthalpies for the individual species:

$$\begin{aligned}\Delta H_{\text{trans}} &= \Delta H^{\text{S}} - \Delta H^{\text{W}} \\ &= \Delta H_{\text{trans}}^{\text{ML}} - \Delta H_{\text{trans}}^{\text{M}^{3+}} - H_{\text{trans}}^{\text{L}^-}\end{aligned}\quad (5)$$

$$\Delta H_{\text{trans}} = \Delta H_{\text{trans}}^{\text{ML}_2} - \Delta H_{\text{trans}}^{\text{ML}} - 2\Delta H_{\text{trans}}^{\text{L}^-}\quad (6)$$

$$\Delta H_{\text{trans}} = \Delta H_{\text{trans}}^{\text{ML}_3} - \Delta H_{\text{trans}}^{\text{ML}_2} - 3\Delta H_{\text{trans}}^{\text{L}^-}\quad (7)$$

The  $\Delta H$  dependences in the solvent can be ascribed primarily to the different hydration–solvation conditions of the metal ions. On the basis of a published report [16], it may be stated that at high dioxane concentration (i.e. 75% dioxane–water) the strengthening of the interaction between the metal ion and the solvent molecules is more than offset by the decrease in



TABLE 4

Thermodynamic functions of metal complexes at 30°C<sup>a</sup>

M <sup>3+</sup>	$-\Delta G_1$ (kcal mol <sup>-1</sup> )	$-\Delta H_1$ (kcal mol <sup>-1</sup> )	$\Delta S_1$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G_2$ (kcal mol <sup>-1</sup> )	$-\Delta H_2$ (kcal mol <sup>-1</sup> )	$-\Delta S_2$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G_3$ (kcal mol <sup>-1</sup> )	$-\Delta H_3$ (kcal mol <sup>-1</sup> )	$-\Delta S_3$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
H <sup>+</sup>	15.69	10.33	17.69						
La	10.21	4.35	19.34	8.89	4.26	15.28	6.93	11.58	15.25
Ce	10.46	4.61	19.31	9.10	4.73	14.42	7.32	14.52	23.76
Pr	10.83	5.08	18.99	9.32	5.16	13.73	7.68	14.90	23.83
Nd	10.96	5.28	18.78	9.54	5.38	13.73	8.34	15.68	24.22
Sm	11.32	5.60	18.88	9.90	5.58	14.26	8.93	16.19	24.06
Eu	11.43	5.28	20.23	9.93	5.43	14.85	9.10	14.80	18.81
Gd	11.36	4.78	21.72	9.76	5.88	12.81	9.18	12.75	11.78
Tb	11.29	4.93	20.99	9.76	4.31	17.99	9.25	10.04	2.61
Dy	11.26	5.05	20.55	10.03	4.61	17.89	9.22	10.01	2.61
Ho	11.39	5.18	20.55	10.25	4.88	17.76	9.40	10.03	2.08
Er	11.52	5.12	21.12	10.44	5.20	17.29	9.62	10.78	3.83
Tm	11.66	5.30	20.99	10.54	5.23	17.52	9.87	10.47	1.98
Yb	11.76	5.32	21.25	10.60	5.40	17.16	10.01	10.68	2.21
Lu	11.65	4.93	22.18	10.51	5.02	18.12	9.68	10.12	1.45

<sup>a</sup>  $\pm(0.13-0.17)$  kcal mol for  $\Delta H_1$ ;  $\pm(0.12-0.18)$  kcal mol<sup>-1</sup> for  $\Delta H_2$ ;  $\pm(0.30-0.48)$  kcal mol<sup>-1</sup> for  $\Delta H_3$ ;  $\pm(0.58-0.66)$  cal mol<sup>-1</sup> K<sup>-1</sup> for  $\Delta S_1$ ;  $\pm(0.39-0.54)$  cal mol<sup>-1</sup> K<sup>-1</sup> for  $\Delta S_2$ ; and  $\pm(0.04-0.70)$  cal mol<sup>-1</sup> K<sup>-1</sup> for  $\Delta S_3$ .

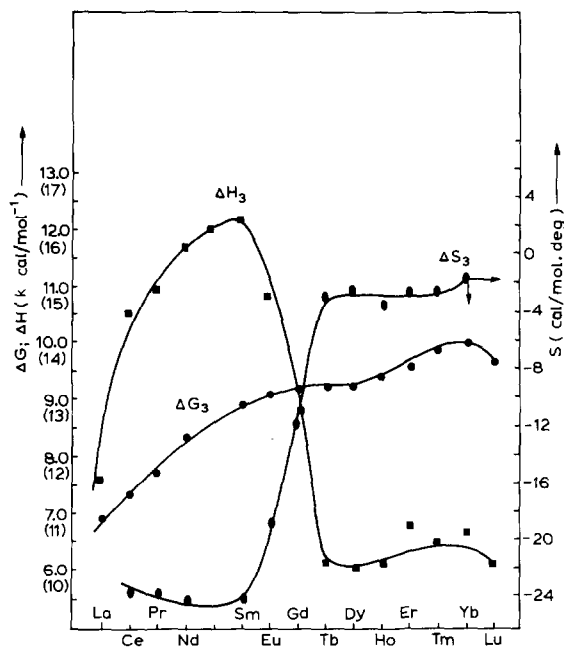


Fig. 3. Variation of the thermodynamic parameters for DPTHC chelates (scale between parentheses is for  $\Delta H_3$ ).

the hydration of the bulky ligand anion. Thus only a minor proportion of the energy released on formation of the strong coordination bond, is utilized against the interaction between the ion and the solvent molecules. Therefore, the complex formation process will be more exothermic, to a greater or lesser extent, in comparison with the process in aqueous medium.

The large entropy contribution as a major driving force for the metal-ligand coordination is substantiated by the relatively large magnitude of  $\Delta S_1$  and  $\Delta S_2$  compared with  $\Delta H_1$  and  $\Delta H_2$  values (Table 4). Williams [17] has pointed out that a high entropy value is usually associated with the combination of a metal ion ( $\text{Ln}^{3+}$ ) with a negatively charged ligand ( $\text{L}^-$ ) involving displacement of the water molecules which then form part of the solvent. Since the water molecules bound to metal ion are highly distorted and oriented, their entropy is low. Thus any process which releases water molecules from this type of strain results in an increase in entropy.

The values of  $\Delta G_1$ ,  $\Delta G_2$  and  $\Delta G_3$  are plotted against the atomic number of the lanthanide elements in Fig. 2; there is a distinct break at gadolinium (a so-called gadolinium break). Changes in the enthalpy and entropy of complex formation when plotted as a function of the atomic number of trivalent lanthanide elements show a complex pattern (Figs. 2 and 3). The values of  $\Delta H_1$  and  $\Delta H_2$  increase from La to Lu with notable breaks (minima) at  $Z = 63-64$ . The values of  $\Delta H_3$  also increase from La to Lu with a pronounced decrease at  $Z = 64-68$ . The variation in the entropy ( $\Delta S_1$ ,

Table 5

Relative partial molal entropy of the complex ions

R	$-S_{R^{3+}}^{\ominus}$	$-(\Delta S_1^{\ominus} + S_{R^{3+}}^{\ominus})$	$-(\Delta S_2^{\ominus} + S_{R^{3+}}^{\ominus})$	$-(\Delta S_3^{\ominus} + S_{R^{3+}}^{\ominus})$
La	39.2	19.9	23.9	54.5
Ce	41.3	22.0	26.9	65.1
Pr	43.0	24.0	29.3	66.8
Nd	44.5	25.7	30.8	68.7
Sm	47.1	28.2	32.8	71.2
Eu	48.4	28.2	33.6	67.2
Gd	49.5	27.8	36.7	61.3
Tb	50.9	29.9	32.9	53.5
Dy	52.3	31.8	34.4	54.9
Ho	53.8	33.3	36.0	55.9
Er	55.2	34.1	37.9	59.0
Tm	56.5	35.5	39.0	58.5
Yb	57.7	36.5	40.5	59.9
Lu	58.8	36.6	40.7	60.3

$\Delta S_2$  and  $\Delta S_3$ ) of DPTHC-Ln<sup>3+</sup> complexes with Z (atomic number of lanthanide elements) shows a clear distinction between two groups of lanthanide elements. The first group is from La to Eu and the second is from Tb to Lu (Figs. 2 and 3). In order to illustrate this variation, we must consider the ligational entropy which is expressed by the relationship

$$\Delta S^{\ominus} = S_{LnX}^{\ominus} - S_{Ln}^{\ominus} - S_X^{\ominus} \quad (8)$$

where the  $\Delta S^{\ominus}$  terms represent standard partial molal entropies of the species LnX, Ln<sup>3+</sup> and X<sup>-</sup> (ligand anion). Of these terms  $S_{LnX}^{\ominus}$  is of particular interest as its variation may be related to the "gadolinium break". Using experimentally obtained values of  $S_{Ln^{3+}}^{\ominus}$  [18] (not corrected for medium) and considering  $S_X^{\ominus}$  constant for certain ligands, values of  $S_{LnX}^{\ominus}$  can be calculated from eqn. (8). The results of these calculations are shown in Table 5. The relative entropy of the complex ions, expressed by the quantity  $S^{\ominus} + S_{Ln^{3+}}^{\ominus}$  in Table 5, is essentially constant for the lanthanides La to Gd; after Gd a second group of constant values is apparent which differs from the first group. A quantitative statement of these results is shown in Table 6. The constancy of the entropies within each of the two group of complex ions (La to Gd and Tb to Lu) would appear to indicate

TABLE 6

Average values for the relative entropies of the complex ions

Element	$(\Delta S_1^{\ominus} + S_{R^{3+}}^{\ominus})$	$(\Delta S_2^{\ominus} + S_{R^{3+}}^{\ominus})$	$(\Delta S_3^{\ominus} + S_{R^{3+}}^{\ominus})$
La-Gd	$-25.11 \pm 3.1$	$-29.5 \pm 3.3$	$-65.0 \pm 5.0$
Tb-Lu	$33.9 \pm 2.3$	$-37.3 \pm 2.8$	$-57.4 \pm 2.4$
Difference	-8.8	-7.8	-7.6

the close similarity in structure and radius of the individual ions within each subgroup.

The data presented here support theories of an expanded solvation sphere through the lanthanide series, as stated in three independent studies [19–21], which divide the lanthanide series into two groups, light lanthanides, lanthanum to gadolinium, and heavy lanthanides, terbium to lutetium. Spedding and Atkinson [22] and Choppin and Graffeo [20] explained this by suggesting two different hydration-sphere structures for the two series. On this basis the heavier lanthanides have a higher hydration number. This would result in more water molecules being released upon complex formation and would account for the higher entropy of the heavier lanthanides. The effect of this change in hydration sphere on the enthalpy of the complex formation would be to cause the lighter lanthanide complexes to form more exothermically than the heavier lanthanide complexes, as shown in Table 4.

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