Thermodynamic parameters of lanthanoid(III) complexation with 3-(α,δ-dicarboxy-n-propylidenehydrazino)-5,6-diphenyl-1,2,4-triazine (DCPT). Part 2

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Abstract

The complex formation equilibria between lanthanoid(III) and DCPT ions have been studied by potentiometry in 75% (v/v) dioxane–water mixture and 0.10 M KNO_3 as constant ionic medium, at 10, 20, 30 and 40 °C. A series of mononuclear protic $[Ln(HL)]^{2+}$, $[Ln(HL)_2]^+$, $[Ln(HL)_3]$, $[LnL(HL)_2]^-$, $[LnL_2(HL)]^{2-}$ and non-protic $[LnL_3]^{3-}$ complex species were found in solutions and their formation constants, ethalpies and entropies were determined. It was established that the stepwise Gibbs energies of the protonated complexes varied in the sequence $-\Delta G_{Ln(HL)} > -\Delta G_{Ln(HL)_2} > -\Delta G_{Ln(HL)_3}$, and the stepwise enthalpies the order was $-\Delta H_{Ln(HL)} > -\Delta H_{Ln(HL)_2} > -\Delta H_{Ln(HL)_3}$, and the entropy markedly increased in the order $\Delta S_{Ln(HL)} > \Delta S_{Ln(HL)_2} > \Delta S_{Ln(HL)_3}$. The results are discussed in relation to changes in the metal–water and metal–ligand bond strength. The variation of the thermodynamic parameters as a function of ionic potential of lanthanide elements is discussed in terms of the different hydration numbers of lighter and heavier lanthanide(III) ions.

Keywords: 3-(α-δ-Dicarboxy-n-propylidene-hydrazino)-5,6-diphenyl-1,2,4-triazine Lanthanide(III) ions; Thermodynamic parameters;

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1. Introduction

We have recently [1] reported the synthesis and properties of iron(II) and iron(III) complexes with 3-(α, δ-dicarboxy-n-propylidenehydrazino)-5,6-diphenyl-1,2,4-triazine (DCPT) as an introduction to the investigation of this chelating agent with a wide variety of metal ions.

It has been reported that DCPT [1] behaves toward iron(II) and iron(III) ions as a monoprotic bidentate O,N-donor, using the carboxylate oxygen and azomethine nitrogen as coordination sites. The only reason for the non-participation of the second carboxylate group (the farthest from triazine moiety) in bonding to the metal ions is the preferable trans arrangement which gives no access for the simultaneous coordination of three sites with the metallic centre. As a result, a number of protonated and non-protonated complex species were formed. It has also been found that both carboxy groups are bonded simultaneously to the two separate iron atoms in the case of the formation of binuclear complexes.

In order to obtain additional information about the formation of protonated and non-protonated complexes, we have expanded our studies to other metal–ligand systems. The thermodynamic study of DCPT–Ln(III) complexes is the aim of the present work.
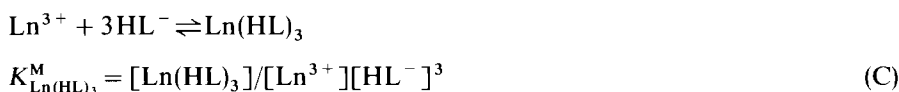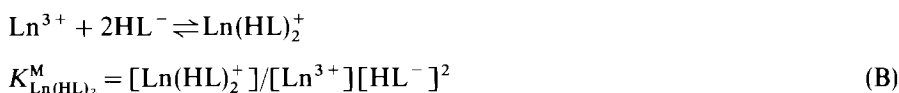

(DCPT)   (I)
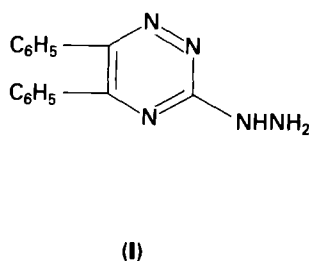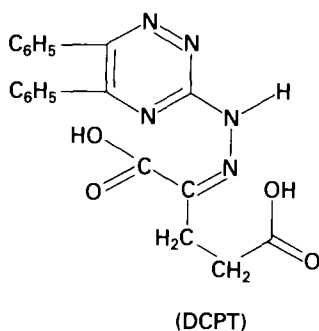
2. Experimental

DCPT was prepared by refluxing a mixture of 3-hydrazino-5,6-diphenyl-1,2,4-triazine(I) (0.01 mol) and α-oxo-glutaric acid (0.01 mol) in absolute ethyl alcohol (50 ml) for 15 min as described in Ref. [1].

For lanthanide nitrates, the potassium hydroxide, the purification of dioxane, and the potentiometric titration procedures have been described elsewhere [2, 3]. The potentiometric titration of 0.003 M DCPT was carried out in the absence and presence of 0.001 M lanthanide ion at 10, 20, 30 and 40 °C and the ionic strength was maintained at 0.10 M KNO_3. All the measurements were performed in 75% (v/v) dioxane–water solvent.

3. Results

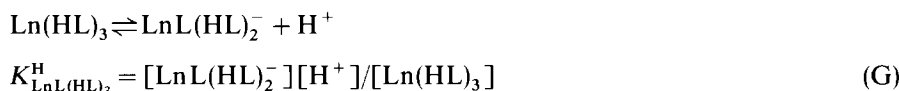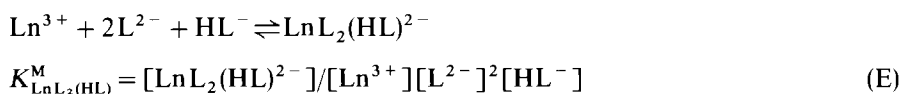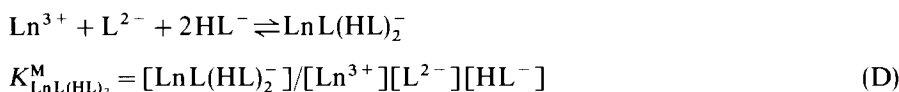The shape of the titration curves of 3:1 molar ratios of DCPT to Ln(III) indicates the formation of a simple mononuclear complex, as well as various protonated complex species. The curves show two separate buffer regions. The first is between $a = 0$ and 3 (a is the number of moles of base added per mole of metal) followed by an inflection point at $a = 3$. The second buffer region is between $a = 3$ and 6, followed by inflection at $a = 6$ (Fig. 1). The equilibria in the first buffer region may be represented by

$$Ln^{3+} + HL^- \rightleftharpoons Ln(HL)^{2+}$$

$$K^M_{Ln(HL)} = [Ln(HL)^{2+}]/[Ln^{3+}][HL^-] \tag{A}$$

$$Ln^{3+} + 2HL^- \rightleftharpoons Ln(HL)_2^+$$

$$K^M_{Ln(HL)_2} = [Ln(HL)_2^+]/[Ln^{3+}][HL^-]^2 \tag{B}$$

$$Ln^{3+} + 3HL^- \rightleftharpoons Ln(HL)_3$$

$$K^M_{Ln(HL)_3} = [Ln(HL)_3]/[Ln^{3+}][HL^-]^3 \tag{C}$$
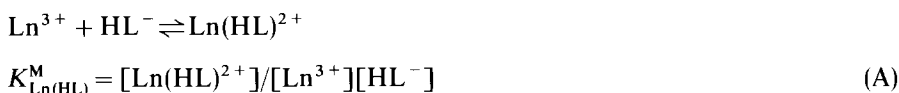
Further addition of base results in the subsequent dissociation of three protons as indicated by the amount of base required per metal chelate. The reactions involved may be described by the equilibria given previously in the case of the DCPT–Fe(III) system [1]

$$Ln^{3+} + L^{2-} + 2HL^- \rightleftharpoons LnL(HL)_2^-$$

$$K^M_{LnL(HL)_2} = [LnL(HL)_2^-]/[Ln^{3+}][L^{2-}][HL^-] \tag{D}$$

$$Ln^{3+} + 2L^{2-} + HL^- \rightleftharpoons LnL_2(HL)^{2-}$$

$$K^M_{LnL_2(HL)} = [LnL_2(HL)^{2-}]/[Ln^{3+}][L^{2-}]^2[HL^-] \tag{E}$$

$$Ln^{3+} + 3L^{2-} + HL^- \rightleftharpoons LnL_3^{3-}$$

$$K^M_{LnL_3} = [LnL_3^{3-}]/[Ln^{3+}][L^{2-}]^3 \tag{F}$$

$$Ln(HL)_3 \rightleftharpoons LnL(HL)_2^- + H^+$$

$$K^H_{LnL(HL)_2} = [LnL(HL)_2^-][H^+]/[Ln(HL)_3] \tag{G}$$

$$LnL(HL)_2^- \rightleftharpoons LnL_2(HL)^{2-} + H^+$$

$$K^H_{LnL_2(HL)} = [LnL_2(HL)^{2-}][H^+]/[LnL(HL)_2^-] \tag{H}$$

$$LnL_2(HL)^{2-} \rightleftharpoons LnL_3^{3-} + H^+$$

$$K^H_{LnL_3} = [LnL_3^{3-}][H^+]/[LnL_2(HL)^{2-}] \tag{I}$$
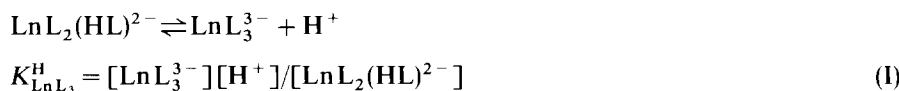
Calculation of the constants $K^M_{M(HL)}$, $K^M_{M(HL)_2}$ and $K^M_{M(HL)_3}$ was carried out using standard procedures based on the calculations of the average number of ligand bound per metal ion, $\bar{n}_{HL}$, and the free ligand concentration [HL], using the first buffer region
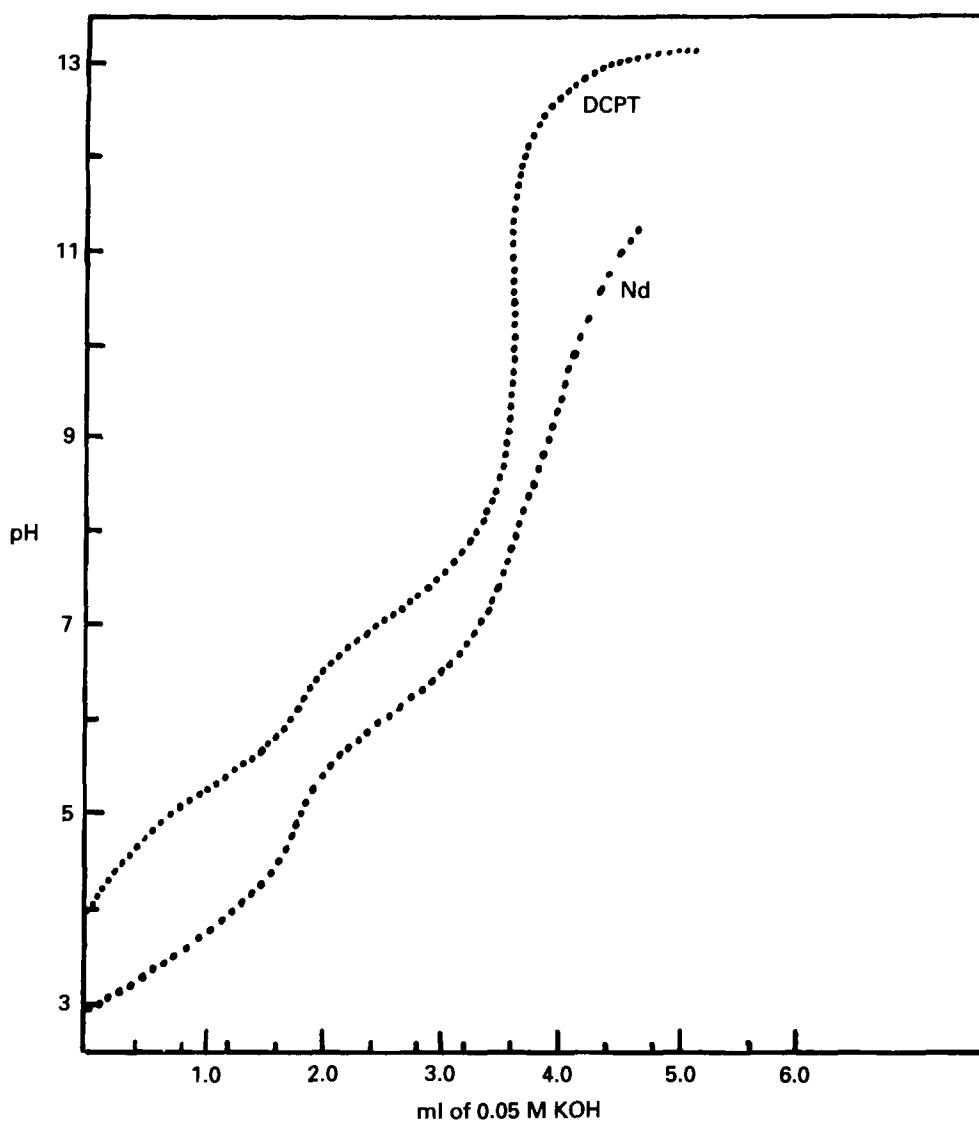
Fig. 1. Potentiometric titration curves of 30 ml DCPT (0.003 M) in the absence and presence of 0.001 M Nd(NO₃)₃.

of the titration curve, then minimising the residuals in the equation

$$\frac{\bar{n}_{HL}}{(1 - \bar{n}_{HL})[HL]} = K^{M}_{M(HL)} + \beta_1 \frac{(2 - \bar{n}_{HL})[HL]}{(1 - \bar{n}_{HL})} \tag{1}$$

$$Y \quad\quad = \quad C \quad + m\, X$$

using least-squares methods. The values of $K^M_{M(HL)_3}$ were obtained using Eq. (2)

$$\frac{\bar{n}_{HL}}{(2-\bar{n}_{HL})[HL]^2} + \frac{K^M_{M(HL)}(\bar{n}_{HL}-1)}{(2-\bar{n}_{HL})[HL]} = \beta_2 \frac{(3-\bar{n}_{HL})}{(2-\bar{n}_{HL})} + \beta_1 \qquad (2)$$

$$\bar{Y} \qquad\qquad = \bar{m}\,\bar{X} \qquad + \bar{C}$$

where $\beta_1 = K^M_{M(HL)} K^M_{M(HL)_2}$ and $\beta_2 = K^M_{M(HL)} K^M_{M(HL)_2} K^M_{M(HL)_3}$. Plots of $\bar{Y}$ versus $\bar{X}$ in Eq. (2) give straight lines, from the slope β_2 and intercept β_1 of which is obtained $K^M_{M(HL)_3}$. The values of $\bar{n}_{HL}$ and [HL] were calculated using Eqs. (3) and (4) respectively

$$HL = \frac{[C_{HL}] - [KOH] - [H^+] + [OH^-]}{[H^+]K^H_1} \qquad (3)$$

$$\bar{n}_{HL} = \frac{[C_{HL}] - [H^+]K^H_1[HL]}{[C_M]} \qquad (4)$$

where $[C_{HL}]$, $[KOH]$ and $[C_M]$ are the molar concentrations of the free ligand, base and metal respectively. The K values for $ML(HL)_2$, $ML_2(HL)$ and ML_3 complex species were obtained using the second buffer region on the titration curve, and replacing [HL] by [L], $\bar{n}_{HL}$ by $\bar{n}_L$, and K^H_1 by K^H_2 in Eqs. (1), (2), (3) and (4).

Computer-assisted algebraic methods were used to solve for the three overlapping complex protonation constants involved in the second buffer region ($K^H_{ML(HL)_2}$, $K^H_{ML_2(HL)}$ and $K^H_{ML_3}$). The values of these constants were calculated from potentiometric titration data by least-squares methods using the following equations

$$\frac{\bar{n}_H}{(1-\bar{n}_H)[H^+]} = K^H_{ML(HL)_2} + \beta\frac{(1-\bar{n}_H)[H^+]}{(1-\bar{n}_H)} \qquad (5)$$

$$\bar{Y}_1 \qquad = \qquad C_1 \qquad + m_1 X_1$$

$$\frac{\bar{n}_H}{(2-\bar{n}_H)[H^+]^2} + \frac{K^H_{ML(HL)_2}(\bar{n}_H-1)}{(2-\bar{n}_H)[H^+]} = \bar{\beta}\frac{(3-\bar{n}_H)}{(2-\bar{n}_H)} + \beta \qquad (6)$$

$$Y_2 \qquad\qquad = m_2 X_2 \qquad + C_2$$

where $\beta = K^H_{ML(HL)_2} K^H_{ML_2(HL)}$ and $\bar{\beta} = K^H_{ML(HL)_2} K^H_{ML_2(HL)} K^H_{ML_3}$. The linear relation between the stability constants and $1/T$ permits the calculation of the enthalpy of the complexation process in accordance with the van't Hoff equation

$$\log K = -(\Delta H/2.303RT) + \text{constant} \qquad (7)$$

Least-squares analysis was used to calculate ΔH and the probable error in the enthalpy terms. The free energy ΔG and entropy change ΔS were calculated from the known relationships

$$-\Delta G = 2.303RT\log K \qquad (8)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (9)$$

The values of the stability constants as well as the thermodynamic parameters (ΔG, ΔH and ΔS) obtained for all complex species are given in Table 1.

Table 1
Thermodynamic parameters for the interaction of DCPT and lanthanide(III) ions: $\mu = 0.10\,M$ (KNO_3); 75% (v/v) dioxane–water solvent; ΔG and ΔH in kJ mol^{-1} and ΔS in J mol^{-1} K^{-1}

Symbol	Equilibrium quotient	La			Pr			Nd			Sm		
		$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS
$K^{M}_{M(HL)}$	$\dfrac{[M(HL)^{(z-1)+}]}{[M^{z+}][HL^{-}]}$	23.9	3.39	67.7	26.4	5.06	70.3	26.5	6.78	65.3	27.0	8.45	61.1
$K^{M}_{M(HL)_2}$	$\dfrac{[M(HL)_2^{(z-2)+}]}{[M^{z+}][HL^{-}]^2}$	20.9	8.45	41.1	23.5	10.16	43.9	23.6	12.30	37.4	25.2	12.39	38.9
$K^{M}_{M(HL)_3}$	$\dfrac{[M(HL)_3^{(z-3)+}]}{[M^{z+}][HL^{-}]^3}$	19.7	10.17	31.6	20.4	11.84	28.2	20.4	13.05	24.4	21.4	16.95	14.6
$K^{M}_{ML(HL)_2}$	$\dfrac{[ML(HL)_2^{(z-4)+}]}{[M^{z+}][L^{2-}][HL^{-}]^2}$	19.0	−4.60	77.8	20.0	−3.39	77.1	20.1	−1.72	72.2	20.2	1.72	61.0
$K^{M}_{ML_2(HL)}$	$\dfrac{[ML_2(HL)^{(z-5)+}]}{[M^{z+}][L^{2-}]^2[HL^{-}]}$	18.1	−6.28	80.5	18.6	−5.06	78.2	18.6	−3.39	72.7	18.6	−2.39	69.2
$K^{M}_{ML_3}$	$\dfrac{[ML_3^{(z-6)+}]}{[M^{z+}][L^{2-}]^3}$	20.0	8.28	93.4	20.0	6.61	87.9	19.7	5.06	81.8	20.0	3.89	78.9
$K^{H}_{ML(HL)_3}$	$\dfrac{[ML(HL)_2^{(z-4)+}][H^{+}]}{[M(HL)_3^{(z-3)+}]}$	39.5	−28.79	35.5	37.9	−33.85	13.4	37.3	−42.30	16.6	37.1	−45.69	−28.4
$K^{H}_{ML_2(HL)}$	$\dfrac{[ML_2(HL)^{(z-5)+}][H^{+}]}{[ML(HL)_2^{(z-4)+}]}$	44.3	−25.40	62.3	42.5	−23.35	63.3	41.7	−33.85	25.8	41.7	−37.24	14.6
$K^{M}_{ML_3}$	$\dfrac{[ML_3^{(z-6)+}][H^{+}]}{[ML_2(HL)^{(z-5)+}]}$	49.3	−23.18	86.1	48.8	−22.01	88.5	47.4	−24.73	74.9	44.7	−30.96	45.2

Table 1 (continued)

Symbol	Equilibrium quotient	Eu			Gd			Tb			Dy		
		$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS
$K^{M}_{M(HL)}$	$\dfrac{[M(HL)^{(z-1)+}]}{[M^{z+}][HL^-]}$	27.5	9.85	58.1	27.0	10.17	55.7	27.7	8.95	61.9	27.6	7.28	66.9
$K^{M}_{M(HL)_2}$	$\dfrac{[M(HL)_2^{(z-2)+}]}{[M^{z+}][HL^-]^2}$	25.3	13.35	39.3	25.8	13.51	40.5	26.5	11.65	49.1	26.6	9.00	58.2
$K^{M}_{M(HL)_3}$	$\dfrac{[M(HL)_3^{(z-3)+}]}{[M^{z+}][HL^-]}$	21.6	15.52	20.0	21.5	14.55	22.8	21.7	13.05	28.6	22.0	12.34	31.9
$K^{M}_{ML(HL)_2}$	$\dfrac{[ML(HL)_2^{(z-4)+}]}{[M^{z+}][L^{2-}][HL^-]}$	20.4	-2.89	57.7	20.5	-2.18	60.4	20.3	2.39	74.8	20.3	3.89	79.9
$K^{M}_{ML_2(HL)}$	$\dfrac{[ML_2(HL)^{(z-5)+}]}{[M^{z+}][L^{2-}]^2[HL^-]}$	18.5	-2.22	53.8	19.1	2.89	72.6	19.3	5.27	81.0	19.0	7.28	86.7
$K^{M}_{ML_3}$	$\dfrac{[ML_3^{(z-6)+}]}{[M^{z+}][L^{2-}]^3}$	19.9	2.89	75.3	20.4	5.48	85.3	20.2	6.95	89.6	20.1	8.45	86.6
$K^{H}_{ML(HL)_2}$	$\dfrac{[ML(HL)_2^{(z-4)+}][H^+]}{[M(HL)_3^{(z-3)+}]}$	35.6	50.79	-50.2	37.0	37.74	-2.6	37.3	28.79	28.2	38.8	25.40	44.3
$K^{H}_{ML_2(HL)}$	$\dfrac{[ML_2(HL)^{(z-5)+}][H^+]}{[ML(HL)_2^{(z-4)+}]}$	39.9	42.30	-7.8	40.5	27.07	44.4	42.1	25.40	55.1	41.7	23.89	58.7
$K^{H}_{ML_3}$	$\dfrac{[ML_3^{(z-6)+}][H^+]}{[ML_2(HL)^{(z-5)-}]}$	46.3	34.69	38.2	46.1	23.18	75.6	47.9	20.29	91.3	49.3	16.74	107.6

Table 1 (continued)

Symbol	Equilibrium quotient	Ho			Er			Tm			Yb		
		$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS
$K_{M(HL)}^{M}$	$\dfrac{[M(HL)^{(z-1)+}]}{[M^{z+}][HL^-]}$	27.9	2.22	84.9	28.5	-2.89	103.4	28.5	4.6	79.1	27.9	8.28	64.9
$K_{M(HL)_2}^{M}$	$\dfrac{[M(HL)_2^{(z-2)+}]}{[M^{z+}][HL^-]^2}$	26.8	6.22	68.0	26.8	3.89	75.7	26.9	7.95	62.8	26.5	12.39	46.5
$K_{M(HL)_3}^{M}$	$\dfrac{[M(HL)_3^{(z-3)+}]}{[M^{z+}][HL^-]^3}$	21.4	10.17	36.9	20.7	7.95	42.6	20.0	12.51	24.6	19.7	15.90	12.6
$K_{ML(HL)_2}^{M}$	$\dfrac{[ML(HL)_2^{(z-4)+}]}{[M^{z+}][L^{2-}][HL^-]^2}$	19.9	7.95	91.8	19.8	8.28	92.6	19.6	4.06	78.1	19.7	2.22	72.4
$K_{ML_2(HL)}^{M}$	$\dfrac{[ML_2(HL)^{(z-5)+}]}{[M^{z+}][L^{2-}]^2[HL^-]}$	19.0	8.96	92.4	18.5	10.67	96.1	18.5	8.12	87.7	17.9	3.56	70.8
$K_{ML_3}^{M}$	$\dfrac{[ML_3^{(z-6)+}]}{[M^{z+}][L^{2-}]^3}$	19.9	10.67	100.9	20.3	12.34	107.6	20.1	8.66	94.9	20.0	6.28	86.8
$K_{ML(HL)_2}^{H}$	$\dfrac{[ML(HL)_2^{(z-4)+}][H^+]}{[M(HL)_3^{(z-3)+}]}$	39.8	19.62	66.5	39.9	169.5	75.8	38.7	36.74	6.3	40.0	42.52	-8.5
$K_{ML_2(HL)}^{H}$	$\dfrac{[ML_2(HL)^{(z-5)+}][H^+]}{[ML(HL)_2^{(z-4)+}]}$	44.1	17.11	89.1	44.6	12.51	105.8	43.5	25.40	59.8	43.6	38.45	17.0
$K_{ML_3}^{H}$	$\dfrac{[ML_3^{(z-6)+}][H^+]}{[ML_2(HL)^{(z-5)+}]}$	50.3	13.56	121.1	53.8	10.17	144.0	52.9	19.83	109.2	52.1	28.79	76.7

$\Delta G \pm (0.2-1.1)\,\text{kJ mol}^{-1}$; $\Delta H \pm (0.02-0.76)\,\text{kJ mol}^{-1}$; $\Delta S \pm (0.02-1.44)\,\text{J mol}^{-1}\,\text{K}^{-1}$.

4. Discussion

A plot of $-\Delta G$, $-\Delta H$ and ΔS versus ionic potential Z^2/r (where Z is the cationic charge and r the ionic radius) for the lanthanide elements is given in Fig. 2. As is clear from this figure, the values of the free energies, enthalpies and entropies run according to the order

$$-\Delta G_{Ln(HL)} > -\Delta G_{Ln(HL)_2} > -\Delta G_{Ln(HL)_3}$$

$$-\Delta H_{Ln(HL)} > -\Delta H_{Ln(HL)_2} > -\Delta H_{Ln(HL)_3}$$

$$\Delta S_{Ln(HL)} > \Delta S_{Ln(HL)_2} > \Delta S_{Ln(HL)_3}$$

The increased values of $\Delta H_{Ln(HL)_n}$ ($n = 1, 2$ and 3) with n can be attributed to stronger metal–ligand bonds formed within higher complexes. It may be generally accepted that metal–water bonds within an aquametal ion weaken when a part of the water molecules within the aquametal ion is replaced with a ligand which has an atom or atoms with a stronger donor property than water [4]. Thus, we can accept that the $Ln-OH_2$ bonds within the mono DCPT–Ln(III) complex are weaker than those within the aqualanthanide(III) ion. Therefore when we introduce the second DCPT molecule to the mono DCPT–Ln(III) complex, the energy (enthalpy) to expel three water molecules from the coordination sphere of the mono-complex may be less than that of aqualanthanide(III) ion. Consequently, the stepwise enthalpy of formation of $Ln(HL)_2^+$ complex becomes more negative than that of the $Ln(HL)^{2+}$ complex. In contrast, when water molecules within the mono DCPT–Ln(III) complex in which the water molecules combine relatively weakly with the metal ion are removed from the coordination sphere, a lower entropy gain may result compared with that for releasing water molecules from the aqualanthanide(III) ion.

If the DCPT molecule is considered to consist of a 3-hydrazino-triazine group condensed with the ketonic group in α-oxo-glutaric acid, then the binding sites in this molecule could be the two carboxylate oxygens or azomethine nitrogen; one of the triazine ring nitrogens is also a possible site. The trans position of the second carboxylate group (the farthest from triazine ring) prevents it from chelating. It has been suggested that the free energy and enthalpy values depend on this O,N-donor ability of DCPT. For this reason the values of ΔG, ΔH and ΔS for the free α-oxo-glutaric acid–Sm(III) complexes were determined under the same experimental conditions, i.e. 75% dioxane–water and 0.10 M KNO_3 ionic strength. Although the basicity of α-oxo-glutaric acid ($pK_1^H + pK_2^H = 5.22 + 6.63 = 11.85$) is nearly the same as for DCPT (11.80), $|\Delta G_{SmHL}|$(DCPT) is larger than ΔG_{SmHL} (α-oxo-glutaric acid) by about 4.56 kJ mol^{-1}. This feature can be explained by comparing the structures of both complexes given in Scheme 1, in which DCPT forms two chelates of five-membered rings. This chelation is expected to be reflected more in the formation entropies, i.e. ΔS_{SmHL}(DCPT) = 61.1 J mol^{-1} K^{-1}, while the corresponding value for ΔS_{SmHL}(α-oxo-glutaric acid) is 121.5 J mol^{-1} K^{-1}. The decrease in the entropy of the former is due to the formation of two chelate rings. In addition, the higher stabilities for the DCPT complexes could be related to the bulky nature of the DCPT molecule compared to
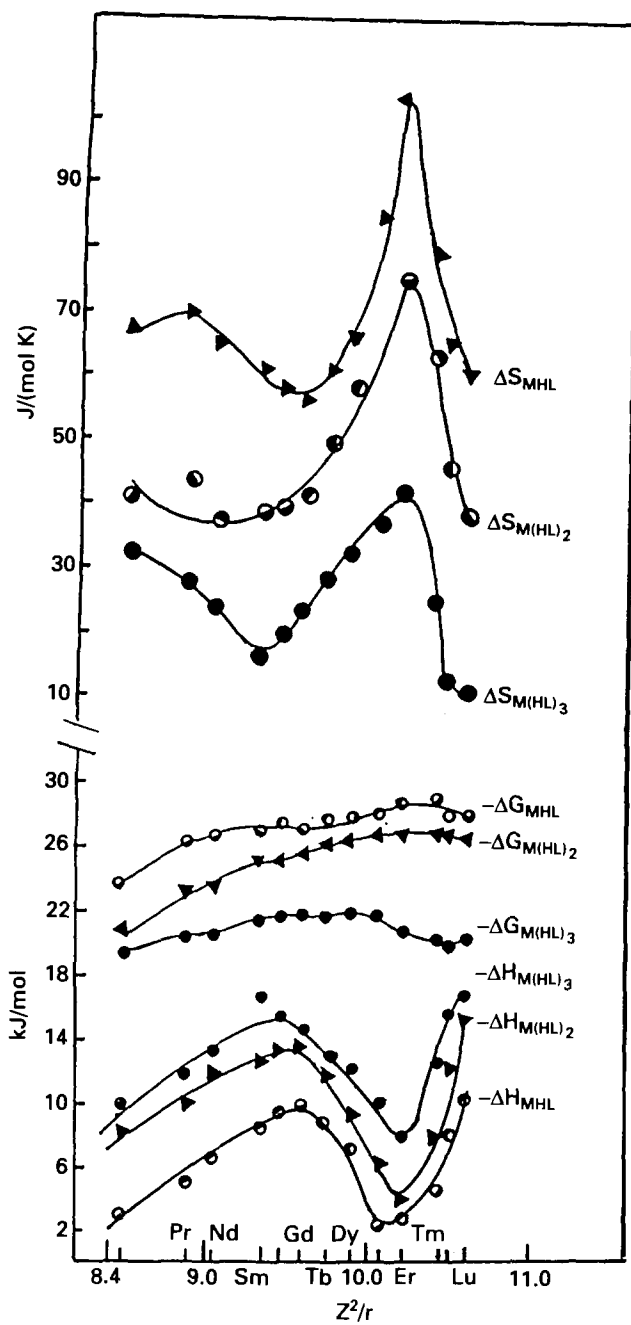
Fig. 2. Thermodynamic parameters ($\Delta G, \Delta H$ and ΔS) in complexation between lanthanoid(III) and DCPT.

α-oxo-glutaric acid. This bulkiness of DCPT causes a strong shielding of the metal ion from external attack by solvent molecules, leading to more stable complexes.

In addition to the above, the O,N-donor ability of DCPT can also be estimated from enthalpy values. It has been shown by Degischer and Nanocallas [5] that for systems involving nitrogen and carboxylate oxygen, the ΔH values reflect the change in the

α-oxo-glutaric acid

(DCPT)
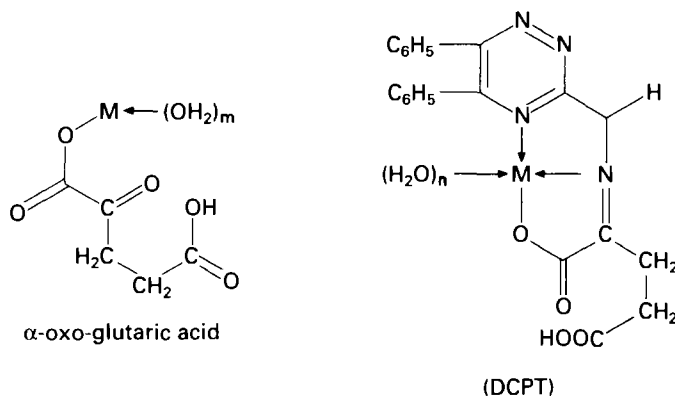
Scheme 1.

bonds made and broken during the reaction. In solution, complex formation derives from solvent-mediated acceptor–donor interactions that can be resolved into two parts: (i) one for which the solvent is responsible (or mainly responsible) and (ii) a second due (or mainly due) to the interactions between the two partners [6]. Considering the fact that the crystal-field produced by an oxygen in α-oxo-glutaric acid should be similar to that of water [7], ΔH will not be significantly affected by the displacement of a water molecule. This could account for the endothermic value obtained for the α-oxo-glutaric–Sm(III) complex (ΔH_{SmHL} glutaric $= 18.00 \, \text{kJ mol}^{-1}$). Because the values of ΔH_{SmHL} for DCPT and α-oxo-glutaric complexes were determined in the same solvent and conditions, we can neglect the solvent interaction described in (i) above. The exothermic ΔH values of Sm(III)–DCPT complexes (3.39–$16.95 \, \text{kJ mol}^{-1}$) indicate that not only the carboxylate oxygen but also the nitrogen atoms act as coordination sites.

The values in Table 1 show that there is a small difference between the values of the thermodynamic parameters ($\Delta G, \Delta H, \Delta S$) for the complex species Ln(HL)_3, LnL(HL)_2^- and $\text{LnL}_2(\text{HL})^{2-}$. This can be explained by the fact that all these reactions consist of the removal of the proton from the second carboxylate group.

The thermodynamic parameters describing the dissociation of the second carboxylate group from the species Ln(HL)_3, LnL(HL)_2^{2-} and $\text{LnL}_2(\text{HL})^-$ show the order $-\Delta G^{\text{H}}_{\text{LnL(HL)}_2} < -\Delta G^{\text{H}}_{\text{LnL}_2(\text{HL})^2} < -\Delta G^{\text{H}}_{\text{LnL}_3}$. This order indicates that after the elimination of the first carboxylate proton, the charge density on the complex species increases and this retards the dissociation of the remaining protons on the carboxylate

groups. This is supported by the orders obtained for the enthalpies and entropies

$$-\Delta H^H_{LnL(HL)_2^-} > -\Delta H^H_{LnL_2(HL)^{2-}} > -\Delta H^H_{LnL_3^{3-}}$$

$$\Delta S^H_{LnL(HL)_2} < \Delta S^H_{LnL_2(HL)^{2-}} < \Delta S^H_{LnL_3^{3-}}$$

In Fig. 2 the variations in the thermodynamic parameters for the protonated complex species $Ln(HL)^{2+}$, $Ln(HL)_2^+$ and $Ln(HL)_3$ as a function of the ionic potential of the lanthanide elements are similar to those previously found for other ligands [8–13], such as triazine [2, 8, 9] and pyridazine [3, 10–13] rings. All curves have an S-shape and can be divided into three regions: an initial region for the lighter lanthanoids (La–Nd); an intermediate region for Sm–Dy; and a final region for the heavier lanthanoids (Ho–Lu). The trends observed in free energy, enthalpy and entropy changes as a function of ionic potentials may be explained in terms of the different hydration numbers of the lighter (coordination number 9) and heavier lanthanoid (coordination number 8) ions [14]. The values obtained for the enthalpy of the heavier lanthanide(III) complexes are less exothermic than those for lighter ones, because less dehydration occurs for these heavier ions when they are complexed. This smaller dehydration of the heavier cations causes comparatively less positive values for the dehydration entropies.

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