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COMPLEXES OF SOME TRIVALENT LANTHANIDES WITH ETHYLCYANOPYRIDYLHYDRAZONOACETATE AND THEIR HYDRAZIDES: STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS *

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ABSTRACT

The stability constants of trivalent lanthanide (La, Ce, Nd, Sm, Gd, Dy and Er) complexes of ethylcyanopyridylhydrazonoacetate (EC-3-PyHA & EC-4-PyHA) and their hydrazides (C-3-PyHAH and C-4-PyHAH) have been determined pH-metrically at different temperatures (25, 30 and 35 ° C) in 10% (v/v) ethanol–aqueous medium at a constant ionic strength of 0.1 M (KNO_3). It was found that the values of the stability constants of the complexes gradually increase from La^{3+} to Er^{3+} and increase with increasing temperature. Conductometric titrations of metal–ligand mixtures confirm the formation of 1 : 2 chelates with all ligands. Thermodynamic functions of the complexes formed show that chelate formation is an endothermic process (positive values of ΔH) and proceeds spontaneously (negative values of ΔG). The entropy changes ΔS have positive values, showing that complex formation is a favourable process.

INTRODUCTION

Ethylcyanoacetate reacts with benzene diazonium chloride in acetate buffer solution to give ethyl-cyano-2-phenylhydrazonoacetate [1–3]. We have prepared ethylcyano(pyridylhydrazono)acetate (EC-3-PyHA and EC-4-PyHA) and their hydrazides (C-3-PyHAH and C-4-PyHAH) using pyridyl diazonium chlorides [4]. It was found previously [5] that the synthesized organic ligands form complexes with some divalent and trivalent transition metal ions (Zn, Cu, Ni, Co, Mn, Fe and Cr). The stability constants of the

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chelates formed were measured pH-metrically, and thermodynamic parameters, as well as ligand field stabilization energies (LFSE), were determined.

Since nothing is mentioned in the literature about the stabilities of the chelate compounds of these ligands with trivalent lanthanide metal ions, we determined their stability constants at different temperatures and calculated the thermodynamic functions ΔG, ΔH and ΔS for the chelate compounds formed in solution. In addition we studied the composition of the formed complexes by conductometric methods.

EXPERIMENTAL

The synthesis and characterization of the ligands was reported previously [4]. The solutions of lanthanide metal nitrates were prepared by dissolving the metal oxides (BDH, 99.9%) in nitric acid and evaporating the solutions to dryness. The residues were dissolved in double-distilled water and the metal contents were determined by EDTA titration using xylenol orange as indicator [6]. The stability constants of trivalent lanthanide (La, Ce, Nd, Sm, Gd, Dy and Er) chelates with EC-3-PyHA, C-3-PyHAH, EC-4-PyHA and C-4-PyHAH were determined in 10% (v/v) ethanol–water medium using pH-metric titrations. Measurements were taken at different temperatures (25, 30 and 35 ° C) to allow calculation of thermodynamic constants ΔH, ΔG and ΔS for the chelate compounds. The values of the hydrogen ion concentrations were corrected for solvent composition, ionic strength and temperature using the equation [7]

$$-\log[\mathrm{H}^+] = \mathrm{pH} = B + \log U_\mathrm{H}$$

where B is the pH-meter reading and $\log U_\mathrm{H}$ is the correction factor. All titrations were carried out under nitrogen atmosphere. The pH-measurements, stability constant calculations and determination of thermodynamic functions were performed as described previously [5]. Conductometric titrations at constant temperature were also performed.

RESULTS AND DISCUSSION

Conductometric study

The titration curves of the ligand/metal ion mixtures show breaks at $m = 2$ (m = number of moles of base equivalent per mole of ligand), indicating the formation of $\mathrm{ML_2}$ species (Fig. 1). The results obtained are in good agreement with the results obtained from pH-metric titrations.

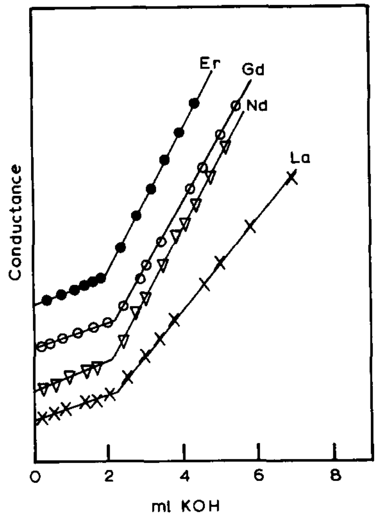

Fig. 1. Conductometric titrations of mixtures of EC-4-PyHA (2×10^{-3} M) and La^{3+}, Nd^{3+}, Gd^{3+} and Er^{3+} in 4:1 ratio at 30 °C.

pH-metric study

Titration curves of the EC-3-PyHA ligand (Fig. 2) are altered in the presence of Ln^{3+} ion (Ln^{3+} = La, Ce, Nd, Sm, Gd, Dy and Er) as a result of

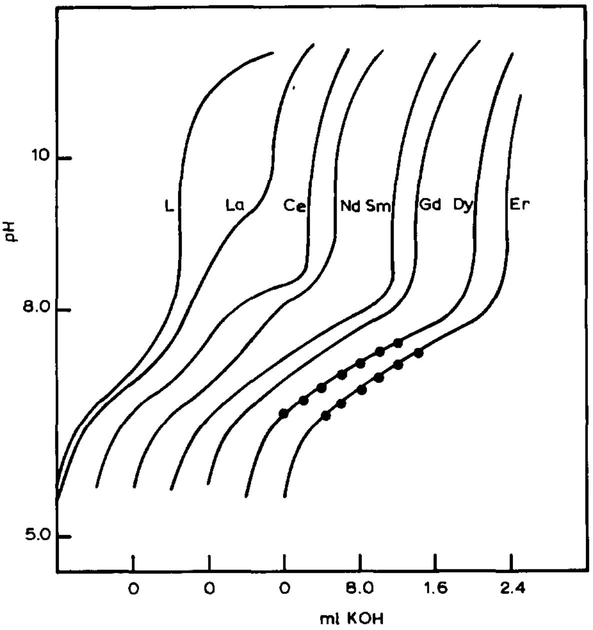

Fig. 2. pH-titration curves of EC-3-PyHA ligand and its lanthanide complexes at 30 °C in 50 ml 10% (v/v) ethanol–water. [L] = 4×10^{-3} M (free ligand); [Metal] = 1×10^{-3} M; ionic strength 0.1 M (KNO_3).

complex formation. The lanthanide ions (1×10^{-3} M) and the organic ligand (4×10^{-3} or 2×10^{-3} M) were titrated against KOH at the desired temperature (± 0.2°C) and an ionic strength of 0.1 M KNO_3 in 10% (v/v) ethanol–water.

The titration curves of the mixtures of Nd^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+} and Er^{3+} with the ligands have a buffering zone extending from $m = 0$ to $m = 1.7$ followed by an inflection, which indicates the formation of an ML_2 species. On the other hand, titration curves of La^{3+} and Ce^{3+} metal ions with both EC-3-PyHA and C-4-PyHAH ligands show two buffer zones, the

TABLE 1

Stability constants of lanthanide complexes at 0.1 M ionic strength (KNO_3) in 10% (v/v) ethanol–water at different temperatures

Ligand	Ion	Temperature (°C)					
		25		30		35	
		log K_1 [a]	log β [a]	log K_1 [a]	log β [a]	log K_1 [a]	log β [a]
EC-3-PyHA	La^{3+}	3.27	6.23	3.33	6.25	3.34	6.31
	Ce^{3+}	3.28	6.20	3.32	6.22	3.35	6.28
	Nd^{3+}	3.28	6.25	3.30	6.26	3.34	6.32
	Sm^{3+}	3.30	6.33	3.34	6.35	3.37	6.37
	Gd^{3+}	3.18	6.09	3.23	6.14	3.36	6.31
	Dy^{3+}	3.20	6.04	3.32	6.31	3.37	6.36
	Er^{3+}	3.34	6.31	3.31	6.32	3.37	6.41
C-3-PyHAH	La^{3+}	3.87	7.28	3.91	7.33	3.98	7.56
	Ce^{3+}	3.85	7.32	3.85	7.35	3.91	7.44
	Nd^{3+}	3.83	7.33	3.84	7.34	3.92	7.53
	Sm^{3+}	3.80	7.25	3.88	7.46	3.94	7.56
	Gd^{3+}	3.81	7.48	3.83	7.50	4.01	7.80
	Dy^{3+}	3.88	7.63	3.96	7.73	4.04	7.85
	Er^{3+}	3.93	7.75	3.99	7.85	4.00	7.93
EC-4-PyHA	La^{3+}	3.90	–	4.08	–	4.08	–
	Ce^{3+}	3.95	–	4.00	–	4.02	–
	Nd^{3+}	3.89	–	3.97	–	3.98	–
	Sm^{3+}	3.97	–	4.22	–	4.25	–
	Gd^{3+}	4.09	–	4.11	–	4.12	–
	Dy^{3+}	4.09	–	4.26	–	4.26	–
	Er^{3+}	4.13	–	4.28	–	4.31	–
C-4-PyHAH	La^{3+}	4.61	8.51	4.64	8.62	4.66	8.75
	Ce^{3+}	4.73	8.76	4.77	8.87	4.81	8.94
	Nd^{3+}	4.71	8.75	4.82	8.94	4.84	8.98
	Sm^{3+}	4.81	9.05	4.92	9.24	5.00	9.28
	Gd^{3+}	4.80	9.12	4.82	9.16	4.88	9.33
	Dv^{3+}	4.84	9.33	4.93	9.44	5.01	9.71
	Er^{3+}	4.89	9.62	4.94	9.67	5.04	9.79

[a] Average values obtained by interpolation at half $\bar{n}$ values and least-square methods.

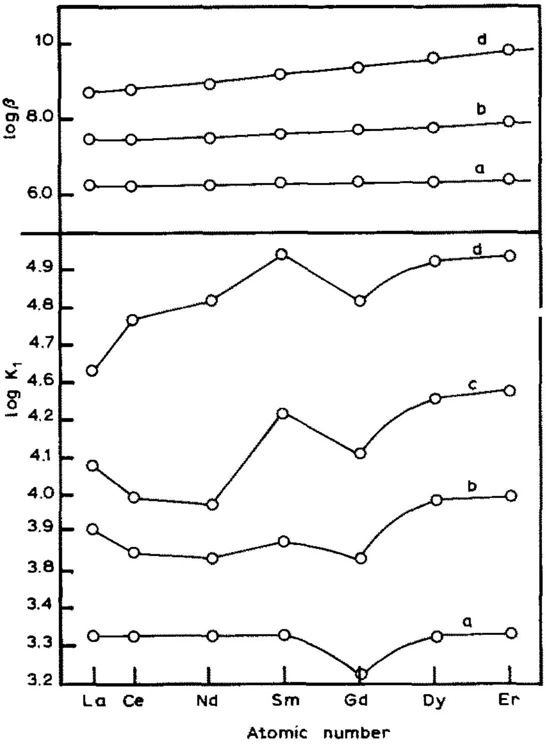

Fig. 3. Stability constants (log K_1 and log β) as a function of lanthanide atomic number for the complexes at 30 °C in 10% (v/v) ethanol–water. (a) EC-3-PyHA, (b) C-3-PyHAH, (c) EC-4-PyHA, (d) C-4-PyHAH.

first at $m = 0.82$ followed by a weak inflection and the second at $m = 1.7$ followed by a sharp inflection, indicating the formation of ML and ML_2 species respectively.

The stability constants (log K_1 and log β) of the formed complexes at different temperatures are given in Table 1. In general, the stabilities of the complexes increase regularly from La^{3+} to Er^{3+}, which may be correlated with the progressive decrease in ionic size. From the relation between lanthanide atomic number and the obtained stability values (log K_1 and log β), we can say that a buffer zone was generally observed at the atomic number of gadolinium. The obtained values (Table 1) of the chelates formed reveals the following order of stability: C-4-PyHAH > EC-4-PyHA > C-3-PyHAH > EC-3-PyHA, the magnitudes of the stabilities being proportional to the values of the ionization constants (pK_a) of the ligands [4].

A plot of the stability constants (log K_1 and log β) for the formed complexes against atomic number of the lanthanide elements is shown in Fig. 3. The observed values of log β (overall stability constant of the formed complexes) gradually increase with increasing lanthanide atomic number (Fig. 3). In the case of EC-4-PyHA/lanthanide ion mixtures, the stability

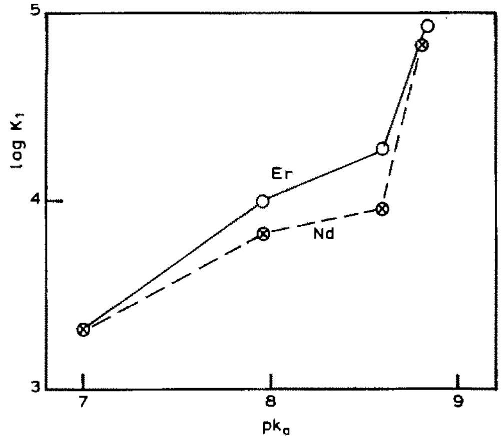

Fig. 4. Stability constants (log K_1) of the Nd^{3+} and Er^{3+} complexes at 30 °C as a function of ionization constant (pK_a) of the free ligand.

constants (log β) cannot be calculated on account of precipitate formation. The deviation of the stability constants from linearity is not unique to the present case, being common for rare earth complexes with several chelating agents [8–10].

However, the stability constants (log K_1) of the lanthanide complexes with each of EC-3-PyHA, C-3-PyHAH, EC-4-PyHA and C-4-PyHAH increase on going from La^{3+} to Er^{3+}, with a break at gadolinium. Electrostatic considerations suggest that the break may be attributed to the discontinuity of the crystal radius at gadolinium [11]. However, this is based on the assumption that the trends in the crystal radii are reflected in the solvated as well as in the coordinated ions, which may not be true [12]. The gadolinium break may alternatively be explained in terms of ligand field theory, it being due to a varying degree of interaction of the 4f orbital with the ligand field [13,14].

Figure 4 shows the relationship between the acid dissociation constants pK_a of the ligands and the stability constants (log K_1) of Nd^{3+} and Er^{3+} chelates (as an example). The stability constant values of Nd^{3+} and Er^{3+} complexes for the different ligands have been found to be related to their basicities. From the results obtained it is clear that the complex structures for different ligands with the same lanthanide ion are different.

Thermodynamic functions

The values of stability constants (Table 1) increase with increasing temperature. The stepwise thermodynamic parameters ΔG, ΔH and ΔS for the formed chelate compounds were calculated from the stepwise stability constants obtained at various temperatures, and are given in Table 2. The

TABLE 2

Thermodynamic functions of lanthanide complexes at 0.1 M ionic strength (KNO_3) in 10% (v/v) ethanol–water

Ligand	Ion	Function					
		$-\Delta G_1$ [a]	ΔH_1 [b]	ΔS_1 [c]	$-\Delta G_2$ [a]	ΔH_2 [b]	ΔS_2 [c]
EC-3-PyHA	La^{3+}	4.71	2.94	24.83	4.19	0.42	14.95
	Ce^{3+}	4.72	2.98	24.89	4.12	0.43	14.73
	Nd^{3+}	4.71	2.52	23.47	4.20	0.42	15.00
	Sm^{3+}	4.75	2.94	24.97	4.23	1.68	19.19
	Gd^{3+}	4.73	7.34	39.24	4.15	1.57	18.48
	Dy^{3+}	4.74	7.18	38.78	4.22	6.46	34.70
	Er^{3+}	4.75	1.33	19.88	4.29	2.99	23.69
C-3-PyHAH	La^{3+}	5.61	4.89	34.09	5.05	7.09	39.39
	Ce^{3+}	5.50	2.58	26.35	4.97	2.51	24.27
	Nd^{3+}	5.52	3.62	29.69	5.09	4.56	31.41
	Sm^{3+}	5.55	5.80	36.94	5.10	6.97	39.25
	Gd^{3+}	5.65	8.40	45.63	5.34	5.04	33.71
	Dy^{3+}	5.70	6.72	40.31	5.37	2.52	25.62
	Er^{3+}	5.64	2.94	27.85	5.54	4.62	32.99
EC-4-PyHA	La^{3+}	5.75	7.56	43.22	–	–	–
	Ce^{3+}	5.67	2.97	27.99	–	–	–
	Nd^{3+}	5.61	3.78	30.49	–	–	–
	Sm^{3+}	5.99	11.76	57.64	–	–	–
	Gd^{3+}	5.81	1.26	22.95	–	–	–
	Dy^{3+}	6.01	7.14	42.68	–	–	–
	Er^{3+}	6.08	7.56	44.27	–	–	–
C-4-PyHAH	La^{3+}	6.57	2.10	28.15	5.77	7.98	44.63
	Ce^{3+}	6.78	3.36	32.92	5.82	4.20	32.54
	Nd^{3+}	6.82	5.46	39.88	5.84	4.20	32.58
	Sm^{3+}	7.05	7.98	48.80	6.03	1.68	25.04
	Gd^{3+}	6.88	3.36	33.24	6.27	5.46	38.10
	Dy^{3+}	7.06	7.14	46.11	6.63	4.62	36.51
	Er^{3+}	7.10	6.10	42.74	6.70	0.85	24.57

[a] Values obtained at $T = 35\,°C$ (kcal mol^{-1}).

[b] Average values obtained using Gibbs–Helmholtz equation (between $T_1 = 298$ and $T_2 = 308$ K) and plots of ln K against $1/T$ (kcal mol^{-1}).

[c] Average values obtained from the corresponding ΔH values and plots of log K against T (cal mol^{-1}).

positive values of enthalpy changes ΔH_1 and ΔH_2 for the 1 : 1 and 1 : 2 lanthanide chelates (Table 2) indicate that the reactions of the elements with the ligands are endothermic.

ΔG values were found to be negative in all cases, showing that complex formation is a spontaneous process. The stepwise entropy changes ΔS_1 and ΔS_2 for all the lanthanide complexes have positive values, indicating that entropy considerations favour complex formation.

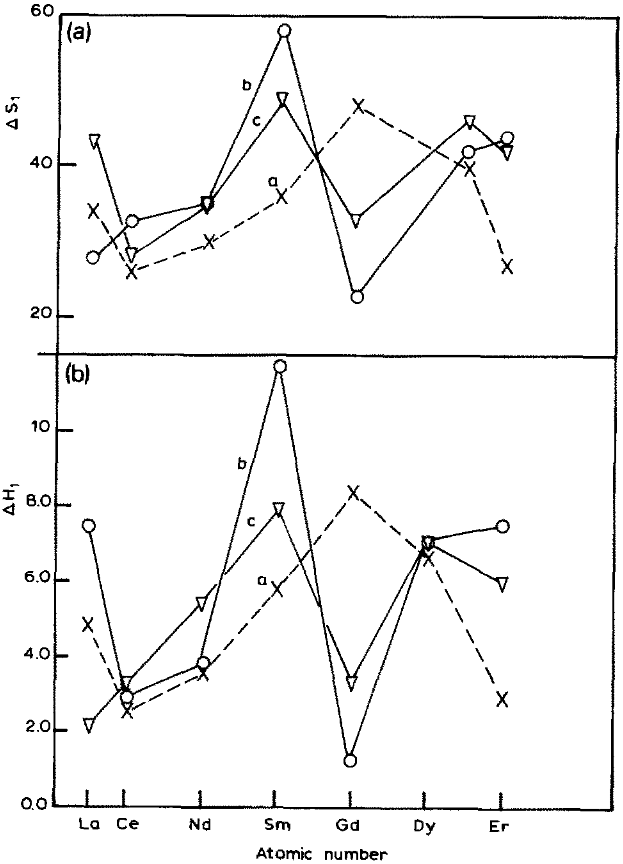

Fig. 5. Variation of ΔH_1 and ΔS_1 for the lanthanide complexes with lanthanide atomic number. (a) C-3-PyHAH, (b) EC-4-PyHA, (c) C-4-PyHAH.

Values of ΔH_1 and ΔS_1 of the formed complexes are shown as a function of the lanthanide atomic number in Fig. 5. From the figure, it is obvious that the variations in enthalpy and entropy are not simple monotonic functions of the atomic number. Both ΔH_1 and ΔS_1 plots for the complexes exhibit discontinuities near the middle of the lanthanide series. This pattern in the curves has been attributed to the different degrees of dehydration of the cations upon complexation [15].

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