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Formation Constants of Binary Complexes of Lanthanides with 2-Hydroxymethylbenzimidazole

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Proton-ligand and metal-ligand formation constants of binary complexes of La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III) with 2-hydroxymethylbenzimidazole have been determined *p*H-metrically in 50% v/v aq dioxane medium at 30°, 40° and 50°C and $I = 0.1$ *M* ($NaClO_4$). The thermodynamic parameters of complex formation have been evaluated. Stabilities (log β_2 values) of the chelates increase with decrease in ionic radius of the metal [Dy(III) > Gd(III) > Y(III) > Nd(III) > Pr(III) > La(III)].

In continuation of our studies on the complexing tendencies of benzimidazoles[1-3], we report herein the formation constants of binary complexes of the type ML_2 [where M = La(III), Pr(III), Nd(III), Gd(III), Dy(III), Y(III) and L = 2-hydroxymethylbenzimidazole (HMB)] in 50% v/v aq dioxane medium and I = 0.1 *M* ($NaClO_4$).

The proton-ligand and metal-ligand formation constants for binary systems were determined using Irving-Rossotti *p*H titration technique[4]. The general experimental details were the same as discussed earlier[1-3]. The *p*H meter readings (B) in the aq dioxane media were corrected by the method of Van Uitert and Haas[5].

From the proton-ligand formation curves ($0.1 < \bar{n}_H < 1.8$) the proton-ligand formation constants log K_{OH} and log K_{NH} evaluated at 30° (12.59 and 5.03), 40° (12.12 and 4.74) and 50°C (11.46 and 4.52) are in accordance with the values reported by Lane and Durham[6].

From the formation curve ($\bar{n}$ vs *p*L), it is found that the log K_1 and log K_2 do not differ much from one another and hence they have been evaluated by the least-square treatment[4] of Eq. (1)

$$\frac{\bar{n}}{(\bar{n}-1)(L)} = \frac{(2-\bar{n})(L)}{(\bar{n}-1)}\beta_2 - K_1 \qquad \ldots (1)$$

Calculations using this method resulted in negative values of K_1 (positive intercept) and hence only log β_2 values are reported in Table 1.

Lane and Quinlan[7] have reported the formation of only 1:1 complexes of La(III) with 2-hydroxymethylnaphthimidazole. The formation of 1:2 complexes of Ln(III) with HMB in the present investigation is quite reasonable because of the lesser steric hindrance of benzimidazole moiety as compared to a naphthimidazole moiety.

Table 1—Formation Constants (log β_2) and Thermodynamic Parameters of Ln–HMB Chelates in 50% v/v aq dioxane medium

[$I = 0.1$ *M* ($NaClO_4$)]

Temp (K)	Dy(III)	Gd(III)	Y(III)	Nd(III)	Pr(III)	La(III)
			log β_2			
303	16.79	16.55	16.47	16.11	15.89	15.36
313	16.63	16.44	16.38	16.01	15.81	15.30
323	16.48	16.35	16.30	15.92	15.74	15.25
			$-\Delta G$ (kJ mol^{-1} at 303 K)			
	97.1	96.0	95.5	93.4	92.2	89.1
			$-\Delta H$ (kJ mol^{-1})			
	28.9	18.8	16.3	17.5	15.3	9.8
			ΔS (JK^{-1} mol^{-1} at 303 K)			
	226.1	254.6	261.5	250.0	253.0	261.5

The order of stabilities (log β_2) of Ln(III)–HMB complexes [Dy(III) > Gd(III) > Y(III) > Nd(III) > Pr(III) > La(III)] is almost in the increasing order of their Z^2/r values indicating that the metal-ligand bond is primarily ionic.

The thermodynamic parameters, ΔG, ΔH and ΔS of formation of Ln–HMB complexes have been evaluated using well known equations and are presented in Table 1. The stabilities are found to decrease with increase in temperature suggesting that the interaction of Ln(III) ions with the ligand is exothermic in nature.

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