TETRAD-EFFECTS IN THE STABILITIES OF LANTHANIDE DTPA 2-PICOLINATE BILIGAND COMPLEXES

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The occurrence of tetrad-effects has been observed in some binary lanthanide complexes. But no satisfactory explanation has been forwarded so far [2]. It may be fruitful to investigate the occurrence of tetrad-effects in the biligand complexes of the lanthanides. In the present communication the results of our studies on the biligand complexes of the type [Ln.A.L] of all the lanthanides with DTPA [A] and 2-picolinic acid [L] are reported.

EXPERIMENTAL

The lanthanides (99.9% purity) were obtained from Indian Rare Earths Ltd. as their nitrates. Other chemicals were of standard purity (B.D.H. AnalaR/Merck G.R./Loba A.R.). All solutions were prepared in double distilled water. The strength of the lanthanide solutions was finally adjusted on the basis of their complexometric titrations with EDTA [3]. The formation constants were determined at 25° by pH titrations at an ionic strength, I= 0.2 (mol dm^{-3}, KNO_3). The solution concentrations (final) were fixed at [M] = [A] = [L] = 1.0 x 10^{-3} mol dm^{-3}. A carbonate free NaOH solution (0.2 mol dm^{-3}) and an Elico digital pH-meter (model LI-120) were used for pH titrations. The formation constant values were calculated using Irving Rossotti method [4] refined by the linear plot method [5] and statistically also by the 'Q-test' [6]. Electronic spectral measurements were carried out on a GCA Mcpherson UV-VIS spectrophotometer (model EU-707/11).

RESULTS AND DISCUSSION

The formation constants of the binary (log K^{M}_{ML} and ternary biligand (log K^{MA}_{MAL}) complexes along with the Δ log K (= log K^{MA}_{MAL} - log K^{M}_{ML}) values are presented in Table 1.

Both Ln^{3+} and $DTPA^{5-}$ are highly charged and the formation of $[Ln\ DTPA]^{2-}$ is facilitated by large electrostatic attraction.

This electrostatic attraction is expected to result in a highly favourable entropy factor resulting in entropy stabilization [7] of the complexes. The addition of the secondary ligand, pic^{-} is accompanied by a coulombic repulsion in view of the similar charges on the combining species. The biligand complexes are, therefore, less stabilized. The Δ log K values are consequently neagative (Table). These Δ log K values for similar biligand complexes with NTA and EDTA [3], lead to the sequence DTPA $\geq$ EDTA > NTA. This indicates that greater negative charge on the (deprotonated) primary ligand results in more negative Δ log K values [9].

The formation constants log K^{MA}_{MAL} of lanthanides show a dip at Gd (Fig.1) which indicates the occurrence of tetrad-effect [1] (or, Gd-break). It is interesting to note that a plot of these formation constants vs standard entropies, S^{o}_{m} (cal deg^{-1} $mole^{-1}$) also yields a similar curve (Fig.1). Gradual increase in the formation constants with the standard entropies of the lanthanides (in two segments) may be seen as an evidence of entropy stabilization of these complexes [7]. The major attempts, made for explaining the occurrence of tetrad-effects, include (i) attributing the break at Gd (III) to a change in coordination number at this stage from nine to eight [10] (ii) correlating the Gd-break with a change in hydration number [11] and

TABLE 1

FORMATION CONSTANTS OF THE BINARY (Ln. PIC) AND BILIGAND (Ln. DTPA. PIC) COMPLEXES OF THE Ln(III) METAL IONS.

Formation constant.	La^{3+} $4f^0$	Ce^{3+} $4f^1$	Pr^{3+} $4f^2$	Nd^{3+} $4f^3$	Sm^{3+} $4f^5$	Eu^{3+} $4f^6$	Gd^{3+} $4f^7$	Tb^{3+} $4f^8$	Dy^{3+} $4f^9$	Er^{3+} $4f^{11}$
Log $K^{Ln}_{Ln.pic}$	4.04	4.16	4.27	4.36	4.56	4.64	4.82	4.88	4.91	5.02
Log $K^{Ln.DTPA}_{Ln.DTPA.pic}$	3.55	3.86	3.95	4.12	4.40	4.55	4.06	4.28	4.39	4.44
Δ Log K..	0.49	0.30	0.32	0.24	0.16	0.09	0.76	0.60	0.52	0.58

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(iii) considering the tetrad-effects as a consequence of changes in total orbital angular momentum of the lanthanides [12]. None of these seems to be fully acceptable [2,13]. The present set of formation constants when correlated with the total orbital angular momentum values, yields an inclined-w ($\mathcal{W}$) plot for the binary [Ln.pic] complexes only (Fig.2), but the plot is not symmetrical as claimed.

The observed electronic spectral bands for uncomplexed lanthanide (Ce^{3+} ion), ligand (pic), and the complexes [Ce. pic], [Ce. DTPA] and [Ce.DTPA.pic] at appropriate pH values are shown in Table 2 alongwith the molar extinction coefficients (log ε) of these

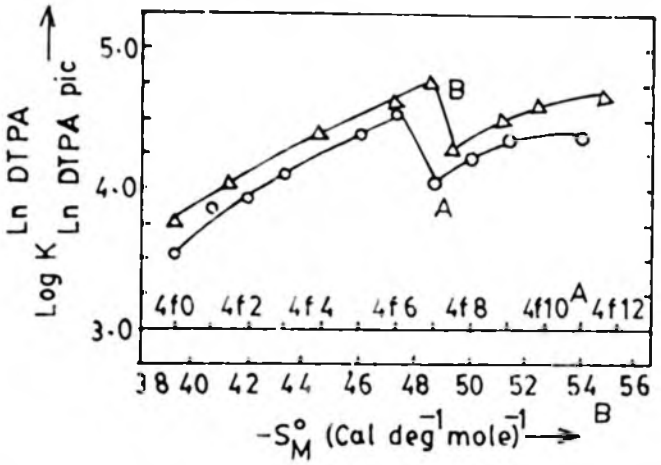


Fig. 1 Variation in formation constant values with (i) number of 4f-electrons (Curve A) and (ii) Standard entropies, $-S^{\circ}_{M}$ (cal deg^{-1} mole^{-1}) (Curve B) of the lanthanides.

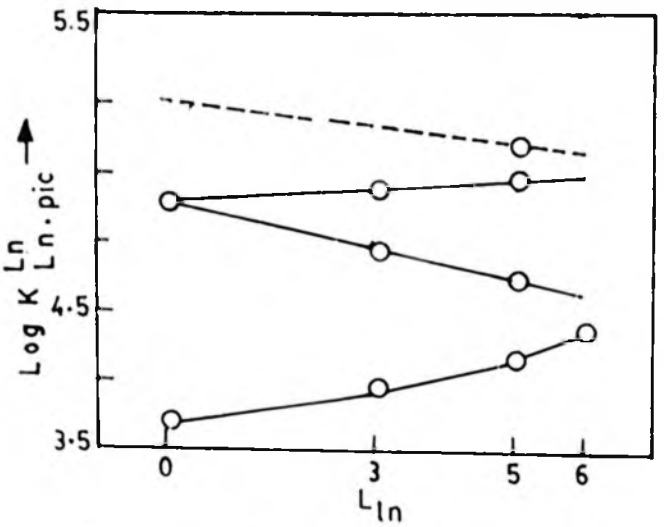


Fig. 2 Inclined-W plot showing the variation in log $K^{Ln.}_{Ln.Pic.}$ values as a function of total orbital angular momentum values, L_{ln} of the lanthanides.

species. The bands for pic show a red shift when compared to the bands [14] (51,540 and 40,000 cm^{-1}) for pyridine in n-hexane. On complexation the bands shift only slightly. In lanthanides the ligand fields split the 4f ground states only to a very small extent 100 cm^{-3}). The value of covalency factor (δ) [15], when calculated for the complex [Ce, DTPA.Pic], works out to $\sim$ 1.67%, which is interestingly slightly lower than the values for [Ce. EDTA. pic] ($\delta \approx 2.101\%$) and [Ce. NTA. pic] ($\delta \approx 2.166\%$). This sequence, DTPA< EDTA< NTA in the values of may δ possibly be a consequence of gradually decreasing metal-ligand bond distances in this order.

TABLE 2

ELECTRONIC SPECTRAL BANDS (IN cm^{-1}) AND MOLAR EXTINCTION COEFFICIENTS (LOG ε) OF THE COMPLEXES

Species	pH (approx)	Bands position/cm^{-1} (log ε) l $mole^{-1}$ cm^{-1} band I	band II	band III
Ce^{3+}	6.5	45,662 (3.06)	40,322 (2.35)	33,112 (2.04)
Pic	6.5	46,089 (3.14)	38,521 (3.24)	-
[Ce.pic]	5.5	45,228 (3.22)	38,521 (3.25)	-
[Ce.DTPA]	4.5	45,662 (3.08)	37,566 (2.31)	34.060 (2.33)
[Ce.DTPA. pic]	5.2	45,475 (3.26)	39,032 (3.32)	-

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