Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1814–1816

NOTE

Intermolecular Inter-ligand Interaction in Mixed Ligand Complexes of Lanthanides(III) Involving Histidine and Some Amino Acids

VIVEK TIWARI* and RASHMI SINGHAI
Department of Chemistry, Dr. H.S. Gour University, Sagar-470 003, India

The formation constant studies on binary and mixed ligand complexes of Pr(III) and Nd(III) involving histidine (hist) as primary ligand and α-alanine (α-ala), valine (val) or leucine (leu) as secondary ligands have been undertaken to evaluate the extra-stablization in the mixed ligand complexes due to possible occurrence of intramolecular inter-ligand interaction. Stability quantifying parameters (Δ log k and ΔΔ log k) indicate significant inter-ligand interaction.

Key Words: Intermolecular, Inter-ligand, Interaction, Mixed ligand complexes, Lanthanides, Histidine, Amino acids, α-Alanine, Valine, Leucine.

Lanthanoids on account of their large size and high coordination number are aptly suited for the formation of their mixed ligand complexes[1]. Similarly in view of their class 'A' character[2] they are also observed to have good complexing abilities for the ligands containing various donor atoms[1]. Besides these the spectral properties of lanthanoids have also been studied with great interest[3] in view of their intense sharp peaks[4], cation solvato dynamics[5], symmetry of the cation coordination polyhedra[6], *f*-shell behaviour[7] and the nephelauxetic effect[8].

The formation constant studies on binary (log K_{ML}) and mixed ligand complexes (log K_{MAL}) of Pr(III) and Nd(III) involving histidine (hist) as primary ligand and α-alanine (α-ala), valine (val) or leucine (leu) as secondary ligands have been evaluated to examine the possibility of the occurrence of intramolecular inter-ligand interaction. Changes in spectral parameters, *viz.*, oscillator strength (P), Judd-Ofelt parameter (τ_λ), changes in inter-electronic repulsion (Racah) parameter (δE^k) and the nephelauxetic ratio ($\delta E^3/\delta E^i$) have also been evaluated in order to examine the changes in spectral parameters as a result of mixed ligand complexation. The changes in spectral parameters have also been attempted to serve as additional spectral evidence for the occurrence of intramolecular ligand-ligand interaction.

All the chemicals used were of AR/ BDH/Fluka AG or standard purity grade. Irving-Rosotti pH titration technique has been used to determine the formation constant of the binary and mixed ligand complexes. Titration sets were prepared in double distilled water and the ionic strength was kept constant at *ca.* 0.2 mol dm^{-3} using *ca.* 1–0 mol dm^{-3} KNO_3. Carbonate-free NaOH *ca.* 0.02 mol dm^{-3} was used in titration sets. The readings were recorded on an Orion-950 autotitrator module with a precision of ±0.001 units. The pH titration readings were subjected to a self-devised PASCAL compiled computer programme to evaluate the formation constant values, which were then subjected to SCOGS computer programme for refinement. The formation constant values thus obtained were used to evaluate the extra-stabilisation parameters to examine the possibility of the occurrence of intramolecular inter-ligand interactions in the mixed ligand complexes.

The values of formation constants for 1 : 1 binary and 1 : 1 : 1 ternary complexes for Pr(III) and Nd(III) along with the Δ log k values and the extra-stabilisation parameters ΔΔ log k, K_I and (%) MAL_{es} are recorded in Table-1. An increase in length or bulk of the non-coordinating side chain of amino acid is expected to lower the stability of the complex due to steric hindrance. The Δ log k values show, in general, less negative values which is indicative of extra-stabilisation of mixed ligand complexes. α-Ala has been considered to be the smallest ligand possessing negligibly small side chain (—CH_3) attached to its aminocarboxylate end which is involved in complexation. This extent of extra-stabilisation has been numerically worked out in terms of ΔΔ log k values (Table-1B).

TABLE-1

FORMATION CONSTANTS OF 1 : 1 BINARY (MA OR ML) AND 1 : 1 : 1 MIXED LIGAND COMPLEXES (MAL) WITH THE Δ log k (PART-A) AND THE STABILITY QUANTIFYING PARAMETER ΔΔ log k, THE EQUILIBRIUM CONSTANTS K_1 AND % MAL_{es} (PART-B) FOR THE POLYMERIC EXCHANGE BETWEEN THE MAL (OPEN) AND THE MAL (CLOSED) FORMS

PART-A

Metal ligand parameter	Pr(III)			Nd(III)		
	$\log K^{M}_{ML}$	$\log K^{MA}_{MAL}$	Δ log K	$\log K^{M}_{ML}$	$\log K^{MA}_{MAL}$	Δ log K
α-Alanine (L)	6.08	5.84	–0.24	6.17	5.90	–0.27
Histidine (A)	4.29	—	—	4.99	—	—
Valine (L)	4.53	4.48	–0.05	4.67	4.60	–0.07
Leucine (L)	4.56	4.43	–0.13	5.01	4.93	0.08

PART-B

Metal ligand parameter	Pr(III)			Nd(III)		
	ΔΔ log K	K_1	(%) MAL_{es}	ΔΔ log K	K_1	(%) MALes
Valine	0.19	0.54	35.43	0.20	0.58	36.89
Leucine	0.11	0.28	22.37	0.18	0.51	33.92

An insight of the extra-stabilization phenomenon suggests a cooperative role played by the substituted side chains. The proximal ends of the elongated substituted side chains develop hydrophobicity and in an act of satisfying this hydrophobicity[10], a folding of the side chains may take place across the central metal. This may lead to the formation of polymeric species, *viz.*, "closed" or "interacted" [MAL_{es}] and "open" or "uninteracted" forms [MAL_{op}] and there may exist an equilibrium between these interacted and uninteracted forms as $MAL_{(op)} \Leftrightarrow MAL_{(int)}$ which is expressed by the constant K_L (numerically equal to $10^{\Delta\Delta \log k_{-1}}$).

A perusal of Table-1 (A and B) clearly suggests that the mixed ligand complexes are extra-stabilized. The magnitude of this extra-stabilization, however, exhibits a sequence val < leu with respect to secondary ligands whereas Pr(III) < Nd(III) with respect to central metal ions.

The extra-stabilization sequence with respect to Ln(III) metal ions may be on account of their relative cationic sizes (ionic radius Pr(III) = 116 pm and Nd(III) = 115 pm) and the cation polyhedra. Both Pr(III) and Nd(III) exhibit tricapped trigonal triprismatic polyhedra having a coordination number of nine.

ACKNOWLEDGEMENTS

The authors are thankful to Head, Department of Chemistry, Dr. H.S. Gour University, Sagar, for facilities. One of us (RS) is thankful to UGC, New Delhi for financial assistance.

REFERENCES

1. J.C. Bailor, Comprehensive Inorganic Chemistry, Pergamon Press, New York, Vol. 4 (1973).
2. T. Moeller, R. Ferrus, G. Feistel, D.F. Martin, L.C. Thompson and W.J. Randall, *Chem. Rev.*, **66**, 1, (1965).
3. R.D. Peacock, *Struct. and Bond.*, **22**, 83 (1976).
4. W.T. Carnall, J.V. Beitz, H. Crosswhite and K. Rajnak, in: S.P. Sinha (Ed.), Spectroscopic Properties of the f-Elements in Compounds and Solutions and Systematics in the Properties of Lanthanoids and Actinoids, Reidel and Publ. Co., Ch. 9, p. 389 (1983).
5. B.R. Judd, in: K.A Gschneidner and L. Eyring (Jr.) (Ed.), Handbook on Physics and Chemistry of Rare Earths, North-Holland Publ. Co., Ch 74 p. 81 (1989).
6. C. Cossy and A.E. Maerbach, *Pure Appl. Chem.*, **60**, 1785 (1988).
7. P.W. Atwins, *Eur. J. Solid State Inorg. Chem.*, **28**, 9, (1991).
8. C.K. Jorgensen, Nephelauxetic Effect in Modern Aspects of Ligand Field Theory, North-Holland, Amesterdam, Ch. 23, p. 293 (1971),
9. R. Singhai, S.N. Limaye and M.C. Saxena, *J. Indian Chem. Soc.*, **74**, 633 (1997); *Proc. Indian Acad. Sci. (Chem. Sci.)*, **107**, 523 (1995); *Spectrochim. Acta (Part A)*, **53**, 353 (1988).
10. M. Tabata and M.Tanaka, *Inorg. Chem.*, **27**, 203 (1988).

(*Received*: 28 October 2002; *Accepted*: 12 May 2003) AJC-3110