Research Article

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF La(III), Ce(III) METAL COMPLEXES WITH PHENYLALANINE

SD. Ballal[1], DG. Kolhatkar[1]* and MN. Deshpande[2]

[1]Department of Chemistry, ShardaMahavidalaya, Parbhani, Maharashtra, India.
[2]Department of Science & Humanities, Government Polytechnic, Hingoli, Maharashtra, India.

ABSTRACT
The complexes of the phenylalanine with metal ions La(III), Ce(III)were prepared in ethanol solution.The ligand (L) and its metal complexes have been characterized by elemental analysis, IR, UV-Visible spectra.The suggesting M :L ratio is 1:3.Octahedral geometries were proposed for La(III),andCe(III) metal ion chelates.

INTRODUCTION
There has been considerable interest organic chelating agent containing O,N,S donor atoms because of the variety of ways in which they are bonded to metal ions. Coordination compounds have been extensively used in analytical, industrial, biological, clinical, biochemical, antimicrobial, anticancer, antibacterial, antifungal and antitumor activity.[1-4] Ligands play an important role in complex formation. Ligand act as electron pair donors to a single cation. The ligand acts as bridging groups to form stable metal chelates. The metal chelate depends on the affinity of the metal ion reacts with towards chelating agent and its concentrations .[5]

EXPERIMENTAL
Preparation of Diaqua-tris(2-amino-3-phenylpropanoicacid) La(III) chelate
A weighed quantity of ligand (PHE)(1.651gm) and metal chloride(3.713 gm) ware separately dissolved in100 ml ethanol and 0.1M solution were prepared[6-9].Clear solutions of lanthanum chloride and phenylalanine were mixed in Stoichiometric ratio of 1:3. Solutions were mixed thoroughly with constant stirring and adjusted to a P^H of 6.7, by adding alcoholic ammonia solution[10]. Resultant mixture was refluxed for three hours and allowed to cool, white colored precipitated out was separated after digestion for half an hour, washed with ethanol for three times, then dried in desiccators, and stored in air tight glass bottle (yield 77.39%)

Preparation of Diaqua-tris-(2-amino-3-phenyl propanoic acid) Ce(III) chelate
A known amount lanthanide metal salt (3.2758gm) and ligand (1.651gm) were separately in100 ml ethanol so as to prepare solution of 0.1 Molar with constant stirring. A clear solution of metal salt was mixed to the ligand solution in 1:3 Stoichiometric ratio and P^H of mixture was adjusted to 6.6 by adding alcoholic ammonia solution. The reaction mixture were refluxed for three hours, faint ash coloured precipitate obtained.The precipitate were filtered through whatmans filter paper, washed with ethyl alcohol and dried in vacuum in a desicattorat room temperature after drying the complex is stored in air tight glass bottle (yield 77.25%).

Analytical data of La(III), Ce(III), metal chelate with phenylalanine

Ligand / Metal Chelates Empirical Formula	Mol. Wt./ (D.P°C)	M:L Ratio/Yield (%)	Molar Cond. (Ω^{-1} cm^2 mol^{-1})	Elemental analysis % Cal (Obs)			
				C	**H**	**N**	**M**
[La(PHE)$_3$2H$_2$O]H$_2$O	684.91 (178)	1:3 77.39 (76.40)	14.50	47.30 (48.10)	5.25 (6.00)	6.13 (6.25)	20.28 (20.45)
[Ce(PHE)$_3$2H$_2$O]H$_2$O	686.12 (186)	1:3 77.25 (74.26)	15.30	44.22 (45.05)	5.24 (5.60	6.12 (7.00)	20.42 (21.00)

RESULT AND DISCUSSION
The ligand phenylalanine (PHE) is used to prepare metal chelates of La(III), Ce(III). After preparation of metal chelates it it's characterized by colour, decomposition point, conductance, elemental analysis, physical, chemical and spectral parameters are determined.

UV – VISIBLE SPECTRAL STUDIES
The electronic spectral data of the chelates are presented in table no.2 and the electronic absorption spectra of metal chelates were recorded in DMSO in the range 200-800 nm.The electronic spectrum of ligand showed two bands around 258 nm, 272 nm characteristic of π→π* and n→π* transitions[11,12]. In the metal chelates, this band is shifted to a lower wave length with increasing intensity. This shift may be attributed to the donated by lone pair of electrons of nitrogen of ligand phenyl alanine to metal ion.

The La(III) chelate exhibits bands around 231nm,275nm,350nm,421nm The broad intense and poorly resolved bands around 421nm may be assigned to LMCT or MLCT. The high intensity band around 231nmand 275 nm are of ligand are assignable to intra ligand π→π* and n→π* transitions. The Ce(III) chelate exhibits bands around 230 nm, 280 nm, 350 nm, 425 nm. The high intensity band around 230nm and 280nm are of ligand are assignable to intra ligand π→π* and *n*→π* transitions. The absorption bands due to the f-f transitions[13,14] the broad intense and poorly resolved bands around 421 nm may be assigned to LMCT.

UV visible spectral data of Lanthanide metal chelates

Sr. No.	Ligand/ Metal Chelate	Absorbance		Transition
		nm	**cm^{-1}**	
1.	Ligand (PHE) (Phenylalanine)	258	387596	π→π*
		272	367648	n→π*
2.	[La(PHE)$_3$2H$_2$O]H$_2$O	231	432900	π→π*
		275	363636	π→π*
		330	285714	n→π*
		421	237529	(LMCT)
3.	[Ce(PHE)$_3$2H$_2$O]H$_2$O	230	434782	π→π*
		380	263157	n→π*
		425	235294	LMCT
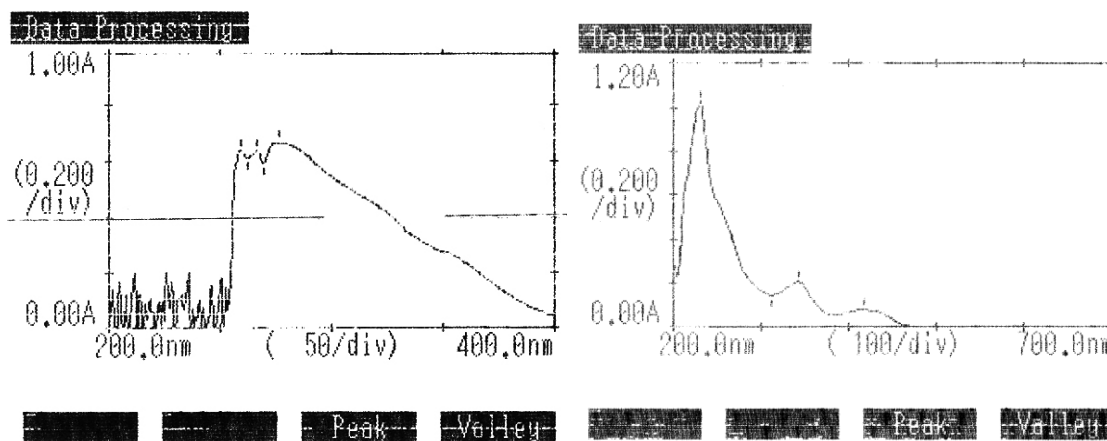
Fig. 1: UV spectra of Phenylalanine   **Fig. 2: UV spectra of [La(Phe)$_3$2H$_2$O]H$_2$O**
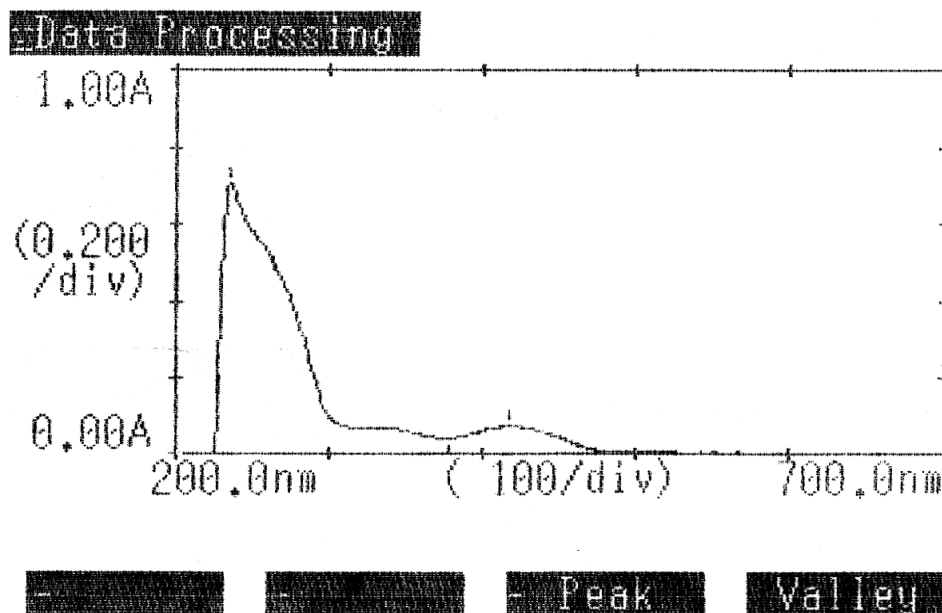
Fig. 3: UV spectra of   [Ce(PHE)$_3$2H$_2$O]H$_2$O

IR CHARACTERIZATION OF METAL CHELATES

Important absorption frequencies of ligand and chelates along with their assignment are presented in the table no.3. The assignments are well supported by literature survey. The comparison of IR spectrum data of La(III), Ce(III) and Nd(III)chelates with ligand Phenylalanine helps in determining bonding pattern in the chelate Studies of infrared spectra for the ligand and its chelates are done.

The FT-IR spectrum of the ligand (PHE), as shown in table, it displays characteristic bands at(3390)cm^{-1}.These bands were attributed to the v (NH$_2$) group[15]. Also a weak band showed at 3248 cm^{-1} assigned to carboxylic (-COOH) group[14]. Theband at 1641 cm^{-1}which shows   v (C=O) group in ligand.

IR spectral study of [La(PHE)$_3$2H$_2$O]H$_2$O chelate

In the spectra of Metal chelates, new broad band at 3502cm^{-1} have appeared, this band indicated the presence of coordinated water molecule[16]. Further, the band observed at 3390cm^{-1} due to (NH$_2$) group in ligand and is shifted towards lower frequency at 3369 cm^{-1} attributed to involvement in coordinate bond[17].A band at 3248cm^{-1} is observed in ligand due to (OH) stretching vibration.

This band is disappeared in the chelates shows deprotonation[18]. Similarly band at 1261cm^{-1} in ligand due to (OH) shifted at 1244 cm^{-1} indicates involvement in coordination. The band at 1641 cm^{-1}which showsv(C=O) group in ligand,its frequency does not change in the IR spectra of chelate.Appearance of new bands in the chelate (M-N) at 449cm^{-1} and (M-O) at 590cm^{-1} [19-20].

IR spectral study of [Ce(PHE)$_3$2H$_2$O]H$_2$O chelate

The new band observed at 3512cm^{-1} due to presence of coordinated water molecule. A band at 3390cm^{-1} is observed in ligand due to -NH$_2$ stretching vibration[21].This band shifted to 3372cm^{-1} indicates involvement in coordination. A band at 3248cm^{-1} is observed in ligand due to (OH) stretching vibration. This band is disappeared in the chelate shows deprotonation. Further the band at 1261cm^{-1} in ligand due to shifted at 1250 cm^{-1} due to deprotonation indicates involvement in coordination. The band at 1641 cm^{-1}which shows   v(C=O) group in ligand shifted to 1634 cm^{-1}.

It indicates C=O group does not involve for coordination.The band due to M-Cl was not found because of instrumental limitation. Appearance of new bands in the chelate (M-N) at 452cm^{-1} and (M-O) at 560cm^{-1} [22-23].

IR Spectral data of Lanthanides metal chelates

Sr. No.	Ligand / Metal Chelate	H_2O cm^{-1}	$-NH_2$ cm^{-1}	OH cm^{-1}	C = O cm^{-1}	C – O cm^{-1}	M – O cm^{-1}	M – N cm^{-1}
1.	Ligand (PHE)	-	3390	3248	1641	1261	-	-
2.	[La(PHE)$_3$2H$_2$O]H$_2$O	3502	3369	-	1641	1244	590	449
3.	[Ce(PHE)$_3$2H$_2$O]H$_2$O	3512	3372	-	1634	1250	560	452
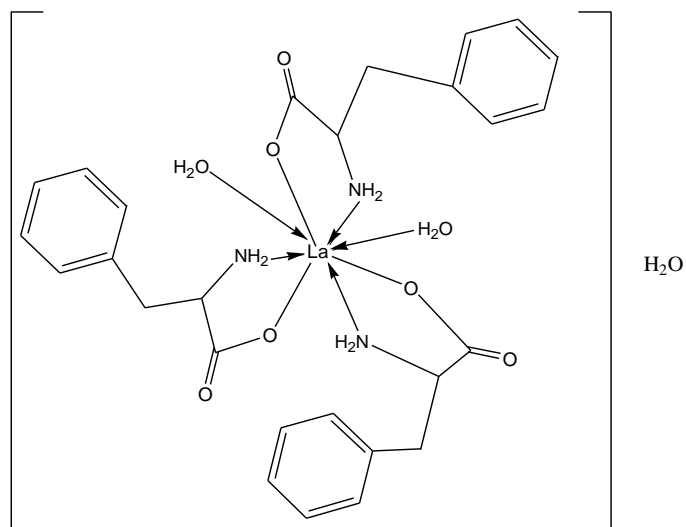
Proposed structure of (Diaqua-tris(2-amino-3-phenyl propanoic acid) La(III) chelate
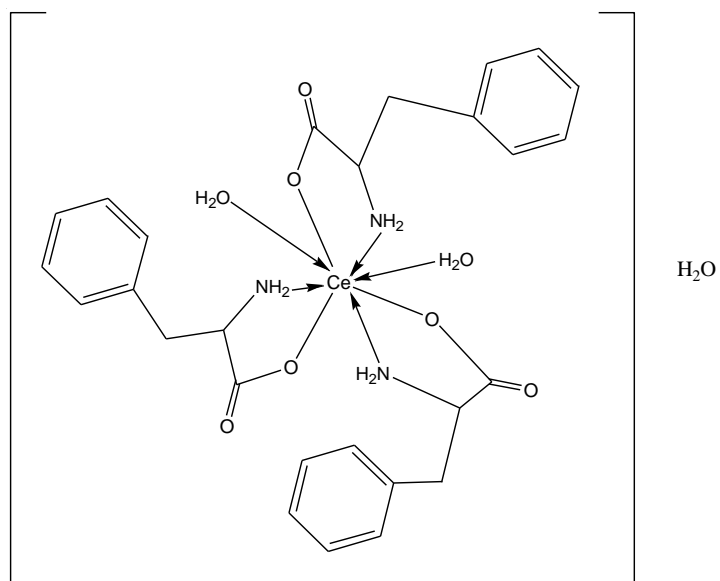
Proposed structure of Diaqua-tris(2-amino-3-phenyl propanoic acid) Ce(III) chelate

SUMMARY AND CONCLUSION

1. The ligand phenylalanine(2-amino-3-phenylpropanoicacid) form metal chelate with lanthanide metal ion viz. La(III) &Ce(III). Coordination no. of these metal ion complex is found to be eight and ligand behave as bidentate in nature.

2. Chelate is insoluble in common organic solvent but they are in soluble in DMSO.

3. Comparative study of infrared spectra of ligand and chelate of metal reveals that the ligand phenylalaninecoordinates to metal ion through nitrogen and oxygen.

4. On the basis of results obtainded from elemental analysis,infraredspectra,electronic spectra and complex formed is 1:3 M: L ratio,

REFERENCES

1. R.N. Patel, N. Singh, K. Shukla, U.K. Chauhan, S. Chakraborty, J. Niclos-Gutierrez,A. Castineiras, J. Inorg. Biochem.98 (2004) 231.
2. Nagajothi A., Kiruthika A., Chitra S. and Parameswari K., International J. Pharma. And Biomedical Sci., (2012), 3,1768.
3. A.H. Fairlamb, G.B. Henderson, A. Cerami, Proc. Natl. Acad. Sci. U.S.A. 86 (1989) 2607
4. R. Bakhtiar, E.I. Ochiai, Gen. Pharmacol. 32 (1999) 525.
5. Bhoopendra Singh, DheerajKumar,International Journal of Scientific and Research Publications, Volume 3, Issue 2, February 2013
6. W.Biltz, Ann. 33, 334 (1904).
7. J.K. Marsh, J.Chem. Soc. 1084 (1947).
8. V.H. Galgali, V.R. Rao and D.D. Khanolkar, I.J. Chem. Soc. 7, 825, (1969).
9. P. Radhakrishna Murthy, V.R. RaoI. J. chem. 6 (8), 465 (1968).
10. J.C. Stites and C.N. MaccurthyJ. Am. Chem. Soc.70, 3142 (1948).
11. J.R. Dyer, Application of Absorption spectroscopy of organic compound 3rdEdn.
12. J.E. Koracic, Spectrochem, Acta part, A, 23, 183, (1967).
13. B.K. Rai and Akhileshbaluni,Asian J. Chem., (2), 725 (2001).
14. W.K. Dutt and A.SenguptaIndianJ. Chem. 11 180 (1973).
15. R. Rajavel, M. SenthilVadivu and C. Anitha, E-Journal of Chemistry, Vol. 5, No. 3, pp. 620-626, (2008).
16. Sangita Sharma, JayeshRamani, JasminBhalodia, NehaPatal, KhushuThakkar and Rajesh Patel, Advance in applied science Research, 2(4) : 374-382, (2011).
17. Suraj B Ade, M.N. Deshpande and D.G. Kolhatkar, International Journal of Research in Pharmaceutical and Biomedicl Science, Vol.3 (2), (2012).
18. R. Shakru, N.J.P. Subhashini, Sathish Kumar K., Shivaraj, J.Chem. Pharm. Res., 2(1) : 38-46 (2010).
19. Sudhir S. SawantVijyaPawar, ShirishJanrao, Ramesh S. Yamgar, Y. Navid, International Jouranl of Research in Pharmacy and Chemistry, 3(3), (2013).
20. Patel K.B., Kharadi G.J., Vyas K.B., Nimavat K.S., International Journal for Pharmaceutical Research Scholars (IJPRS), V-1, I-2, (2012).
21. A.P. Mishra and Rajendra K. Jain, J. Chem. Pharm. Res. 2(6) : 51-61 (2010).
22. J.H. Deshmukh, M.N. Deshpande, Asian Journal of Chemistry., Vol. 22, 3, 1760-1768 (2010).
23. Morey Jaishree, Unique Journal of Pharmaceutical and Biological Sciences, 01(03), 36-39, (2013).