Asian Journal of Chemistry Vol. 15, No. 1 (2003), 139–143

Synthesis and Reactivity of Quadridentate Schiff Base Chelates of Lanthanide(III) Ions

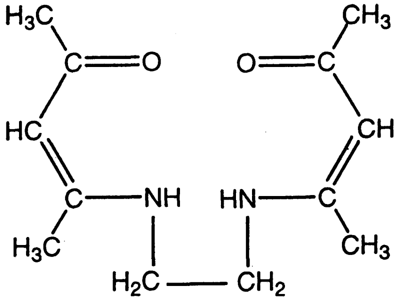
V. BALASUBRAMANIAN*, A. LOGANAYAGI†, R. NANTHINI†, A. RAVI†,
N. KARTHIKEYAN and S. MUTHUKUMARAN
Department of Chemistry, Presidency College, Chennai-600 005, India

α-Naphthylisocyanation reactions are first conducted on Schiff base chelates of lanthanide(III) ion. The results of reaction reactivity clearly indicate that α-naphthylisocyanate attacks at the coordinated Schiff base chelates and after prototropic rearrangement forms α-naphthylamido derivatives. The results are investigated and based on spectroscopic results. The structures of the chelates are proposed.

Key Words: Lanthanide(III), Schiff base, Chelates, Reactivity.

INTRODUCTION

There are several detailed views of reactions of coordinated ligand which clearly indicate that the Schiff bases formed between acetylacetone and elthylenediamine form complexes with almost all transition metal ions. It is abbreviated to ac_2en (Fig. 1). It is a well known tetradentate reagent. The reactions conducted on quadridentate Schiff base complexes of transition metal ions are common. This paper describes the synthesis and reactivity of lanthanide(III) Schiff base (ac_2en.) chelates of La(III), Ce(III), Eu(III). Similar chelates with lanthanides are less reported[1–3].



bis(acetylacetone)ethylenediamine
Fig.. 1

---

†Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India.

Dutt *et al.*[1] prepared the above metal-chelates by mixing the metal ions in the ligand in the ratio 1 : 3, but Arvind *et al.*[2] reported that the above metal-chelates are obtained by mixing metal and ligand in the ratio 1 : 1. A product is obtained in which only tetradentate ligand has coordinated but literature survey clear indicates no reaction conducted on lanthanide chelates made up of qudridentate bis(acetylacetone)ethylenediamine complexes. In this paper, α-naphthylisocyanation reactions have been attempted on bis(acetylacetone)ethylenediamine chelates of trivalent lanthanides, involving lanthanum(III), cerium(III) and europium(III).

EXPERIMENTAL

The materials and methods employed for the preparation and physico-chemical studies of the various complexes reported in this work are elemental analysis and IR. The Schiff base N,N′-ethylene bis(acetylacetoneimine) was prepared by condensing the diamine with acetylacetone[4].

Preparation of the Parent Lanthanide Chelates

Lanthanide(III) chlorides (4.5 mmoles) in 15 mL methanol were mixed with (ac.ac)en (4.4 mmoles) in the same solvent (20 mL) with vigorous stirring at room temperature. The molar ratio of metal and ligand was kept at 1 : 1. The mixture was then refluxed for about 3 h and subsequently heated over a water bath to evaporate the solvent. A few drops of ether were added when a precipitate separated out. The precipitate was redissolved in CH_3OH and reprecipitated with ether. The process was repeated a few times and then finally the precipitate was dried *in vacuo* over P_2O_5 for several days.

Preparation of α-Naphthylisocyanated Chelates

$[Ln(ac_2.en.\alpha\text{-naphthylNCO})Cl_3]$ (Ln = La, Ce or Eu)

The respective lanthanide chelates and α-naphthylisocyanate are mixed in the ratio 1 : 1 and 1 : 2 in dry benzene. The above mixture was refluxed on a water bath for about seven days. The precipitated α-naphthylisocyanated derivatives were separated.

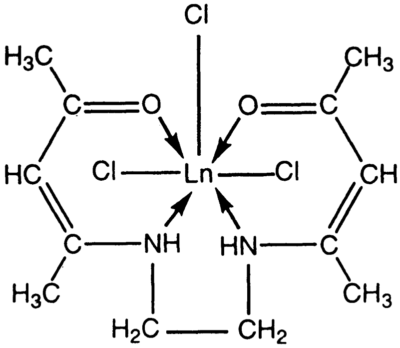
RESULTS AND DISCUSSION

The molar conductance range for 1 : 1 electrolytes at 10^{-3} M dilution in DMSO are reported[5] as 50–70 $ohm^{-1}\ cm^2\ mole^{-1}$. But in our conductive studies has been obtained a molar conductance of 20–30 $ohm^{-1}\ cm^2\ mole^{-1}$ in DMSO at 10^{-3} M dilution for some non-electrolyte complexes of trivalent lanthanides. The above studies on lanthanide complexes show that these complexes are non-electrolytes and therefore all the three chlorides are in the inner coordination sphere. The preparation of lanthanide complexes is represented by the following equation.

$$LnCl_3 + ac_2.en \xrightarrow[\text{(Methanol)}]{CH_3OH} [Ln(ac_2.en)Cl_3]$$

(Ln = La, Ce or Eu)

The analysis for carbon, hydrogen, metals and chlorides fits the formula (Table-1). It shows that the ligand $ac_2.en$ interacts in the keto form, which is in contrast with the reaction of the ligand with the transition metal[6, 7] where it reacts in its enolic form. The presence of one tetradentate ligand $ac_2.en$ and three chloride ions in the coordination sphere of the complexes (Fig. 2) gives an indication that the lanthanide ion may be seven-coordinate in solid state which supports the literature findings[8, 9].



$[Ln(ac_2en)Cl_3]$

Fig. 2

TABLE-1

ELEMENTAL ANALYSIS OF PARENT AND REACTED LANTHANIDE CHELATES

S.No.	Chelates	Yield (%)	m.p. (°C)	% Analysis: Found (Calcd.)			
				Ln	C	N	H
1.	$[La(ac_2en.\alpha\text{-}naphthylNCO)Cl_3]$	60	170	19.76 (19.82)	58.16 (58.20)	7.94 (7.98)	4.82 (4.85)
2.	$[Ce(ac_2en)Cl_3]$	80	135	29.68 (29.76)	31.87 (31.98)	5.87 (5.95)	4.15 (4.25)
3.	$[Ce(ac_2en\cdot\alpha\text{-}naphthylNCO)Cl_3]$	55	160	19.90 (19.94)	58.08 (58.11)	7.94 (7.97)	4.78 (4.84)
4.	$[Eu(ac_2en)Cl_3]$	80	171	31.58 (31.50)	29.88 (29.87)	5.75 (5.80)	4.11 (4.14)
5.	$[Eu(ac_2en\cdot\alpha\text{-}naphthylNCO)Cl_3]$	60	185	21.25 (21.28)	57.11 (57.14)	7.79 (7.84)	4.71 (4.76)

ac_2en = bis(acetylacetone)ethylenediamine (keto form).

Structure and Bonding of the Parent Lanthanide Chelates

IR spectra of $ac_2.en$ and $[Ln(ac_2.en)Cl_3]$ have been compared in order to characterize the lanthanide chelates (Table-2). It shows bands at 1590 cm^{-1} (C═O stretching), 1510 cm^{-1} (C═C and C═N stretching) and 1220 cm^{-1} (—OH in hydrogen bonding)[6]. The non-bonded ligand must have both the keto and enol forms and hence IR shows two strong bands around 760 and 740 cm^{-1} which are due to the C—H deformation of the double bonded carbon in the hydrogen bonded ring. On complexation, the 1519 cm^{-1} ν(CO) band increases to 1616–1570 cm^{-1} and ν(C═C) and ν(C═N) bands splits into 3 (or 4) bands. The strong band around the region 1220 cm^{-1} in the ligand (due to —OH in H bonding) disappears in all the metal-chelates. In the metal-chelates the band around 454–430 cm^{-1} is assignable to ν(Ln—O) mode. The bands around 781 cm^{-1} and 1190 cm^{-1} are assignable to π(C—H) and δ(C—H) respectively[10–15].

TABLE-2

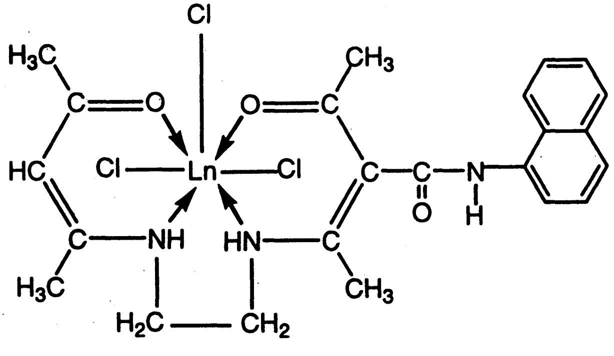
CHARACTERISTIC IR FREQUENCIES (cm^{-1}) OF A PARENT AND REACTED LANTHANIDE CHELATES

S.No.	Chelates	ν(C=O) Coordinated	ν(C=N)	π(CH)	δ(CH)	Amido	
						ν(C=O)	ν(N—H)
1.	[La(ac₂en)Cl₃]	1616 s	1526 s	781 w	1190 s	—	—
2.	[La(ac₂en·α-naphthylNCO)Cl₃]	1616 s	1526 s	—	—	1725 s	3500–2900 m, b
3.	[Ce(ac₂en)Cl₃]	1590 s	1532 s	781 w	1187 s	—	—
4.	[Ce(ac₂en·α-naphthylNCO)Cl₃]	1577 s	1532 s	—	—	1683 s	3500–2800 m, b
5.	[Eu(ac₂en)Cl₃]	1570 s	1530 s	790 w	1192 s	—	—
6.	[Eu(ac₂en·α-naphthylNCO)Cl₃]	1570 s	1532 s	—	—	1690 s	3500–2800 m, b

Structure and Bonding of α-Naphthylamido Substituted Chelates

Comparing the IR spectrum of parent chelates and the reacted chelates, α-naphthylisocyanated derivatives show the absence of bands due to π(C—H) and δ(C—H) indicating substitution of α-naphthylisocyanate at γ(C—H) position. Further, a new band around 1725–1690 cm^{-1} and a broad band centering around 3500–2800 cm^{-1} are assignable to ν-amido(CO) and ν-amido(NH) respectively. Therefore it is tentatively assumed that α-naphthylisocyanate adds on γ(CH) and after prototropic rearrangement forms α-naphthylamido derivatives[10–15].

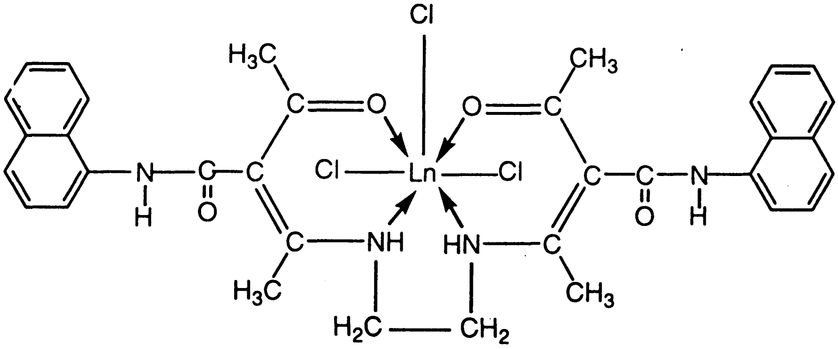
Therefore based on the above evidence the following tentative structures are assigned to α-naphthylisocyanated lanthanide chelates (Fig. 3).



[Ln(Al·en·Al·α-naphthylNCO)Cl₃] Mono α-naphthylisocyanated [Ln(ac₂en)Cl₃] Ln = La(III), Ce(III), Eu(III)

Fig. 3.

The close examination of IR spectra of complexes formed between the parent complexes and α-naphthylisocyanate in 1 : 1 ratio exhibits IR bands due to π(C—H) and δ(C—H) with reduced intensity indicating partial substitution (Fig. 4).



[Ln(Al·α-naphthyl·en·Al·α-naphthylNCO)Cl_3] Di α-naphthylisocyanated[Ln(ac_2en)Cl_3]
Ln = La(III), Ce(III), Eu(III)
Fig. 4

REFERENCES

1. N.K. Dutt and K. Nag, *J. Inorg. Nucl. Chem.*, **30**, 3273 (1968).
2. Arvind, M. Sayeed, K. Iftikhar and N. Ahmad, *Synth. React. Inorg. Met-Org. Chem.*, **12**, 55 (1982).
3. ———, *Indian J. Chem.* (in press).
4. P.J. McCarthy, R.J. Hovey, K. Vend and A.E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).
5. N.N. Greenwood, B.P. Stanghan and A.E. Nilson, *J.Chem. Soc. (A)*, 2209 (1968).
6. K. Ueno and A.E. Martell, *J. Phys. Chem.*, **59**, 998 (1955).
7. S.F.H. Rizvi and N. Ahmad, *Acta Chim. (Budapest)*, **94**, 195 (1977).
8. K. Iftikhar, M. Sayeed and N. Ahmad, *Bull. Chem. Soc. (Japan).*, **53**, 2258 (1982).
9. J. Selbin, N. Ahmad and N. Bhacca, *Inorg. Chem.*, **10**, 1383 (1971).
10. V. Balasubramanian, N.S. Dixt and C.C. Patel, *J. Inorg. Nucl. Chem.*, **41**, 122 (1979).
11. ———, *National Acad. Sci. Letters*, **1**, 173 (1978).
12. ———, *Indian J. Chem.*, **20A**, 667 (1981).
13. V. Balasubramanian, R.R. Iyengar and C.C. Patel, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **90**, 33 (1981).
14. V. Balasubramanian and C.C. Patel, *Synth. React. Inorg. Met.-Org. Chem.*, **12**, 11 (1982).
15. V. Balasubramanian, A. Loganayagi, M. Muneeswaran and N. Karthikeyan, *Asian J. Chem.*, **12**, 157 (2000).

(*Received*: 20 May 2002; *Accepted*: 27 July 2002) AJC-2808