

## Synthesis and Characterization of some Lanthanide(III) Chelates with *O*-Hydroxyacetophenone Oxime

M. MOHAN\*, J. P. TANDON\*\* and N. S. GUPTA

Department of Chemistry, N.R.E.C. College, Khurja-203131 (U.P.), India

Received June 5, 1985

### Abstract

A series of trivalent lanthanide chelates of the type  $[\text{Ln}(\text{Hoaox})_3\text{X}_2](\text{X})$  (where  $\text{Ln}^{3+} = \text{La, Pr, Nd, Sm, Gd or Dy}$ ;  $\text{Hoaox} = O$ -hydroxyacetophenone oxime and  $\text{X}^- = \text{NO}_3$  or  $\text{Cl}$ ) have been synthesized by the direct reaction of *O*-hydroxyacetophenone oxime with lanthanide(III) nitrates or chlorides in 2,2'-dimethoxypropane and ethanol. The chelates have been characterized by elemental analysis, conductance, X-ray powder diffraction patterns, magnetic and spectral studies. The elemental analyses reveal the presence of 1:3 (metal:ligand) stoichiometry and molar conductance data in ethanol indicate 1:1 electrolytes in all lanthanide(III) chelates. The lanthanide(III) chelates are X-ray isomorphous and possess orthorhombic type of lattice with slightly different unit cell parameters. The magnetic values show little deviation from Van Vleck values. The electronic spectra, recorded at room temperature in methanol, are dominated by ligand absorption bands and exhibit only slight shift and marked enhancement in the intensity of the bands. IR spectral data suggest the *cis*-coordination of the neutral Hoaox ligand molecules through the oxygen atom of the phenolic hydroxylic group, oxime group nitrogen atom and monodentate nitrate coordination to all lanthanide(III) chelates. Thermogravimetric studies have also been carried out.

### Introduction

In continuation of our studies on metal complexes of oxime containing ligands [1], we are reporting herein, for the first time, the synthesis of lanthanide(III) nitrate and chloride chelates with *O*-hydroxyacetophenone oxime (Hoaox) and their characterization by elemental analysis, conductance, X-ray powder diffraction patterns, magnetic, electronic and vibrational spectral and thermogravimetric studies.

### Experimental

#### Materials

Lanthanide(III) nitrates, chlorides and *O*-hydroxyacetophenone were obtained from K and K Laboratories, New York, and were used as such without further purification. Solvents were of reagent grade and were purified by usual methods.

#### Synthesis of *O*-Hydroxyacetophenone Oxime(Hoaox)

A solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (0.70 mol) and sodium hydroxide (0.70 mol) in 50 cm<sup>3</sup> of 50% aqueous methanol was added to a boiling solution of *O*-hydroxyacetophenone (0.65 mol) in 150 cm<sup>3</sup> of methanol. The resulting solution mixture was refluxed for 2 h, cooled and diluted with 150 cm<sup>3</sup> of water. The mixture was filtered and the white solid, so obtained, was washed thoroughly with water and then recrystallized from methanol. The authenticity of the compound was judged by elemental analysis (Table I) and physical methods (m.p. 116° and infrared study).

#### Synthesis of the Chelates

The following general procedure was used to isolate all the lanthanide(III) chelates. Lanthanide(III) nitrate or chloride (0.06 mmol) was dissolved in 120 cm<sup>3</sup> of ethanol and 20 cm<sup>3</sup> of 2,2'-dimethoxypropane and heated for half an hour under reflux. Hoaox (0.18 mmol) was dissolved in the same solvent mixture by heating and added to the metal salt solution. The resulting solution mixture was then heated under reflux for 6 h with continuous stirring and the volume of the solution was reduced to 20 cm<sup>3</sup> by evaporation. On cooling the solution to room temperature, a crystalline solid was obtained which was filtered, washed with a little of ethanol and diethylether then dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ .

#### Characterization of Chelates

##### Analysis

Carbon, hydrogen and nitrogen analyses were obtained through the courtesy of Micro Analytical Laboratory, C.D.R.I., Lucknow. Lanthanides were

\*Author to whom correspondence should be addressed.  
\*\*Department of Chemistry, The University of Rajasthan, Jaipur-302004, India.

TABLE I. Analytical, Molar Conductance and Magnetic Data for Lanthanide(III) Chelates

Compound	Colour	Melting point (°C)	Analysis (Found (Calc.)) (%)				$\Lambda_M$ ( $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ )	$\mu_{\text{eff}}, \mu_B$ at 298 °K
			C	H	N	M		
Hoaox	white	116.0	62.98 (63.37)	6.12 (5.96)	9.48 (9.30)			
[La(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	white	82.5	37.12 (37.02)	3.40 (3.47)	10.82 (10.80)	17.78 (17.85)	43	diamagnetic
[Pr(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	light green	80.0	37.15 (36.95)	3.52 (3.46)	10.89 (10.77)	18.00 (18.07)	40	3.45
[Nd(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	light pink	81.5	36.92 (36.77)	3.52 (3.45)	10.85 (10.72)	18.42 (18.45)	40	3.50
[Sm(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	cream	84.5	36.52 (36.48)	3.35 (3.42)	10.72 (10.64)	19.20 (19.05)	42	1.52
[Gd(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	white	87.0	36.27 (36.17)	3.52 (3.39)	10.35 (10.55)	19.85 (19.75)	37	7.86
[Dy(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	cream	83.5	35.86 (35.93)	3.44 (3.37)	10.59 (10.48)	20.22 (20.27)	37	10.20
[La(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	white	117.5	41.16 (41.24)	3.92 (3.86)	6.09 (6.01)	19.92 (19.89)	39	diamagnetic
[Pr(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	green	115.0	41.00 (41.12)	3.88 (3.85)	6.00 (5.99)	19.25 (19.92)	37	3.60
[Nd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	light violet	110.5	41.24 (40.94)	3.92 (3.82)	5.90 (5.97)	20.56 (20.50)	39	3.48
[Sm(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	cream	112–5	40.96 (40.57)	3.90 (3.80)	5.75 (5.91)	21.32 (21.19)	38	1.54
[Gd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	white	109.5	40.22 (40.18)	3.82 (3.77)	5.80 (5.86)	21.82 (21.94)	40	7.87
[Dy(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	cream	113.0	39.80 (39.99)	3.62 (3.74)	5.75 (5.81)	22.64 (22.50)	41	10.22

analysed by EDTA titrations after decomposition of the chelates according to the reported procedure [2].

#### Conductance

The electrolytic molar conductances of all the lanthanide(III) chelates at *ca.*  $1 \times 10^{-3}$  M concentration level in ethanol were determined at room temperature ( $30 \pm 1$  °C), using Toshniwal conductometric bridge type CL01/01 having an immersion type cell (cell constant  $0.66 \text{ cm}^{-1}$ ).

#### X-Ray powder patterns

X-ray powder diffractograms of chelates were obtained on a Philips (automatic) diffractometer PW 1130100, The Netherlands (X-ray Generator). The target Cu K $\alpha$  was used with Ni filters and the wavelength of the source was 1.5418 Å. Reflections up to  $60^\circ$  were recorded in almost every case. The density of the chelates was determined by the displacement method.

#### Magnetic moment measurements

Magnetic susceptibilities of all the chelates were measured at room temperature on a standard Faraday balance, using HgCo(NCS)<sub>4</sub> [3] as susceptibility standard. Diamagnetic corrections were estimated by using Pascal's constants [4].

#### Spectral measurements

Electronic spectra of all the chelates in methanol at room temperature were measured on a Cary-14 spectrophotometer. Infrared spectra ( $4000\text{--}200 \text{ cm}^{-1}$ ) of the ligand and its lanthanide(III) chelates were recorded on a Perkin Elmer 180 spectrophotometer in CsI.

#### Thermogravimetric analysis

Thermogravimetric analysis of all the chelates was carried out on a Stanton (mass flow type) automatic recording thermogravimetric balance at Guru Nanak Dev University, Amritsar.

TABLE II. Cell Parameters, Density and Number of Molecules per Unit Cell of some Lanthanide(III) Chelates

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Density (gm/cm <sup>3</sup> )	<i>Z</i>	$\alpha = \beta = \gamma$ (°)
[La(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	10.71	31.77	12.84	1.76	6	90
[Dy(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	7.69	32.72	18.32	1.75	6	90
[Nd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	11.51	20.73	15.93	1.85	6	90
[Gd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	6.47	32.86	18.32	1.85	6	90

## Results and Discussion

The interaction of lanthanide(III) nitrates and chlorides with *O*-hydroxyacetophenone oxime (Hoaox) in the 1:3 ratio in a mixture of ethanol and 2,2'-dimethoxypropane afforded the chelates of the general formula [Ln(Hoaox)<sub>3</sub>X<sub>2</sub>](X (where Ln<sup>3+</sup> = La, Pr, Nd, Sm, Gd or Dy and X<sup>-</sup> = NO<sub>3</sub> or Cl<sup>-</sup>), as in Table I. All the chelates are pale white to cream in colour except praseodymium and neodymium which are green and violet, respectively. All the chelates are nonvolatile, soluble in methanol, ethanol DMF and DMSO, insoluble in rest common organic solvents and decompose in water. When exposed to the open air, all the chelates show a tendency to hydrolyse and become pasty. The conductance data (Table I) reveal 1:1 electrolytic nature of all the chelates in ethanol [5], indicating that one of the anions remains in the outer sphere of these chelates and does not participate in coordination to the metal ion.

The fine powdered samples of some lanthanide(III) chelates have been used to record their X-ray powder diffraction patterns and the observed '*d*' values have been indexed from the diffractograms\*. All the chelates have been found to belong to the 'orthorhombic' type of lattice. The unit cell dimensions *a*, *b* and *c* and the number of molecules per unit cell *Z* have been evaluated and are summarized in Table II.

The paramagnetic behaviour of the lanthanide(III) ions is consistent with the presence of unpaired 4f electrons. Since these electrons are well-shielded by 5s<sup>2</sup>5p<sup>6</sup> octet both in their spin and orbital motion, the magnetic movement of a chelate should indicate whether these 4f electrons take part in bond formation or not. The magnetic moments of the present lanthanide(III) chelates, as in Table I, show little deviation from Van Vleck values [6] and those reported for 8-hydrated sulphates [7]. Thus, the magnetic moments of the new chelates are within the predicted range and observed in lanthanide compounds.

In the UV region (400–200 nm), Hoaox exhibits two absorption bands at 43 105 (log  $\epsilon$  = 3.62) and

33 898 (log  $\epsilon$  = 2.28) cm<sup>-1</sup>, which can be assigned [8] to *n* →  $\sigma^*$  and *n* →  $\pi^*$  transitions, respectively. The high absorption by the ligand as compared to the lanthanide(III) ions masks any splitting of the band and only the slight wavelength and intensity variations are significant in the chelates. The spectra of the lanthanide(III) chelates are dominated by ligand absorption bands.

In the visible region, the lanthanide(III) chelates exhibit the alternations in the intensity or shifts in the position of the absorption bands, sometimes both. The relevant energies and *J* level assignments are given in Table III. Lanthanum(III) and gadolinium(III) chelates have no significant absorption band. The so called 'hypersensitive' bands are bracketed in Table III. The energies at which the various bands appear are lower as compared to the aquo ion. This red shift has been ascribed to a nephelauxetic effect [9]. The extent of the red shift is related to covalence in the metal–ligand bond. Sinha [10] has proposed a scale to express this covalence. Sinha's parameter,  $\delta$  (%) is given by the relation.

$$\delta(\%) = (1 - \beta)/\beta \times 100$$

where

$$\beta = \frac{1}{n} \sum \nu_{\text{complex}}^i / \nu_{\text{aquo}}^i$$

The values calculated using the above equation are presented in Table III. The bonding parameter,  $b^{1/2}$ , the magnitude of which suggests the comparative involvement of the 4f orbital metal–ligand bond, is correlated to nephelauxetic ratio ( $\beta$ ) by the expression [11]:

$$b^{1/2} = (1 - \beta)^{1/2}/2$$

The positive values of bonding parameters (Table III), suggest the occurrence of some covalent character in the metal–ligand bond. The magnitude of the parameters  $\beta$ ,  $\delta$  and  $b^{1/2}$  increase with the increase in the atomic number of lanthanides and is in accordance with the lanthanide contraction.

The observed shapes of hypersensitive bands for the present chelates provide some clue regarding the coordination number around the lanthanide(III) ion [12]. A comparison of the shapes of the hypersensitive bands of Karraker's octacoordinated species in

\*The X-ray data can be obtained from the authors on request.

TABLE III. Electronic Spectral Data of Lanthanide(III) Chelates

Compound	Frequency ( $\text{cm}^{-1}$ )	$\log \epsilon$ (max)	Assignment
Hoaox	43105	3.62	$n \rightarrow \sigma^*$
	33898	2.28	$n \rightarrow \pi^*$
[La(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	43478	4.25	$n \rightarrow \sigma^*$
	33898	3.15	$n \rightarrow \pi^*$
[Pr(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) $\beta = 0.9975$ $\delta = 0.2506$ $b^{1/2} = 0.02500$	43478	3.58	$n \rightarrow \sigma^*$
	33898	2.10	$n \rightarrow \pi^*$
	22730	4.25	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$
	22220	5.60	$\rightarrow {}^3\text{P}_1$
	20835	7.89	$\rightarrow {}^3\text{P}_0$
	16950	12.38	$\rightarrow {}^1\text{D}_2$
[Nd(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) $\beta = 0.9932$ $\delta = 0.6753$ $b^{1/2} = 0.04123$	43478	4.15	$n \rightarrow \sigma^*$
	33890	2.98	$n \rightarrow \pi^*$
	19230	4.58	${}^4\text{I}_{9/2} \rightarrow {}^4\text{P}_{1/2}$
	18967	6.35	$\rightarrow {}^4\text{G}_{4/2}$
	17360	8.40	$\rightarrow [{}^4\text{G}_{5/2}, {}^2\text{G}_{5/2}]$
	16950	8.26	$\rightarrow {}^2\text{H}_{9/2}$
[Sm(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) $\beta = 0.9930$ $\delta = 0.7049$ $b^{1/2} = 0.04183$	43478	3.98	$n \rightarrow \sigma^*$
	33898	2.50	$n \rightarrow \pi^*$
	25000	3.75	${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{9/2}$
	24700	3.97	$\rightarrow {}^6\text{P}_{3/2}$
	23800	4.45	$\rightarrow {}^4\text{I}_{13/2}$
	21430	3.10	$\rightarrow [{}^4\text{I}_{11/2}, {}^4\text{M}_{15/2}]$
	20460	2.98	$\rightarrow {}^4\text{I}_{9/2}$
	19950	2.10	$\rightarrow {}^4\text{G}_{7/2}$
[Gd(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	43478	4.00	$n \rightarrow \sigma^*$
	33898	2.25	$n \rightarrow \pi^*$
[Dy(Hoaox) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> $\beta = 0.9925$ $\delta = 0.7498$ $b^{1/2} = 0.04330$	43480	3.50	$n \rightarrow \sigma^*$
	33870	2.10	$n \rightarrow \pi^*$
	23410	3.68	${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$
	22150	3.10	$\rightarrow {}^4\text{I}_{15/2}$
	21340	3.98	$\rightarrow {}^4\text{F}_{9/2}$
[La(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	43480	3.60	$n \rightarrow \sigma^*$
	33898	2.59	$n \rightarrow \pi^*$
[Pr(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl) $\beta = 0.9975$ $\delta = 0.2506$ $b^{1/2} = 0.02500$	43480	5.25	$n \rightarrow \sigma^*$
	33900	3.70	$n \rightarrow \pi^*$
	22730	4.25	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$
	22220	5.98	$\rightarrow {}^3\text{P}_1$
	20835	7.60	$\rightarrow {}^3\text{P}_0$
	16950	12.89	$\rightarrow {}^1\text{D}_2$
[Nd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl) $\beta = 0.9932$ $\delta = 0.6753$ $b^{1/2} = 0.04123$	43480	4.98	$n \rightarrow \sigma^*$
	33898	3.65	$n \rightarrow \pi^*$
	19230	4.72	${}^4\text{I}_{9/2} \rightarrow {}^4\text{P}_{1/2}$
	18967	6.10	$\rightarrow {}^4\text{G}_{4/2}$
	17360	9.25	$\rightarrow [{}^4\text{G}_{5/2}, {}^2\text{G}_{5/2}]$
	16950	8.42	$\rightarrow {}^2\text{H}_{9/2}$
[Sm(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl) $\beta = 0.9930$ $\delta = 0.7021$ $b^{1/2} = 0.04183$	43480	3.50	$n \rightarrow \sigma^*$
	33898	2.42	$n \rightarrow \pi^*$
	25000	3.60	${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{9/2}$
	24698	4.25	$\rightarrow {}^6\text{P}_{3/2}$
	23805	4.98	$\rightarrow {}^4\text{I}_{13/2}$

(Continued)

TABLE III. (Continued)

	21425	3.10	$\rightarrow [{}^4I_{11/2}, {}^4M_{15/2}]$
	20460	2.60	$\rightarrow {}^4I_{9/2}$
	19950	1.85	$\rightarrow {}^4G_{7/2}$
[Gd(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	43478	2.58	$n \rightarrow \sigma^*$
	33890	1.39	$n \rightarrow \pi^*$
[Dy(Hoaox) <sub>3</sub> (Cl) <sub>2</sub> ](Cl)	43478	3.25	$n \rightarrow \sigma^*$
$\beta = 0.9923$	33878	2.10	$n \rightarrow \pi^*$
$\delta = 0.7734$	23410	2.98	${}^6H_{15/2} \rightarrow {}^4G_{11/2}$
$b^{1/2} = 0.04387$	22150	3.35	$\rightarrow {}^4I_{15/2}$
	21335	2.88	$\rightarrow {}^4F_{9/2}$

aqueous solution with those present in neodymium(III) chelates in methanol reveals considerable similarity. This, probably, indicates that the coordination number around the neodymium(III) ion in the present chelate is also eight. Since neodymium chelates are isomorphous with those of other lanthanide(III) chelates, the coordination number eight is also suggested for other lanthanide(III) chelates.

The free ligand, Hoaox, exhibits multiple bands in the 3300–2700  $\text{cm}^{-1}$  range which are assigned [13] to the intermolecular H-bonded OH of the NOH group. All the lanthanide(III) chelates exhibit the sharp intensity bands in the 3450–3350, 3200–3140, 3060–3000 and 2900–2760  $\text{cm}^{-1}$  range which are assigned [13] to the free  $\nu(\text{OH})$ , H-bonded  $\nu(\text{OH})$ ,  $\nu(\text{C}-\text{H})$ , coupled  $\nu(\text{OH})$ , and overtone  $\nu(\text{C}=\text{N})$  stretching vibrations, respectively. The  $\nu(\text{C}=\text{N})$  (acyclic) and  $\nu(\text{N}-\text{O})$  stretching vibrations in the free ligand are observed at 1580 and 948  $\text{cm}^{-1}$ , respectively. These stretching vibrations are shifted to higher frequency in the lanthanide(III) chelates, appearing at *ca.* 1640 and *ca.* 1050  $\text{cm}^{-1}$ , respectively. The shift of the bands towards the high frequency sides suggests that the oxime proton is not heterolyzed and there is a contribution from neutral  $>\text{C}=\text{NOH}$  groups in the present lanthanide(III) chelates [13].

The absorption band observed at 1280  $\text{cm}^{-1}$  in the free ligand which shifts only to *ca.* 1290  $\text{cm}^{-1}$  in the lanthanide(III) chelates, is assigned to phenolic  $\nu(\text{C}-\text{O})$  stretching vibration. The slight shift of  $\nu(\text{C}-\text{O})$  in the chelates may be ascribed to delocalization of electron density from the oxygen atom to the lanthanide(III) ion, resulting in a slightly ionic character of the C–O bond and consequently slight increase in the  $\nu(\text{C}-\text{O})$  frequency.

The infrared spectra of the lanthanide(III) nitrate chelates of Hoaox exhibits sharp to weak intensity bands at *ca.* 1320, *ca.* 1010, *ca.* 720, 1440 *ca.* 710 and *ca.* 820  $\text{cm}^{-1}$  which are assigned [14, 15] to the frequencies of  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  of the coordinated ( $C_{2v}$ ) nitrate group(s). The appearance of the bands at *ca.* 830 and *ca.* 1350  $\text{cm}^{-1}$  indicates [14,

[15] the presence of the ionic ( $D_{3h}$ ) nitrate group(s). Thus, the lanthanide chelates have both ionic and coordinated nitrate groups and, therefore, have been formulated as  $[\text{Ln}(\text{Hoaox})_3(\text{NO}_3)_2]\text{NO}_3$  on conductance data and steric grounds. Furthermore, the appearance of the weak bands at 1740 and 1720  $\text{cm}^{-1}$  confirms [14, 15] the monodentate coordination of the nitrate groups in these chelates.

In the far-infrared spectral region, Hoaox exhibits the strong to medium intensity bands at 400, 330, 312, 300 and 250  $\text{cm}^{-1}$ , whereas all the chelates show bands of varying intensity at *ca.* 400, *ca.* 310, *ca.* 290 and *ca.* 250  $\text{cm}^{-1}$ , assigned to ligand absorption bands. In addition to the vibrations, two spectral bands associated with  $\nu(\text{Ln}-\text{N})$  (ligand) vibration at *ca.* 245 and *ca.* 215  $\text{cm}^{-1}$  and two bands at *ca.* 220 and *ca.* 210  $\text{cm}^{-1}$  due to  $\nu(\text{Ln}-\text{Cl})$  and  $\nu(\text{Ln}-\text{O})$  ( $\text{NO}_3$ ) vibrations of varying intensity are observed. This assignment suggests [16] the *cis*-coordination of the ligand molecules in all the present lanthanide(III) chelates.

The thermogravimetric analysis shows that the decomposition of the present chelates takes place in two steps. The chelates are stable upto *ca.* 180 °C after which the total loss in the temperature range 180–270 °C corresponds to one molecule of Hoaox. Further decomposition takes place with the liberation of other molecules of ligand in the temperature range 270–380 °C leaving  $\text{Ln}(\text{NO}_3)_3$  or  $\text{LnCl}_3$  and finally forming  $\text{Ln}_2\text{O}_3$  at 590 °C.

Thus, on the basis of the above evidence, it can be concluded that the lanthanide(III) ions are surrounded by three neutral ligand molecules, each bound in a bidentate N, O fashion and two anions forming a coordination number of eight.

#### Acknowledgements

The authors are grateful to the authorities of C.D.R.I., Lucknow, India, for recording electronic and IR spectra. Thanks are also due to the authorities of Delhi University, Delhi, India for X-ray powder diffraction results.

## References

- 1 M. Mohan, J. P. Tandon and N. S. Gupta, *Synth. React. Inorg. Met. Org. Chem.*, **15**, 375 (1985) and refs. therein.
- 2 A. K. Srivastava, V. B. Rana, M. Mohan, M. P. Swami and P. C. Jain, *J. Inorg. Nucl. Chem.*, **37**, 723 (1975).
- 3 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
- 4 F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metal Complexes', Chapman and Hall, London, 1961.
- 5 W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- 6 J. H. Van Vleck and A. Frank, *Phys. Rev.*, **34**, 494 (1929); **34**, 1625 (1929).
- 7 D. M. Yost, H. Russel and C. S. Garner, 'The Rare Earth Elements and their Compounds', Wiley, New York, 1957, Chap. 2.
- 8 C. N. R. Rao, 'Ultra-Violet and Visible Spectroscopy', Butterworth, London, 1975, p. 80.
- 9 C. K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).
- 10 S. P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).
- 11 D. E. Henrie and C. R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).
- 12 D. G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967); *J. Inorg. Nucl. Chem.*, **31**, 2851 (1969); **33**, 3713 (1971).
- 13 M. Mohan and B. D. Paramhans, *Indian J. Chem.*, **19A**, 759 (1980).
- 14 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
- 15 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem.*, **49**, 1957 (1971).
- 16 J. R. Ferraro, 'Low-Frequency Vibrations of Inorganic and Coordination Compounds', Plenum, New York, 1971.