Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1334–1344

Synthesis, Spectral and Thermal Studies on Lanthanum(III) Complexes of Piperidin-4-ones

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The diamagnetic lanthanum(III) nitrate (La^1–La^{10}) and chloride (La^{11}–La^{20}) complexes of piperidin-4-ones (L^1–L^{10}) of general formula $[La(L)_2(NO_3)_3(H_2O)_2]$ and $[La(L)Cl_3(H_2O)_2]$ have been prepared and characterized by various physico-chemical studies like elemental analysis, molecular weight determination, molar conductance, thermal and spectral studies. Molar conductance data indicate that these complexes are non-electrolytes. IR spectral data show the presence of water molecules and thermal studies confirm that these water molecules are coordinated. IR spectra also reveal that the nitrate groups are coordinated to the metal ion as bidentate ligands. IR and NMR spectral studies suggest that piperidin-4-ones coordinate with metal ions only through ring nitrogen and not through carbonyl group.

Key Words: Piperidin-4-ones, Lanthanum, Complexes, Thermal, Spectral.

INTRODUCTION

Recently the coordination chemistry of lanthanide complexes has attracted many research workers due to the biological, chemical and industrial application of these complexes[1–4]. We have already reported the synthesis and characterization of samarium(III)[5], cerium(III)[6], gadolinium(III)[7], terbium(III) and dysprosium(III)[8] completes of piperidin-4-ones. Lanthanides being hard acids would be expected to show preference to bonding *via* the ketocarbonyl oxygen rather than the ring nitrogen in case of piperidin-4-ones. However, it has been unambiguously confirmed that only the ring nitrogen of piperidin-4-ones is coordinated to lanthanide(III) ions[5–8]. In continuation of our work., we now report the synthesis and characterization of lanthanum(III) complexes of piperidin-4-ones

EXPERIMENTAL

Various substituted 2,6-diphenylpiperidin-4-ones (L^1–L^{10}) were prepared following reported procedures[9, 10]. The complexes have been prepared by a general procedure: A mixture of lanthanum(III) nitrate (1.7 g, 5 mmol) and piperidin-4-

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one (10 mmol) in ethanol (50 mL). was refluxed on a water bath for 4 h. Subsequently, the solvent was distilled off under reduced pressure. The residue was repeatedly washed with hot ethanol, acetone and ether and dried over phosphorus(V) oxide *in vacuo*. Lanthanum(III) chloride complexes of piperidin-4-one have been prepared by a similar procedure using lanthanum(III) chloride.

The lanthanum content of the complexes was determined by complexometric EDTA titration[11] using xylenol orange as an indicator at pH 6. Elemental analyses (C, H and N) were determined using a Carlo-Erba 1106 microanalytical instrument. Conductance measurements were performed on 10^{-3} mol L^{-1} solutions of the complexes in acetonitrile using a type CM-82 Elico conductivity bridge with a dip type conductivity cell fitted with a platinum electrode (cell constant = 1.0 cm^{-1}). The molecular weight determinations have been carried out by the depression of freezing point method using camphor as the solvent in which the complexes are completely soluble. The experiments were repeated thrice for each complex and the average values have been taken. The results were found to agree with the calculated values within ± 2% error. The IR spectra of the ligands and their metal complexes were recorded on a Shimadzu FT-IR 8000 spectrophotometer in the 4000–400 cm^{-1} region using the KBr disc technique. The ^1H and ^{13}C NMR spectra were run at room temperature on a model 400 JEOL GSE spectrometer operating at 399.65 MHz or 100.40 MHz, respectively. The simultaneous TG-DTA measurements were carried out in air, using 3–5 mg samples at a heating rate of 10°C min^{-1} in the temperature range from ambient to 800°C using a platinum cup as the sample holder.

RESULTS AND DISCUSSION

Analytical and conductance data in Tables 1 and 2 lead to general formula of the complexes as $[La(L)_2(NO_3)_3(H_2O)_2]$ and $[La(L)Cl_3(H_2O)_2]$ for lanthanum(III) nitrate and lanthanum(III) chloride complexes respectively. These complexes are colourless, sparingly soluble in methanol, dimethylformamide, dimethylsulphoxide and acetonitrile and insoluble in ether, acetone and chloroform. The nitrate complexes are non-hygroscopic and stable in air while the chloride complexes are hygroscopic and stable in the absence of air. All these complexes have negligible conductivity values (Tables 1 and 2), indicating that they are non-electrolytes. The observed molecular weights of these complexes are found to agree with the calculated formula weights, confirming that these complexes are nonelectrolytes (van't Hoff factor = 1).

The IR spectral data of lanthanum(III) nitrate and chloride complexes are given in Tables 3 and 4, respectively. The piperidin-4-ones have been shown to exist in the chair conformation with alkyl and phenyl groups in equatorial orientations[9, 10]. The sharp band around 3300 cm^{-1} due to N—H stretching of the ligands (L^1–L^5) has been shifted to higher frequency (*ca.* 3400 cm^{-1}) as a broad band for nitrate complexes [La^1–La^5] and is shifted to lower frequency for chloride complexes [La^{11}–La^{15}], respectively[12]. The lower frequency absorption in chloride complexes can be explained as follows: Hydrogen bonding between the anion present and the proton of the NH group decreases the N—H stretching frequency

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE LANTHANUM(III) NITRATE COMPLEXES

Complex		m.w., Found (Calcd.)	Yield (%)	Decomp. temp. (°C)	Element, Found (Calcd.) (%)				Conductance (ohm^{-1} cm^2 mol^{-1})
No.	Formula (Empirical formula)				La	C	H	N	
(La^1)	$[La(L^1)_2(NO_3)_3(H_2O)_2]$ $(LaC_{34}H_{38}N_5O_{13})$	862.72 (863.17)	65	> 320	16.25 (16.09)	47.57 (47.27)	4.15 (4.44)	8.35 (8.11)	2.5
(La^2)	$[La(L^2)_2(NO_3)_3(H_2O)_2]$ $(LaC_{36}H_{42}N_5O_{13})$	893.17 (891.20)	75	178–180	15.75 (15.50)	48.50 (48.47)	4.50 (4.75)	7.23 (7.86)	3.7
(La^3)	$[La(L^3)_2(NO_3)_3(H_2O)_2]$ $(LaC_{38}H_{46}N_5O_{13})$	919.75 (919.23)	75	> 340	15.00 (15.11)	49.75 (49.61)	5.00 (5.04)	7.75 (7.62)	4.5
(La^4)	$[La(L^4)_2(NO_3)_3(H_2O)_2]$ $(LaC_{40}H_{50}N_5O_{13})$	949.18 (947.26)	70	240	14.76 (14.66)	50.15 (50.67)	5.56 (5.32)	7.76 (7.39)	4.7
(La^5)	$[La(L^5)_2(NO_3)_3(H_2O)_2]$ $(LaC_{38}H_{46}N_5O_{13})$	921.56 (919.23)	80	> 240	15.25 (15.11)	49.50 (49.61)	5.16 (5.04)	7.57 (7.62)	5.2
(La^6)	$[La(L^6)_2(NO_3)_3(H_2O)_2]$ $(LaC_{36}H_{42}N_5O_{13})$	893.76 (891.20)	65	> 300	15.89 (15.59)	48.74 (48.47)	4.38 (4.75)	7.68 (7.86)	3.5
(La^7)	$[La(L^7)_2(NO_3)_3(H_2O)_2]$ $(LaC_{38}H_{46}N_5O_{13})$	918.37 (919.23)	70	> 300	15.35 (15.11)	49.84 (49.67)	5.37 (5.04)	7.86 (7.62)	4.6
(La^8)	$[La(L^8)_2(NO_3)_3(H_2O)_2]$ $(LaC_{40}H_{46}N_5O_{13})$	949.00 (947.26)	70	> 300	14.25 (14.66)	50.46 (50.67)	5.53 (5.32)	7.66 (7.39)	5.7
(La^9)	$[La(L^9)_2(NO_3)_3(H_2O)_2]$ $(LaC_{42}H_{54}N_5O_{13})$	977.75 (975.29)	65	> 320	14.28 (14.24)	51.76 (51.68)	5.86 (5.58)	7.63 (7.18)	6.8
(La^{10})	$[La(L^{10})_2(NO_3)_3(H_2O)_2]$ $(LaC_{40}H_{46}N_5O_{13})$	949.37 (947.26)	70	> 320	14.37 (14.66)	50.53 (50.67)	5.46 (5.32)	7.57 (7.39)	7.9

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF THE LANTHANUM(III) CHLORIDE COMPLEXES

Complex		m.w., Found (Calcd.)	Yield (%)	Decomp. temp. (°C)	Element, Found (Calcd.) (%)				Conductance (ohm^{-1} cm^2 mol^{-1})
No.	Formula (Empirical formula)				La	C	H	N	
(La^{11})	[La(L^1)(Cl)$_3$(H$_2$O)$_4$] (C$_{17}$H$_{25}$NO$_3$Cl$_3$La)	570.85 (568.45)	70	> 300	24.25 (24.31)	36.00 (35.89)	4.50 (4.43)	2.57 (2.46)	2.7
(La^{12})	[La(L^2)(Cl)$_3$(H$_2$O)$_4$] (C$_{18}$H$_{27}$NO$_5$Cl$_3$La)	584.75 (582.47)	90	220	23.65 (23.72)	37.10 (37.08)	4.75 (4.67)	2.50 (2.40)	7.2
(La^{13})	[La(L^3)(Cl)$_3$(H$_2$O)$_4$] (C$_{19}$H$_{29}$NO$_5$Cl$_3$La)	597.25 (596.49)	85	210	23.00 (23.17)	38.05 (38.22)	5.00 (4.90)	2.25 (2.35)	2.1
(La^{14})	[La(L^4)(Cl)$_3$(H$_2$O)$_4$] (C$_{20}$H$_{31}$NO$_5$Cl$_3$La)	612.25 (610.50)	80	> 260	22.56 (22.64)	39.45 (39.31)	5.26 (5.12)	2.46 (2.29)	1.5
(La^{15})	[La(L^5)(Cl)$_3$(H$_2$O)$_4$] (C$_{19}$H$_{29}$NO$_5$Cl$_3$La)	595.75 (596.49)	90	240	23.34 (23.17)	38.51 (38.22)	4.76 (4.90)	2.53 (2.35)	3.5
(La^{16})	[La(L^6)(Cl)$_3$(H$_2$O)$_4$] (C$_{18}$H$_{27}$NO$_5$Cl$_3$La)	584.20 (582.47)	70	> 240	23.95 (23.72)	37.00 (37.08)	4.76 (4.67)	2.52 (2.40)	2.6
(La^{17})	[La(L^7)(Cl)$_3$(H$_2$O)$_4$] (C$_{19}$H$_{29}$NO$_5$Cl$_3$La)	598.17 (596.49)	75	> 240	23.25 (23.17)	38.00 (38.22)	4.75 (4.90)	2.47 (2.35)	3.5
(La^{18})	[La(L^8)(Cl)$_3$(H$_2$O)$_4$] (C$_{20}$H$_{31}$NO$_5$Cl$_3$La)	612.00 (610.50)	75	> 300	22.76 (22.64)	39.76 (39.31)	5.45 (5.12)	2.15 (2.29)	4.5
(La^{19})	[La(L^9)(Cl)$_3$(H$_2$O)$_4$] (C$_{21}$H$_{33}$NO$_5$Cl$_3$La)	626.15 (624.52)	70	> 280	22.35 (22.13)	40.56 (40.35)	5.75 (5.32)	2.47 (2.24)	2.1
(La^{20})	[La(L^{10})(Cl)$_3$(H$_2$O)$_4$] (C$_{20}$H$_{31}$NO$_5$Cl$_3$La)	609.85 (610.50)	75	> 240	22.85 (22.64)	39.95 (39.31)	5.37 (5.12)	2.66 (2.29)	3.7

TABLE-3

IMPORTANT IR ABSORPTION BANDS (cm^{-1}) OF THE LIGANDS AND LANTHANUM(III) NITRATE COMPLEXES

Complex No.	$\nu(C{=}O)^a$	$\nu(C{=}O)^b$	ν(N—H)	ν(O—H)	δ(HOH)	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5	$(\nu_4-\nu_1)$	$(\nu_3-\nu_5)$
(La^1)	1700 s	1720 s	3500 s	3200–3600 b	1637 m	1480 s	1302 s	1053 m	818 w	—	—	178	—
(La^2)	1699 s	1726 s	3545 s	3200–3600 b	1624 m	1480 s	1302 s	1051 m	818 w	752 s	700 s	178	52
(La^3)	1701 s	1730 s	3545 s	3200–3600 b	1637 m	1468 s	1298 s	1051 m	816 w	—	—	170	—
(La^4)	1700 s	1728 s	3543 s	3200–3600 b	1639 m	1480 s	1302 s	1038 m	818 w	750 s	698 s	178	52
(La^5)	1701 s	1732 s	3545 s	3200–3600 b	1624 m	1480 s	1300 s	1051 m	818 w	—	—	180	—
(La^6)	1726 s	1730 s	—	3200–3600 b	1624 m	1480 s	1302 s	1039 m	817 w	—	—	178	—
(La^7)	1722 s	1727 s	—	3200–3600 b	1637 m	1480 s	1300 s	1051 m	818 w	—	—	180	—
(La^8)	1720 s	1725 s	—	3200–3600 b	1637 m	1480 s	1302 s	1040 m	816 w	—	—	178	—
(La^9)	1710 s	1718 s	—	3200–3600 b	1624 m	1480 s	1300 s	1051 m	818 w	—	—	180	—
(La^{10})	1713 s	1722 s	—	3200–3600 b	1624 m	1480 s	1301 s	1038 m	815 w	—	—	179	—

[a] for ligands, [b] for complexes, s = strong, b = broad, m = medium, w = weak

and the magnitude of this shift depends on the size of the anion[13] and decreases as $Cl^- > NO_3^-$. Forsberg and Moeller observed similar results[14]. The Bohlmann bands[15] which occur in the region 3000–2800 cm^{-1} were found to be absent in the IR spectra of the corresponding complexes. The absence of these bands reveals that there may be a conformational change of piperidinone ring due to its complexation with the lanthanum ion through the lone pair of electrons of ring nitrogen. Thus it is concluded that the ring nitrogen is coordinated to lanthanum(III) ion with some conformational change. In the case of NCH_3 containing ligands (L^6–L^{10}), in addition to the absence of Bolhmann bands, the absorption due to the C—H stretching frequencies of NCH_3 are also shifted to higher frequency in the corresponding complexes, suggesting the involvement of ring nitrogen in complexation.

TABLE-4

IMPORTANT IR ABSORPTION BANDS (cm^{-1}) OF THE LIGANDS AND LANTHANUM(III) CHLORIDE COMPLEXES

Complex	ν(C═O)[a]	ν(C═O)[b]	ν(N—H)	ν(O—H)	δ(HOH)
(La^{11})	1700 s	1720 s	3220 s	3000–3600 b	1640 s
(La^{12})	1699 s	1722 s	3227 s	3000–3600 b	1624 s
(La^{13})	1701 s	1724 s	3225 s	3000–3600 b	1624 s
(La^{14})	1700 s	1725 s	3215 s	3000–3600 b	1640 s
(La^{15})	1701 s	1724 s	3215 s	3000–3600 b	1630 s
(La^{16})	1726 s	1729 s	—	3000–3600 b	1625 s
(La^{17})	1722 s	1730 s	—	3000–3600 b	1636 s
(La^{18})	1720 s	1725 s	—	3000–3600 b	1640 s
(La^{19})	1710 s	1720 s	—	3000–3600 b	1636 s
(La^{20})	1713 s	1720 s	—	3000–3600 b	1630 s

[a]for ligands, [b]for complexes, s = strong, b = broad

The carbonyl stretching frequency of the ligands (L^1–L^5) appears around 1700 cm^{-1}. This absorption is shifted to higher frequency by about 20–31 cm^{-1} in the corresponding complexes (La^1–La^5) and (La^{11}–La^{15}). The higher frequency shift indicates that the carbonyl group is not involved in complexation. The higher frequency shift may be due to conformational changes that occur as a result of coordination of the ring nitrogen. The corresponding shift in the complexes (La^6–La^{10}) and (La^{16}–La^{20}) are found to be only 5–10 cm^{-1}. This suggests that the conformational change is larger for piperidin-4-ones containing N—H group than for those containing NCH_3 group. This may be due to the difference in the preferential orientation of the nitrogen lone pair in these two types of piperidin-4-ones[16].

A broad absorption band in the region 3600–3200 cm^{-1} due to (O—H) stretching vibration (merged with NH absorption) and a medium intensity band around 1630 cm^{-1} due to (H—O—H) bending vibration[17] are indicative of the presence of water molecules in these complexes. In addition to these two bands, another sharp medium intensity band in the region around 615 cm^{-1} is observed in the spectra of La(III) nitrate complexes This new band may be assigned for the rocking mode of vibration of water molecules.

Analysis of the IR spectra of lanthanum(III) nitrate complexes with respect to nitrate group reveals that (i) the peak around 1380 cm^{-1} due to ionic nitrate group[17] is absent in the spectra of all the complexes and (ii) the magnitudes of $(\nu_4 - \nu_1)$ and $(\nu_3 - \nu_5)$ are 170–180 cm^{-1} and 52–89 cm^{-1}, respectively, indicating the presence of bidentate nitrate groups. Thus, it is concluded that all the three nitrate groups in these complexes are coordinated with La(III) ions in a bidentate manner[18, 19].

The band observed in the region 550–543 cm^{-1} and 420–415 cm^{-1} is attributed to (La—N) and (La—O) bonding, respectively[20]. The IR spectra of lanthanum(III) chloride complexes exhibit an additional band around 510 cm^{-1} which may be assigned to (La—Cl) bond.

The ^1H NMR data in DMSO-d_6 as solvent for the ligand (L^2) and its diamagnetic lanthanum(III) nitrate complex (La^2) are presented in Table-5. Analysis of the spectral data reveals that the signals H(2), H(6) and N—H and aromatic protons are shifted downfield in the complex. The ring nitrogen atom acquires a partial positive charge when its lone pair of electrons is involved in coordination and, consequently, the electron withdrawing nature of nitrogen is increased. This explains the observed downfield shifts. The signals of H(3), H(5) and C(3)-CH_3 protons are found to be slightly upfield. This may be due to the change in conformation of the piperidin-4-one ring as a result of complexation. The presence of water in this complex is indicated by the proton signal at δ 3.18.

TABLE-5
^1H NMR SPECTRAL DATA OF THE LIGAND (L^2) AND COMPLEX (La^2)

Compd.	H(2)	H(3) and H(5)	H(6)	C(3)-CH_3	NH	Aromatic protons
(L^2)	3.55 (d, 1H)	2.54–2.66 (m, 3H)	4.00 (dd, 1H)	0.80 (d, 3H)	2.04 (s, 1H)	7.20–7.42 (m, 10H)
(La^2)	4.78 (s, 1H)	2.51–2.70 (m, 3H)	4.78 (s, 1H)	0.76 (d, 3H)	Same as H(3) and H(5)	7.40–7.57 (m, 10H)

The ^{13}C NMR data in DMSO-d_6 as solvent for the ligand (L^2) and the corresponding lanthanum(III) nitrate complex (La^2) are recorded in Table-6. A perusal of the spectral data indicates that the C(4) (carbonyl carbon) signal has not undergone any change in the complex suggesting that the carbonyl group is not involved in complex formation. Thus, both ^{13}C NMR and IR spectral observations complement each other in explaining the non-participation of the carbonyl group in complex formation. The other carbon signals show only a marginal shift and this may probably be due to the change in conformation. The downfield shift of the H(2) and H(6) ^1H NMR signals and the upfield shift of the ^{13}C NMR signals of C(2) and C(6) in the complex show that the heterocyclic ring deviates from the normal chair conformation on complexation[21].

Thermal curves (TG-DTA) of all the lanthanum(III) nitrate complexes are similar. The thermal data of a few complexes are given in Table-7. A thorough scrutiny of the thermal curves indicates that these complexes undergo decomposition in four steps. The thermal curves of (La^2) and (La^4) show an endothermic peak at 173 and 186°C, respectively. The mass loss at this temperature corresponds to two coordinated water molecules[22]. The loss of piperidin-4-one molecules takes place in the second step of decomposition. This is shown by an exothermic curve in the temperature range 275–300°C. Generally, the decompositions of the organic ligands of lanthanide(III) complexes are violently exothermic while the corresponding complexes containing metal ions other than lanthanides show only endothermic effects[23]. This violent reaction may be attributed to the high oxygen content of the anion (NO_3^-) present in these complexes[24, 25]. The residue, lanthanum(III) nitrate, undergoes decomposition in the next step. This is shown by a very strong exothermic peak in the region between 400–500°C. The residue corresponds to lanthanum oxide nitrate, $La_5O_7(NO_3)$. It has also been reported[26] that lanthanum(III) nitrate on thermal decomposition gives lanthanum(III) oxide through the formation of lanthanum oxide nitrate. Finally, $La_5O_7(NO_3)$ undergoes further decomposition in the temperature range 650–750°C giving rise to La_2O_3.

TABLE-6

^{13}C NMR SPECTRAL DATA OF THE LIGAND (L^2) AND COMPLEX (La^2)

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(3)—CH_3	Aromatic carbons
(L^2)	68.53	51.43	209.20	50.73	61.79	10.10	142.67, 141.79, 128.48, 128.35, 127.81, 127.58, 126.38
(La^2)	66.48	52.72	209.42	51.90	59.60	10.50	136.27, 135.42, 129.98, 128.88, 128.72, 128.02, 127.40

The changes observed in the decomposition of these complexes are represented by the following sequence of reactions:

$$[La(L)_2(NO_3)_3(H_2O)_2] \xrightarrow[-2H_2O]{170\text{–}186^\circ C} [La(L)_2(NO_3)_3] \xrightarrow[-2L]{275\text{–}300^\circ C} La(NO_3)_3$$

$$\xrightarrow{400\text{–}500^\circ C} La_5O_7NO_3 \xrightarrow{650\text{–}750^\circ C} La_2O_3$$

Thermal analyses have not been carried out for lanthanum(III) chloride complexes because of their hygroscopic nature.

TABLE-7

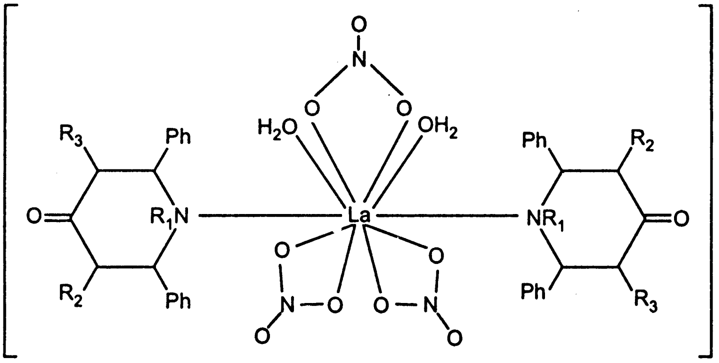
THERMAL ANALYSIS DATA OF THE LANTHANUM(III) NITRATE COMPLEXES[a]

Complex		DTA peak temp. (°C)	Thermogravimetry		Decomposition product
No.	Formula		TG Temp. Range (°C)	Weight loss Found (Calcd.) %	
(La^2)	$[La(C_{18}H_{19}NO)_2(NO_3)_3(H_2O)_2]$	173+	170–190	4.00 (4.04)	$[La(C_{18}H_{19}NO)_2(NO_3)_3]$
		248–	200–300	63.00 (63.54)	$La(NO_3)_3$
		422–	400–500	80.50 (80.51)	$La_5O_7NO_3$
		473–			
		751–	700–775	82.00 (81.72)	La_2O_3
(La^3)	$[La(C_{19}H_{21}NO)_2(NO_3)_3(H_2O)_2]$	185+	175–190	4.00 (3.92)	$[La(C_{19}H_{21}NO)_2(NO_3)_3]$
		329–	320–400	65.00 (64.66)	$La(NO_3)_3$
		353–			
		517–	450–650	81.00 (81.10)	$La_5O_7NO_3$
		630–			
		736–	650–750	82.00 (82.28)	La_2O_3
(La^4)	$[La(C_{20}H_{23}NO)_2(NO_3)_3(H_2O)_2]$	186+	170–200	4.00 (3.80)	$[La(C_{20}H_{23}NO)_2(NO_3)_3]$
		279–	250–300	66.00 (65.70)	$La(NO_3)_3$
		331–	300–425	82.00 (81.66)	$La_5O_7NO_3$
		449–			
		705–	650–750	83.00 (82.80)	La_2O_3
(La^5)	$[La(C_{19}H_{21}NO)_2(NO_3)_3(H_2O)_2]$	195+	185–200	4.00 (3.92)	$[La(C_{19}H_{21}NO)_2(NO_3)_3]$
		275–	250–300	64.50 (64.66)	$La(NO_3)_3$
		361–	350–500	81.00 (81.10)	$La_5O_7NO_3$
		472–			
		710–	650–750	82.00 (82.28)	La_2O_3
(La^8)	$[La(C_{20}H_{23}NO)_2(NO_3)_3(H_2O)_2]$	176+	170–190	4.00 (3.80)	$La(C_{20}H_{23}NO)_2(NO_3)_3$
		315–	300–450	65.25 (65.70)	$La(NO_3)_3$
		427–			
		516–	500–650	82.00 (81.66)	$La_5O_7NO_3$
		623–			
		732–	700–750	83.00 (82.80)	La_2O_3
(La^9)	$[La(C_{21}H_{25}NO)_2(NO_3)_3(H_2O)_2]$	195+	180–200	4.00 (3.69)	$[La(C_{21}H_{25}NO)_2(NO_3)_3]$
		328–	300–450	67.00 (66.68)	$La(NO_3)_3$
		434–			
		556–	525–650	82.00 (82.19)	$La_5O_7NO_3$
		635–			
		705–	700–725	84.00 (83.30)	La_2O_3

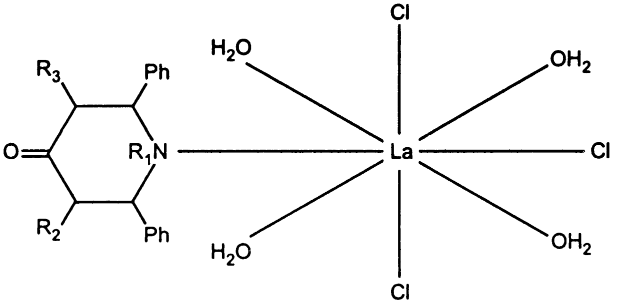
+ Endothermic; – Exothermic.

Conclusions

The formulae assigned for lanthanum(III) nitrate and chloride complexes, namely, $[La(L)_2(NO_3)_3(H_2O)_2]$ and $[La(L)Cl_3(H_2O)_4]$, respectively, are in accordance with the elemental analyses, conductance and thermal data. IR spectral studies indicate the absence of ionic nitrate groups. The IR and NMR spectral data suggest that the coordinating site of piperidin-4-one is only the ring nitrogen and not the carbonyl group. The IR spectra and thermal curves of these complexes show the coordination of water molecules. All these observations lead to the conclusion that La(III) ion is 10-coordinate in nitrate complexes and 8-coordinate in chloride complexes. The following probable structures are suggested for the nitrate and chloride complexes.



Structure of La(III) chloride complexes



Structure of La(III) nitrate complexes

ACKNOWLEDGEMENTS

We thank Dr. B. Sampath Kumar, Principal and Secretary, PSG College of Arts and Science for providing facilities. We also thank Tamilnadu State Government for the award of scholarship to C. Theivarasu.

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(*Received*: 27 September 2003; *Accepted*: 3 March 2004) AJC-3366