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Synthesis and Physico-chemical Investigations of Some Seven Coordinated Complexes of Lanthanides(III) Chloride Derived from Hydrazones of Isonicotinic Acid Hydrazide

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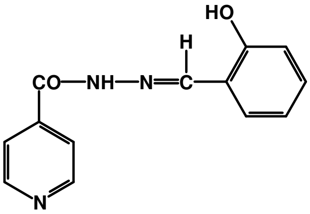
The present work describes the synthesis of lanthanide(III) chloride coordination complexes of hydrazones of isonicotinic acid hydrazide *viz.*, N-isonicotinamido-2-hydroxybenzalaldimine (INH-SAL), N-isonicotinamido-3-methoxy-4-hydroxybenzalaldimine (INH-VAN), N- isonicotinamido-2-hydroxy-1-naphthalaldimine (INH-Naph) with with general composition $[Ln(L)_2Cl_3]$ (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy; L = INH-SAL, INH-VAN or INH-Naph). All these coordination compounds were characterized by elemental analyses, molar mass determination, magnetic susceptibility, infrared and electronic spectra. The infrared studies show that all the three hydrazones behave as bidentate with carbonyl-oxygen and azomethine nitrogen as two coordination sites. In all these coordination compounds the central metal displays a coordination number seven. Thermal properties of these compounds were also investigated.

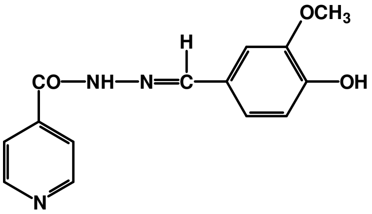
Key Words: Lanthanide(III), Hydrazones, Complexes.

INTRODUCTION

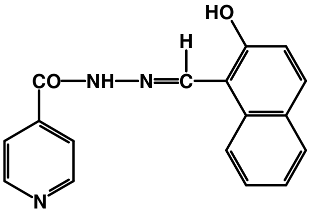
The stereochemistry of the lanthanide(III) has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed[1,2]. This structural versatility arises from the lack of strong crystal field effects for the 4*f* electronic configurations as well as from the large ionic radii of these metal ions which change markedly with either oxidation number or atomic number for lanthanides (III)[3]. Because of their large size, the lanthanide ions generally have higher coordination number varying from 6 to 10. In present work we describe some seven coordinated complexes of lanthanides(III) chlorides derived from hydrazones of isonicotinic acid hydrazide, *viz.*, N-isonicotinanido-2′-hydroxybenzalaldimine (INH-SAL), N-isonicotinamido-3′-methoxy-4′-hydroxybenzalaldimine (INH-VAN) and N-isonicotnamido-2′-hydroxy-1′-naphthalaldimine (INH-Naph) (Fig. 1).



N-Isonicotinamido-2-hydroxybenzalaldimine (INH-SAL)



N-Isonicotinamido-3-methoxy-4-hydroxybenzalaldimine (INH-VAN)



N-Isonicotinamido-2′-hydroxy-1′-naphthalaldimine (INH-Naph)

Fig. 1.

EXPERIMENTAL

The lanthanide(III) chlorides were obtained from Rare Earth Products Ltd. (India) and were used without further purification. All the three hydrazones of isonicotinic acid hydrazide, *i.e.* INH-SAL, INH-VAN and INH-Naph were synthesized in the laboratory by following general method. Isonicotnic acid hydrazide (0.01 mol) was dissolved in 25 mL of 95 % alcohol. To this solution, aromatic aldehydes, *viz.*, salicylaldehyde, vanillin or 2-hydroxy-1'-naphthaldehyde (0.01 mL) was added in 95 % ethanol (25 mL). The reaction mixture was refluxed on a water bath for about 2 h. The partial removal of solvent on a water bath followed by cooling produced crystalline product, which was suction filtered, washed with cold alcohol and dried under vacuum (yield ~ 80-85 %).

Synthesis of the coordination compounds

[$LnCl_3$.2(INH-SAL] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy): All the complexes were synthesized as follows the solution of respective lanthanide(III) chloride (1 mmol) and the ligand (2.1 mmol) in hot methanol

(15 mL each) were mixed and refluxed on a water bath for *ca.* 2 h. On cooling in an ice bath, the resulting solid complex was separated out. It was repeatedly washed with diethyl-ether and dried in a desiccator over P_4O_{10}.

[$LnCl_3$.2(INH-VAN] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy): A methanolic solution of the ligand was refluxed for 1 h and then a methanolic solution of the trivalent lanthanide chloride was added (metal to ligand in 1:2 molar ratio). The reaction mixture was refluxed for *ca.* 2 h and then kept for slow heating on the hot plate till a thick layer of the precipitate settled down. The supernatent liquid was decanted off and the product was dried. It was then washed several times with methanol to remove any excess of the metal chloride and/or ligand. Finally the complexes were dried *in vacuo* over P_4O_{10}.

[$LnCl_4$.2(INH-Naph] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy): All the complexes of INH-Naph were synthesized by the following method. The corresponding metal chloride (1 m mol) was dissolved in anhydrous ethanol (20 mL) and added to the refluxing solution of the ligand (2 mol) in anhydrous ethanol (30 mL). The reaction mixture was refluxed for *ca.* 2-3 h, when a coloured mass separated out. The precipitate was filtered off, washed with ethanol and ether and finally dried *in vacuo* over P_4O_{10}.

Physico-chemical techniques: The lanthanide metal contents was estimated as its oxide by direct combustion in a platinum crucible. The estimation was further confirmed by dissolving the product of direct combustion in dil. HCl. The acid extract was transferred into a flask, pH was adjusted to 5.5-6.4 by the addition of acetic acid-sodium acetate buffer and was then titrated against 0.1M EDTA using xylenol-orange as an indicator. The results from both the methods were compared and found within the experimental errors. Nitrogen was esximated in the laboratory by the Kjeldahl method. The chlorine was estimated by Volhard's method[4]. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy ± 0.01 ºC in the laboratory. The conductivity measurements were carried out using a Toshniwal conductivity Bridge (type CL 01/01) and a dip type cell operated at 230 volts AC mains. All the measurments were done at room temperature in $PhNO_2$. The magnetic measurements were carried out at room temperature with Evan's balance and anhydrous copper sulfate was used as a calibrant. The infrared spectra of the complexes were recorded on a Perkin-Elmer infrared spectrometer model 521 in CsI in the range of 4000-200 cm^{-1} at C.D.R.I., Lucknow, India. A Hilger Unispek spectrophotometer with 1 cm quartz cell was employed for recording the visible spectra of Pr^{3+}, Nd^{3+} and Sm^{3+} complexes. Thermogravimetric analysis was carried out in static air with open sample holder and a small paltinum boat, the heating rate was 6º min^{-1}.

RESULTS AND DISCUSSION

The reaction of non-aqueous solution of lanthanide(III) chlorides with INH-SAL, INH-VAN or INH-Naph resulting complexes of the general composition $[Ln(L)_2Cl_3]$ (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy; L = INH-SAL, INH-VAN or INH-Naph). The analytical data of the present complexes are presented in Table-1. The complexes are anhydrous which is evident from analytical, infrared and thermal studies. All these complexes are quite stable and can be stored for long period. The complexes are generally soluble in common organic solvents but partially soluble in diethyl-ether. TG curves indicate no changes upto 130 ºC, suggesting the absence of either coordinated or uncoordinated water molecule in these complexes. The molar conductance of these complexes in nitrobenzene are presented in Table-1. The molar conductance values are too low to account for any dissociation, therefore, the complexes are non-electrolytes. Data on the molecular weight of the complexes in nitrobenzene are given in Table-1 along with the values calculated on the basis of established formula of the complexes. The ratio of molecular weight observed for $LnCl_3.2L$ to that calcualted is *ca.* 0.98 which shows that the complexes are monomeric in nature.

The magnetic moment values observed in present lanthanide coordination compounds are given in Table-1 show that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons. All other tripositive lanthanide ions are paramagnetic due to the presence of 4*f*-electrons, which are effectively shielded by $5s^2$ $5p^6$ electrons. The comparison of these observed values with those observed for 8-hydrated sulfate[5] and those calculated for uncomplexed ion[6] indicates that the 4*f*-electrons do not participate in any bond formation of these complexes[7,8]. The magnetic moments of the present complexes (Table-1) are within the range predicted and observed in the compounds of paramagnetic ions as reported earlier[9,10].

Infrared spectra: All the three hydrozones are expected to act as tridentate one, the possible coordination sites being pyridine-nitrogen, azomethine-nitrogen and amide group. The infrared frequencies in the present ligands associated with amide group (carbonyl-oxygen), azomethine-nitrogen (C = N) and hetrocyclic-nitrogen are expected to lie influenced on complex formation with metal ions have been discussed.

Generally all amides, show two absorption bands, (i) the carbonyl absorption band near 1640 cm^{-1} known as amide-I band and (ii) strong band in the 1600-1500 cm^{-1} region, known as amide-II band. The origin of these bands in hydrazides, the carbonyl absorption, responsible for the amide-I band is likely to be lowered in frequently by the NH group as in normal amides[11]. The amide-I band in isonicotinoylhydrazine derivatives, however,

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF LANTHANIDE(III) CHLORIDE COMPLEXES

Complex	Elemental analysis (%): Found (Calcd.)			Ω M (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)	m.w.
	M	N	Cl			
$LaCl_3$.2(INH-SAL)	18.92 (19.10)	11.49 (11.54)	14.57 (14.63)	3.2	Diamag	727.5 (722.0)
$PrCl_3$.2(INH-SAL)	19.27 (19.32)	11.47 (11.51)	14.51 (14.59)	3.6	3.60	729.5 (724.0)
$NdCl_3$.2(INH-SAL)	19.59 (19.65)	11.40 (11.46)	14.47 (14.53)	4.1	3.58	732.5 (728.0)
$SmCl_3$.2(INH-SAL)	20.26 (20.31)	11.31 (11.37)	14.36 (14.42)	3.7	1.66	738.5 (731.0)
$GdCl_3$.2(INH-SAL)	20.98 (21.05)	11.21 (11.26)	14.22 (14.28)	3.3	7.90	745.5 (739.0)
$TbCl_3$.2(INH-SAL)	21.19 (21.27)	11.18 (11.23)	14.19 (14.24)	3.5	9.25	747.5 (743.0)
$DyCl_3$.2(INH-SAL)	21.57 (21.63)	11.12 (11.18)	14.12 (14.18)	4.3	10.53	751.0 (745.0)
$LaCl_3$.2(INH-VAN)	17.59 (17.65)	10.61 (10.66)	13.46 (13.52)	3.9	Diamag	787.5 (782.0)
$PrCl_3$.2(INH-VAN)	17.78 (17.85)	10.58 (10.63)	13.41 (13.48)	3.7	3.62	789.5 (784.0)
$NdCl_3$.2(INH-VAN)	18.08 (18.17)	10.53 (10.59)	13.36 (13.43)	4.1	3.52	792.5 (786.0)
$SmCl_3$.2(INH-VAN)	18.70 (18.78)	10.46 (10.51)	13.28 (13.33)	3.8	1.60	798.5 (793.0)
$GdCl_3$.2(INH-VAN)	19.43 (19.49)	10.36 (10.42)	13.16 (13.22)	3.6	7.95	805.5 (799)
$TbCl_3$.2(INH-VAN)	19.64 (19.69)	10.35 (10.40)	13.11 (13.18)	3.5	9.18	807.5 (802)
$DyCl_3$.2(INH-VAN)	19.98 (20.03)	10.29 (10.35)	13.07 (13.13)	4.2	10.78	811.0 (805)
$LaCl_3$.2(INH-Naph)	16.71 (16.79)	10.10 (10.15)	12.78 (12.87)	3.8	Diamag	827.5 (822)
$PrCl_3$.2(INH-Naph)	16.92 (16.99)	10.05 (10.12)	12.75 (12.83)	4.1	3.59	829.5 (825)
$NdCl_3$.2(INH-Naph)	17.22 (17.29)	10.03 (10.09)	12.70 (12.79)	3.7	3.64	832.5 (826)
$SmCl_3$.2(INH-Naph)	17.74 (17.88)	9.95 (10.01)	12.63 (12.70)	4.2	1.62	838.5 (832)
$GdCl_3$.2(INH-Naph)	18.49 (18.56)	9.87 (9.93)	12.50 (12.59)	2.9	7.92	845.5 (839)
$TbCl_3$.2(INH-Naph)	18.68 (18.76)	9.84 (9.91)	12.47 (12.56)	4.1	9.21	847.5 (841)
$DyCl_3$.2(INH-Naph)	18.98 (19.09)	9.82 (9.87)	12.43 (12.51)	3.9	10.82	851.0 (846)

TABLE-2
KEY INFRARED BANDS (cm^{-1}) OF LANTHANIDE(III) CHLORIDE COMPLEXES OF HYDRAZONES OF ISONICOTINIC ACID HYDRAZIDE

Compound	ν(OH)	ν(NH) asym & sym	Amide-I	ν(C = N) (azomethine)	Amide-II + δ(NH)	ν(Ln-N) /ν(Ln-O)
(INH-SAL)	3405 m 3380 m	3290 m 3220 m	1660 vs	1620 vs	1560 s 1550 s	-
LaCl$_3$.2(INH-SAL)	3405 m 3382 m	3292 m 3220 m	1620 vs	1560 s	1550 w 1525 m	440 w 370 w
PrCl$_3$.2(INH-SAL)	3402 m 3380 m	3290 m 3220 m	1610 vs	1565 s	1530 vs	450 m, br 360 w
NdCl$_3$.2(INH-SAL)	3402 m 3382 m	3295 m 3220 m	1620 vs	1570 s	1555 s	430 w 360 w
SmCl$_3$.2(INH-SAL)	3400 m 3380v	3290 m 3222 m	1600 vs,br	1570 s	1525 m	460 m 360 w
GdCl$_3$.2(INH-SAL)	3405 m 3382 m	3292 m 3222 m	1600 vs,br	1572 s	1535 sh	430 m 365 w
TbCl$_3$.2(INH-SAL)	3405 m 3380 m	3295 m 3220 m	1600 vs,br	1560 s	1530 sh 1575 m	455 m 360 w
DyCl$_3$.2(INH-SAL)	3402 m 3382 m	3292 m 3220 m	1605 s	1572 s	1525 m	440 w 370 w
(INH-VAN)	3480 m 3420 w	3300 m 3220 w	1670 vs 1630 vs	1585 s	1540 m 1530 m	-
LaCl$_3$.2(INH-VAN)	3482 m 3420 w	3305 m 3222 w	1650 s 1598 s	1540 s	1538 m 1525 sh	450 m 375 w
PrCl$_3$.2(INH-VAN)	3480 m 3423 w	3300 m 3200 w	1620 s	1530 s	1522 m 1520 sh	440 m 380 w
NdCl$_3$.2(INH-VAN)	3482 m 3422 w	3302 m 3220 w	1612 s	1532 s	1522 m 1510 sh	442 m 378 w
SmCl$_3$.2(INH-VAN)	3480 m 3420 w	3300 m 3222 w	1617 s	1530 s	1520 m 1505 sh	437 m 375 w
GdCl$_3$.2(INH-VAN)	3482 m 3425 w	3302 m 3222 w	1610 s	1500 vs,br	1510 m 1502 sh	430 m 380 w
TbCl$_3$.2(INH-VAN)	3480 m 3420 w	3303 m 3220 w	1617 vs	1532 s	1510 m 1500 sh	432 m 382 w
DyCl$_3$.2(INH-VAN)	3482 m 3420 w	3302 m 3220 w	1615 s	1537 s	1512 m 1500 sh	422 m 382 w
(INH-Naph)	3410 m 3382 m	3290 m 3225 m	1660 vs	1590 s	1560 m 1550 sh	-
LaCl$_3$.2(INH-Naph)	3439 s 3382 m	3292 s 3216 m	1637 s 1605 m	1542 m	1557 sh	410 w 375 w
PrCl$_3$.2(INH-Naph)	3417 s 3385 m	3290 s 3230 m	1636 s	1570 s	1555 sh	405 w 382 w
NdCl$_3$.2(INH-Naph)	3412 m 3380 m	3292 m 3225 m	1635 s	1567 s	1555 m	410 w 370 w
SmCl$_3$.2(INH-Naph)	3430 m 3390 m	3292 m 3240 m	1630 s 1605 s	1547 s	1555 sh	410 m 375 w
GdCl$_3$.2(INH-Naph)	3428 s 3380 m	3290 m 3230 m	1638 m 1608 s	1548 s	1552 sh	415 w 380 w
TbCl$_3$.2(INH-Naph)	3412 m 3382 m	3292 m 3225 m	1632 s	1547 s	1552 m	405 w 370 w
DyCl$_3$.2(INH-Naph)	3415 m 3380 m	3290 m 3220 m	1335 s	1545 s	1550 sh	410 w 382 w

appear at 1660-1640 cm^{-1}. In the infrared spectra of the complexes a considerable negative shift in ν(C = O) is observed indicating a decrease in the stretching force-constant of C=O as a consequence of coordination through the carbonyl oxygen atom of the free base. The amide-II band appears at the normal position in the NH-deformation rather than C-N link. In isonicotinoyl-hydrazine derivatives, the absorption in 1565-1560 cm^{-1} region has been assigned to amide-II absorption. The NH stretching absorption in free ligands occur[12] at *ca.* 3290 and 3220 cm^{-1} which remains unaffected after complexation. This precludes the posibility of coordination tarough imine nitrogen atom. Another important band occurs in the range 1590 cm^{-1} attibuted to ν(C = N) (azomethine) mode[13,14]. In spectra of all the complexes this band is shifted to lower wave number and appears in 1550-1530 cm^{-1} region, respectively indicating the involvement of N-atom of the azomethine group in coordination[13-15]. In spectra of INH-SAL and INH-Naph the stretching frequency at *ca.* 3400 cm^{-1} is attributed to ν(OH). In all the complexes of INH-SAL and INH-Naph the hydroxyl frequency appears at the same region as in the free ligands clearly indicting that the -OH group is not taking part in the coordination. The strong hands observed at 1575-1520 and 1080-1000 cm^{-1} are tentatively assigned[16,17] to asymmetric and symmetric ν(C=C) + ν(C=N) of pyridine ring and pyridine ring breathings and deformations remain practically inchanged in frequency and band intensities revealing non-involvement of pyridinic-nitrogen and metal bond.

The overall infrared spectral evidence suggests that the ligands act as a bidentate ligands and coordinate through amide-oxygen and azomethine nitrogen atoms forming a five membered chelate ring. the far infrared spectral bands in the ligands are practically unchanged in these complexes. But some new bands with medium to weak intensities appear in the region 460-350 cm^{-1} in the complexes under study, which are tentatively assigned to ν(Ln-N)/ν(Ln-O) modes[18-20]. In the present studies ν(Ln-Cl) has been assigned in the 285-270 cm^{-1} region.

Electronic spectra: The spectral data for the solutions of the present lanthanide(III) complexes investigated in acetonitrile are recorded in Table-3 and for comparison, data for an aqueous salt solution are also given. Lanthanum(III) has no significant absorption in the visible region. The absorption bands of praseodymium(III), neodymium(III), samarium(III), gadolinium(III) and dysprosium(III) in the visible and near infrared region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$, $^8S_{7/2}$ and $^6H_{15/2}$ to the excited J-levels of 4*f*-configuration, respectively. Some red shift or nephelauxetic effect is observed in CH_3CN solution of these coordintion compounds. This red shift is usually accepted as an evidence of a higher degree of covalency than existing in the aquo compounds[21,22].

In all the complexes marked enhancement in the intensity of the bond has been observed. This red-shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From these β-values the covalence factor ($b^{1/2}$), Sinha parameter (δ %) (metal-ligand covalency, per cent) and the covalency angular overlap parameter (η) have been calculated using the following expression[22,23].

TABLE-3
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELATED BONDING PARAMETERS OF LANTHANIDE(III) COMPLEXES OF INH-SAL AND INH-VAN

Ln^{3+}	$LnCl_3$ electronic spectral bands	$Ln(L)_2Cl_3$ electronic spectral bands	J-levels	(1-β)	β	$b^{½}$	δ %	η
			INH-SAL Complexes					
Pr^{3+}	22470	22390	$^3H_4 \rightarrow {}^3P_2$	0.00356	0.9964	0.02983	0.3572	0.0019
	21325	21230	$\rightarrow {}^3P_1$	0.00445	0.9955	0.03335	0.4470	0.0023
	20750	20620	$\rightarrow {}^3P_0$	0.00626	0.9937	0.03956	0.6299	0.0032
	17000	16880	$\rightarrow {}^1D_2$	0.00705	0.9929	0.04198	0.7100	0.0036
Nd^{3+}	19550	19480	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.00358	0.0064	0.02991	0.3592	0.0019
	17360	17260	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.00576	0.9942	0.03794	0.5793	0.0030
	13660	13630	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.00219	0.9978	0.02339	0.2194	0.0012
	12470	12430	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.00320	0.9967	0.02828	0.3210	0.0017
Sm^{3+}	24870	24830	$^6H_{5/2} \rightarrow {}^4F_{9/2}$	0.00160	0.9983	0.02000	0.1602	0.0009
	24000	23835	$\rightarrow {}^6P_{5/2}$	0.00687	0.9931	0.04144	0.6917	0.0035
	21550	21520	$\rightarrow {}^4I_{13/2}$	0.00139	0.9986	0.01864	0.1391	0.0008
			INH-VAN Complexes					
Pr^{3+}	22470	22370	$^3H_4 \rightarrow {}^3P_2$	0.00445	0.9955	0.03335	0.4470	0.0023
	21325	21220	$\rightarrow {}^3P_1$	0.00492	0.9950	0.03507	0.4944	0.0026
	20750	20600	$\rightarrow {}^3P_0$	0.00722	0.9927	0.04248	0.7273	0.0037
	17000	16850	$\rightarrow {}^1D_2$	0.00882	0.9911	0.04695	0.8899	0.0045
Nd^{3+}	19550	19460	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.00460	0.9953	0.03391	0.4621	0.0024
	17360	17250	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.00633	0.9936	0.03978	0.6370	0.0033
	13660	13620	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.00292	0.9970	0.02701	0.2928	0.0016
	12470	12410	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.00481	0.9951	0.03467	0.4834	0.0025
Sm^{3+}	24870	24820	$^6H_{5/2} \rightarrow {}^4F_{9/2}$	0.00201	0.9979	0.02241	0.2014	0.0011
	24000	23810	$\rightarrow {}^6P_{5/2}$	0.00791	0.9920	0.04446	0.7979	0.0041
	21550	21510	$\rightarrow {}^4I_{13/2}$	0.00185	0.9981	0.02150	0.1853	0.0010

$$b^{1/2} = \frac{1}{2}\left[(1-\beta)^{1/2}\right]$$

$$\delta(\%) = \left[(1-\beta)/\beta\right] \times 100$$

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

The positive values for (1-β) and d% in these coordination compounds (Table-3) suggest that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were found to be positive indicating covalent bonding.

Thermal studies: $LnCl_3$.2(INH-SAL) (Ln = La, Pr, Gd or Tb): Thermoanalytical results are presented in Table-4. As is clear from the careful analysis of pyrolysis curves, the complexes do not possess water of crystallization. The thermal curves indicate that *ca.* 220 ºC, the compounds start to lose mars with partial evaporation of the organic ligand up to a temperature 285 ºC, the mass loss corresponds to one mole of organic ligand. The residues obtained after heating up to 830 ºC to constant weight are very close to that expected for the lanthanide oxide[24,25].

$LnCl_3$.2(INH-VAN) (Ln = Pr, Nd, Sm or Dy): The weight loss curves of these complexes suggest that they do not show the presence water molecule either in or out of the coordination sphere. The analysis of these curves suggest that above 230 ºC, the compounds start to loss mass with partial evaporation of the organic ligand up to a temperature of 290 ºC. The mass loss corresponds to one molecule of INH-VAN and in the temperature range 360-460 ºC, another molecule of INH-VAN in also lost. The residues obtained after heating up to 825 ºC, to constant weight is very close to that expected for the lanthanide oxides[24,25] (Table-4).

TABLE-4
THERMOANALYTICAL RESULTS OF SOME LANTHANIDE(III) CHLORIDE COMPLEXES OF HYDRAZONES

Complex	Sample weight (mg)	Residual mass (mg)	LIgand mass loss (%)				Residual (%)	
			220-285 ºC*		350-455 ºC†		820 ºC‡	
			Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$LaCl_3$.2(INH-SAL)	25.60	5.64	33.12	33.82	66.25	67.16	22.40	22.06
$PrCl_3$.2(INH-SAL)	29.80	6.83	33.03	33.42	66.07	66.82	23.34	22.94
$GdCl_3$.2(INH-SAL)	2.60	5.63	32.32	32.72	64.65	65.39	24.27	23.86
$TbCl_3$.2(INH-SAL)	21.20	5.25	32.24	32.58	64.48	64.96	25.01	24.78
$PrCl_3$.2(INH-VAN)	22.80	4.87	34.32	34.69	68.65	69.32	21.57	21.36
$NdCl_3$.2(INH-VAN)	28.20	5.89	34.19	34.46	68.39	68.92	21.19	20.92
$SmCl_3$.2(INH-VAN)	30.10	6.47	33.93	34.26	67.87	68.20	21.79	21.52
$DyCl_3$.2(INH-VAN)	25.30	5.72	33.41	33.89	66.83	67.16	22.99	22.62
$LaCl_3$.2(INH-Naph)	22.10	4.28	35.16	35.36	70.33	70.86	19.69	19.40
$PrCl_3$.2(INH-Naph)	26.90	5.37	34.95	35.29	69.90	70.26	20.18	19.98
$GdCl_3$.2(INH-Naph)	24.20	5.12	34.41	34.80	68.83	69.28	21.40	21.18
$TbCl_3$.2(INH-Naph)	29.20	6.36	34.33	34.68	68.67	68.98	22.06	21.80

*Calculated for loss of one molecule of hydrazone.

†Calculated for loss of both molecule of hydrazones.

‡Calculated as lanthanide oxide Ln_2O_3 (Ln - La, Nd or Gd), Tb_4O_7

$LnCl_3.2$(INH-Naph) (Ln = La, Nd, Gd or Tb): The thermogravimetric curves of these complexes indicate that *ca.* 250 ºC, the complexes start to lose mass with partial evaporation of the organic ligand up to the temperatuer of 305 ºC, the loss of mass corresponds to one molecule of organic ligand. At temperature close to 475 ºC, another coordinated organic ligand is also lost (Table-4). The residues obtained after heating *ca.* 830 ºC to constant weight corresponding to lanthanide oxide[24,25].

Stereochemistry: The non-electrolytic behaviour of the complexes suggests that all the chloro ions are coordinated to the central metal ion. The infrared studies reveal that all the three hydrazones, *i.e.*, INH-SAL, INH-VAN and INH-Naph are N,O-donors and coordinated in a bidentate manner. Thus on the basis of stoichlometric ratio of metal to cordinating ligands and other studies, it is revealed that the lanthanide ion is surrounded by 2-oxygen atoms (from carbony group of INH), 2-nitrogen atoms of azomethine groups and 3-anionic chloro ligands produce a coordination number seven for the lanthanide atom[2] Fig. 2.

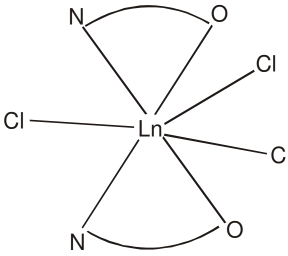


Fig. 2. Proposed structures of $[Ln(L)_2Cl_3]$. (C.N. = 7)

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