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SOME HIGH COORDINATION COMPOUNDS OF LANTHANIDES(III) DERIVED FROM N-ISONICOTINAMIDOSALICYALDIMINE

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ABSTRACT. A new series of lanthanide(III) nitrates, isothiocyanates and perchlorates coordination complexes of N-isonicotinamidosalicyaldimine (INH-SAL) with the general composition $LnX_3.n(INH\text{-}SAL)$ (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy; X = NO_3^-, n = 2; X = NCS^-, n = 2 or 3 and X = ClO_4^-, n = 4) have been reported. All the complexes were characterized by chemical analyses, conductance, molar weight, magnetic moment measurements, infrared and electronic spectra. IR spectra indicate that the ligand behaves as a neutral N,O-donors. Thermal properties of the complexes have also been studied.

INTRODUCTION

Metal coordination compounds of >C=N- containing ligands are known to possess biological activity and are potent inhibitors for many enzymatic reactions [1]. A large number of lanthanide(III) complexes of >C=N- containing chelating agents have been synthesized and studied by several workers [1]. Coordination numbers of lanthanides(III) complexes are usually greater than six and usually vary from six to twelve. This coordination variation in lanthanide complexes is well established and may be attributed to steric factors and electrostatic force of attraction and repulsion's rather than to the directional orientation of bonds by the deep seated 4f-orbitals of metal ion [1]. Thus it is expected that the large lanthanide ions have a tendency to allow accommodation of more than six donor atoms in the coordination sphere. To verify this view in the present work, we wish to report some seven, eight, nine and ten-coordinated complexes of trivalent lanthanide ions with N-isonicotinamidosalicylaldimine (INH-SAL) (Figure 1).

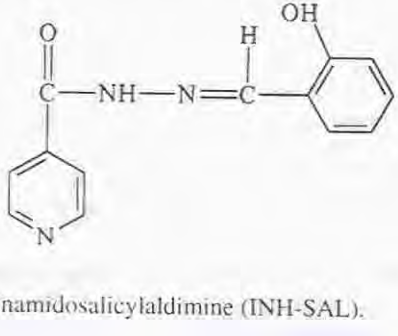


Figure 1. N-Isonicotinamidosalicylaldimine (INH-SAL).

EXPERIMENTAL

Reagents. The lanthanide(III) nitrates and oxides were obtained from Rare Earth Products Ltd. (India) and were used without further purification. The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess acid [2]. The lanthanide isothiocyanates were prepared by adding a warm ethanolic solution of lanthanide nitrates to warm ethanol solution of KCNS. The precipitate of KNO_3 rapidly coagulated. The volume of the solution was reduced on a water bath, cooled, filtered and the filtrate was used for complexation [3]. The ligand (INH-SAL) was prepared in the laboratory as follows: isoniazid (1.1 mmol) was dissolved in 20 mL of 95% ethanol. To this solution, salicyalaldehyde (1 mmol) was added in 95% ethanol (20 mL). The reaction mixture was refluxed on a water bath for ~2 h. The partial removal of the solvent on a water bath, followed by cooling on ice, produced light yellow crystalline product, which was suction filtered, washed with cold alcohol and dried under vacuum over P_4O_{10} (yield ~85%), light yellow crystals, m.p.186 ^{0}C.

Analyses. The carbon, hydrogen and nitrogen analyses of the complexes were performed at micro-analytical laboratory. The metals were estimated as their oxides by direct combustion in a platinum crucible. The molecular weight of the complexes was determined either cryoscopically [4] or by Rast camphor method [4]. The conductivity measurements were carried out using a Toshniwal Conductivity Bridge (Type CI 01\01) and a dip type cell operated at 220 volts AC mains. The magnetic measurements were carried out at room temperature with a Gouy's balance and $[HgCo(SCN)_4]$ was used as a calibrant. The infrared spectra of the complexes were recorded on a Perkins Elmer Infrared Spectrophotometer model 521 in CsI in the range 4000-200 cm^{-1}. A hilger Uvispek spectrophotometer with 1-cm quartz cell was employed for recording the visible spectra of Pr^{3+}, Nd^{3+} and Sm^{3+} complexes. Thermogravimetric analyses of lanthanide(III) complexes was carried out in static air, with open sample holders and a small platinum boat, the heating rate was 6 ^{0}C min^{-1}.

Synthesis of complexes

$Ln(NO_3)_3$.2(INH-SAL) (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy). An ethanolic (95%) solution (20 mL) of the ligand (2.1 mmol) was added with constant stirring to a hot ethanolic solution (10 mL) of respective lanthanide(III) nitrate (1 mmol) and the reaction mixture was refluxed on a water bath for 2 h. The yellow precipitate obtained was separated by filtration, washed with ethanol and finally dried at 110 ^{0}C.

$Ln(NCS)_3$.n(INH-SAL) (n = 2, Ln = La or Pr; n = 3, Ln = Nd, Sm, Gd, Tb or Dy). The absolute ethanolic solution (10 mL) of lanthanide isothiocyanate (1 mmol) was added in drops to the hot ethanolic solution (20 mL) of ligand (3 mmol) within 10 min with vigorous stirring. The solution was then allowed to stand for 24 h at room temperature (35 ^{0}C). The precipitate was filtered, washed with absolute ethanol and dried in vacuo over P_4O_{10}.

$Ln(ClO_4)_3$.4(INH-SAL) (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy). Lanthanide(III) perchlorate (1 mmol) and (INH-SAL) (4.1 mmol) was dissolved separately in hot ethanol (20 mL each). The reaction mixture was refluxed for 3 h and the solution was concentrated to the viscous mass, which was washed several times with small portions of hot benzene to remove the excess of

ligand. The finally divided solid mass was finally washed with diethyl ether and collected and dried over P_4O_{10}.

RESULTS AND DISCUSSION

The reaction of ethanolic solution of lanthanide salts with N-isonicotinamidosalicyalaldimine (INH-SAL) resulted in the formation of complexes of the general composition LnX_3.n(INH-SAL) (Ln = La, Pr, Nd, Sm, Gd, Tb, Tb or Dy ; X = NO_3, n = 2; X = NCS^-, n = 2 or 3; X = ClO_4^-, n = 4). The analytical data (Table 1) indicate that the complexes are pure and consistence with the proposed structures. The molar conductance (Table 1) of nitrato and isothiocyanato complexes are too low to account for any dissociation, therefore the complexes are non-electrolytes. The perchlorato complexes behave as 1:3 electrolytes suggesting all the three-perchlorato groups are present out side the coordination sphere [4]. The molecular weight of the complexes in nitrobenzene [4] or by Rast camphor method [4] are given in Table 1 along with values calculated on the basis of established formula of the complexes [4]. The ratio of molecular weight observed for $Ln(NO_3)_3$.2(INH-SAL) and $Ln(NCS)_3$.2(INH-SAL) or $Ln(NCS)_3$.3(INH-SAL) to that calculated is ~0.98 which shows that the complexes are monomeric in solution. In case of $Ln(ClO_4)_3$.4(INH-SAL), the ratio is found to be ~ 0.25 suggesting 4 species are formed in the perchlorato complexes. The magnetic moments (Table 1) are normal for complexes of these ions indicating that 4f-electrons do not participate in the bond formation. This is due to effective shielding of 4f-electrons from external forces [5,6].

Infrard spectra. The ligand (INH-SAL) is expected to act as tridentate one, the possible coordination sites being pyridinic-nitrogen, (heterocyclic-nitrogen) azomethine-nitrogen (C=N) and amide-group (carbonyl-oxygen). The key IR bands are summarized in Table 2. Generally all amides show four absorption bands [7], band-I, ν(C=O); band-II, [ν(C-N) + δ(N-H)], band-III, δ(N-H) and band-IV due to ϕ(C=O). The origin of these bands in hydrazides, the carbonyl absorption, responsible for the amide-I band is likely to be lowered [8] in frequency by the NH group as in normal amides. The (C=O) amide-I band in INH-derivative, however, appears at ~1660 cm^{-1}. In the IR 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 (C-N) amide-II band appears at the normal position in the NH-deformation frequency mode. In INH-SAL the absorption in 1560-1550 cm^{-1} region has been assigned to amide-II absorption. The ν(N-H) stretching absorption in free ligand occurs at ~3290 cm^{-1} and 3220 cm^{-1} [9] which remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom. Another important band occuring at 1602 cm^{-1} in the free ligand attributed to ν(C=N) of the azomethine mode [10, 11]. In spectra of all the complexes this band is shifted to lower wave number and appears in the reference 1550-1530 cm^{-1} region indicating the coordination of N-atom of the azomethine group [3,11].

The strong bands observed at 1575-1520 cm^{-1} and 1080-1000 cm^{-1} are tentatively assigned [12, 13] to antisymmetric and symmetric ν(C=C) + ν(C=N) of pyridine ring and pyridine ring breathings and deformations and remain practically unchanged in frequency and band intensities revealing non-involvement of the pyridinic-nitrogen in bond formation. In the spectra of INH-SAL, the stretching frequency in 3400 cm^{-1} region is attributed to ν(OH). In all the metal complexes, the hydroxyl frequency appears at the same region as in the free ligand clearly indicating that the -OH group did not take part in coordination. The overall IR spectral evidence suggests that the ligand INH-SAL act as a bidentate ligand and coordinates through amide-oxygen and azomethine-nitrogen atoms forming a five-membered chelate ring. The far IR spectral bands in the ligand are practically unchanged in these complexes. But some new bands with medium to weak intensities appear in the regions 450-360 cm^{-1} in the complexes under study, which are tentatively assigned to ν(Ln-O)/ν(Ln-N) modes [14, 15].

Table 1. Analytical, conductivity, molecular weight and magnetic moment data of lanthanide(III) complexes of INH-SAL.

Complex	Analysis: found (calculated) %				ΩM (ohm^{-1}cm^2 mole^{-1})	Exp. Mol. Wt. (Formula Wt.)	μ eff (B.M.)
	M	C	H	N			
La(NO$_3$)$_3$.2(INH-SAL)	17.06 (17.22)	38.25 (38.66)	2.68 (2.72)	15.48 (15.61)	3.9	800 (807)	Diamagnetic
Pr(NO$_3$)$_3$.2(INH-SAL)	17.27 (17.42)	38.17 (38.56)	2.76 (2.71)	15.44 (15.57)	3.6	802 (809)	3.66
Nd(NO$_3$)$_3$.2(INH-SAL)	17.59 (17.73)	38.06 (38.42)	2.66 (2.70)	15.38 (15.51)	4.1	804 (812)	3.51
Sm(NO$_3$)$_3$.2(INH-SAL)	18.15 (18.33)	37.93 (38.14)	2.64 (2.68)	15.27 (15.40)	4.0	809 (818)	1.62
Gd(NO$_3$)$_3$.2(INH-SAL)	18.87 (19.03)	37.50 (37.72)	2.63 (2.66)	15.13 (15.27)	3.9	819 (825)	7.85
Tb(NO$_3$)$_3$.2(INH-SAL)	19.06 (19.22)	37.40 (37.72)	2.63 (2.66)	15.10 (15.23)	3.4	820 (827)	9.93
Dy(NO$_3$)$_3$.2(INH-SAL)	19.41 (19.56)	37.33 (37.56)	2.60 (2.64)	15.06 (15.17)	4.3	822 (836.5)	10.19
La(NCS)$_3$.2(INH-SAL)	17.32 (17.48)	43.53 (43.77)	2.72 (2.76)	15.71 (15.84)	4.3	789 (795)	Diamagnetic
Pr(NCS)$_3$.2(INH-SAL)	17.53 (17.69)	43.44 (43.66)	2.71 (2.76)	15.67 (15.80)	4.7	791 (797)	3.59
Nd(NCS)$_3$.3(INH-SAL)	13.69 (13.83)	48.27 (48.41)	3.12 (3.17)	16.00 (16.13)	3.7	1033 (1041)	3.57
Sm(NCS)$_3$.3(INH-SAL)	14.18 (14.32)	47.98 (47.72)	3.12 (3.15)	15.90 (16.04)	3.6	1040 (1047)	1.59
Gd(NCS)$_3$.3(INH-SAL)	14.70 (14.89)	47.32 (47.56)	3.09 (3.13)	15.80 (15.93)	4.3	1016 (1054)	7.81
Tb(NCS)$_3$.3(INH-SAL)	14.89 (15.05)	44.28 (44.52)	3.08 (3.12)	15.76 (15.90)	4.2	1047 (1056)	9.83
Dy(NCS)$_3$.3(INH-SAL)	15.16 (15.33)	44.26 (44.46)	3.07 (3.11)	15.71 (15.85)	3.6	1051 (1059.5)	10.34
La(ClO$_4$)$_3$.4(INH-SAL)	9.76 (9.91)	44.28 (44.52)	3.08 (3.13)	11.82 (11.98)	76.3	346 (1401.5)	Diamagnetic
Pr(ClO$_4$)$_3$.4(INH-SAL)	9.96 (10.04)	44.26 (44.46)	3.08 (3.13)	11.85 (11.97)	77.4	347 (1403.5)	3.64
Nd(ClO$_4$)$_3$.4(INH-SAL)	10.13 (10.23)	44.16 (44.36)	3.07 (3.12)	11.84 (11.94)	79.3	348 (1406.5)	3.61
Sm(ClO$_4$)$_3$.4(INH-SAL)	10.52 (10.61)	43.97 (44.17)	3.07 (3.11)	11.79 (11.89)	77.4	349 (1412.5)	1.63
Gd(ClO$_4$)$_3$.4(INH-SAL)	10.96 (11.06)	43.74 (44.17)	3.04 (3.09)	11.74 (11.83)	78.2	350 (1419.5)	7.92
Tb(ClO$_4$)$_3$.4(INH-SAL)	11.07 (11.18)	43.63 (43.69)	3.04 (3.09)	11.72 (11.81)	79.1	350 (1421.5)	9.39
Dy(ClO$_4$)$_3$.4(INH-SAL)	11.32 (11.47)	43.52 (43.78)	3.03 (3.09)	11.69 (11.78)	76.9	351 (1425)	10.53

Table 2. Key IR data (cm^{-1}) of lanthanide(III) complexes of INH-SAL.

Complex	ν(C=O) amide-I	ν(C=N) azomethine	ν(Ln-O)/ν(Ln-N)
INH-SAL	1660 s	1602 vs	--
La(NO$_3$)$_3$.2(INH-SAL)	1620 vs	1560 s	440 w, 370 w
Pr(NO$_3$)$_3$.2(INH-SAL)	1610 vs	1565 s	450 m, br, 360 w
Nd(NO$_3$)$_3$.2(INH-SAL)	1620 s	1570 s	430 w, 360 w
Sm(NO$_3$)$_3$.2(INH-SAL)	1600 vs, br	1570 s	460 m, 360 w
Gd(NO$_3$)$_3$.2(INH-SAL)	1600 vs, br	1572 s	430 m, 365 w
Tb(NO$_3$)$_3$.2(INH-SAL)	1600 vs, br	1560 s	455 m, 360 w
Dy(NO$_3$)$_3$.2(INH-SAL)	1605 s	1572 s	440 m, 370 m
La(NCS)$_3$.2(INH-SAL)	1600 s	1540 m	450 m, 375 w
Pr(NCS)$_3$.2(INH-SAL)	1620 s	1530 m	440 m, 380 w
Nd(NCS)$_3$.3(INH-SAL)	1612 s	1535 s	442 m, 375 w
Sm(NCS)$_3$.3(INH-SAL)	1617 s	1530 s	437 m, 375 w
Gd(NCS)$_3$.3(INH-SAL)	1610 vs	1520 vs, br	430 m, 380 w
Tb(NCS)$_3$.3(INH-SAL)	1617 vs	1535 s	432 m, 382 w
Dy(NCS)$_3$.3(INH-SAL)	1615 s	1540 s	422 m, 382 w
La(ClO$_4$)$_3$.4(INH-SAL)	1620 vs	1555 s	415 m, 392 w
Pr(ClO$_4$)$_3$.4(INH-SAL)	1622 vs	1560 s	415 m, 390 w
Nd(ClO$_4$)$_3$.4(INH-SAL)	1630 s, 1610 sh	1547 s	422 m, 370 w
Sm(ClO$_4$)$_3$.4(INH-SAL)	1632 s, 1615 sh	1550 s	422 m, 382 w
Gd(ClO$_4$)$_3$.4(INH-SAL)	1630 s, 1620 sh	1545 s	415 m, 370 w
Tb(ClO$_4$)$_3$.4(INH-SAL)	1632 s	1545 s	422 m, 375 w
Dy(ClO$_4$)$_3$.4(INH-SAL)	1625 s	1555 s	425 m, 380 w

Anions. For lanthanide(III) nitrates complexes the occurrence of two strong absorptions at ~1525-1400 cm^{-1} and 1325-1285 cm^{-1} region is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group, respectively, suggesting that the nitrate groups lie inside the coordination sphere [16, 17]. Other absorption associated with the covalent nitrate groups is also observed in the spectra of the complexes. If the (ν_4 - ν_1) difference is taken as an approximate measure of the covalency of the nitrate group [17], a value of ~200 cm^{-1} for the complexes studied suggest strong covalency for the metal-nitrate bonding. Though considerable work has been carried out in order to establish the nature of coordinated nitrate by infrared studies, it is not possible to identify the type of bonding with certainty since the symmetry of the nitrate group remains the same (C_{2v}) whether it acts as a monodentate or bidentate group [18]. According to Lever *et al.* [19] bidentate coordination involves a greater distortion from D_{3h} symmetry than unidentate coordination, therefore, bidentate complexes should show a large separation of (ν_1 + ν_4). By an investigation of the spectra of a number of compounds of known crystal structure, Lever *et al.* [19] showed this to be true, the separation for monodentate nitrate groups appeared to be 5-26 cm^{-1} and that for bidentate group 25-66 cm^{-1}. In the present work, the authors have tried to apply the frequency assignment to the present lanthanide(III) nitrate complexes. A separation of ~30-50 cm^{-1} in the combination bands in 1800-1700 cm^{-1} region suggest a bidentate nitrate coordination. The bidentate character of nitrato groups has already been established by X-ray [20] and neutron diffraction studies [21]. Thus, we suggest that in the present work the nitrate groups are bidentate (Table 3).

Table 3. Infrared absorption frequencies (cm^{-1}) of NO_3^- in $Ln(NO_3)_3.2(INH\text{-}SAL)$.

Complex	$(\nu_2+\nu_3)$	$(\nu_2+\nu_5)$	$(\nu_2+\nu_3)-(\nu_2+\nu_5)$	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5
$La(NO_3)_3.2(INH\text{-}SAL)$	1782vw	1735vw	47	1510s, 1502s, br	1300sh, 1292vs	1050m, br 1025m	820m	740s	700w
$Pr(NO_3)_3.2(INH\text{-}SAL)$	1785vw	1750vw	35	1530vs	1315vs	1050m	820w	755s	700m
$Nd(NO_3)_3.2(INH\text{-}SAL)$	1770vw	1730vw	40	1525m	1320m	1070m, 1040m	810w	735s	700w
$Sm(NO_3)_3.2(INH\text{-}SAL)$	1785vw	1743vw	42	1510sh, 1500s	1320m, 1280s	1050s, br	820m, 810m	740s	700w
$Gd(NO_3)_3.2(INH\text{-}SAL)$	1788vw	1750vw	38	1510sh, 1500s	1320m, 1300w	1040m, br 1020m	818m	740s	700w
$Tb(NO_3)_3.2(INH\text{-}SAL)$	1780vw	1740vw	40	1500s	1325s	1040m	820s, 810s	740s	698w
$Dy(NO_3)_3.2(INH\text{-}SAL)$	1745vw	1745vw	45	1510s, br	1325m, 1300sh	1050m, br	820m, 810m	740s	700w

The thiocyanate ion has been studied widely by infrared spectroscopy. The various criteria proposed for determining the mode of bonding have been discussed by Nakamoto [8]. Bailey *et al.* [22] suggested that the region near or above 2100 cm^{-1} is for S-bonding, which below this is for N-bonding. The bonding regions (ν_2) 860-780 cm^{-1} and 720-690 cm^{-1} were assigned for M-NCS and M-SCN group, respectively. The NCS frequency (ν_3) is also different for the two isomers that is 490-450 cm^{-1} is for the M-NCS and 440-400 cm^{-1} is for M-SCN group. Bridging thiocyanate usually give higher CN stretching frequencies than terminal NCS group [8, 23]. Table 4 shows the IR absorption C-N stretching (ν_1), C-S stretching (ν_3) and N-C-S bending (ν_2) are identified. These frequencies are associated with the terminal N-bonding isothiocyanate ion [22-24].

Table 4. Infrared absorption frequencies (cm^{-1}) of NCS^- in $Ln(NCS)_3.n(INH\text{-}SAL)$.

Complex	ν(CN)	ν(CS)	δ(NCS)
$La(NCS)_3.2(INH\text{-}SAL)$	2042 vs	845 m	470 w
$Pr(NCS)_3.2(INH\text{-}SAL)$	2040 vs	840 m	472 w
$Nd(NCS)_3.3(INH\text{-}SAL)$	2025 vs	837 m	465 w
$Sm(NCS)_3.3(INH\text{-}SAL)$	2042 vs	842 m	472 w
$Gd(NCS)_3.3(INH\text{-}SAL)$	2045 vs	840 m	480 w
$Tb(NCS)_3.3(INH\text{-}SAL)$	2035 vs	840 m	442 w
$Dy(NCS)_3.3(INH\text{-}SAL)$	2040 vs	842 m	475 w

The occurrence of two strong bands at 1100-1080 cm^{-1} and 630-620 cm^{-1} regions, in the spectra of lanthanide(III) perchlorate complexes (attributed to ν_3 and ν_4 vibrations of ionic perchlorate) suggests the presence of perchlorate groups outside the coordination sphere of the complexes (Table 5) [25,26]. This view is also supported by the data on conductance and molecular weight determination.

Table 5. Infrared absorption frequencies (cm^{-1}) of ClO_4^- in $Ln(ClO_4)_3$.4(INH-SAL).

Complex	ν_3	ν_4
$La(ClO_4)_3$.4(INH-SAL)	1100 s	625 s
$Pr(ClO_4)_3$.4(INH-SAL)	1105 s	620 s
$Nd(ClO_4)_3$.4(INH-SAL)	1095 s	622 s
$Sm(ClO_4)_3$.4(INH-SAL)	1090 s	625 s
$Gd(ClO_4)_3$.4(INH-SAL)	1100 s	630 s
$Tb(ClO_4)_3$. 4(INH-SAL)	1102 s	625 s
$Dy(ClO_4)_3$.4(INH-SAL)	1100 s	620 s

Electronic spectra. The electronic spectra of the complexes (Table 6) showed a shift in band position towards the lower wave numbers as compared to those of the aquo complexes. The bands observed in the case of Pr^{3+}, Nd^{3+} and Sm^{3+} complexes could be assigned to the transitions from $^3H_4$, $^4I_{9/2}$ and $^4H_{5/2}$ (ground levels) to the excited J-levels of the respective $4f^n$ configurations. The present data also show that the nephelauxetic values for different J-levels vary considerably. The (1-β) values are used to estimate Sinha's covalency parameter (δ%) [27]. Another bonding parameter $b^{1/2}$ which measures the amount of metal 4f orbital to ligand mixing in these compounds and the covalency angular overlap parameter (η) were also calculated. The values of (1-β), $b^{1/2}$, δ% and η at corresponding transitions are also included in Table 6. The positive values for (1-β) and δ% in these coordination compounds suggest a bonding between the metal and an aquo ion. The values of the parameter bonding ($b^{1/2}$) and the angular overlap parameter (η) were found to be positive indicating covalent bonding [6].

Table 6. Electronic spectral data (cm^{-1}) and related bonding parameters of Lanthanide (III) nitrate complexes of INS-SAL.

Complexes	$Ln(NO_3)_3$ electronic spectral bands	Complex electronic spectral bands	Energy levels	(1-β)	β	$b^{1/2}$	δ%	η
$Pr(NO_3)_3$.2(INH-SAL)	22470	22300	$^3H_4 \rightarrow {}^3P_2$	0.0076	0.9924	0.0434	0.7617	0.0038
	21280	21000	$\rightarrow {}^3P_1$	0.0131	0.9869	0.0573	1.3325	0.0066
	20830	20640	$\rightarrow {}^3P_0$	0.0091	0.9909	0.0477	0.9204	0.0046
	16950	16760	$\rightarrow {}^1D_2$	0.0112	0.0529	0.0529	1.1327	0.0056
$Nd(NO_3)_3$.2(INH-SAL)	19420	19240	$^4I_{9/2} \rightarrow {}^3G_{9/2}$	0.0093	0.0481	0.0481	0.9346	0.0046
	17390	17210	$\rightarrow {}^4G_{5/2}, {}^4G_{7/2}$	0.0103	0.0508	0.0508	1.0045	0.0052
	13420	13200	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.0164	0.0640	0.0640	1.6663	0.0083
	12500	12340	$\rightarrow {}^4F_{3/2}, {}^4H_{9/2}$	0.0128	0.0565	0.0565	1.2966	0.0064
$Sm(NO_3)_3$.2(INH-SAL)	24850	24700	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0060	0.0388	0.0388	0.6066	0.0030
	24100	23800	$\rightarrow {}^6P_{5/2}$	0.0124	0.0557	0.0557	1.2596	0.0062
	21600	21440	$\rightarrow {}^4I_{5/2}$	0.0074	0.0430	0.0430	0.2455	0.0037

Thermal Studies

[Ln(INH-SAL)$_2$(NO$_3$)$_3$] (Ln = Pr, Gd, Tb or Dy). Thermogravimetric curves of these complexes indicate no changes up to 130 °C suggesting the absence of either coordinated or uncoordinated water molecule in these complexes. These complexes are stable up to 240 °C.

All the complexes undergo decomposition in two stages (see equation below) between 300 °C and 400 °C until stable lanthanide oxides are formed (Pr_6O_{11}, Gd_2O_3, Tb_4O_7 and Dy_2O_3) at about 820 °C.

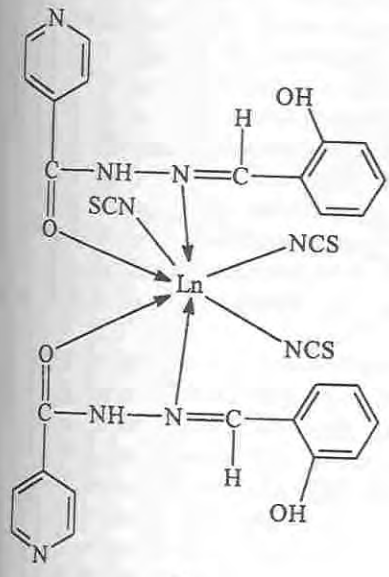
$$Ln(NO_3)_3.2(INH\text{-}SAL) \xrightarrow{\sim 300\ ^{\circ}C} Ln(NO_3)_3(INH\text{-}SAL) \xrightarrow{\sim 400\ ^{\circ}C} Ln(NO_3)_3$$

$$\xrightarrow{\sim 810\ ^{\circ}C} \text{Lanthanide oxide}$$

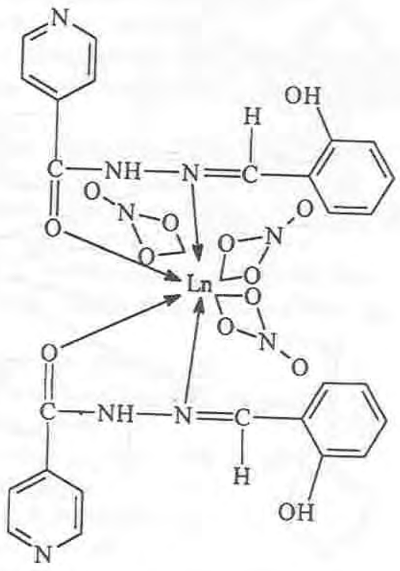
[Ln(INH-SAL)$_n$(NCS)$_3$] (Ln = Nd, Gd or Tb). The thermogravimetric curves clearly indicate that these complexes are non-hygroscopic in nature. All the complexes are stable up to 215 °C, beyond this temperature a loss of 45.6-46.06% in weight corresponding to loss of 2 moles of (INH-SAL) is observed. At 455 °C, all the organic ligand molecules are lost. The residues obtained at ~810 °C to constant weight are very close to that expected for the lanthanide oxides, viz., Nd_2O_3, Gd_2O_3 or Tb_4O_7 [28, 29].

[Ln(INH-SAL)$_4$(ClO$_4$)$_3$] (Ln = La Nd, Gd, or Dy). The thermogravimetric curves indicate that above 190 °C the complexes start to loss mass with partial evaporation of the organic ligand. In the temperature range 190-280 °C, a weight loss is ~42% corresponding to a loss of 2.5 moles in INH-SAL; while at 390 °C, the loss of ~68% corresponds to a total loss of INH-SAL molecules. Finally at ~810 °C stable lanthanide oxide Ln_2O_3 (Ln = La, Nd, Gd or Tb) are formed [28, 29].

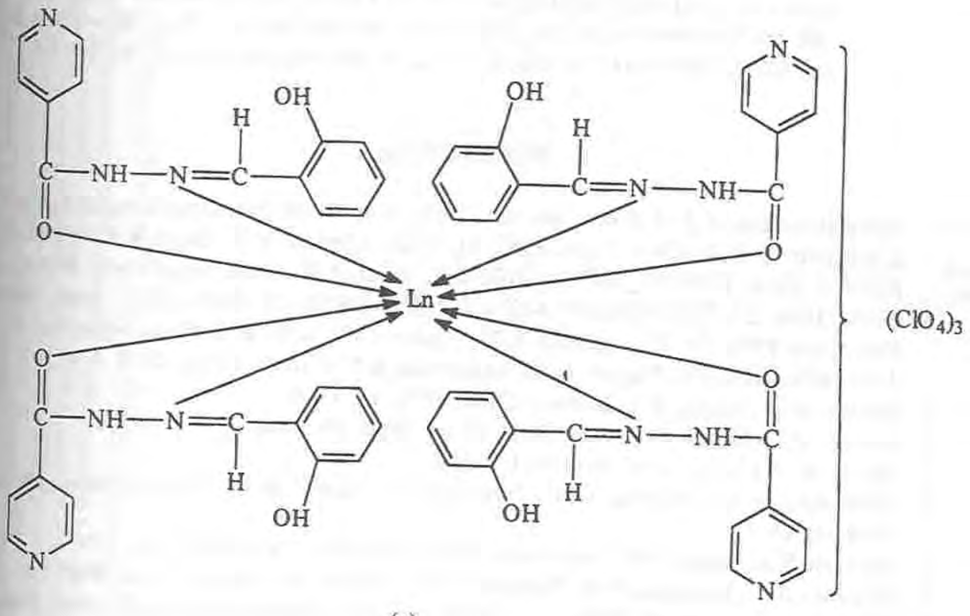
Stereochemistry of the complexes. Coordination numbers of the lanthanide ions are normally from 6 to 9, but are often higher with ligands of small bidentate ligands, such as nitrates. In [Ln(INH-SAL)$_2$(NO$_3$)$_3$] complexes, the electrolytic conductivity data indicate that the nitrato complexes in nitrobenzene behave as non-electrolytes. Thus, all the NO_3^- ions are present in the coordination sphere. The IR data reveals the bidentate nature of NO_3^- in these complexes. The organic ligand (INH-SAL) also behaves as bidentate ligand coordinating to the lanthanide via oxygen of the amide group and nitrogen of the azomethine group. Thus, in these complexes 8-oxygen atoms and 2-nitrogen atoms surround the central metal ion and thus produce a coordination number ten in these complexes. In [Ln(INH-SAL)$_n$(NCS)$_3$] complexes, the conductance and molecular weight data indicate that these complexes do not dissociate in nitrobenzene and form a monomeric species. The IR data suggests that all the three NCS ions bonded to the metal ion via N-atom. Thus in case of La or Pr, these ions are linked by five-nitrogen atoms (2 of azomethine group and 3 of isothiocyanate ions) and two oxygen atoms, while Nd, Sm, Gd, Tb or Dy are surrounded by six nitrogen atoms and three oxygen atoms. These studies concluded a coordination number seven for La and Pr and nine for Nd-Dy. An increase in the coordination number on going from La to Dy may be explained in terms of increasing ionic potential from La to Dy [30]. In literature, a number of lanthanide perchlorato complexes with bidentate organic ligands have been reported, in which the coordination number of lanthanide ions is found to be eight [30]. In the present complexes [Ln(INH-SAL)$_4$(ClO$_4$)$_3$], a coordination number eight has been postulated for lanthanide ions. The probable structures of these complexes are presented as follows:



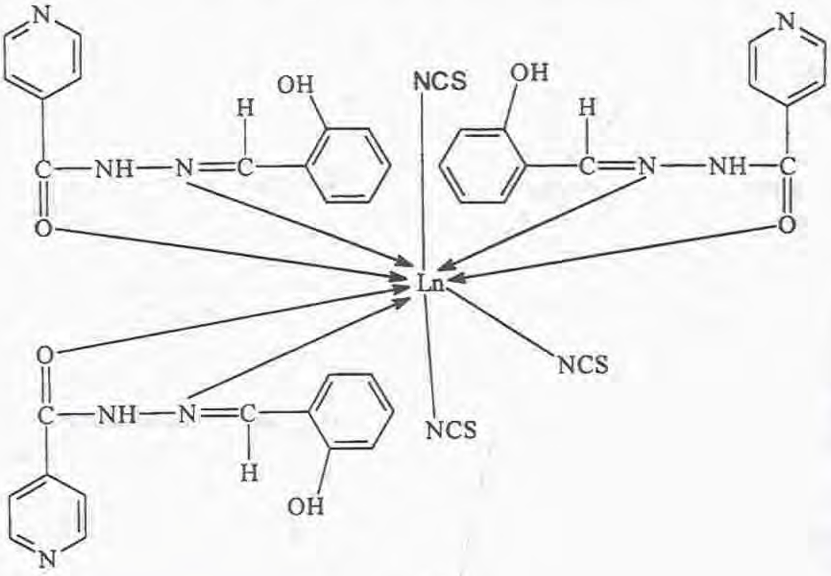
(a)



(b)



(c)



(d)

Figure 2. Proposed structures of the complexes: (a) [Ln(INH-SAL)$_2$(NCS)$_3$] (Ln = La or Pr) (CN = 7), (b) [Ln(INH-SAL)$_2$(NO$_3$)$_3$] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy) (CN = 10), (c) [Ln(INH-SAL)$_4$(ClO$_4$)$_3$] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy) (CN = 8), and (d) [Ln(INH-SAL)$_3$(NCS)$_3$] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy) (CN = 9).

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