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MAGENTO-SPECTRAL STUDIES ON SOME LANTHANIDE(III) NITRATE AND ISOTHIOCYANATE COMPLEXES OF HYDRAZONES OF ISONICOTINIC ACID HYDRAZIDE

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ABSTRACT. A new series of 28 lanthanide(III) nitrate and isothiocyanate complexes of hydrazones of isonicotinic acid hydrazide, *viz.*, N-isonicotinamide-*p*-dimethylaminobenzalaldimine (INH-PDAB) and N-isonicotinamide-3-methoxy-4-hydroxybenzalaldimine (INH-VAN) with the general composition, $Ln(L)_n X_3$ (L = INH-PDAB or INH-VAN, X = NO_3, n = 2, Ln = La, Pr, Nd, Sm, Gd, Tb or Dy; X = NCS, n = 2, Ln = La or Pr; n = 3, Ln = Nd, Sm, Gd, Tb, or Dy) have been reported. All the complexes were characterized by chemical analysis, conductance, molar weight, magnetic moment measurements, IR and electronic spectra. IR spectra indicate that the ligands behave as neutral O,N-donors. Thermal properties of the complexes have also been studied.

INTRODUCTION

Isonicotinic acid hydrazide (isoniazid, INH) is a drug of proven therapeutical importance and is used against a wide spectrum of bacterial ailments, *viz.*, tuberculosis [1]. Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH [2]. The studies on complexing behaviour of hydrazones of isonicotinic acid hydrazide towards metal ions is comparatively very less [3,4]. In the present work, we describe the synthesis and characterization of lanthanide nitrate and isothiocyanate complexes with N-isonicotinamido-*p*-dimethylaminobenzalaldimine (INH-PDAB, **1**) and N-isonicotinamido-3-methoxy-4-hydroxybenzalaldimine (INH-VAN, **2**).

EXPERIMENTAL

Reagents

The lanthanide nitrates were obtained from Rare Earth Products Ltd. (India) and were used without further purification. The lanthanide thiocyanates were prepared by adding a warm ethanolic solution of KNCS. 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 [5].

The ligands INH-PDAB and INH-VAN were synthesized [4] as follows: Isonicotinic acid

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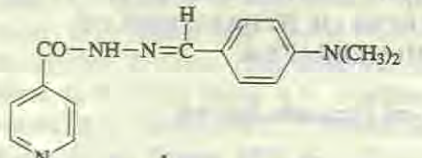
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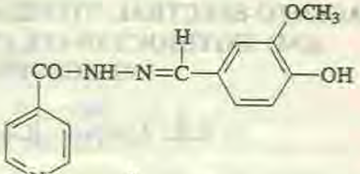
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hydrazide (0.01 mol) was dissolved in 30 mL of 95% ethanol. To this solution an aromatic aldehyde (*p*-dimethylaminobenzaldehyde or vanillin) (0.01 mol) in the same solvent was added. The mixture was refluxed on a water bath for 2 h. Partial removal of the solvent on a water bath followed by cooling produced crystalline product, which was suction filtered, washed with cold ethanol and dried under vacuum (yield *ca* 85%).

Synthesis of complexes

[Ln(NO$_3$)$_3$.2(INH-PDAB)] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy). Lanthanide(III) nitrate (2 mmol) was dissolved in acetone (20 mL) and the ligand INH-PDAB (4.1 mmol) was suspended in acetone (150 mL) and refluxed on a water bath until it was completely dissolved. The lanthanide nitrate solution was slowly added to it. The resulting solution was further refluxed for 2 h. The precipitated complex was filtered, washed several times with hot acetone and dried *in vacuo* over P_4O_{10}.

[Ln(NCS)$_3$.n(INH-PDAB)] (n = 2, Ln = La or Pr; n = 3, Ln = Nd, Sm, Gd, Tb or Dy). To a solution of the lanthanide isothiocyanate (1 mmol) in methanol (10 mL) a solution of the ligand (3 mmol) in hot methanol (30 mL) was added dropwise with constant stirring. The reaction was continued for 3 h. The solution volume was then reduced to 10 mL by evaporation, and a precipitate formed on addition of a small amount of anhydrous diethyl ether. This was filtered off, washed with ether and dried *in vacuo*.

[Ln(NO$_3$)$_3$.2(INH-VAN] (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy). An ethanolic (95%) solution (20 mL) of the Schiff base (4 mmol) was added with stirring to a hot ethanolic solution (10 mL) of the lanthanide(III) nitrate (2 mmol) and the reaction mixture was refluxed on a water bath for 2 h. The yellow precipitate thus obtained was separated by filtration, washed with ethanol and finally dried at 110°.

[Ln(NCS)$_3$.n(INH-VAN] (n = 2, Ln = La or Pr; n = 3, Ln = Nd, Sm, Gd, Tb or Dy). The absolute ethanolic solution (10 mL) of lanthanide thiocyanate (1 mmol) was added dropwise into the hot ethanolic solution (20 mL) of the Schiff base (3 mmol) within 10 min with vigorous stirring. The solution was then allowed to stand for 24 h at r.t. (35°). The precipitate was filtered, washed with absolute ethanol, and dried *in vacuo*.

All the physico-chemical studies of the complexes were made following procedures reported earlier [4,6].

The metal was determined as its oxide by direct combustion in a platinum crucible. The C, H, and N analyses were performed at C.D.R.I., Lucknow. The molecular weights of the complexes were determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of ±0.01° accuracy. Conductivity measurements were carried out using a Toshniwal Conductivity Bridge (type CL 01/01) and a dip type cell operated at 220 volts AC.

All measurements were done at room temperature in nitrobenzene. Magnetic measurements were carried out at r.t. with a Gouy balance and $[Hg.Co(SCN)_4]$ was used as a calibrant. IR spectra of the complexes were recorded on a Perkin Elmer Infrared Spectrophotometer model-521 in CsI in the range 4000-200 cm^{-1}. A Hilger Uvispek Spectrophotometer with a 1 cm quartz cell was employed for recording the visible spectra of the Pr^{3+}, Nd^{3+} and Sm^{3+} complexes. Thermogravimetric analyses were carried out in static air, with open sample holders and a small platinum boat, the heating rate was 6°/min.

RESULTS AND DISCUSSION

The general composition of all the complexes correspond to $LnX_3.nL$ (L = INH-PDAB or INH-VAN, $X = NO^-_3$, n = 2, Ln = La, Dy; $X = NCS^-$, n = 2, Ln = La or Pr; n = 3, Ln = Nd, Sm, Gd, Tb or Dy). The analytical data of the complexes are summarized in Table 1. The complexes are fairly stable and non-hygroscopic in nature and could be stored for a long time. Thermogravimetric curves indicated no changes up to 140° suggesting the absence of coordinated or uncoordinated water molecule in these complexes. The molar conductance values of these complexes are too low to account for any dissociation, therefore, the complexes are non-electrolytic in nature. Data on the molecular weight of the complexes in nitrobenzene are presented in Table 1 along with values calculated on the basis of established formula of the complexes. The ratio of molecular weight observed for $Ln(NO_3)_3.2L$ and $Ln(NCS)_3.2L$ or $Ln(NCS)_3.3L$ to that calculated is *ca* 0.98 which shows that the complexes are monomeric in solution.

The values of the magnetic moments are close to the theoretical values indicating that the 4f orbitals are well shielded and do not take part in bonding. The magnetic moment of these complexes (Table 1) when plotted against increasing atomic numbers of the lanthanides, show the characteristic unequal double humped curve.

Infrared spectra. The ligands are expected to be tridentate, the possible coordination sites being pyridine-nitrogen, azomethine-nitrogen and the amide group. However, comparison of the IR spectra of the ligands and the complexes, suggest that both ligands are bidentate with the carbonyl-oxygen and azomethine-nitrogen as two coordinating sites. In INH-VAN the -OH group is not taking part in the coordination. This behaviour is similar to the Schiff bases of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with 4-aminoantipyrine [7-9]. The partial IR data are presented in Table 2. The presence of various ring vibrations and C-H absorptions make the spectra fairly complicated for complete assignments of individual bands.

The amide-I band in INH derivatives appears at *ca* 1660-1640 cm^{-1}. In the IR spectra of the complexes a considerable negative shift in $\nu(C=O)$ is observed indicating a decrease in the stretching force constant of the C=O bond 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 frequency mode. In INH-derivatives, the absorption in 1565-1560 cm^{-1} region has been assigned to amide-II absorption. The band due to NH stretching in free ligands occurs [10] at *ca* 3290 and 3220 cm^{-1} and remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom. Another important band which occurs in the region of 1590 cm^{-1} is attributed to $\nu(C=N)$ (azomethine) mode [7-9]. In the spectra of all the complexes this band is shifted to lower frequency and appears in the 1550-1520 cm^{-1} region indicating the involvement of the N atom of the azomethine group in coordination [7-9].

Table 1. Elemental analysis, conductivity, molecular weight and magnetic moment data of lanthanide(III) complexes of INH-PDAB and INH-VAN.

Complex	Found (Calc.) %				Ω_M Ohm^{-1}cm^{2}mol^{-1}	Exp. Mol. Wt. (Calc.)	μ_{eff} (B.M.)
	Metal	C	H	N			
$La(NO_3)_3.2(INH\text{-}PDAB)$	16.22 (16.14)	41.96 (41.81)	3.69 (3.71)	17.98 (17.88)	3.9	852 (861)	Diamag.
$Pr(NO_3)_3.2(INH\text{-}PDAB)$	16.41 (16.33)	41.85 (41.71)	3.68 (3.70)	17.95 (17.84)	4.3	853 (863)	3.59
$Nd(NO_3)_3.2(INH\text{-}PDAB$	16.73 (16.62)	41.71 (41.57)	3.66 (3.69)	17.89 (17.78)	4.6	860 (866)	3.62
$Sm(NO_3)_3.2(INH\text{-}PDAB)$	17.31 (17.20)	41.41 (41.28)	3.63 (3.66)	17.78 (17.66)	3.8	863 (872)	1.64
$Gd(NO_3)_3.2(INH\text{-}PDAB)$	17.97 (17.86)	41.17 (40.95)	3.60 (3.64)	17.63 (17.51)	4.9	870 (879)	7.94
$Tb(NO_3)_3.2(INH\text{-}PDAB)$	18.12 (18.04)	41.07 (40.86)	3.60 (3.63)	17.60 (17.48)	4.1	873 (881)	9.28
$Dy(NO_3)_3.2(INH\text{-}PDAB)$	18.49 (18.37)	40.86 (40.70)	3.58 (3.61)	17.53 (17.41)	3.7	875 (884.5)	10.51
$La(NCS)_3.2(INH\text{-}PDAB)$	16.48 (16.37)	46.87 (46.64)	3.72 (3.76)	18.24 (18.13)	4.3	840 (849)	Diamag.
$Pr(NCS)_3.2(INH\text{-}PDAB)$	16.67 (16.56)	46.73 (46.53)	3.72 (3.76)	18.20 (18.09)	4.9	843 (851)	3.54
$Nd(NCS)_3.3(INH\text{-}PDAB)$	12.95 (12.83)	51.52 (51.33)	4.22 (4.27)	18.83 (18.71)	4.1	1113 (1122)	3.50
$Sm(NCS)_3.3(INH\text{-}PDAB)$	13.41 (13.29)	51.20 (51.06)	4.21 (4.25)	18.73 (18.61)	5.0	1120 (1128)	1.61
$Gd(NCS)_3.3(INH\text{-}PDAB)$	13.95 (13.83)	50.98 (50.74)	4.17 (4.22)	18.62 (18.50)	5.7	1125 (1135)	7.80
$Tb(NCS)_3.3(INH\text{-}PDAB)$	14.09 (13.98)	50.87 (50.65)	4.17 (4.22)	18.58 (18.46)	3.8	1130 (1137)	9.80
$Dy(NCS)_3.3(INH\text{-}PDAB)$	14.36 (14.24)	50.73 (50.50)	4.15 (4.20)	18.53 (18.41)	4.1	1132 (1140.5)	10.26
$La(NO_3)_3.2(INH\text{-}VAN)$	16.15 (16.03)	38.92 (38.75)	3.03 (2.99)	14.63 (14.53)	3.9	860 (867)	Diamag.
$Pr(NO_3)_3.2(INH\text{-}VAN)$	16.34 (16.22)	38.80 (38.66)	3.02 (2.99)	14.61 (14.49)	3.6	861 (869)	3.73
$Nd(NO_3)_3.2(INH\text{-}VAN)$	16.63 (16.51)	38.64 (38.53)	3.01 (2.98)	14.54 (14.44)	4.3	863 (872)	3.52
$Sm(NO_3)_3.2(INH\text{-}VAN)$	17.19 (17.08)	38.37 (38.26)	3.00 (2.96)	14.46 (14.35)	4.2	870 (878)	1.63
$Gd(NO_3)_3.2(INH\text{-}VAN)$	17.85 (17.64)	38.19 (37.96)	2.97 (2.93)	14.35 (14.23)	3.9	877 (885)	7.68
$Tb(NO_3)_3.2(INH\text{-}VAN)$	18.10 (17.92)	38.02 (37.88)	2.97 (2.93)	14.33 (14.20)	3.3	880 (887)	9.27
$Dy(NO_3)_3.2(INH\text{-}VAN)$	18.36 (18.24)	37.90 (37.73)	2.95 (2.91)	14.25 (14.14)	4.6	881 (890.5)	10.43
$La(NCS)_3.2(INH\text{-}VAN)$	16.37 (16.25)	43.71 (43.50)	3.07 (3.04)	14.84 (14.73)	4.3	847 (855)	Diamag.
$Pr(NCS)_3.2(INH\text{-}VAN)$	16.57 (16.45)	43.59 (43.40)	3.06 (3.03)	14.81 (14.70)	4.9	850 (857)	3.69
$Nd(NCS)_3.3(INH\text{-}VAN)$	12.87 (12.73)	47.92 (47.74)	3.49 (3.44)	14.96 (14.85)	3.9	1123 (1131)	3.62
$Sm(NCS)_3.3(INH\text{-}VAN)$	13.33 (13.19)	47.96 (47.49)	3.49 (3.43)	14.89 (14.77)	3.8	1128 (1137)	1.69
$Gd(NCS)_3.3(INH\text{-}VAN)$	13.84 (13.72)	47.39 (47.20)	3.45 (3.40)	14.81 (14.68)	4.6	1136 (1144)	7.71
$Tb(NCS)_3.3(INH\text{-}VAN)$	13.99 (13.87)	47.30 (47.12)	3.45 (3.40)	14.79 (14.65)	4.2	1137 (1146)	9.61
$Dy(NCS)_3.3(INH\text{-}VAN)$	14.26 (14.13)	47.20 (46.96)	3.44 (3.39)	14.74 (14.61)	3.8	1140 (1149.5)	10.39

The strong bands observed at 1575-1520 cm^{-1} and 1080-1000 cm^{-1} are tentatively assigned [3,11,12] to antisymmetric and symmetric ν(C=C) and ν(C=N) of pyridine ring and pyridine ring breathing and deformations, respectively. These bands remain practically unchanged after complexation. These observation suggest the non-involvement of pyridinic-nitrogen in complex formation. In the spectrum of INH-VAN, the band at 3500-3400 cm^{-1} is attributed to ν(OH). In the complexes of INH-VAN, the -OH group frequency appears at the same region as in the free ligand clearly indicating that the -OH group is not taking part in the coordination. The overall IR spectral evidence suggests that both ligands act as bidentate ligands and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five-membered chelate ring. The far IR spectral bands in the ligands are practically unchanged in these complexes. But some new bands with medium to weak intensities appear in the region 440-360 cm^{-1} in the complexes under study which are assigned to ν(Ln-O)/ν(Ln-N) modes [13,14].

Table 2. Partial IR data (cm^{-1}) of lanthanide(III) complexes of INH-PDAB and INH-VAN.

Complex	ν(OH)	ν(NH)	Amide-1	ν(C=N) azomethine	ν(Ln-O)/ν(Ln-N)
INH-PDAB	-	3300m, 3200m	1655s	1588vs	-
La(NO$_3$)$_3$.2(INH-PDAB)	-	3300m, 3222m	1630s, 1610m	1565s	430m, 380w
Pr(NO$_3$)$_3$.2(INH-PDAB)	-	3310m, 3205m, 3300sh	1635m	1560s	425m, 382w
Nd(NO$_3$)$_3$.2(INH-PDAB)	-	3300m, 3280m	1650m, 1615s	1560s, 1570sh	400m, 340w
Gd(NO$_3$)$_3$.2(INH-PDAB)	-	3300m, 3280w, 3210w	1635m, 1618m	1570s, 1550sh	430m, 380w
Tb(NO$_3$)$_3$.2(INH-PDAB)	-	3300m, 3280m, 3200w	1640m, 1610sh	1570s	435w, 360w
Dy(NO$_3$)$_3$.2(INH-PDAB)	-	3320m, 3280m	1650m, 1600vs, br	1570s	420m, 380w
La(NCS)$_3$.2(INH-PDAB)	-	3305m, 3200m	1650m, 1620m	1545m br	420m, 348m
Pr(NCS)$_3$.2(INH-PDAB)	-	3305m, 3205m	1620s, 1600s	1535m	422m, 348m
Nd(NCS)$_3$.3(INH-PDAB)	-	3303m, 3205m	1620s, 1600s	1540m	420w, 362m
Sm(NCS)$_2$.3(INH-PDAB)	-	3302m, 3200m	1630m, 1605m	1540m	430w, 380w
Gd(NCS)$_3$.3(INH-PDAB)	-	3300m, 3250m	1635m, 1615m	1535m	435w, 375w
Tb(NCS)$_3$.3(INH-PDAB)	-	3305m, 3200m	1630m, 1610m	1542m	440m, 380w
Dy(NCS)$_3$.3(INH-PDAB)	-	3300m, 3205m	1632m, 1612m	1540m	437m, 382w
INH-VAN	3480m, 3420w	3300m, 3220w	1700vs, 1630vs	1585s	-
La(NO$_3$)$_3$.2(INH-VAN)	3482m, 3420w	3305m, 3220w	1670vs, 1605w	1525m	440w, 370w
Pr(NO$_3$)$_3$.2(INH-VAN)	3480m, 3422w	3302m, 3220w	1670s, 1610vs	1530vs	450m, br, 360w
Nd(NO$_3$)$_3$.2(INH-VAN)	3482m, 3420w	3300m, 3200w	1680s, 1620s	1555s	430w, 360w
Sm(NO$_3$)$_3$.2(INH-VAN)	3480m, 3422w	3302m, 3220w	1670vs, 1600vs, br	1525m	460m, 360w
Gd(No$_3$)$_3$.2(INH-VAN)	3480w, 3420w	3300m, 3222w	1670s, 1600vs, br	1535sh	430m, 365w
Tb(NO$_3$)$_3$.2(INH-VAN)	3480m, 3420w	3300m, 3225w	1665vs, 1600vs, br	1530sh, 1515m	455m, 360w
Dy(NO$_3$)$_3$.2(INH-VAN)	3480m, 3420w	3300m, 3220w	1660s, 1605s	1525m	440w, 370w
La(NCS)$_3$.2(INH-VAN)	3480m, 3420w	3305m, 3222w	1650s, 1598s	1540m	450m, 375w
Pr(NCS)$_3$.2(INH-VAN)	3480m, 3423w	3300m, 3220w	1620s	1530m	440m, 380w
Nd(NCS)$_3$.3(INH-VAN)	3482m, 3422w	3302m, 3220w	1612s	1532s	442m, 378w
Sm(NCS)$_3$.3(INH-VAN)	3480m, 3420w	3300m, 3222w	1617s	1530s	437m, 375w
Gd(NCS)$_3$.3(INH-VAN)	3482m, 3425w	3302m, 3222w	1610s	1520vs, br	430m, 380w
Tb(NCS)$_3$.3(INH-VAN)	3480m, 3420w	3303m, 3220w	1617vs	1532s	432m, 382w
Dy(NCS)$_3$.3(INH-VAN)	3482m, 3420w	3302m, 3220w	1615vs	1537s	422m, 382w

Anion. In lanthanide(III) nitrate complexes the occurrence of two strong absorptions at *ca* 1525-1480 cm^{-1} and 1320-1285 cm^{-1} region is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate groups, respectively, suggesting that the nitrate groups lie inside the coordination sphere [15,16]. A value of *ca* 200 cm^{-1} (ν_4 - ν_1) for these complexes suggest strong covalency for the metal-nitrate bonding [16]. Other absorptions associated with the covalent nitrate groups are also observed in the spectra of the complexes. According to Lever [17], bidentate coordination involves a greater distortion from D_{3h} symmetry than unidentate coordination, therefore, bidentate complexes should show a large separation of $(\nu_1 + \nu_4)$. In the present complexes, a separation of *ca* 55-30 cm^{-1} in the combination bands in the 1800-1700 cm^{-1} region conclude the bidentate nitrate coordination. The bidentate character of nitrato groups has been established by X-ray [18] and neutron diffraction studies [19,20].

In thiocyanato complexes the SCN$^-$ is known to form complexes through the hard N-end or the soft S-end or behaves as a bridging ligand mainly depending on (i) the nature of the central atom, (ii) the nature of other ligands in the coordination spheres, (iii) environmental and kinetic mechanistic controls. Earlier studies [21] on various metal thiocyanato complexes have proved that three fundamental frequencies: C-N stretch (ν_1), C-S stretch (ν_3) and N-C-S bending (ν_2) appear in 2080-2040, 860-780 and 480-465 cm^{-1} regions for N-bonded NCS, and at 2120-2080, 720-760 and 470-410 cm^{-1} regions for S-bonded SCN, respectively. For bridging thiocyanate, ν_1 occurs generally at higher frequency than that of terminal thiocyanate while ν_3 occur at intermediate frequencies. In these complexes the ν_1 (2045-2030 cm^{-1}), ν_2 (835-815 cm^{-1}) and ν_3 (472-460 cm^{-1}) frequencies are inferred for terminal N-bonded isothiocyanate ion [21].

Electronic spectra. . Spectral data obtained for solutions of Pr, Nd and Sm nitrate complexes of INH-PDAB in acetonitrile are recorded in Table 3. Lanthanum(III) has no significant absorption in the visible region. The absorption bands of praseodymium(III), neodymium(III) and samarium(III) in the visible and near IR region appear due to transitions from the ground levels of $^3H_4$, $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J level of 4f configuration, respectively. Some red shift or nephelauxetic effect is observed in acetonitrile solution of these coordinating compounds. This red shift is usually accepted as evidence of a higher degree of covalency than existing in the aquo compounds [22,23]. In all the complexes, marked enhancement in the intensity of the bands has been observed. We have also calculated various parameters like nephelauxetic ratio (β), bonding parameter $(b^{1/2})$, Sinha's parameter $(\delta\%)$ and covalency angular overlap parameter (η). The values of the nephelauxetic ratio is smaller than 1 and the positive values of the bonding parameter and Sinha's parameter indicate the occurrence of some covalent character in the metal-ligand bond [24]. Comparatively smaller magnitude of $b^{1/2}$ values also show the involvement of the 4f orbital in metal-ligand bond to a very low degree [25].

Table 3. Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) nitrate complexes of INH-PDAB.

Complex	$Ln(NO_3)_3$ electronic spectral bands	Complex electronic spectral bands	Energy levels	$(1-\beta)$	β	$b^{1/2}$	$\delta\%$	η
$Pr(NO_3)_3.(INH\text{-}PDAB)_2$	22470	22310	$^3H_4 \rightarrow {}^3P_2$	0.0071	0.9928	0.0596	0.7171	0.0037
	21280	21000	$\rightarrow {}^3P_1$	0.0131	0.9868	0.0810	1.3325	0.0067
	20830	20650	$\rightarrow {}^3P_0$	0.0086	0.9913	0.0657	0.8715	0.0044
	16950	16760	$\rightarrow {}^1D_2$	0.0112	0.9887	0.0074	1.1326	0.0057
$Nd(NO_3)_3.(INH\text{-}PDAB)_2$	19420	19260	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.0082	0.9917	0.0641	0.8298	0.0042
	17390	17160	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.0132	0.9867	0.0813	1.3397	0.0067
	13420	13200	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.0163	0.9836	0.0905	1.6663	0.0083
	12500	12330	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.0136	0.9864	0.0824	1.3787	0.0069
$Sm(NO_3)_3.(INH\text{-}PDAB)_2$	24850	24720	$^6H_{5/2} \rightarrow {}^4F_{5/2}$	0.0052	0.9947	0.0511	0.5257	0.0027
	24100	23820	$\rightarrow {}^6P_{5/2}$	0.0116	0.9883	0.0761	1.1745	0.0059
	21600	21470	$\rightarrow {}^4I_{13/2}$	0.0060	0.9939	0.0548	0.6045	0.0031

Thermal studies. Thermal properties of some representative complexes have been investigated by thermogravimetric (TG) analysis. In [Ln(INH-PDAB)$_2$(NO$_3$)$_2$] (Ln = Pr, Nd, Gd, or Dy) complexes, the TG curves indicate that above 280° the complexes start to lose mass with partial evaporation of the ligand up to a temperature of 345°; the loss of mass corresponds to one mole of organic ligand. At temperature close to 475° both the organic ligand molecules are lost. The residues obtained after heating to constant weight at 810°, are very close to those expected for the lanthanide oxides (Pr_6O_{11}, Nd_2O_3, Gd_2O_3 and Dy_2O_3) [26,27].

In [Ln(INH-VAN)$_3$(NCS)$_3$] (Ln = Nd, Gd, Tb or Dy), there is no apparent weight loss up to 140°, clearly indicating the absence of water molecules in these coordination compounds. At 265-330° there is a loss of 1.7 moles of organic ligand, and at 450° total loss of organic ligand has occurred. Finally, at *ca* 810° stable lanthanide oxides are formed (Nd_2O_3, Gd_2O_3, Tb_4O_7 and Dy_2O_3).

Stereochemistry. The electrolytic conductivity data indicate that the nitrato complexes behave as non-electrolytes in nitrobenzene. Thus all the NO_3^- are present in the coordination sphere. Molecular weight measurements (cryoscopically in freezing nitrobenzene) indicate the monomeric nature of these complexes. IR data reveal the bidentate nature of NO_3^- in these complexes. Both the organic ligands, i.e., INH-PDAB and INH-VAN, behave as bidentate ligands coordinating to the lanthanide via oxygen of the amide group and nitrogen of the azomethine group. Thus in these complexes the central metal ion is surrounded by eight oxygen atoms and two nitrogen atoms and produce a coordination number of ten [28].

In thiocyanato complexes the conductance and molecular weight data indicate that these complexes do not dissociate in nitrobenzene and form a monomeric species. IR data suggest that all the three NCS$^-$ ions are bonded to the metal ion via the nitrogen atom. Thus in case of La and Pr, these ions are linked by five nitrogen atoms (2 of azomethine groups and 3 of isothiocyanate ions) and two oxygen atoms, while Nd and Dy are surrounded by six nitrogen and three oxygen atoms. These studies concluded a coordination number of seven for La and Pr and nine for Nd and Dy. An increase in the coordination number, in going from La to Dy may be explained in terms of increasing ionic potential from La to Dy [28].

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