SYNTHESIS AND STRUCTURAL STUDIES OF SOME TRIVALENT LANTHANIDE COMPLEXES OF ISONICOTINIC ACID HYDRAZIDE

T. R. RAO, I. A. KHAN and R. C. AGGARWAL
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India.

ABSTRACT

Trivalent lanthanides have been found to form complexes with isonicotinic acid hydrazide (INH) of the type $M(INH)_3X_3$ [X = Cl, SCN; M = La(III), Pr(III), Nd(III), Sm(III) and Gd(III)]. The complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared and electronic spectral studies. The nephelauxetic ratio ($\bar{\beta}$), covalency (δ) and bonding parameter ($b^{1/2}$) have been calculated from the electronic spectra. Infrared spectral studies reveal that INH acts as a neutral bidentate chelating ligand in all the complexes and that thiocyanate is N-bonded.

INTRODUCTION

ISONICOTINIC ACID HYDRAZIDE (INH) has attracted the attention of several investigators since the report that INH has antitubercular properties and that its complexation with Cu^{2+} results in a ten-fold increase of the activity[1]. Recently, Dutt and Sen Gupta[2] have reported the preparation of rare-earths complexes of INH of the formulae $Ln(ClO_4)_3.5INH$ and $Ln(ClO_4)_3.3INH.H_2O$ and they reported monodentate behaviour of INH in the complexes through the heterocyclic nitrogen.

Interestingly, Zinner and co-workers report[3] that INH acts as a bidentate ligand in its $Ln(NO_3)_3$ complexes, coordinating through carbonyl oxygen and amide nitrogen, based on the single crystal x-ray structure of $Sm(NO_3)_3.3INH\cdot 3H_2O$. As the INH, thus, seems to show varied bonding behaviour, it will be worthwhile studying the bonding behaviour in its complexes with Ln(III) chlorides and thiocyanates. A thorough survey of the literature shows that a few complexes of INH with some Ln(III) chlorides are reported[4] but the studies seem to be incomplete as the synthesis of a few complexes with the general composition, $M(INH)_2Cl_3$ and their IR spectra are only reported. Hence, in continuation of our previous studies on the transition metal complexes of INH and related ligands[5-9] we now report here, a systematic study on the synthesis and structural investigations of complexes of INH with lanthanide (III) chlorides and thiocyanates.

EXPERIMENTAL

Starting Materials–Lanthanide trichlorides obtained from the Indian Rare Earths Ltd., Kerala (India), were used as such. Isonicotinic acid hydrazide used was of Schüchardt, West Germany. All other chemicals used were of BDH, AR grade.

Preparation of the Complexes–The lanthanide chloride complexes were synthesized by mixing the ethanolic solutions of the appropriate Ln(III) chloride (2 mmol) and INH (6 mmol) and refluxing the resulting solution on a water bath for ca. 30 min. The microcrystalline complexes obtained were filtered, washed successively with cold ethanol and ether and dried *in vacuo*.

All the Ln(III) thiocyanate complexes were prepared by mixing acetonitrile solutions of 2 mmol of the appropriate metal thiocyanate (obtained by metathetic reaction of $LnCl_3$ and KSCN in anhydrous ethanol) and INH (6 mmol). The complexes precipitated instantaneously were filtered, washed successively with acetonitrile and ether and dried *in vacuo*.

Analysis of the Complexes–Lanthanides were gravimetrically estimated as oxides[10] as well as oxalates after decomposing the organic matter with aquaregia and subsequently with conc. sulphuric acid. The chloride and thiocyanate were determined gravimetrically as AgCl and AgSCN, respectively while hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. Nitrogen was microanalysed.

Physical Measurements–Magnetic susceptibility measurements were carried out at room temperature on a Cahn-Faraday electrobalance and molar conductance was determined on a WTW conductivity meter equipped with a magic eye. The infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, model-621 while the electronic spectra were obtained on a Cary-14 Spectrophotometer.

RESULTS AND DISCUSSION

The analytical data (table 1) shows that INH forms 3:1 adducts with Ln(III) salts. All the complexes reported in table 1 are moderately hygroscopic. Samarium(III) complexes are found to melt at specific temperatures while all others decompose on heating. The complexes are soluble in water, methanol, acetone and DMF but are insoluble in non-polar organic solvents like benzene and carbon tetrachloride.

The molar conductances of the complexes (table 1) in 0.001M methanolic solution indicate their non-electrolytic nature[11]. However, a 1:1 electrolytic behaviour has been observed in 0.001M DMF solutions presumably due to the replacement of one of the coordinated chloride/thiocyanate by the solvent molecule.

The room temperature magnetic moments of the complexes (table 1) show a very little deviation from van Vleck values [12] indicating very little participation of the 4f-electrons in bond formation in these complexes.

Electronic Spectra–The electronic f-f transition bands normally show weak perturbation due to complexation; an increase in intensity, shifts to the red region and splitting of some bands are observed on complex formation. The position and shapes of electronic spectral bands of Pr(III), Nd(III) and Sm(III) complexes both in the solid state (nujol) and in solutions of DMF and methanol are almost similar, except for the relative broadness of the mull spectra. This suggests that the complexes maintain the same stereochemistry in solid and solution phases. While the La(III), and Gd(III) complexes have shown no absorption in the visible region, the other complexes have shown various bands appearing at lower energies as compared to those in aquo complexes. The magnitude of the bathochromic shift of the bands in each case indicates a meagre nephelauxetic effect upon complex formation[13]. The nephelauxetic effect ($\bar{\beta}$), the bonding parameter ($b^{1/2}$) and the Sinha's parameter (δ) have been calculated[14,15]. The bonding parameter, $b^{1/2}$, reflects the extent of participation of 4f-orbitals in complexation; greater the magnitude of the parameter, greater is the contribution of 4f-orbitals[14]. The $b^{1/2}$ values obtained for the present complexes indicate a decreasing order of 4f-orbital participation in the series Pr(III), Nd(III), Sm(III). The average value of the Sinha's parameter (δ) obtained in each case is positive and smaller than unity, indicating the presence of a weak covalent bonding character in the complexes.

Infrared Spectra–The coordination sites of the ligand involved in the present complexes have been de-

Table 1 *Analytical Data and General Behaviour of Ln(III) Complexes of INH*

Complex	Colour	M.P. (°C)	Found (calcd.) % Metal	Cl/SCN	N	N_2H_4	Molar conductance (mohs cm^2 $mole^{-1}$)		μ_{eff} (B.M.)
$La(INH)_3Cl_3$	Cream colour	195[d]	20.85 (21.16)	16.30 (16.22)	19.18 (19.20)	14.58 (14.62)	2.9[a]	42.4[b]	Diamag.
$Pr(INH)_3Cl_3$	Pale green	202[d]	21.23 (21.40)	16.22 (16.17)	19.09 (19.20)	14.14 (14.58)	4.8[a]	40.7[b]	3.16
$Nd(INH)_3Cl_3$	Pale violet	180[d]	21.80 (21.79)	16.04 (16.09)	19.00 (19.04)	14.38 (14.50)	5.1[a]	53.1[b]	3.24
$Sm(INH)_3Cl_3$	Cream colour	170	22.14 (22.51)	15.73 (15.95)	18.68 (18.87)	14.30 (14.37)	8.0[a]	64.9[b]	1.95
$Gd(INH)_3Cl_3$	White	210[d]	23.28 (23.33)	15.65 (15.78)	18.70 (18.68)	14.19 (14.22)	8.4[a]	88.5[b]	8.03
$La(INH)_3(SCN)_3$	White	> 280	19.02 (19.18)	24.01 (24.03)	23.02 (23.21)	13.15 (13.26)	3.8[a]	51.4[b]	Diamag.
$Pr(INH)_3(SCN)_3$	White	195[d]	19.33 (19.41)	23.78 (23.97)	23.06 (23.14)	13.19 (13.22)	3.1[a]	41.8[b]	3.08
$Nd(INH)_3(SCN)_3$	White	240[d]	19.43 (19.79)	23.68 (23.86)	22.97 (23.03)	13.11 (13.17)	8.2[a]	98.0[b]	4.38
$Sm(INH)_3(SCN)_3$	White	260	20.15 (20.44)	23.64 (23.66)	22.66 (22.84)	12.98 (13.05)	7.5[a]	94.4[b]	2.04
$Gd(INH)_3(SCN)_3$	White	254[d]	21.09 (21.23)	23.37 (23.41)	22.49 (22.63)	12.90 (12.93)	8.7[a]	90.3[b]	7.20

[a] values in methanolic solution; [b] values in DMF solution; [d] decomposes.

Table 2 *Electronic Spectral Data of Ln(III) Complexes of INH*

Complex	Band maximum (cm^{-1}) complex (X = Cl)	complex (X = SCN)	Assignment	Spectral parameters* X = Cl	X = SCN
$Pr(INH)_3X_3$	16805	16805	$^3H_4 \rightarrow {}^1D_2$	$\bar{\beta} = 0.962$	$\bar{\beta} = 0.962$
	20530	20530	$\rightarrow {}^3P_0$	$\delta = 3.98$	$\delta = 3.98$
	21100	21100	$\rightarrow {}^3P_1$	$b^{1/2} = 0.138$	$b^{1/2} = 0.138$
	22220	22220	$\rightarrow {}^3P_2$		
$Nd(INH)_3X_3$	11490	11490	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	$\bar{\beta} = 0.978$	$\bar{\beta} = 0.974$
	12445	12420	$\rightarrow {}^4F_{5/2}$	$\delta = 2.25$	$\delta = 2.71$
	13330	13330	$\rightarrow {}^4F_{7/2}$	$b^{1/2} = 0.105$	$b^{1/2} = 0.115$
	14600	14560	$\rightarrow {}^4F_{9/2}$		
	15900	—	$\rightarrow {}^2H_{11/2}$		
	17090	17080	$\rightarrow {}^4G_{5/2}$		
			${}^2G_{7/2}$		
	19050	18957	$\rightarrow {}^4G_{9/2}$		
	20960	20830	$\rightarrow {}^2G_{9/2}$		
	21190	21050	$\rightarrow {}^4G_{11/2}$		
	21550	21510	$\rightarrow {}^2P_{1/2}$		
	23265	23150	$\rightarrow {}^2D_{5/2}$		
$Sm(INH)_3X_3$	—	17090	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	$\bar{\beta} = 0.998$	$\bar{\beta} = 0.994$
	20920	20700	$\rightarrow I_{11/2}$	$\delta = 0.160$	$\delta = 0.553$
	21510	21370	$\rightarrow {}^4I_{13/2}$	$b^{1/2} = 0.028$	$b^{1/2} = 0.052$
	—	22730	$\rightarrow {}^4G_{9/2}$		
	24510	24510	$\rightarrow {}^4L_{13/2}$		

* $\bar{\beta} = n^{-1} \sum_n = 1\ \nu comp/\nu aq$; $b^{1/2} = [\frac{1}{2}(1-\bar{\beta})]^{1/2}$; $\delta = [(1-\bar{\beta})/\bar{\beta}] \times 100$

termined by a careful comparison of the acetonitrile solution spectrum of the ligand with the solid state spectra of the complexes. The amide I, amide II, amide III and ν(N-N) bands are observed at 1670, 1560, 1330 and 980 cm^{-1} in the solution spectrum of the ligand and in 1650–1625, 1545–1530, 1360–1340 and 1030–1020 cm^{-1} regions respectively in the nujol spectra of all the complexes. A negative shift in amide I and II bands and a positive shift in amide III band in the spectra of all the complexes compared with that of the ligand indicate coordination through carbonyl oxygen[16]. The observed positive shift in the ν(N-N) mode in the spectra of all the complexes suggests the $>$N–N$<$ moiety coordination either through the –NH– group or through the terminal $-NH_2$ group of the hydrazide[17]. However, the observed negative shifts in the bands of NH_2 stretching, rocking and wagging vibrations in the spectra of all the complexes compared to those of the free ligand at 3340, 1140 and 890 cm^{-1} respectively show the coordination of $-NH_2$ group with the metal ions. The bands appearing at 995, 658 and 400 cm^{-1} in the spectrum of the parent ligand due to the ring skeletal vibration, in-plane and out-of-plane ring deformation modes respectively remain almost unaltered in the spectra of all the complexes indicating the non-involvement of ring nitrogen in coordination with the metal ions.

A very strong band appearing in the spectra of all the thiocyanato complexes in the 2060–2030 cm^{-1} region can be assigned to ν(CN) of terminally bonded thiocyanato groups[18]. The M–NCS bonding is more decisively suggested by the ν(CS) and δ(NCS) modes appearing in the 835–830 and 490–480 cm^{-1} regions in the spectra of these complexes. The non-ligand bands appearing in the 485–450 and 350–330 cm^{-1} regions in the spectra of all the complexes are tentatively assigned to ν(M–O) and ν(M–N) modes respectively[19].

Based on the elemental analysis and various physico-chemical data, a coordination number 'nine' has been proposed around the metal ion in all the complexes where INH acts as a neutral bidentate ligand coordinating through carbonyl oxygen and terminal nitrogen of the hydrazide moiety.

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