

Synthesis and Magneto-Spectral Investigations of Some Six and Nine Coordinated Complexes of Lanthanides(III) Derived from 4[N-(2'-Hydroxy-1'-Naphthalidene)amino]Antipyrinethiosemicarbazone

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The present work describes the synthesis and characterization of some six and nine coordinated complexes of trivalent lanthanide(III) with 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone (HNAAPTS). All the complexes have the general composition $\text{LnX}_{3,n}(\text{HNAAPTS})$ ($\text{X} = \text{NO}_3^-$, $n = 1$; $\text{X} = \text{NCS}^-$ or ClO_4^- , $n = 2$). The complexes were characterized through elemental analyses, molar mass, conductivity measurements, magnetic susceptibilities, and infrared and electronic spectra. Infrared spectra revealed that HNAAPTS acts as a neutral tridentate (N,N,S) donor. The coordination number in these complexes is either six or nine depending on the nature of the anionic ligand.

Keywords: Lanthanides(III), Thiosemicarbazone, Coordination compounds

INTRODUCTION

Schiff base metal complexes have played a major role in the development of coordination chemistry. A large number of transition metal complexes of thiosemicarbazones have been reported [1-3]. However, very few reports are available on trivalent lanthanide complexes of thiosemicarbazones [4,5]. In the present work we report some six and nine coordinated complexes of lanthanides(III) coordination compounds of 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinethiosemicarbazone (HNAAPTS) (Fig.1).

EXPERIMENTAL

The lanthanide nitrates and oxides were obtained from Rare

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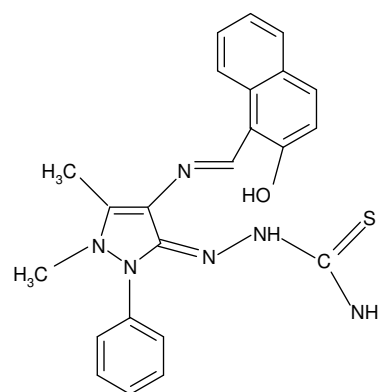


Fig. 1. 4[N-(2'-hydroxy-1'-naphthalidene)amino] antipyrinethiosemicarbazone.

Earth Products Ltd. (India) and used without further purification. The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid (AR)

and evaporating off the excess of acid [6]. The lanthanide thiocyanates were prepared by adding a warm ethanolic solution of lanthanide nitrates to warm ethanolic solutions 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 [7]. The ligand HNAAPTS was synthesized in the laboratory as previously described [8].

Synthesis of the Complexes

$\text{Ln}(\text{NO}_3)_3(\text{HNAAPTS})$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). All the complexes were synthesized by the following general method. A solution of the respective lanthanide(III) nitrate (1 mmol) and HNAAPTS (1.1 mmol) in hot methanol (15 ml each) were mixed and refluxed in a waterbath for ~2 h. On cooling in an ice bath, the resulting solid complex was separated out. It was repeatedly washed with methanol and diethyl-ether and dried in a desiccator over P_4O_{10} .

$\text{Ln}(\text{NCS})_3 \cdot 2(\text{HNAAPTS})$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). These complexes were synthesized as follows: A methanolic solution of the ligand was refluxed for 1 h and then a methanolic solution of the trivalent lanthanide isothiocyanate was added (metal to ligand in 1:2 mol ratio). The reaction mixture was refluxed for ~2 h and then heated slowly on a hot plate until a thick layer of the precipitate settled down. The supernatant liquid was decanted off and the product was separated out. It was then washed several times with warm methanol to remove any excess of metal salt and/or ligand. Finally the complex was dried *in vacuo* over P_4O_{10} .

$\text{Ln}(\text{ClO}_4)_3 \cdot 2(\text{HNAAPTS})$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The corresponding metal perchlorate (1 mmol) was dissolved in 10 ml of anhydrous ethanol and then was added to the refluxing solution of ligand (2.1 mmol) in anhydrous ethanol (20 ml). The reaction mixture was refluxed for ~2-3 h, until a colored solid mass separated out. The precipitate was filtered, washed with ethanol and finally with diethyl ether and dried *in vacuo* over P_4O_{10} .

Analyses

The lanthanide metal content was estimated as its oxide by direct combustion in a platinum crucible. The conductivity measurement was carried out using a Toshniwal conductivity

bridge (type CL 01/01) and a dip type cell operated at 220 volts AC mains at room temperature. The molecular weights of the complexes were determined in the laboratory cryoscopically in freezing PhNO_2 using a Beckmann thermometer with an accuracy ± 0.01 °C. The magnetic measurements were carried out at room temperature with a Gouys balance and anhydrous copper sulfate was used as a calibrant. The infrared spectra of the complexes were determined using a Perkins Elmer infrared spectrophotometer model 521 in KBr in the range of 4000-200 cm^{-1} . A Hilger Uvispeck spectrophotometer with a 1 cm quartz cell was employed for recording the visible spectra of Pr^{3+} , Nd^{3+} , and Sm^{3+} complexes.

RESULTS AND DISCUSSION

The reaction of non-aqueous solutions of lanthanide(III) salts with HNAAPTS resulted in the formation of the complexes of the general composition $\text{LnX}_{3.n}(\text{HNAAPTS})$ ($\text{X} = \text{NO}_3$, $n = 1$; $\text{X} = \text{NCS}$ or ClO_4 , $n = 2$; Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The complexes are anhydrous in nature, which is evident from their analytical and infrared studies. The complexes are generally soluble in common organic solvents, but insoluble in diethyl-ether. The analytical data are presented in Tables 1-3. The molar conductance of nitrate 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 in nitrobenzene. Data on the molecular weight of the complexes in nitrobenzene are presented in Tables 1-3, along with the values calculated on the basis of established molecular formulas of the complexes. The ratio of observed molar masses to the calculated masses for $\text{Ln}(\text{NO}_3)_3 \cdot (\text{HNAAPTS})$ or $\text{Ln}(\text{NCS})_3 \cdot 2(\text{HNAAPTS})$ is ~0.98, which shows that the complexes are monomeric in solution. In the case of $\text{Ln}(\text{ClO}_4)_3 \cdot 2(\text{HNAAPTS})$, the ratio is found to be 0.25. This data further support that four species are formed in the perchlorato complexes.

The magnetic moment values observed in the present lanthanide(III) complexes are summarized in Table 4. The data shows that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electron configuration and absence of unpaired electrons. All other triple positive

Some Six and Nine Coordinated Complexes of Lanthanides(III)

Table 1. Analytical, Conductivity and Molecular Weight Data of Lanthanide(III) Nitrate Complexes of HNAAPTS

Compound	Found (Calcd.) Analysis (%)			Λ_m (ohm ⁻¹ cm ² mol ⁻¹)	Electrolytic nature	Average molecular weight	Formula weight
	Ln	N	S				
La(NO ₃) ₃ ·(HNAAPTS)	18.29 (18.41)	16.52 (16.68)	8.40 (8.47)	2.1	Non-electrolyte	750	755
Pr(NO ₃) ₃ ·(HNAAPTS)	18.48 (18.62)	16.48 (16.64)	8.38 (8.45)	1.9	Non-electrolyte	752	757
Nd(NO ₃) ₃ ·(HNAAPTS)	18.78 (18.94)	16.40 (16.57)	8.36 (8.42)	1.7	Non-electrolyte	755	760
Sm(NO ₃) ₃ ·(HNAAPTS)	19.40 (19.58)	16.30 (16.44)	8.27 (8.35)	2.0	Non-electrolyte	761	766
Gd(NO ₃) ₃ ·(HNAAPTS)	20.18 (20.31)	16.18 (16.30)	8.19 (8.27)	1.9	Non-electrolyte	769	773
Tb(NO ₃) ₃ ·(HNAAPTS)	20.34 (20.51)	16.08 (16.23)	8.17 (8.25)	1.7	Non-electrolyte	770	775
Dy(NO ₃) ₃ ·(HNAAPTS)	20.70 (20.87)	16.02 (16.18)	8.15 (8.22)	1.8	Non-electrolyte	773	778.5
Ho(NO ₃) ₃ ·(HNAAPTS)	20.98 (21.12)	15.98 (16.13)	8.13 (8.19)	2.1	Non-electrolyte	777	781

Table 2. Analytical, Conductivity and Molecular Weight Data of Lanthanide(III) Isothiocyanate Complexes of HNAAPTS

Compound	Found (Calcd.) Analysis (%)				Λ_m (ohm ⁻¹ cm ² mol ⁻¹)	Electrolytic nature	Average molecular weight	Formula weight
	Ln	N	S	NCS				
La(NCS) ₃ ·2(HNAAPTS)	11.72 (11.84)	17.73 (17.90)	13.52 (13.64)	14.68 (14.83)	3.1	Non-electrolyte	1168	1173
Pr(NCS) ₃ ·2(HNAAPTS)	11.86 (12.00)	17.70 (17.87)	13.49 (13.61)	14.65 (14.80)	2.9	Non-electrolyte	1166	1175
Nd(NCS) ₃ ·2(HNAAPTS)	12.08 (12.22)	17.65 (17.82)	13.45 (13.58)	14.62 (14.77)	2.7	Non-electrolyte	1172	1178
Sm(NCS) ₃ ·2(HNAAPTS)	12.52 (12.66)	17.60 (17.73)	13.39 (13.51)	14.56 (14.69)	2.8	Non-electrolyte	1177	1184
Gd(NCS) ₃ ·2(HNAAPTS)	13.02 (13.18)	17.51 (17.63)	13.30 (13.43)	14.48 (14.60)	2.7	Non-electrolyte	1185	1191
Tb(NCS) ₃ ·2(HNAAPTS)	13.17 (13.32)	17.47 (17.60)	13.27 (13.41)	14.42 (14.58)	2.4	Non-electrolyte	1188	1193
Dy(NCS) ₃ ·2(HNAAPTS)	13.40 (13.58)	17.42 (17.55)	13.24 (13.37)	14.40 (14.54)	1.9	Non-electrolyte	1191	1196.5
Ho(NCS) ₃ ·2(HNAAPTS)	13.53 (13.76)	17.38 (17.51)	13.18 (13.34)	14.38 (14.51)	2.4	Non-electrolyte	1193	1199

Table 3. Analytical, Conductivity and Molecular Weight Data of Lanthanide(III) Perchlorate Complexes of HNAAPTS

Compound	Found (Calcd.) Analysis (%)				Λ_m ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Electrolytic nature	Average molecular weight	Formula weight
	Ln	N	S	ClO ₄				
La(ClO ₄) ₃ ·2(HNAAPTS)	10.60 (10.71)	12.84 (12.94)	4.88 (4.93)	22.80 (23.00)	78.4	1:3	323	1297.5
Pr(ClO ₄) ₃ ·2(HNAAPTS)	10.74 (10.85)	12.82 (12.92)	4.87 (4.92)	22.78 (22.97)	79.3	1:3	324	1299.5
Nd(ClO ₄) ₃ ·2(HNAAPTS)	10.96 (11.05)	12.76 (12.89)	4.86 (4.91)	22.71 (22.91)	77.7	1:3	325	1302.5
Sm(ClO ₄) ₃ ·2(HNAAPTS)	11.35 (11.46)	12.84 (12.83)	4.82 (4.89)	22.62 (22.81)	76.9	1:3	325	1308.5
Gd(ClO ₄) ₃ ·2(HNAAPTS)	11.82 (11.93)	12.65 (12.77)	4.80 (4.86)	22.50 (22.69)	77.2	1:3	326	1315.5
Tb(ClO ₄) ₃ ·2(HNAAPTS)	11.97 (12.06)	12.53 (12.75)	4.79 (4.85)	22.46 (22.65)	78.2	1:3	326	1317.5
Dy(ClO ₄) ₃ ·2(HNAAPTS)	12.20 (12.30)	12.50 (12.71)	4.78 (4.84)	22.42 (22.59)	79.3	1:3	328	1321.0
Ho(ClO ₄) ₃ ·2(HNAAPTS)	12.35 (12.46)	12.58 (12.69)	4.76 (4.83)	22.40 (22.55)	77.2	1:3	329	1323.5

Table 4. Permanent Magnetic Moments (B.M.) of Lanthanide Ions and their Coordination Compounds with HNAAPTS at Room Temperature (35 °C)

Ln ³⁺	Theoretical			Measured		
	Hund	Van Vleck	Ln ₂ (SO ₄) ₃ ·8H ₂ O	Ln(NO ₃) ₃ ·HNAAPTS	Ln(NCS) ₃ ·2(HNAAPTS)	Ln(ClO ₄) ₃ ·2(HNAAPTS)
La	0.00	0.00	0.00	Diamagnetic	Diamagnetic	Diamagnetic
Pr	3.60	3.62	3.48	3.61	3.38	3.60
Nd	3.62	3.68	3.52	3.59	3.57	3.59
Sm	0.84	1.55	1.53	1.66	1.59	1.63
Gd	7.94	7.94	7.81	7.91	7.81	7.87
Tb	9.70	9.70	9.40	9.27	9.47	9.21
Dy	10.60	10.60	10.30	10.48	10.61	10.56
Ho	10.60	10.60	10.40	10.39	10.43	10.52

charged lanthanide complexes are paramagnetic due to the presence of 4f-electrons, which are effectively shielded by 5s² and 5p⁶ electrons. The comparison of these observed values

with those observed for 8-hydrated sulfate [9] and those calculated for uncomplexed ions [10] indicates that 4f-electrons do not participate in any bond formation in these

complexes.

Infrared Spectra

The important infrared bands of free ligand and its lanthanide(III) complexes are summarized in Table 5. The strong bands in free ligand observed at 3420 and 3310 cm^{-1} due to ν (NH) remained unaffected after complexation. The ligand band at 1600 cm^{-1} (C=N of imine nitrogen) shifted to lower wavenumbers on complexation suggests involvement of unsaturated nitrogen atoms of two azomethine groups in bonding with the metal ion [11]. Other bands observed in free ligand are at 1320, 1195 cm^{-1} due to ν (C=S) + ν (C=N) + ν (C-N), 1120, 1095 cm^{-1} due to δ (NCS) + CS bending and 840, 820 cm^{-1} due to ν (C=S) stretchings [12]. Coordination of sulfur with metal ion would result in displacement of electrons toward the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation (C=S) stretching vibrations should decrease and that of (C=N) should increase [13]. In the present complexes, the bands at 1320 and 1195 cm^{-1} increased by 50-60 cm^{-1} . Similarly bending modes of (N-C-S) and (C=S) also increased, but to a lesser extent. On the other hand, on complexation the infrared bands at 840 and 820 cm^{-1} shifted to lower wavenumbers with reduced intensity. All these peculiar changes on complexation confidently preclude any unambiguous ascertainment of metal-sulfur bonding. The possibility of thione-thiol tautomerism ($\text{H-N-C-S} \rightleftharpoons \text{C-N-S-H}$) in the present ligand has been ruled out, for there were no bands around 2700-2500 cm^{-1} , characteristic of thiol groups displayed in the infrared absorption [14]. In the far infrared region, ν (Ln-N) and ν (Ln-S) were also assigned to the 430-330 cm^{-1} region [4,5].

For lanthanide(III) nitrate complexes, the occurrence of two strong absorptions in the 1525-1515 cm^{-1} and 1310-1290 cm^{-1} regions are attributed to vibrational modes ν_4 and ν_1 of the covalently bonded nitrate groups, respectively, suggesting that the nitrate groups lie inside the coordination sphere [15,16]. Other absorptions associated with the covalent nitrate groups are also observed in the spectra of the metal-complexes. If the ($\nu_4-\nu_1$) difference is taken as an approximate measure of the covalency of the nitrate group [16], a value of $\sim 200 \text{ cm}^{-1}$ for the present complexes studied herein suggest strong covalency for the metal-nitrate bonding. To identify the monodentate or bidentate nature, we applied the Lever

separation method [17] in the present nitrate complexes. A separation of $\sim 30\text{-}40 \text{ cm}^{-1}$ in the combination bands ($\nu_1 + \nu_4$) (Table 6) in the 1800-1700 cm^{-1} region supports the bidentate nitrate coordination. The bidentate character of nitrate groups has been established by X-ray and neutron diffraction studies [18,19]. Hence, we conclude the nitrate groups in the present complexes are of bidentate nature. In present lanthanide(III) thiocyanate complexes, the (C-N) stretching frequency appears in 2065-2040 cm^{-1} region, which lies on the border line for distinguishing between sulfur and nitrogen bonding in the thiocyanate. Although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded, the frequency of the (C-S) stretching vibration has also been used to diagnose the bonding mode in thiocyanate group. The (C-S) bond identified in 840-780 cm^{-1} region further confirms that the thiocyanate group is N-bonded [20,21]. The δ (N-C-S) (ν_2) is also identified in these complexes (Table 7). In lanthanide(III) perchlorato complexes, the occurrence of two strong bands (Table 8) in the 1110-1080 cm^{-1} and 630-620 cm^{-1} regions is attributed to ν_3 and ν_4 vibrations [22,23]. This suggests that tetrahedral symmetry of ClO_4^- has not been disturbed on complexation and the ClO_4^- ions are not bonded to the lanthanide metal ion.

Electronic Spectra

Typical spectral data for the solutions of the present lanthanide(III) complexes of HNAAPTS have been investigated in acetonitrile (Tables 9,10) 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 of $^3\text{H}_4$, $^4\text{I}_{9/2}$, $^6\text{H}_{5/2}$, $^8\text{S}_{7/2}$ and $^6\text{H}_{15/2}$ to the excited J-levels of the 4f-configuration respectively. Some red shift or nephelauxetic effect is observed in the acetonitrile solutions of these complexes. This red shift is usually accepted as evidence of a higher degree of covalency than the presence of aquo compounds [24,25]. 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 the β values the

Table 5. Infrared Absorption Frequencies (cm^{-1}) of Ln(III) Coordination Compounds of HNAAPTS

Section 1.01 Complex	ν (NH)	ν (C=N)	ν (C=S) + ν (C=N) + ν (C-N)	δ (NCS) + CS-bending	ν (N-N)	ν (C=S)	ν (Ln-N) + ν (Ln-S)
HNAAPTS	3420 s 3310 s	1600 vs	1320 s, 1195 m	1120 m 1095 m	1060 m	840 s 820 s	- -
La(NO ₃) ₃ ·(HNAAPTS)	3415 m 3312 m	1575 s	1365 s, 1240 m	1170m 1130 m	1072 m	772 s 755 s	430 m 320 w
Pr(NO ₃) ₃ ·(HNAAPTS)	3422 m 3310 m	1570 s	1360 s, 1245 m	1172 m 1125 m	1070 m	700s 750 s	425 m 330 w
Nd(NO ₃) ₃ ·(HNAAPTS)	3418 m 3310 m	1562 s	1360 s, 1230 m	1165 m 1125 w	1068 m	700 s 680 m	422 m 325 w
Sm(NO ₃) ₃ ·(HNAAPTS)	3415 m 3315 m	1565 s	1362 s, 1242 m	1175 m 1130 m	1072 m	770 s 752 s	430 m 330 w
Gd(NO ₃) ₃ ·(HNAAPTS)	3415 m 3315 m	1568 s	1362 s, 1240 m	1172 m 1130 m	1070 m	765 s 750 m	415 m 320 w
Tb(NO ₃) ₃ ·(HNAAPTS)	3410 m 3305 m	1565 s	1370 s, 1245 m	1170 m 1125 m	1072 m	770 s 752 m	425 m 310 w
Dy(NO ₃) ₃ ·(HNAAPTS)	3420 m 3315 m	1562 s	1365 m, 1242 m	1172 m 1130 m	1060 m	772 m 755 m	430 m 320 w
Ho(NO ₃) ₃ ·(HNAAPTS)	3415 m 3310 m	1560 s	1362 m, 1235 m	1172 m 1125 m	1070 m	772 m 752 m	415 m 330 w
La(NCS) ₃ ·2(HNAAPTS)	3416 m 3312 m	1565 s	1365 s 1240 m	1175 m 1130 m	1070 m	772 s 755 s	425 m 350 w
Pr(NCS) ₃ ·2(HNAAPTS)	3420 m 3315 m	1562 s	1360 s 1248 m	1165 m 1125 w	1072 m	770 s 750 s	430 m 340 w
Nd(NCS) ₃ ·2(HNAAPTS)	3418 m 3305 m	1560 s	1362 s 1232 m	1172 m 1125 m	1075 m	772 s 695 s	440 m 335 w
Sm(NCS) ₃ ·2(HNAAPTS)	3415 m 3315 m	1565 s	1365 s 1240 s	1168 m 1130 w	1068 m	770 s 752 s	435 m 320 w
Gd(NCS) ₃ ·2(HNAAPTS)	3422 m 3310 m	1560 s	1362 s 1242 m	1172 m 1130 m	1070 m	765 m 750 m	442 m 325 w
Tb(NCS) ₃ ·2(HNAAPTS)	3415 m 3312 m	1555 s	1360 s 1248 m	1170 m 1125 m	1072 m	770 s 752 m	445 m 330 w
Dy(NCS) ₃ ·2(HNAAPTS)	3422s 3315 s	1560 s	1362 s 1242 s	1170 m 1130 w	1070 m	782 m 755 m	437 m 332 w
Ho(NCS) ₃ ·2(HNAAPTS)	3422 s 3312 m	1562 s	1360 m 1242 m	1178 m 1132 m	1075 m	772 m 750 m	445 m 318 w
La(ClO ₄) ₃ ·2(HNAAPTS)	3422 m 3310 m	1562 s	1362 m 1242 m	1172 m 1130 m	1070 m	765 s 750 m	425 m 370 w
Pr(ClO ₄) ₃ ·2(HNAAPTS)	3415 m 3310 m	1560 s	1362 m 1235 m	1165 m 1125 m	1072 m	772 m 752 m	415 m 332 w
Nd(ClO ₄) ₃ ·2(HNAAPTS)	3418 m 3310 m	1562 s	1360 s 1230 m	1165 m 1125 w	1068 m	765 s 750 s	435 m 335 w
Sm(ClO ₄) ₃ ·2(HNAAPTS)	3415 m 3315 m	1568 s	1362 s 1240m	1170 m 1125 m	1070 m	772 s 750 m	440 m 325 w
Gd(ClO ₄) ₃ ·2(HNAAPTS)	3418 m 3315 m	1565 s	1370 s 1245 m	1172 m 1130 m	1072 m	765 s 750 m	452 m 312 w
Tb(ClO ₄) ₃ ·2(HNAAPTS)	3418 m 3310 m	1568 s	1362 s 1240 m	1172 m 1130 m	1065 m	772 m 755 m	435 m 320 w
Dy(ClO ₄) ₃ ·2(HNAAPTS)	3420 s 3312 m	1575 s	1365 s 1240 m	1170 m 1130 w	1072 m	772 s 755 s	440 m 322 w
Ho(ClO ₄) ₃ ·2(HNAAPTS)	3415 m 3315 m	1568 s	1362 s 1240 m	1172 m 1130 m	1070 m	765 s 750 m	415 m 320 w

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Table 6. Infrared Absorption Frequencies of Nitrate Groups in Ln(NO₃)₃.HNAAPTS

Complex	(ν ₂ + ν ₅)	(ν ₂ + ν ₆)	(ν ₂ + ν ₅) - (ν ₂ + ν ₆)	ν ₄	ν ₁	ν ₂	ν ₆	ν ₃	ν ₅
La(NO ₃) ₃ .HNAAPTS	1790 vw	1740 vw	50	1500 s	1300 s	1028 m	815 m	725 m	695 w
Pr(NO ₃) ₃ .HNAAPTS	1785 vw	1740 vw	45	1502 s	1290 m	1030 m	810 m	745 s	690 w
Nd(NO ₃) ₃ .HNAAPTS	1790 vw	1750 vw	40	1510 s	1302 s	1025 m	805 sh	735 s	692 w
Sm(NO ₃) ₃ .HNAAPTS	1785 vw	1740 vw	45	1490 s	1300 s	1028 m	810 m	738 s	690 w
Gd(NO ₃) ₃ .HNAAPTS	1788 vw	1742 vw	46	1495 s	1295 m	1030 m	815 m	735 s	690 w
Tb(NO ₃) ₃ .HNAAPTS	1785 vw	1740 vw	45	1500 s	1300 m	1022 m	820 m	750 s	692 w
Dy(NO ₃) ₃ .HNAAPTS	1790 vw	1740 vw	50	1505 s	1305 s	1020 m	822 m	752 s	695 w
Ho(NO ₃) ₃ .HNAAPTS	1780 vw	1740 vw	40	1510 s	1300 s	1035 m	823 m	755 s	698 w

Table 7. Infrared Absorption Frequencies (cm⁻¹) of Isothiocyanato Groups in Ln(NCS)₃.2(HNAAPTS)

Complex	ν (C-N)	ν (C-S)	δ (N-C-S)
La(NCS) ₃ .2(HNAAPTS)	2050 s	857 m	465 m
Pr(NCS) ₃ .2(HNAAPTS)	2052 s	860 m	460 m
Nd(NCS) ₃ .2(HNAAPTS)	2065 s	850 m	470 m
Sm(NCS) ₃ .2(HNAAPTS)	2050 s	840 m	465 m
Gd(NCS) ₃ .2(HNAAPTS)	2055 s	837 m	460 m
Tb(NCS) ₃ .2(HNAAPTS)	2060 s	845 m	-
Dy(NCS) ₃ .2(HNAAPTS)	2065 s	852 m	470 w
Ho(NCS) ₃ .2(HNAAPTS)	2062 s	845 m	475 w

Table 8. Infrared Absorption Frequencies (cm⁻¹) of Perchlorato Groups in Ln(ClO₄)₃.2(HNAAPTS)

Complex	ν ₃	ν ₄
La(ClO ₄) ₃ .2(HNAAPTS)	1085 s	625 s
Pr(ClO ₄) ₃ .2(HNAAPTS)	1090 s	622 s
Nd(ClO ₄) ₃ .2(HNAAPTS)	1100 s,br	620 s
Sm(ClO ₄) ₃ .2(HNAAPTS)	1095 s	625 s
Gd(ClO ₄) ₃ .2(HNAAPTS)	1105 s,br	630 s
Tb(ClO ₄) ₃ .2(HNAAPTS)	1100 s	625 s
Dy(ClO ₄) ₃ .2(HNAAPTS)	1090 s,br	632 s
Ho(ClO ₄) ₃ .2(HNAAPTS)	1095 s	625 s

Table 9. Electronic Spectral Data (cm⁻¹) and Related Bonding Parameters of Lanthanide(III) Isothiocyanate Complexes of HNAAPTS

Ln ³⁺	Ln(NCS) ₃ Electronic Spectral Bands	[Ln(HNAAPTS) ₂ (NCS) ₃] Electronic Spectral Bands	<i>J</i> -Levels	(1-β)	β	b ^{1/2}	δ%	η
Pr ³⁺	22400	22240	³ H ₄ → ³ P ₂	0.0071	0.9928	0.0422	0.7191	0.0036
	21230	21030	→ ³ P ₁	0.0094	0.9906	0.0485	0.9509	0.0047
	20800	20600	→ ³ P ₀	0.0096	0.9904	0.0490	0.9703	0.0048
	16900	16700	→ ¹ D ₂	0.0118	0.9882	0.0543	1.1971	0.0059
Nd ³⁺	19400	19200	⁴ I _{9/4} → ² G _{9/2}	0.0103	0.9897	0.0507	1.0407	0.0051
	17400	17200	→ ⁴ G _{5/2} , ² G _{7/2}	0.0115	0.9885	0.0536	1.1613	0.0058
	13400	13240	→ ² S _{3/2} , ⁴ F _{7/2}	0.0119	0.9881	0.0546	1.2084	0.0060
	12500	12240	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.0208	0.9792	0.0721	2.1241	0.0105
Sm ³⁺	24900	24700	⁴ H _{5/2} → ⁴ P _{9/2}	0.0080	0.9920	0.0448	0.8095	0.0040
	24000	23820	→ ⁶ P _{5/2}	0.0075	0.9925	0.0433	0.7556	0.0037
	21600	21440	→ ⁴ P _{13/2}	0.0074	0.9926	0.0430	0.7455	0.0037

Table 10. Electronic Spectral Data (cm⁻¹) and Related Bonding Parameters of Lanthanide(III) Perchlorato Complexes of HNAAPTS

Ln ³⁺	Ln(ClO ₄) ₃ Electronic Spectral Bands	[Ln(HNAAPTS) ₂ (ClO ₄) ₃] Electronic Spectral Bands	<i>J</i> -Levels	(1-β)	β	b ^{1/2}	δ%	η
Pr ³⁺	22470	22340	³ H ₄ → ³ P ₂	0.0057	0.9943	0.0380	0.5813	0.0023
	21325	21200	→ ³ P ₁	0.0058	0.9942	0.0382	0.5894	0.0029
	20750	20620	→ ³ P ₀	0.0062	0.9938	0.0395	0.6299	0.0031
	17000	16850	→ ¹ D ₂	0.0068	0.9912	0.0469	0.8898	0.0044
Nd ³⁺	19600	19450	⁴ I _{9/4} → ² G _{9/2}	0.0076	0.9924	0.0437	0.7709	0.0038
	17380	17250	→ ⁴ G _{5/2} , ² G _{7/2}	0.0074	0.9926	0.0432	0.7526	0.0037
	13680	13580	→ ² S _{3/2} , ⁴ F _{7/2}	0.0073	0.9927	0.0427	0.7353	0.0036
	12470	12380	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.0072	0.9928	0.0424	0.7262	0.0036
Sm ³⁺	24870	24740	⁴ H _{5/2} → ⁴ P _{9/2}	0.0052	0.9948	0.0361	0.5247	0.0026
	24000	23800	→ ⁶ P _{5/2}	0.0083	0.9917	0.0456	0.8400	0.0041
	21550	21450	→ ⁴ P _{13/2}	0.0046	0.9954	0.0340	0.4661	0.0023

covalence factors (b^{1/2}), Sinha parameter (δ%) (metal-ligand covalency percent) and the covalency angular overlap parameter (η) have been calculated using the expressions below [25,26].

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

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

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

The positive values for (1-β) and δ% in these coordination compounds (Tables 9,10) suggest that the bonding between

the metal and the ligand is covalent compared to 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.

Stereochemistry

[Ln(HNAAPTS)(NO₃)₃] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The conductance measurements of these coordination compounds in nitrobenzene indicate the non-ionic nature of these species. Hence all the three nitrate groups are present inside the coordination sphere. Infrared data reveal the bidentate nature of NO₃⁻, thus the lanthanide ion is surrounded by six oxygen atoms of three bidentate nitrate ions, two nitrogens and one sulfur atom of HNAAPTS, thus producing a coordination number of nine for the lanthanide ion [27].

[Ln(HNAAPTS)₂(NCS)₃] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The non-electrolytic behavior and infrared studies of these coordination compounds suggest that all the NCS⁻ ions are coordinated to the metal ion *via* N-atoms. HNAAPTS is a neutral tridentate ligand (N,N,S-donor) and thus a coordination number of nine for the lanthanide ion has been suggested in all these coordination compounds.

[Ln(HNAAPTS)₂](ClO₄)₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The molar conductance of these coordination compounds in nitrobenzene indicate that they behave as 1:3 electrolytes. Hence, none of the three perchlorate ions are bonded to the lanthanide ions and all three are present outside the coordination sphere. Infrared spectra of all these coordination compounds further indicate the absence of water or ethanol and, hence, a coordination number of six has been assigned to each of the lanthanide ions in these coordination compounds.

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