

MAGNETO AND SPECTRAL BEHAVIOUR OF LANTHANIDE(III) PERCHLORATE COMPLEXES OF N-ISONICOTINAMIDOANISALALDIMINE

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A new series of lanthanide(III) perchlorate complexes of N-isonicotinamidoanisalaldimine (INH-SAL) with the general composition $[\text{Ln}(\text{INH-SAL})_3(\text{ClO}_4)_3]$ (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy) were synthesized and characterized by elemental analyses, conductance, molecular weight, infrared and electronic spectral data. INH-SAL acts as a bidentate (N, O) chelating agents. The tentative coordination number eight has been assigned. Thermal behaviour of some representative chelates have also been investigated.

Key Words: N-Isonicotinamidoanisalaldimine; Ln(III) Complexes; Magnetic; Infrared; Electronic

Introduction

Schiff bases may form stable complexes with lanthanide because of the availability of both nitrogen and oxygen atoms for coordination¹. The literature survey clearly reveals that no report has been published on lanthanide(III) complexes of hydrazones of isonicotinic acid hydrazide. Thus in the present communication we report our results on lanthanide(III) perchlorate complexes of N-isonicotinamidoanisalaldimine (INH-SAL).

The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess of acid. The ligand INH-SAL was synthesized in the laboratory by condensation of isonicotinic acid hydrazide with *p*-anisaldehyde (yield — 82%; m.f. $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$; colour-light yellow; m.pt. 127°C).

The metal complexes were synthesized by treating a methanolic solution of the corresponding lanthanide(III) perchlorate with a hot methanolic solution of the ligand in required stoichiometric ratio. The reaction mixture was refluxed on a water bath for 3 hrs. The solvent was partially distilled off and then the mixture was cooled to room temperature. The separated precipitates were suction filtered, washed with ethanol and dried under vacuum at room temperature over P_4O_{10} . The analyses and physical measurements were made as reported earlier².

The analytical data of the complexes are presented in Table I. The molar conductance values of the complexes in PhNO_2 (76.9–81.9) $\Omega^{-1} \text{cm}^2\text{mol}^{-1}$ show that the complexes are 1:3 electrolytes. The molecular weights in freezing PhNO_2 also support the similar electrolytic behaviour of the complexes. The

magnetic moment values observed in the present study and given in Table I show that lanthanum complexes are diamagnetic in nature^{2,3}.

Table I
Analytical, conductivity, molecular weight and magnetic moments data of lanthanide(III) perchlorato-complexes of INH-SAL

Complex	Found (Calcd.) %			Ω_M ($\text{ohm}^{-1}\text{cm}^2$ mole^{-1})	Mol. wt. Found (Calcd.)	μ_{eff} B.M.
	Ln	N	Anion			
La(ClO_4) ₃ ·4(INH-SAL)	9.61 (9.53)	11.57 (11.52)	20.57 (20.48)	76.9	363 (1457.5)	Diamag.
Pr(ClO_4) ₃ ·4(INH-SAL)	9.74 (9.65)	11.56 (11.51)	20.54 (20.45)	77.9	364 (1459.4)	3.63
Nd(ClO_4) ₃ ·4(INH-SAL)	9.93 (9.84)	11.53 (11.48)	20.49 (20.41)	78.6	365 (1462.5)	3.59
Sm(ClO_4) ₃ ·4(INH-SAL)	10.28 (10.21)	11.50 (11.44)	20.39 (20.32)	79.1	366 (1468.5)	1.60
Gd(ClO_4) ₃ ·4(INH-SAL)	10.71 (10.64)	11.43 (11.38)	20.31 (20.23)	80.1	368 (1475.5)	7.91
Tb(ClO_4) ₃ ·4(INH-SAL)	10.84 (10.76)	11.42 (11.37)	20.28 (20.20)	81.9	369 (1477.5)	9.31
Dy(ClO_4) ₃ ·4(INH-SAL)	11.08 (10.97)	11.39 (11.34)	20.22 (20.15)	77.6	370 (1481.0)	10.51

Infrared Spectra

The amide-I band in INH-SAL appears at 1690 and 1640 cm^{-1} . In the i.r. spectra of the complexes a considerable negative shift in $\nu(\text{C}=\text{O})$ is observed indicating a decrease in the stretching force-constant of $\text{C}=\text{O}$ 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 $\text{C}-\text{N}$ link. In INH-SAL, the absorption at *ca.* 1565 cm^{-1} region has been assigned to amide-II absorption. The NH -stretching absorption in free ligands occurs⁴ at *ca.* 3290 and 3220 cm^{-1} , which remains unaffected after complexation. Another important band occurs at *ca.* 1590 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ (azomethine) mode^{5,6}, shifted to lower wave number after complexation and appears in 1550-1530 cm^{-1} region respectively indicating the involvement of N-atom of the azomethine group in coordination^{5,6}.

The overall i.r. spectral evidence suggests that the ligand acts as a bidentate ligand and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five-membered chelate ring. Some new bands with medium to weak intensities appear in the far i.r. region (440-360 cm^{-1}) in the complexes are assigned to $\nu(\text{Ln}-\text{O})/\nu(\text{Ln}-\text{N})$ modes^{10,11}.

In all the complexes only two strong ν_3 and ν_4 bands are observed at 1110-1080 cm^{-1} region and 630-620 cm^{-1} region respectively, for perchlorate

Table II
Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) perchlorate complexes of INH-ANSL

Complex	$\text{Ln}(\text{ClO}_4)_3$ electronic spectral bands	Complex electronic spectral bands	Energy levels	$(1-\beta)$	β	b^2	$\delta\%$
$\text{Pr}(\text{ClO}_4)_3 \cdot 4(\text{INH-ANSL})$	22470	22360	$^4\text{H}_4 \rightarrow ^3\text{P}_2$	0.00489	0.99570	0.04944	0.49140
	21325	21210	$\rightarrow ^3\text{P}_1$	0.00539	0.99460	0.05191	0.54192
	20750	20620	$\rightarrow ^3\text{P}_0$	0.00626	0.99373	0.05594	0.62994
	17000	16860	$\rightarrow ^1\text{D}_2$	0.00823	0.99176	0.06414	0.82983
$\text{Nd}(\text{ClO}_4)_3 \cdot 4(\text{INH-ANSL})$	19600	19480	$^2\text{I}_{9/2} \rightarrow ^2\text{G}_{9/2}$	0.00612	0.99387	0.05531	0.61577
	17380	17260	$\rightarrow ^4\text{G}_{5/2}, ^2\text{G}_{7/2}$	0.00690	0.99309	0.05873	0.69480
	13680	13640	$\rightarrow ^2\text{S}_{3/2}, ^4\text{F}_{7/2}$	0.00292	0.99707	0.03820	0.29285
	12470	12420	$\rightarrow ^4\text{F}_{5/2}, ^4\text{H}_{9/2}$	0.00400	0.99599	0.04472	0.40161
$\text{Sm}(\text{ClO}_4)_3 \cdot 4(\text{INH-ANSL})$	24870	24740	$^6\text{H}_{5/2} \rightarrow ^4\text{F}_{9/2}$	0.00522	0.99477	0.05108	0.52474
	24000	23700	$\rightarrow ^6\text{P}_{5/2}$	0.01250	0.98750	0.07905	1.26582
	21550	21510	$\rightarrow ^4\text{I}_{13/2}$	0.00185	0.99814	0.03041	0.18534
	22400	22260	$^5\text{I}_8 \rightarrow ^5\text{G}_6, ^5\text{F}_1$	0.00625	0.99375	0.05590	0.62893
$\text{No}(\text{ClO}_4)_3 \cdot 4(\text{INH-ANSL})$	19310	18980	$\rightarrow ^5\text{F}_4$	0.01708	0.98291	0.09241	1.73769
	15740	15610	$\rightarrow ^5\text{F}_5, ^5\text{S}_2$	0.00825	0.99174	0.06422	0.83187
	13510	13380	$\rightarrow ^5\text{I}_4$	0.00962	0.99037	0.06935	0.97135

ion indicating that tetrahedral symmetry has not been disturbed on complexation, and the perchlorate ions are not bonded to metal ion^{10,11}.

Electronic Spectra

Typical spectral data for solutions of the present complexes investigated in acetonitrile is recorded in Table II and for comparison, data for an aqueous salt solution are also given. The absorption bands of praseodymium(III), neodymium(III), samarium(III), gadolinium(III) and dysprosium(III) in the visible and near i.r. 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 4f-configuration, respectively. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From the β -values the covalence factor $b^{1/2}$ and the Sinha parameter δ % (metal-ligand covalency percent) were also calculated. The positive values for $(1 - \beta)$ and δ % in these compounds 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} were found to be positive indicating covalent bonding^{12,13}.

Thermal Studies

The t.g. curves of $[Ln(INH-ANSL)_4](ClO_3)_5$ (Ln = La, Nd, Gd or Dy) indicate that above 240°C, the complexes start to lose mass with partial evaporation of the organic ligand. In the temperature range 250-320°C, a weight loss is ca. 44% corresponds to loss of 2.5 moles of organic ligand; which at ca. 430°C, the loss is ca. 70% corresponds to total loss of organic ligand molecules. Finally, at ca. 810°C, stable lanthanide oxides (Ln_2O_3) are formed¹⁴.

In conclusion, the conductance measurement and i.r. studies reveal that the lanthanide ion has a coordination number eight.

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