

Synthesis and spectroscopic investigations of complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide

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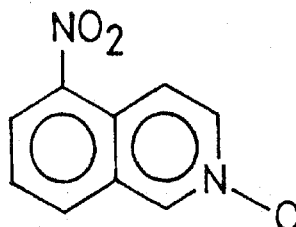
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Abstract. New complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide (NIQNO) of the type $\text{Ln}(\text{NIQNO})_3(\text{NO}_3)_3$ where $\text{Ln} = \text{La}-\text{Yb}$ and Y have been synthesised and characterised by analyses, conductance, infrared, proton NMR and electronic spectra. The molar conductance and IR data point to the coordinated nature of the nitrate groups in all the complexes studied. IR spectral analysis along with the proton NMR spectra of the ligand and its (diamagnetic) La^{3+} and Y^{3+} complexes unequivocally proves that the coordination of the ligand to the tripositive lanthanide ions taken place through the oxygen of the N-O group. From a comparison of the visible electronic spectral shapes of the Nd^{3+} and Ho^{3+} complexes, a probable coordination number of eight can be assigned to all the complexes.

Keywords. Lanthanide nitrate complexes; 5-nitroisoquinoline-2-oxide; infrared; proton NMR; electronic spectra.

1. Introduction

Investigations on the lanthanide complexes of substituted pyridine-1-oxides with substituents other than the methyl group, have led to the conclusion that substituents at the 4-position of the heterocyclic ring are capable of introducing a steric hindrance to coordination and consequently affect the ligand to metal ratio as compared to that in the substituted pyridine-1-oxide complexes (Navaneetham and Soundararajan 1981). To understand the effect of the substituents on the coordination number around the metal ion due to the differences in their nature such as their position in the ring, the bulkiness, electron-donating or -withdrawing tendency, new complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide have been synthesised and studied by analyses, conductance, IR, proton NMR and electronic spectra.



2. Experimental

2.1 Materials

Isoquinoline was obtained from Fluka Chemicals, Germany. Lanthanide oxides (99.99% pure) were obtained from the American Potash and Chemicals, USA. All the solvents were purified by standard methods.

5-nitroisoquinoline was prepared by nitration of isoquinoline-2-oxide as described by (Katritzky *et al* 1957) for 4-nitropyridine-1-oxide and recrystallized from chloroform solution (m.p. 219–220°C; Lit., Ochiai and Ishikawa 1945, 220–222°C). Hydrated lanthanide nitrates were prepared as reported earlier (Rajasekar and Soundararajan 1979).

2.2 Preparation of the complexes

A solution of lanthanide nitrate (1 mmole) in hot ethyl acetate (15 ml) was added slowly with stirring to a boiling solution NIQNO (15 mmoles) in ethyl acetate (200 ml). The stirring was continued for 5 minutes. The precipitated complex was filtered through a sintered crucible (G_3), washed with hot chloroform followed by diethyl ether and finally dried over phosphorus(V) oxide in a vacuum desiccator.

2.3 Analytical and physical methods

The metal and anion content of the complexes were estimated by EDTA titrations using xylenol-orange as indicator (Lyle and Rahman 1963). The anion was estimated by gravimetric precipitation with nitron as described by (Welcher 1947). The ligand was estimated spectrophotometrically at 204 nm using the calibration curve method (Willard *et al* 1965). The analytical data are presented in table 1. The IR spectra of the ligand and its lanthanide complexes in nujol (in the region 400–4000 cm^{-1}) were recorded on a Perkin-Elmer model 397 spectrophotometer. The important IR bands and their assignments are given in table 2. Proton NMR spectra of the ligand and its diamagnetic La^{3+} and Y^{3+} complexes were recorded on a Bruker WH-270 spectrometer operating in the FT mode, using CD_3CN as solvent and TMS as the internal reference (table 3). Electronic spectra of Nd^{3+} and Ho^{3+} complexes in acetonitrile were recorded in the visible region on a Hitachi uv-3400 model spectrophotometer. The solid state spectra for the same complexes

Table 1. Analytical and conductivity data for the complexes of the general formula $\text{Ln}(\text{NIQNO})_3(\text{NO}_3)_3$.

Ln^{3+}	% Metal		% Ligand		% Anion		* Molar conductance in CH_3CN
	Found	Calc.	Found	Calc.	Found	Calc.	
La	15.48	15.52	63.84	63.69	20.70	20.78	14
Nd	16.14	16.02	63.53	63.32	20.84	20.66	13
Ho	17.84	17.91	61.64	61.89	20.40	20.20	24
Er	18.19	18.12	61.90	61.74	20.04	20.15	17
Yb	18.56	18.63	61.41	61.35	20.22	20.02	18
Y	9.28	9.41	—	—	—	—	20

* Values in $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, at 25°C

Table 2. Important infrared frequencies (in cm^{-1}) and their assignments for NIQNO and its nitrate complexes.

NIQNO	La	Nd	Ho	Er	Yb	Y	Assignment
—	1790 <i>vw</i>	1785 <i>vw</i>	1790 <i>w</i>	1785 <i>w</i>	1785 <i>w</i>	1785 <i>w</i>	($\nu_2 + \nu_3$)
—	1760 <i>vw</i>	1760 <i>vw</i>	1765 <i>vs</i>	1765 <i>vs</i>	1765 <i>vs</i>	1768 <i>s</i>	nitrate
—	1728 <i>w</i>	1728 <i>vw</i>	1728 <i>vs</i>	1728 <i>vs</i>	1730 <i>vs</i>	1730 <i>s</i>	($\nu_2 + \nu_5$) nitrate
1522 <i>vs</i>	1528 <i>vs</i>	1528 <i>vs</i>	1528 <i>vs</i>	1525 <i>vs</i>	1522 <i>vs</i>	1525 <i>s</i>	ν_4 nitrate + ligand
1340 <i>s</i>	1332 <i>vs</i>	1335 <i>vs</i>	1338 <i>v</i>	1335 <i>vs</i>	1335 <i>s</i>	1330 <i>vs</i>	ν_{NO} deformation
—	1310 <i>s</i>	1305 <i>s</i>	1325 <i>vs</i>	1305 <i>s</i>	1305 <i>vs</i>	1295 <i>s</i>	ν_1 nitrate
—	1030 <i>vs</i>	1030 <i>vs</i>	1030 <i>vs</i>	1025 <i>vs</i>	1028 <i>vs</i>	1028 <i>s</i>	ν_2 nitrate
840 <i>m</i>	845 <i>w</i>	850 <i>vw</i>	845 <i>m</i>	845 <i>m</i>	845 <i>m</i>	845 <i>m</i>	δ_{NO}
739 <i>m</i>	740 <i>m</i>	742 <i>m</i>	745 <i>vs</i>	742 <i>vs</i>	745 <i>vs</i>	745 <i>vs</i>	γ_{CH}

Table 3. Proton NMR data for NIQNO and its La^{3+} and Y^{3+} complexes in CD_3CN .

Compound	Chemical shifts with respect to TMS (δ)					
	1H	3H	4H	6H	7H	8H
NIQNO	8.84	8.48	7.94	8.38	7.71	8.17
La^{3+}	9.68	8.54	8.11	8.42	7.84	8.26
Y^{3+}	9.68	8.65	8.15	8.56	7.89	8.34

in nujol were recorded in the same region were run on a Cary-14 instrument. Electrolytic conductance measurements in acetonitrile solutions of the complexes were carried out with a Siemens conductivity bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentration of the solutions used were of the order of 10^{-3} M.

3. Results and discussion

Analytical data for the newly prepared complexes listed in table 1 indicate that three molecules of the ligand are associated with each metal ion. All the complexes are soluble in DMSO, DMF and acetonitrile (Ho^{3+} , Er^{3+} and Yb^{3+} complexes are slightly insoluble) and insoluble in chloroform, benzene and carbon tetrachloride. Molar conductance values suggest that all the three nitrate groups are non-ionic in nature (Geary 1971).

The absence of the two IR active bands of the nitrate ion D_{3h} symmetry in all the complexes at 720 and 1390 cm^{-1} provides confirmatory evidence to the conductance measurements that all the nitrate groups are non-ionic in nature. Nitrate groups are capable of bonding to a metal ion in monodentate or bidentate fashion, in either case the symmetry is lowered from D_{3h} to C_{2v} . The two situations cannot, in general, be unambiguously distinguished on the basis of the IR data alone. The combination bands of the nitrate group which generally appear in the 1700–1800 region have been used for structural assignments of the nitrate groups (Curtis and Curtis 1965; Lever *et al* 1971). In the present complexes, the presence of three weak

bands in the said region and the separation between them suggest that both mono and bidentate nitrate groups are present in the complexes studied.

The band at 1340 cm^{-1} assigned to N–O stretching frequency of the ligand shifts to lower frequencies (ca. $5\text{--}8\text{ cm}^{-1}$) in the spectra of the complexes indicating the binding of the N-oxide oxygen to the tripositive lanthanide ion. The $\nu\text{N--O}$ and C–H out-of-plane vibrations at 840 cm^{-1} and 739 cm^{-1} of the ligand shift to higher frequencies revealing the coordination of the N–O group to the metal ion in the NIQNO complexes of lanthanide nitrates.

Additional evidence for the participation of the oxygen of the N–O moiety in coordination with the lanthanide ion is found in the proton NMR spectra of the ligand and its diamagnetic complexes (La^{3+} and Y^{3+}) (table 3). The assignments have been made relative to the reported assignments for 5-nitroisoquinoline (Aramarego and Batterharn 1966).

All proton signals in the La^{3+} and Y^{3+} complexes show downfield shifts, confirming the coordination of the N-oxide moiety to the lanthanide ion. The observed deshielding is a consequence of the drainage of electron density towards the lanthanide ion in the complexes. The downfield shifts observed in the Y^{3+} complexes are greater than those in La^{3+} complexes, showing the stronger coordination of the ligand through the oxygen of the N-oxide moiety to the metal ion. The variation in the magnitude of deshielding of the heterocyclic ring protons in the lanthanide nitrate complexes (La^{3+} and Y^{3+}) of NIQNO (in comparison with IQNO complexes, Rajasekar 1986), is a consequence of the influence of the substituents at the 5-position of the isoquinoline-2-oxide ring on the strength of the metal-ligand bond.

Electronic spectral data are given in table 4. The sharp *f-f* bands exhibit red shifts with respect to the aquo ions consequent on complex formation. The red shift called the nephelauxetic shift, is a measure of the covalency in the metal-ligand bond. Sinha (1966, 1971) has proposed a δ scale to express the covalent character of the metal-ligand bond, which is given by the relation,

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

where β is the average value of the ratio ν complex/ ν aquo. The δ values calculated for Nd^{3+} and Ho^{3+} complexes of NIQNO are presented in table 4. The shapes of the hypersensitive bands of the Nd^{3+} and Ho^{3+} complexes resemble

Table 4. Electronic spectral data and their assignments (in DMSO).

Nd^{3+}		Ho^{3+}	
<i>J</i> level	Energy (KK)	<i>J</i> level	Energy (KK)
$4G_{9/2}$	19.53	$5F_3$	20.52
$4G_{7/2}$	19.02	$5F_4, 5F_{5/2}$	18.47
$2G_{7/2}$	17.13	$5F_5$	15.35
$4G_{5/2}$	$\delta = 0.9897$		$\delta = 1.07$

markedly the shapes of the eight-coordinate lanthanide perchlorate complexes of N-(2-pyrimidyl)benzamide (Rajasekar 1980).

The position, shape and relative intensities were found to be identical both in the solid state spectra recorded in Nujol and in the solution spectra taken in acetonitrile. In short, the same eight-coordinate geometry is observed in both the states and, hence, the compatibility in the solid state properties, such as infrared and solution properties as well as conductivity and NMR.

On the basis of the available evidence, a tentative coordination number of eight can be suggested for all the complexes of NIQNO.

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