

Lanthanide perchlorate complexes of 2-acetamidopyridine-1-oxide

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Abstract. 2-acetamidopyridine-1-oxide (AcAmPyO) complexes of six lanthanide perchlorates, with the general composition $\text{Ln}(\text{AcAmPyO})_3(\text{ClO}_4)_3$, have been synthesized and characterized by analysis, molar conductance, infrared, proton NMR and electronic spectral data. Infrared and conductance studies indicate the ionic nature of the anion. The coordination of the ligand through the N-O and C=O moieties is shown by the infrared and proton NMR spectral analysis.

Keywords. Lanthanide perchlorate complexes; 2-acetamidopyridine-1-oxide; IR spectra; proton NMR; electronic spectra.

1. Introduction

A survey of the literature in the field of lanthanide coordination chemistry reveals that although lanthanide complexes with neutral bidentate pyridine-1-oxide ligands like picolinamide-1-oxide (Navaneetham and Soundararajan 1979) are known, pyridine-1-oxide ligands containing the $-\text{NHCOCH}_3$ (acetamido) group have not been employed for complexation with lanthanides. We report in this paper the synthesis and characterization of new perchlorate complexes of six lanthanides with 2-acetamidopyridine-1-oxide (AcAmPyO).

2. Experimental

2.1 Materials

2-aminopyridine was obtained from Aldrich Chemical Company, USA and used as such. Hydrated lanthanide perchlorates were obtained as reported earlier (Behrendt and Madan 1976).

2.2 Synthesis of AcAmPyO

2-aminopyridine (0.1 mol) was refluxed with freshly distilled acetic anhydride (0.11 mol) for two hours. Acetic acid and acetic anhydride were removed by distillation at 100 mm/Hg pressure. The solid residue was recrystallized from ether to get colourless plates of 2-acetamido pyridine (m.p. 66°C ; Lit. $66-7^\circ\text{C}$). The acetamidopyridine was then N-oxidised adopting the method described by Ochidi (1967)

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for the preparation of quinoline-1-oxide. The crude product was recrystallized from acetone m.p. 132°C (Lit. 131–32°C).

2.3 Preparation of the complexes

To a hot solution of AcAmPyO (12 mmol) in ethylacetate (50 ml), a solution of hydrated lanthanide perchlorate (1 mmol) also taken in ethylacetate (5 ml) was added with stirring. Stirring in the hot condition was continued for 10 minutes. The solvent was then decanted and the sticky mass thus obtained was washed thrice with hot chloroform (10 ml) to remove any unreacted ligand, washed twice with dry diethyl ether (15 ml), and finally dried *in vacuo* (≈ 3 mm/Hg) at 80–85°C for about 30 minutes to get the dry solid complex.

2.4 Analyses

The metal and anion contents in all the complexes were estimated as reported previously (Serra *et al* 1976); ligand was estimated spectrophotometrically at 230 nm using the calibration curve method.

2.5 Physical measurements

Conductance measurements in acetonitrile, infrared spectra in mulls, proton NMR spectra of the ligand and its La³⁺ complex in CD₃CN and electronic spectra both in solution (acetonitrile) and solid state (mulls) were obtained by the methods described previously elsewhere (Rajasekar and Soundararajan 1981).

3. Results and discussion

Analytical data for the newly prepared complexes listed in table 1 indicate that five molecules of the ligand are associated with each tripositive lanthanide ion Ln(AcAmPyO)₅(ClO₄)₃. Molar conductance values in acetonitrile indicate that all the six complexes behave as 1:3 electrolytes (Geary 1971). The complexes are hygroscopic and soluble in polar solvents such as methanol, acetone, acetonitrile, DMSO and DMF but insoluble in CCl₄, chloroform and benzene.

Table 1. Analytical and molar conductance data for the AcAmPyO complexes of lanthanides.

Complex	Metal (%)		Ligand (%)		ClO ₄ ⁻ (%)		Λ_M^+
	Found	Calcd.	Found	Calcd.	Found	Calcd.	
La(AcAmPyO) ₅ (ClO ₄) ₃	14.48	11.60	62.53	63.48	24.80	24.92	389.2
Nd(AcAmPyO) ₅ (ClO ₄) ₃	11.87	11.99	62.56	63.19	—	—	363.8
Gd(AcAmPyO) ₅ (ClO ₄) ₃	12.80	12.94	61.89	62.52	—	—	350.2
Dy(AcAmPyO) ₅ (ClO ₄) ₃	13.18	13.31	61.75	62.25	24.38	24.44	342.3
Ho(AcAmPyO) ₅ (ClO ₄) ₃	13.36	13.48	61.52	62.13	—	—	348.8
Yb(AcAmPyO) ₅ (ClO ₄) ₃	13.93	14.05	61.10	61.72	—	—	349.8

⁺ Molar conductance in acetonitrile (Ohm⁻¹ cm² mol⁻¹).

3.1 IR spectra

The presence of a very strong band in the region 1085–1105 cm⁻¹ (ν_3) and a medium unsplit one in the region 620–622 cm⁻¹ (ν_4) in the IR spectra of all the complexes (table 2) confirms evidence of non-coordinated perchlorates from conductivity measurements. Coordination of the perchlorate groups would result in a lowering of the symmetry from T_d symmetry and a splitting of these bands.

The shifts in ν_{N-O} , amide I and amide II, δ_{N-O} and the γ_{C-H} bands of the ligand in the complexes indicate the coordination of the N-oxide and C=O groups of the ligand to the tripositive lanthanide ion. The ν_{N-O} and the amide I bands are lowered by 5 cm⁻¹, while the amide II, δ_{N-O} and γ_{C-H} bands are shifted to higher frequencies by 5, 10 and 15 cm⁻¹, respectively, in the complexes. These positive shifts amply demonstrate a decrease in the π -electron density of the amide groups and the heterocyclic ring as a result of the bidentate binding of the ligand, through the N-oxide and amide carbonyl groups, to the lanthanide ion.

3.2 Proton NMR spectra

Additional evidence for the coordination of the ligand is provided by the proton NMR spectra of the ligand and La³⁺ complex (diamagnetic). The spectral data are given in table 3. The downfield shifts of all the ring proton signals observed in the La³⁺ complex (compared to the ligand) concomitantly prove the coordination of the ligand to the metal ion via the N–O and C=O groups.

3.3 Electronic spectra

The electronic spectral assignments of Nd³⁺ and Ho³⁺ complexes along with their J-level assignments are presented in table 4.

Table 2. Important infrared frequencies (in cm⁻¹) and their assignments for AcAmPyO and its complexes.

Ligand	La	Nd	Gd	Dy	Ho	Yb	Assignment
3175–	3325–	3300–	3300–	3325–	3325–	3325–	ν_{NH}
3400 <i>wb</i>	3425 <i>wb</i>	3400 <i>wb</i>	3400 <i>wb</i>	3425 <i>wb</i>	3425 <i>wb</i>	3425 <i>wb</i>	
1710 <i>s</i>	1705 <i>m</i>	1702 <i>m</i>	1702 <i>m</i>	1705 <i>m</i>	1708 <i>m</i>	1705 <i>m</i>	Amide I
1575 <i>m</i>	1580 <i>m</i>	1580 <i>m</i>	1582 <i>m</i>	1580 <i>m</i>	1585 <i>m</i>	1580 <i>w</i>	Amide II
1278 <i>m</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1275 <i>w</i>	ν_{N-O}
—	1090 <i>s</i>	1090 <i>s</i>	1090 <i>s</i>	1090 <i>s</i>	1105 <i>s</i>	1085 <i>s</i>	ν_{3ClO_4}
860 <i>w</i>	870 <i>w</i>	870 <i>w</i>	870 <i>w</i>	870 <i>w</i>	865 <i>w</i>	865 <i>w</i>	δ_{N-O}
745 <i>w</i>	755 <i>w</i>	755 <i>w</i>	758 <i>w</i>	755 <i>w</i>	760 <i>w</i>	758 <i>w</i>	γ_{C-H}
—	620 <i>m</i>	620 <i>m</i>	620 <i>m</i>	622 <i>m</i>	621 <i>m</i>	620 <i>m</i>	ν_{4ClO_4}

Abbreviations: *w* = weak; *s* = strong; *m* = medium; *b* = broad.

Table 3. Proton NMR spectral data for AcAmPyO and its La³⁺ complex in CD₃CN (chemical shifts in δ w.r.t. TMS).

Compound	3H	4H	5H	6H
AcAmPyO	6.97	7.22	6.69	8.18
La ³⁺ complex	7.03	7.34	6.71	8.27

Table 4. Electronic spectral data for AcAmPyO complexes of Nd³⁺ and Ho³⁺

Nd ³⁺		Ho ³⁺	
J level	Energy(KK)	J level	Energy(KK)
⁴ G _{7/2}	19.05	⁵ F _{1'} ⁵ G ₆	22.15
⁴ G _{5/2'} , ² G _{7/2}	17.13	⁵ F ₃	20.31
β =	0.9942	β =	0.9928
δ =	0.5870	δ =	0.7239

The various bands exhibit red shifts with respect to the aquo ion and the nephelauxetic shifts are in the range found for many lanthanide complexes. Sinha (1966) has proposed a δ scale to express and metal-ligand covalency, which is given by the relation

$$\delta(\text{percent}) = [(1-\beta)/\beta] \times 100,$$

where β is the average value of $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The positive values of δ suggest a certain amount of covalency in the metal-ligand band in the six lanthanide complexes. The shapes of the hypersensitive bands resemble those of the ten coordinate lanthanide nitrate complexes of 2-N-acetylaminopyridine (Rajasekar 1980). The marked similarities in the positions and the shapes of the bands in the solid state and in solution point to similarities in the coordination environment around the lanthanide ions in both the states and, hence, the compatibility in the solid state properties such as infrared and solution properties as well as conductivity and proton NMR.

On the basis of these available pieces of evidence a tentative coordination number of ten can be suggested for all the six lanthanide perchlorate complexes of AcAmPyO.

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