

## Complexes of lanthanide nitrates with 2-N-(6-picoly)-benzamide

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**Abstract.** New complexes of lanthanide nitrates with 2-N-(6-picoly)-benzamide of the formulae  $\text{Ln}_3[\text{6-pic-BA}]_3[\text{NO}_3]_6$  ( $\text{Ln} = \text{Y}$  and  $\text{La-Yb}$ ) have been prepared and characterised by chemical analysis, infrared, molar conductance and electronic spectral data. Molar conductance data along with IR data point to the presence of co-ordinated nitrate groups. IR spectra prove the bidentate co-ordination of the ligand to the metal ion, through the oxygen of the secondary amide and the nitrogen of the heterocyclic ring. Electronic spectral studies in the visible region suggest an eight co-ordinate geometry around the metal ions.

**Keywords.** Lanthanide nitrates; 2-N-(6-picoly) benzamide; hypersensitive bands.

### 1. Introduction

Recently, we have started a programme of preparing complexes of lanthanides with heterocyclic amides, having the oxygen of the amide moiety and the heterocyclic nitrogen designed in such a fashion so as to function as a potential bidentate ligand. To start with, we have synthesised and characterised lanthanide nitrate complexes with 2-N-(pyridyl)-benzamide (Rajasekar and Soundararajan 1980). In order to study the effect of the methyl group at the 6-position of the ring in 2-N-(6-picoly) benzamide on the stoichiometry and other physical properties of the complexes formed compared to the 2-N-(pyridyl)-benzamide complexes, we have synthesised and characterised complexes of lanthanide nitrates with 6-pic-BA and report the same in this paper.

### 2. Materials and methods

#### 2.1. Materials

2-amino-6-picoline was obtained from Aldrich Chemicals, USA. Lanthanide oxides (99.9% pure) were obtained from Indian Rare Earths, Kerala State. All the other chemicals used were of reagent grade. The solvents were purified by standard methods.

## 2.2. Preparation of the ligand 6-pic-BA

The ligand was prepared according to the method given by Zeide (1920) by the benzylation of 2-amino-6-picoline. M.P. 89° C, Lit. 90° C.

## 2.3. Preparation of the hydrated lanthanide nitrates

The hydrated lanthanide nitrates were prepared by dissolving the corresponding oxides in 50% nitric acid and evaporating the solution on a steam-bath.

## 2.4. Preparation of lanthanide nitrate complexes

Hydrated lanthanide nitrate (1 mm) dissolved in ethylacetate (5 ml) was treated with the ligand (4 mm). The solution was evaporated on a steam-bath, washed twice with hot chloroform (10 ml) to remove the excess of ligand, if any, and finally dried at the pump (*ca* 3 mm/Hg) at 60° C for about 45 min to get the complex.

## 2.5. Analyses

The metal content of the complexes was estimated by EDTA titrations using xylenol orange as the indicator (Kolthoff and Elwing 1963). The nitrate content was estimated as nitron nitrate (Vogel 1962). The analytical data are presented in table 1.

## 2.6. Physical methods

The IR spectra of the ligand and complexes in nujol mull in the region 400–4000 cm<sup>-1</sup> were recorded on a Carl-Zeiss UR-10 spectrophotometer. Conductance measurements in acetonitrile were carried out in a Siemen's conductivity bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 0.001 M (table 1).

Table 1. Analytical and molar conductance data of 6-pic-BA complexes.

Complex	Metal % Found (Calc.)	Nitrate % Found (Calc.)	Carbon % Found (Calc.)	Hydrogen % Found (Calc.)	Λ*
La <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	21.49 (21.62)	28.76 (28.92)	24.10 (24.26)	1.60 (1.87)	36
Pr <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	21.76 (21.86)	28.97 (28.83)	24.31 (24.18)	1.73 (1.86)	46
Nd <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	22.16 (22.26)	28.70 (28.70)	24.01 (24.07)	1.60 (1.85)	23
Ho <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	24.71 (24.65)	27.76 (27.81)	23.32 (23.32)	1.93 (1.79)	32
Er <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	24.90 (24.92)	27.70 (27.71)	23.14 (23.24)	1.61 (1.79)	51
Yb <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	24.73 (24.67)	27.38 (27.47)	22.99 (23.04)	1.93 (1.77)	48
Y <sub>3</sub> [6-pic-BA] <sub>3</sub> [NO <sub>3</sub> ] <sub>6</sub>	14.88 (15.00)	31.21 (31.37)	26.14 (26.31)	2.11 (2.02)	34

\* Molar conductance—ohms<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

Electronic spectra of Nd and Ho complexes in acetonitrile were recorded in the visible region on a Unicam SP-700A spectrophotometer.

### 3. Results and discussion

Analytical data show that the complexes have the composition  $\text{Ln}_2[6\text{-pic-BA}]_3[\text{NO}_3]_6$  ( $\text{Ln} = \text{Y}$  and  $\text{La-Yb}$ ). The complexes are soluble in ethanol, methanol, acetone and acetonitrile, but insoluble in benzene, chloroform and carbon tetrachloride. The composition of the complexes shows that the presence of methyl group at 6-position introduces considerable steric hindrance and brings down the number of ligand molecules attached to the metal from two in the 2-N-(pyridyl)-benzamide complexes to one and half in the present complexes.

Molar conductance values in acetonitrile indicate that the nitrate groups are all non-ionic (Geary 1971).

The principal IR bands and the appropriate assignments are shown in table 2. The presence of amide I band at two frequencies, viz. a strong band at  $1675\text{ cm}^{-1}$  and a weak band at  $1685\text{ cm}^{-1}$  would probably be due to the presence of ligand in two different forms. On complexation, the amide I band shifts to a lower frequency as a result of the co-ordination of the ligand through the oxygen of the secondary amide. This is further substantiated by the increase observed in the amide II, amide III and amide IV band frequencies of the complexes compared to the ligand.

Table 2. Important IR bands and their assignment of 6-pic-BA complexes.

6-pic-BA	La	Pr	Nd	Ho	Er	Yb	Y	Assignment
..	1775vw	1775vw	1775vw	1775vw	1780vw	1770vw	1770vw	$\nu_2(\text{A}_1) + \nu_2(\text{A}_1)$ nitrate
	1740vw	1740vw	1740vw	1740vw	1740vw	1746vw	1745vw	$\nu_2(\text{A}_1) + \nu_2(\text{B}_2)$ nitrate
1675vs	1645vs	1650s	1650s	1650s	1650s	1650s	1650s	Amide I
1685w	1635w	1630w	1635w	1635w	1635w	1630w	1635w	
1605vs	1610s	1610s	1614s	1611s	1611s	1610s	1610s	Ring C=C, C=N
1535s	1540s	1540s	1540s	1575vs	1570vs	1570vs	1575vs	Amide II
..	1468vs	1470vs,	1460vs	1470s,	1470s,	1460s	1468s	$\nu_4(\text{B}_2)$ nitrate
		br		br	br			
..	1350m	1350w	1350m	1350w	1350w	1351w	1350w	$\nu_1(\text{A}_1)$ nitrate
1280vs	1290m	1305s,	1290m	1305s,	1305s,	1305s,	1305s,	Amide III
		br		br	br	br	br	
1010s	1038s	1040vs	1038vs	1040vs	1040vs	1040vs	1040vs	$\nu_2(\text{A}_1)$ nitrate + ligand
1008sh	1012w	1012w	1012sh	1012sh	1012sh	1012sh	1012sh	
..	840m	820s	820s	820s	820s	820s	820s	$\nu_2(\text{B}_1)$ nitrate
650s	680br	670m	670m	670m	670m	670m	675m	Amide IV
610vs	620w	625w	625w	625w	625w	625w	625w	Ring in-plane deformation
420w	450s	450s	450s	447s	445s	440s	440s	Ring out-of-plane deformation

Abbreviations : s = strong; vs = very strong; m = medium; w = weak; sh = shoulder.

The  $\nu_{C=C}$  and  $\nu_{C=N}$  stretching vibrations of the pyridine ring are found at a higher frequency in the complexes compared to the ligand. This is due to an increase in double bond character of the C=C and C=N bond. An increase in the characteristic ring breathing, ring-in-plane and out-of-plane deformation modes is also observed in all the complexes and such shifts have invariably been noticed in complexes involving pyridine co-ordination. These go to indicate that both the amide oxygen and heterocyclic nitrogen take part in the co-ordination and the ligand acts in a bidentate chelating fashion.

Nitrate groups are capable of bonding to a metal ion in a unidentate or a bidentate fashion. The two situations cannot, in general, be unambiguously distinguished on the basis of the IR data alone.

In the absence of Raman data, 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 two weak bands in the above said region clearly show that the nitrate groups are co-ordinated to the metal ions in a bidentate fashion. It has been shown that *f*-block transition metal prefers bidentate co-ordination of the nitrate groups to monodentate or ionic, which can be attributed to the favourable metal–nitrate interaction for given degree of nitrate–nitrate repulsion (Haque *et al* 1971).

The electronic spectral data of Nd<sup>3+</sup> and Ho<sup>3+</sup> complexes are presented in table 3 along with the *J* level assignments. Sinha's (1966) covalency parameter  $\delta$  have been calculated and the positive value of  $\delta$  suggests a certain amount of covalency in the metal–ligand bond. The hypersensitive bands in the complexes revealed some splitting on running an expanded spectrum. The shape, position and relative intensities were identical in the solid state spectra taken in nujol mull and solution spectra recorded in acetonitrile. Also, the shapes of the hypersensitive bands resemble markedly the shapes reported in the literature by Karrakar (1967, 1968) for some eight-co-ordinate  $\beta$ -diketonates.

Table 3. Electronic spectral data of 6-pic-BA complexes and their assignments.

Nd <sup>3+</sup>		Ho <sup>3+</sup>	
J level	Energy (KK)	J level	Energy (KK)
<sup>4</sup> G <sub>5/2</sub>	17.06	<sup>4</sup> F <sub>3</sub>	20.41
<sup>4</sup> G <sub>7/2</sub>	18.87	<sup>4</sup> K <sub>6</sub>	22.22
<sup>4</sup> G <sub>9/2</sub>	19.42	..	..
$\beta = 0.9862$		$\beta = 0.9955$	
$\delta = 1.399$		$\delta = 0.45$	

With the available data presented here, an eight co-ordinate geometry can be assigned tentatively for all the complexes.

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