

## Some lanthanide metal complexes of n-isonicotinamidosalicylaldimine

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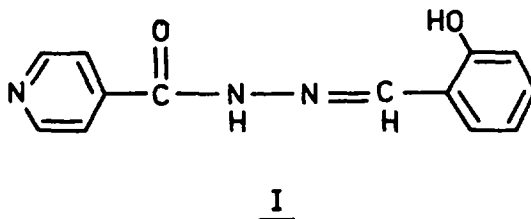
MS received 21 December 1985; revised 11 March 1985

**Abstract.** Trivalent lanthanide complexes of the type  $K[ML_2]$  where  $M = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III)$  and  $Dy(III)$  and  $H_2L = N$ -isonicotinamidosalicylaldimine, have been prepared and characterised. The nephelauxetic ratio ( $\beta$ ), covalency ( $\delta$ ) and bonding parameter ( $b^2$ ) of  $K[NdL_2]$  have been calculated. Infrared spectral studies reveal that  $N$ -isonicotinamidosalicylaldimine acts as a dibasic tridentate ligand. A coordination number six has been proposed for the lanthanide metal ions.

**Keywords.** Lanthanide metal complexes;  $N$ -isonicotinamidosalicylaldimine; tridentate ligand; coordination number.

### 1. Introduction

The ligand  $N$ -isonicotinamidosalicylaldimine (*I*) has been reported to behave as a uninegative bidentate and dinegative tetradentate species with  $3d$ -metal ions (Narang and Aggarwal 1975) and neutral bidentate and uninegative tridentate species with a main group element like  $Sn(IV)$  (Aggarwal and Vara Prasad Rao 1982). No report has been made on the coordinating behaviour of  $N$ -isonicotinamidosalicylaldimine towards lanthanides. In continuation of our earlier work on transition metal and lanthanide complexes of pyridine based hydrazides and their derivatives (Aggarwal and Rao 1977, 1978; Rao *et al* 1985, 1986), we report here the synthesis and structural investigations on  $N$ -isonicotinamidosalicylaldimine complexes of  $La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III)$  and  $Dy(III)$ .



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## 2. Experimental

### 2.1 Starting materials

Lanthanide trichlorides obtained from the Indian Rare Earths Ltd., Kerala were used as such, and N-isonicotinamidosalicylaldimine was prepared as described in the literature (Sacconi 1953).

### 2.2 Preparation of the complexes

All the complexes were prepared by mixing together aqueous-ethanolic solutions of the ligand (2 mmol), KOH (4 mmol) and the appropriate metal chloride (1 mmol) and adjusting the pH of the solution to  $\sim 7.5$  by the addition of a few drops of dil. HCl. The precipitated complexes were digested on a water bath for about 30 min, filtered, washed successively with water, and ethanol and dried at room temperature.

### 2.3 Analyses of the complexes

Lanthanides were gravimetrically estimated as oxides as well as oxalates after decomposing the organic matter with aqua regia and subsequently with concentrated  $H_2SO_4$  (Kolthaff *et al* 1963). Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. Nitrogen was microanalysed.

### 2.4 Physical measurements

Magnetic susceptibility measurements were carried out at room temperature on a Cahn-Faraday electrobalance and the molar conductance was determined on a WTW conductivity meter. The infrared spectra were recorded on Perkin-Elmer spectrophotometer, model 621 while the electronic spectra were obtained on a Cary-14 spectrophotometer.

## 3. Results and discussion

The analytical data (Table 1) of the complexes indicate 1:2 metal to ligand stoichiometry with the general formula  $K[ML_2]$  where  $M = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III)$  and  $Dy(III)$  and each ligand in the complex coordinates as a dinegative species as evidenced by IR and PMR spectra discussed later. The simultaneous behaviour of N-isonicotinamidosalicylaldimine as a uninegative and a dinegative species in the same complex molecule, as reported for its isomer (N-picolinamidosalicylaldimine) in Ln(III) complexes (Dutta and Das 1983), has been completely ruled out on the basis of spectral data. Further, in order to estimate quantitatively the ionic cation involved, we have prepared a new series of complexes,  $Li[ML_2]$ , [ $M = Pr(III), Nd(III), Sm(III)$  and  $Eu(III)$ ] following the same synthetic routes as those of  $K[ML_2]$  except that LiOH.  $H_2O$  has been used in place of KOH. The lithium present in the complexes has been qualitatively confirmed by the flame test as well as quantitatively estimated as  $2Li_2O, 5Al_2O_3$ . The results agree well with the empirical formula  $Li[ML_2]$ . Further, their magnetic and spectral data have been observed to be identical with those of the corresponding  $K[ML_2]$  complexes.

**Table 1.** Elemental analysis and general behaviour of N-isonicotinamidosalicylaldimine complexes.

Complex	Analysis found (Calc.) %			Molar conductance (mhos cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (BM)
	M	N	N <sub>2</sub> H <sub>4</sub>		
K[LaL <sub>2</sub> ]	21.03 (21.17)	12.50 (12.80)	9.65 (9.75)	25.37	Diamag.
K[PrL <sub>2</sub> ]	21.20 (21.41)	12.48 (12.76)	9.62 (9.72)	29.50	3.38
K[NdL <sub>2</sub> ]	21.59 (21.64)	12.43 (12.70)	9.55 (9.67)	38.35	3.63
K[SmL <sub>2</sub> ]	22.40 (22.52)	12.25 (12.58)	9.50 (9.56)	32.45	2.17
K[EuL <sub>2</sub> ]	22.39 (22.71)	12.30 (12.55)	—	46.61	4.06
K[GdL <sub>2</sub> ]	23.15 (23.32)	12.32 (12.45)	9.38 (9.49)	40.12	7.62
K[DyL <sub>2</sub> ]	23.41 (23.91)	12.28 (12.36)	9.36 (9.41)	38.94	9.88

Complex K[LaL<sub>2</sub>] is light yellow and all the other complexes are yellow.

All the complexes are non-melting below 300°C and are insoluble in water and common organic solvents. They are, however, sparingly soluble in hot DMF and DMSO. The molar conductance values of their saturated solutions in DMF (< 0.001 M) lie in the range 25.37–46.61 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> which are close to those reported for 1:1 electrolytes (Geary 1971). Thermal studies (ambient – 135°C) made on the complexes indicate no loss of weight.

### 3.1 Magnetic moments

The magnetic moments of Ln(III) complexes show little deviation from the Van Vleck values (Van Vleck and Frank 1929) since the 4f-electrons are well shielded by 5s<sup>2</sup>p<sup>6</sup> octet both in their spin and orbital motion and consequently indicate very little participation of the 4f-electrons in bond formation. All the complexes in the present study with the exception of K[LaL<sub>2</sub>] show magnetic moments (table 1) corresponding to Van Vleck values (Van Vleck and Frank 1929).

### 3.2 Electronic spectra

The f-f transition bands show normally weak perturbation due to complexation. Spectra have been recorded for the neodymium(III) complex in its solid state as well as as saturated solution in DMF. The solid state and the solution spectra are similar indicating no appreciable change around the metal ion on going from the solid to the solution state. The hypersensitive bands (<sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>G<sub>5/2</sub>, <sup>2</sup>G<sub>7/2</sub>) show significant red shift compared to those of aquoneodymium(III) complex (Choppin *et al* 1966). The magnitude of the bathochromic shift of the bands indicates a meagre nephelauxetic effect upon complex formation (Misumi *et al* 1968). The nephelauxetic effect ( $\beta$ ), bonding parameter ( $b^1$ ) and Sinha's parameter ( $\delta$ ) have been calculated (table 2) from the spectrum (Henrie and Choppin 1968; Sinha 1966). The nephelauxetic parameter ( $\beta$ ) is less than one which shows the covalent nature of the bonding between the metal ion and the ligand. Jorgensen ascribed the nephelauxetic effect to a decrease in coulombic interaction between the f electrons on the lanthanide atoms, that is, expansion of the electron clouds (Jorgensen 1962). The bonding parameter ( $b^1$ ) shows a moderate

**Table 2.** Electronic spectral data of the Nd(III) complex of N-isonicotinamidosalicylaldimine.

Band max (cm <sup>-1</sup> )	Assignment	*Spectral parameter
11430	<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>3/2</sub>	
12426	→ <sup>4</sup> F <sub>5/2</sub>	
13385		
13515	→ <sup>4</sup> F <sub>9/2</sub>	$\bar{\beta} = 0.9867$
13605		$b^{\ddagger} = 0.0815$
16475	→ <sup>2</sup> H <sub>11/2</sub>	$\delta = 1.347$
16950	—	
17155	<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub>	
19010	→ <sup>4</sup> G <sub>9/2</sub>	

\*Spectral parameters are calculated for hypersensitive transition,

$${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}; \bar{\beta} = 1/n \sum_{n=1}^{\infty} \text{complex/aquo}$$

$$b^{\ddagger} = [\frac{1}{2}(1 - \bar{\beta})]^{\ddagger}; \% \delta = [(1 - \bar{\beta}/\beta) \times 100]$$

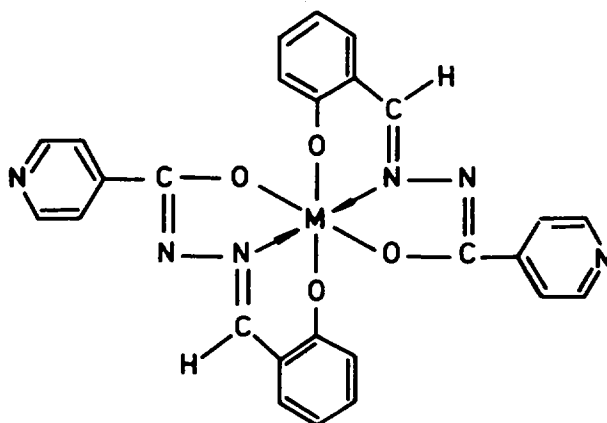
amount of 4f ligand orbital mixing in the complex. Sinha's parameter is positive indicating the presence of weak covalent bonding in the Nd(III) complex.

### 3.3 PMR spectra

The PMR spectrum of N-isonicotinamidosalicylaldimine in DMSO-*d*<sub>6</sub> displays signals at  $\delta$ 12.18, 11.07, 8.71 and 7.45–6.20 assignable to the phenolic, imine (NH), azomethine and aromatic protons, respectively. In the spectrum of K[LaL<sub>2</sub>], signals due to phenolic and imine protons totally disappear, while those of the azomethine and aromatic protons appear with slight broadening at almost the same positions as in the ligand. These observations can best be interpreted in terms of the loss of the amide proton through enolization and the deprotonation of the phenolic OH group and the subsequent coordination of the ligand as a dinegative tridentate species bonding through the enolic oxygen, azomethine nitrogen and the phenolic oxygen. The absence of any shift in the aromatic proton signals indicates the noninvolvement of the pyridine nitrogen in coordination.

### 3.4 Infrared spectra

The bonding sites of the ligand involved in coordination with the metal ion have been determined by a careful comparison of the IR spectra of the ligand and the complexes. The peaks appearing in the spectrum of the parent ligand at 1670, 1610, 1560, 1285 and 1270 cm<sup>-1</sup> may respectively be assigned to amide I,  $\nu$ (C=N), amide II, amide III and  $\nu$ (C–O) modes (Aggarwal and Vara Prasada Rao 1982). All the amide bands disappear in the spectra of the complexes suggesting the destruction of the >C=O group by enolization and subsequent coordination of the enolic oxygen, while the  $\nu$ (C=N) and  $\nu$ (C–O) modes undergo negative and positive shifts, respectively, of the order of



**Figure 1.** Structure of  $[ML_2]^-$ . M = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Dy(III).

20–25  $\text{cm}^{-1}$  indicating coordination through the azomethine nitrogen and phenolic oxygen atoms. The destruction of the  $>\text{C}=\text{O}$  group via amide  $\rightleftharpoons$  imidol tautomerism is further shown by the appearance of new peaks characteristic of  $\nu(\text{NCO}^-)$  in the regions 1535–1530 and 1395–1390  $\text{cm}^{-1}$ . Further, the bands due to the ring skeletal bending and in-plane and out-of-plane deformation modes of the pyridine ring appearing at 990, 675 and 440  $\text{cm}^{-1}$  in the spectrum of the ligand remain almost unaltered in the spectra of all the complexes suggesting the noncoordination of the pyridine nitrogen.

The nonligand bands appearing in the 330–310 and 400–370  $\text{cm}^{-1}$  regions in the spectra of all the complexes may tentatively be assigned to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  modes respectively (Charpantier and Moeller 1970; Ngsee *et al* 1977). Based on elemental analysis and various physico-chemical studies, the structure shown in figure 1 has been proposed for the  $\text{K}[\text{LnL}_2]$  complexes.

### Acknowledgements

The authors are thankful to the Head of the Chemistry Department, for encouragement. One of them (IAK) thanks the CSIR, New Delhi, for a fellowship.

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