

# Lanthanide complexes with pyridinecarboxylic acids – Spectroscopic and thermal studies

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## ABSTRACT

The effect of 14 lanthanides on the structure and the electronic system of isonicotinic acid was studied using IR (KBr), IR (ATR), Raman, UV–Vis, spectrofluorometric, elemental analysis and thermogravimetric (TG/DTG) methods. The influence of the lanthanides ions on the electronic charge distribution of the ligand is discussed. The nephelauxetic parameters and the degree of covalency in the lanthanide–ligand bonds were established. Moreover, the molecular structures of the lanthanide complexes with isonicotinic, nicotinic, picolinic and benzoic acids were compared, with a particular emphasis on the changes within the aromatic ring of metal complexes.

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## 1. Introduction

Pyridinecarboxylic acids are a biologically important group of ligands. The location of the nitrogen atom in the aromatic ring in the ortho, meta and para positions causes formation of metal complexes with different types of coordination. The isonicotinic ligand may act as (a) a bidentate bridging ligand (Fig. 1 IC), terbium [1] and europium [2] complexes, (b) bidentate chelating (Fig. 1 IB) e.g., terbium [1] and europium [2] complexes, (c) monodentate (Fig. 1 IA) e.g., magnesium [3] and zinc [4] complexes, or (d) tridentate bridging and chelating (Fig. 1 ID), e.g., in a lanthanum complex [5]. Additionally, the nitrogen atom from the aromatic ring may participate in metal coordination (Fig. 1 IE–H) [6–11]. In the lanthanide nicotinate, the carboxylate group may be (a) bidentate bridging (Fig. 1 IIC), e.g., dysprosium [12] and cerium [13] compounds, (b) bidentate chelating (Fig. 1 IIB) e.g., in a dysprosium complex [12], or (c) monodentate (Fig. 1 IIA) e.g., zinc [14] and molybdenum [15] compounds. In the nicotinate complexes, the lanthanide ions may be bonded only through the nitrogen atom (Fig. 1 IIE) [16,17] or by the nitrogen atom and a monodentate carboxylate group (Fig. 1 IIF) [18,19].

In the picolinic acid molecule, the nitrogen atom is in the ortho position relative to the carboxylic group. Thereby, the metal cation may be coordinated through the N-atom and COO<sup>−</sup> group at the

same time. This causes the formation of a five-membered chelating ring, which may be crucial for maintaining the stability of the complex. The coordination mode in picolinic acid complexes may be (a) monodentate through the carboxylate group and nitrogen atom (Fig. 1 IIIC), e.g., terbium [20] and iron [21] complexes, (b) bidentate chelating (Fig. 1 IIIB), e.g., in a cadmium compound [22], (c) bidentate bridging with additional bonding through the nitrogen atom (Fig. 1 IIIC), e.g., in a holmium complex [23] or (d) monodentate and bidentate chelating (Fig. 1 IIID), e.g., in a uranium compound [24].

Pyridinecarboxylic acids are of great biological importance. Nicotinic and picolinic acids are synthesized from tryptophan. Picolinic acid is regarded as a natural chelator which facilitates assimilation, e.g., for chromium(III) and zinc(II) ions [25,26]. Nicotinic acid (niacin, vitamin B3) takes part in the synthesis and degradation of carbohydrates, fatty acids and amino acids, as well as other metabolic transformations [27]. Nicotinic acid blocks the degradation of lipids in fat tissue, thereby reducing the level of free fatty acids in the blood [28,29]. Isonicotinic acid derivatives were formerly used to treat mental illness – most of them were withdrawn from sale because of their negative effects on the liver [30].

In our previous papers the effect of different metal ions on the electronic system of pyridinecarboxylic acids was studied [31–36]. The spectroscopic studies (FT-IR, FT-Raman, NMR) and quantum chemical calculations (theoretical IR, NMR spectra, electronic charge distribution, aromatic indices) showed that alkali [31] and alkaline [32] metal ions disturb the electronic charge distribution

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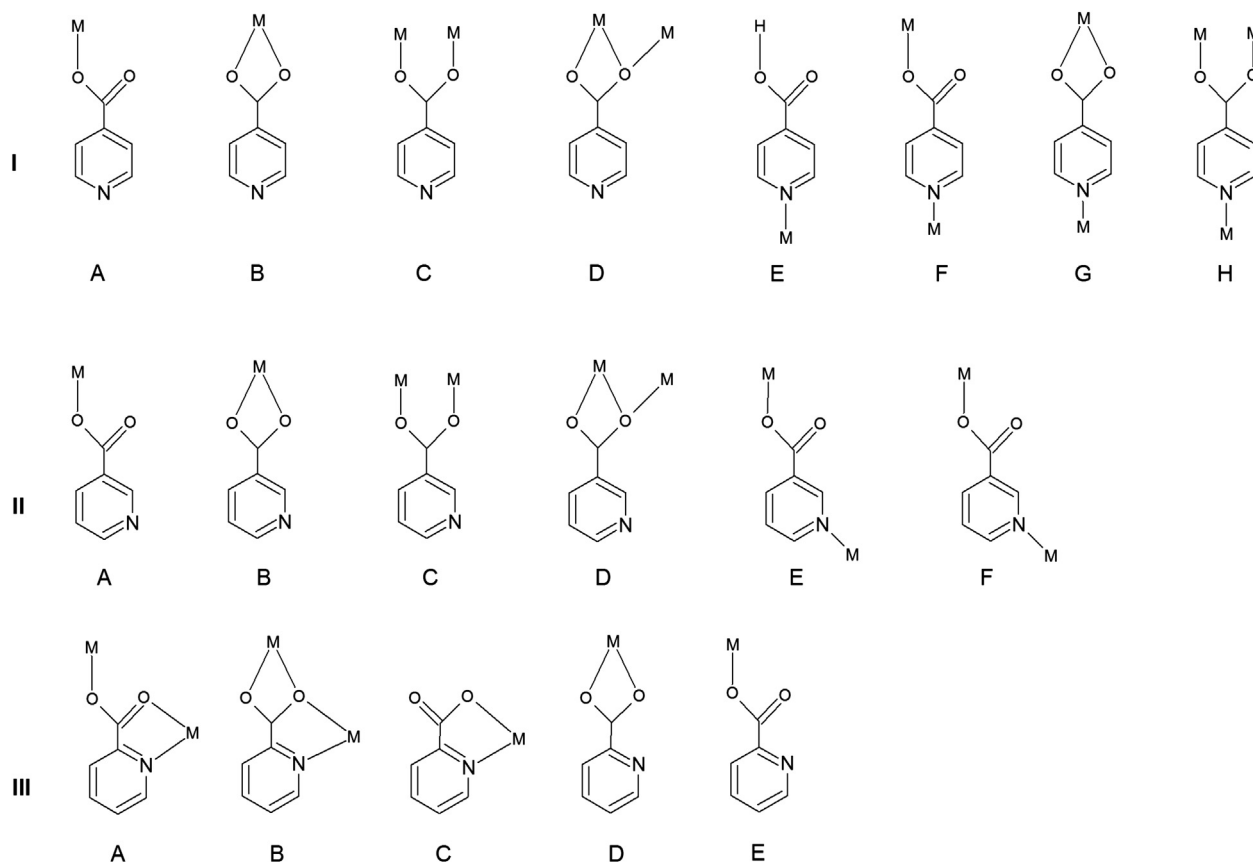


Fig. 1. Type of coordination of the isonicotinate (I), nicotinate (II) and picolinate (III) metal complexes.

of picolinic acid and the degree of disturbance increases in the order  $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$  and  $\text{Mg} \rightarrow \text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba}$ . Moreover, spectroscopic studies revealed that 3d transition metal ions (i.e., Cu(II), Fe(III) and Ni(II) ions) stabilize the electronic system of picolinic acid [33]. Similar results were obtained for benzoic, salicylic and nicotinic acids [37–41]. The dependency between the electronic charge distribution in the studied complexes and the location of the elements in the periodic table was established [37]. Namely, alkali and heavy toxic metal ions (e.g., Ag(I), Pb(II), Hg(I) and Hg(II) ions) disturb the electronic charge distribution in the studied ligands, whereas 3d and 4f metal ions (e.g., Cr(III), Fe(III) and Ln(III)) stabilize it. The stabilization of the aromatic system in lanthanide complexes is associated with the nephelauxetic effect. The nephelauxetic effect [42–44] is to expand the probability of finding an electron in the central ion. This effect, typical for ions with partially filled subshells, is caused by the penetration of electrons from the ligand into the unfilled orbitals of the central ion. Donor electrons cause a decrease in the effective charge of the nucleus, changing its central field. The central ion electrons, subjected to the effective charge of the nucleus, increase the radial dimensions of their orbitals, which causes a weakening of the inter-electron repulsion. The measure of the expansion of the cloud of electron density of the metal under the influence of a ligand in the complex is the nephelauxetic parameter [44–47]. In the La–Lu series, the degree of covalency of the bonds increases, whereas the delocalization of the “f” orbitals decreases [45]. The covalency of bonds in complexes is determined by the nephelauxetic effect of the ligands [43,44].

In the present work the physicochemical properties of a series of 14 lanthanide isonicotinates and selected lanthanide nicotinates, picolinates and benzoates were studied by spectroscopic and thermogravimetric methods.

## 2. Material and methods

### 2.1. Sample preparation

A 10 ml of water solution of lanthanide chlorides (that contain 0.2 mol of the lanthanide ions) was added to a 10 ml water solution of sodium isonicotinate (0.6 mol), so the metal:ligand stoichiometric ratio was 1:3. After a few days precipitates of the lanthanide isonicotinates formed. The precipitates were filtered and washed with distilled water. The solid residue was dried in a dryer at 90 °C for 48 h. In the same way the neodymium nicotinate, picolinate and benzoate were obtained. The sodium salts of the pyridinecarboxylates were synthesized by mixing the appropriate volume of sodium hydroxide and the pyridinecarboxylic acids (the stoichiometric ratio was 1:1). The mixtures were slowly evaporated on a water bath and the solid residue was dried at 90 °C for 48 h.

### 2.2. Measurements

The FT-IR spectra were recorded with the KBr pellet method in the range 400–4000  $\text{cm}^{-1}$  (the resolution was 4  $\text{cm}^{-1}$ ) using an Equinox 55 FT-IR spectrometer. The ATR FT-IR spectra were registered in the same range with the use of an Alfa spectrophotometer (Bruker). In this paper the changes in the positions of individual bands from the IR spectra of the tested compounds were discussed. Sometimes, quite small differences in the shifts of the corresponding bands from the spectra of the series of compounds were observed. In order to check the effect of the KBr matrix on the band locations, the ATR spectra were also registered and compared. No effect of the KBr matrix on the band shifts was observed.

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