

# Hydrolytic synthesis of novel lanthanide(III) complexes with pyridine-2,6-dicarboxylic acid: Characterization of the structure and the physical properties



Nuša Hojnik<sup>a,\*</sup>, Matjaž Kristl<sup>a</sup>, Amalija Golobič<sup>b</sup>, Zvonko Jagličič<sup>c</sup>, Miha Drofenik<sup>a,d</sup>

<sup>a</sup> University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

<sup>b</sup> University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, SI-1000 Ljubljana, Slovenia

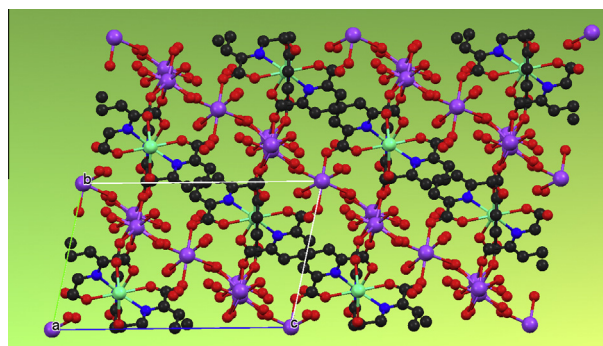
<sup>c</sup> Institute of Mathematic, Physics and Mechanics, Jadranska 19, SI-1000 Ljubljana, Slovenia and Faculty of Civil and Geodetic Engineering, Jamova 2, SI-1000 Ljubljana, Slovenia

<sup>d</sup> Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

## HIGHLIGHTS

- Two new complexes were hydrolytically synthesized in aqueous solutions at basic pH.
- Crystal structures are identified as  $\text{Na}_3[\text{Ln}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$ .
- Coordination polyhedron is a tricapped trigonal prism with O atoms in the corners.
- Mononuclear rare-earth ions display paramagnetic behavior.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 13 May 2014

Received in revised form 18 July 2014

Accepted 11 September 2014

Available online 21 September 2014

### Keywords:

Lanthanides

Pyridine-2,6-dicarboxylic acid

Magnetic properties

X-ray structure determination

Hydrogen bonds

## ABSTRACT

The coordination compounds of pyridine-2,6-dicarboxylic acid and two lanthanide(III) ions,  $\text{Ho}^{3+}$  and  $\text{Dy}^{3+}$ , were hydrolytically synthesized in aqueous solutions at a slightly basic pH, and then characterized by thermogravimetric analysis, IR spectroscopy, magnetic measurements as well as X-ray powder and single-crystal diffraction analysis. The elemental analyses were performed to check the purity of the compounds. The formula for these compounds is identified as  $\text{Na}_3[\text{Ln}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ho}$ , **1**;  $\text{Ln} = \text{Dy}$ , **2**) in agreement with the X-ray structural analysis and all the other experimental data. The absence of the  $1709\text{ cm}^{-1}$  band corresponding to  $\nu(\text{C}=\text{O})$  in the IR spectra of the compounds evidences the deprotonating of the carboxyl group. The very strong inductive effect of the metal ion that is readily coordinated by the carboxylate group of the zwitterionic ligand is responsible for the formation of the product. The single-crystal X-ray structural analysis revealed that compounds **1** and **2** are isostructural. Their structure can be described as interchanging layers of complex anions  $[\text{Ln}(\text{Pydc})_3]_3$  ( $\text{Ln} = \text{Ho}$  and  $\text{Dy}$  for **1** and **2**, respectively) and layers of hydrated sodium cations. In complex anions the holmium and dysprosium atoms are coordinated by three crystallographically independent pyridinedicarboxylate ligands in tridentate-chelate mode, via one O atom of both carboxylate groups and the ring N atom. The coordination number is nine and the coordination polyhedron is a tricapped trigonal prism with O atoms at the corners.

© 2014 Elsevier B.V. All rights reserved.

\* Corresponding author.

E-mail address: [nusa.hojnik@um.si](mailto:nusa.hojnik@um.si) (N. Hojnik).

## Introduction

Pyridinedicarboxylic acid, which can act as a potential scorpionate ligand [1–3], exists in six isomeric forms, i.e., (pyridine-2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dicarboxylic acid). These isomers can play an important role in building crystal structures. In addition, structural studies of these complex compounds in connection with the chemical systematics of these coordination compounds are potentially valuable in various fields, e.g., in host guest chemistry and crystal engineering, luminescence, catalysis, molecular magnetism, sensors, and nonlinear optics, etc. [4–13]. Here we report on the synthesis and provide a full characterization of newly prepared, mononuclear complexes of pyridine-2,6-dicarboxylic acid (Pydc) and the lanthanide(III) ions  $\text{Ho}^{3+}$  and  $\text{Dy}^{3+}$ . The carboxylate groups at the 2- and 6-positions of the pyridine ring can be fully or partially deprotonated for coordination to metals. The carboxylate groups bearing various bridging modes can efficiently induce a magnetic exchange. The geometry of these groups can possess three potential coordinating [N,O,O] donor sites to form stable chelates [14] with various metal ions, functioning as a bidentate [15,16], tridentate [17,18], or bridging ligand [19,20] in complexes. During a more general study we investigated Pydc, which is known to be able to act as a tridentate ligand. The reason for this is probably related to the position of the carboxylate groups, which are sufficiently close to the nitrogen in the pyridinedicarboxylic acid. The control of certain reaction parameters, such as the pH value, the solvent concentration, the molar ratio, and the geometry and flexibility of the ligands, plays a crucial role in the structure-formation processes and the reaction yield [21,22]. A survey of recent literature indicates that a ligand-controlled hydrolysis was successfully used in the structural characterization of water clusters in organic as well as metal-organic compounds. Some of these complexes have great potential for further applications to generate mixed ligands [23–25]. All the compounds described in this paper contain a large number of crystallization water molecules via extensive O–H–O interactions. Similar compounds prepared under low-pH conditions and characterized crystallographically have already been published [26–28].

## Experimental part

### Synthesis

All the reactants of A.R. grade were obtained commercially and used without further purification.

### $\text{Na}_3[\text{Ho}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$ **1**

During the two-step synthesis the ligand was first converted, with the addition of NaOH, to its mono-anionic form, the pyridyl and carboxylate groups of which are both capable of metal coordination. The lanthanide salt solution was prepared by dissolving  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  (0.5 mmol) in 10 mL of water, and a freshly prepared aqueous solution of NaOH (1.0 M) was added with stirring to the point of precipitation. A ligand solution was prepared by dissolving pyridine-2,6-dicarboxylic acid (1 mmol) in 10 mL of water and adding an aqueous solution of NaOH (1.0 M). The pH of the ligand solution was adjusted to above 8. This solution was then added dropwise to the solution of lanthanide salt. The resulting mixture was stirred at 90 °C for 1 h and then filtered while hot. Brownish-pink single crystals, suitable for analysis, were obtained by the slow evaporation of the solvent over a period of several weeks.

Yield: 48%. Elemental analysis (%) calcd. for  $\text{Na}_3[\text{Ho}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$  ( $M_r = 981.44$ ): C, 25.53; H, 3.79; N, 4.25. Found: C, 25.70; H, 3.77; N, 4.27.

### $\text{Na}_3[\text{Dy}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$ **2**

This complex was prepared with the procedure described for **1** using  $\text{Dy}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (0.5 mmol) and pyridine-2,6-dicarboxylic acid (1 mmol). Colorless single crystals, suitable for analysis, were obtained.

Yield: 45%. Elemental analysis (%) calcd. for  $\text{Na}_3[\text{Dy}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$  ( $M_r = 979.01$ ): C, 25.59; H, 3.77; N, 4.26. Found: C, 25.76; H, 3.78; N, 4.29.

### Thermal and elemental analysis

A thermogravimetric analysis was carried out on a METTLER TGA/SDTA851<sup>e</sup> system in the temperature range 30–1100 °C in a nitrogen flow (100 mL/min) with a heating rate of 10 K/min using  $\text{Al}_2\text{O}_3$  crucibles.

Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyzer at the University of Ljubljana.

### XRPD analysis

X-ray powder-diffraction data for the products of the thermal decomposition were collected with an AXS-Bruker/Siemens/D5005 diffractometer using  $\text{Cu K}\alpha$  radiation at 293 K. Finely ground samples were placed on a Si single-crystal holder and measured in the range  $10^\circ < 2\theta < 70^\circ$ . The diffraction data was analyzed using the EVA program and the PDF Datafile.

### IR analysis

The experimental IR spectra were recorded with a Shimadzu IRAffinity-1 spectrometer in the range 4000–400  $\text{cm}^{-1}$  using the KBr pellet method. The data were collected with Shimadzu IRsolution version 1.50.

**Table 1**  
Summary of crystallographic data and structure analyses.

Compound	<b>1</b>	<b>2</b>
Empirical formula	$\text{Na}_3[\text{Ho}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$	$\text{Na}_3[\text{Dy}(\text{Pydc})_3] \cdot 14\text{H}_2\text{O}$
$M_r$	981.44	979.01
Cell setting, space group	Triclinic, P-1, No. 2	Triclinic, P-1, No. 2
Temperature (K)	150(2)	293(2)
$a$ (Å)	10.2390(3)	10.3188(3)
$b$ (Å)	10.9385(3)	10.9967(3)
$c$ (Å)	17.1431(5)	17.2589(4)
$\alpha$ (°)	74.429(3)	74.635(2)
$\beta$ (°)	77.191(3)	77.397(2)
$\gamma$ (°)	72.869(3)	72.735(2)
$V$ (Å <sup>3</sup> )	1746.15(9)	1782.50(8)
$Z$	2	2
$D_x$ ( $\text{Mg m}^{-3}$ )	1.867	1.824
Radiation type, wavelength (Å)	Mo $\text{K}\alpha$ , 0.71073	Mo $\text{K}\alpha$ , 0.71073
$\mu$ ( $\text{mm}^{-1}$ )	2.407	2.235
$F(000)$	984	982
Crystal form, color	Prism, brownish pink	Prism, colorless
Crystal size (mm)	0.40 × 0.35 × 25	0.38 × 0.22 × 18
Absorption correction	Multiscan	Multiscan
No. of measured and indep. reflc.	17,475, 9076	17,945, 9249
No. of ( $F^2 > 2.0\sigma(F^2)$ ) reflections	7777	6748
$R_{\text{int}}$	0.029	0.033
$\theta$ range (°)	2.8–27.5	2.7–27.5
Full-matrix refinement on $F^2$		
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.039, 0.092, 1.10	0.034, 0.089, 1.07
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ ( $\text{e Å}^{-3}$ )	3.46, −1.45	0.93, −0.87
No. of parameters	494	494
No. of contributing reflections	9076	9249

Download English Version:

<https://daneshyari.com/en/article/1402147>

Download Persian Version:

<https://daneshyari.com/article/1402147>

[Daneshyari.com](https://daneshyari.com)