

Thermal and spectroscopic studies of sodium and light lanthanide (III) complexes with 2,4-pyridinedicarboxylate anion

Zofia Rzączyńska · Anna Danczowska-Burdon

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Abstract Pyridine-2,4-dicarboxylic acid (lutidinic acid) is next one after pyridine-2,5-dicarboxylic acid of the six isomers which lanthanide complexes were studied thermally and spectrally. New complexes synthesized with light lanthanides (III) with general formula $\text{Ln}_2\text{L}_3 \cdot n\text{H}_2\text{O}$, where $n = 7.5; 8; 8.5; 9$, were obtained. Sodium salt was obtained as hexahydrated compound. Hydrated complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), and Gd(III) are thermally stable up to 303–313 K. Dehydration process run for all compounds in one stage, anhydrous compounds decompose through appropriate light lanthanides (III) oxalates, oxocarbonates, carbonates to metal oxides. Theoretical IR and Raman studies were carried out in order to identify precisely characteristic group bands vibrations present on IR and Raman spectra.

Keywords Lanthanide complexes · Pyridinedicarboxylates · 2,4-pyridinedicarboxylates · Lutidinic acid · Thermal decomposition

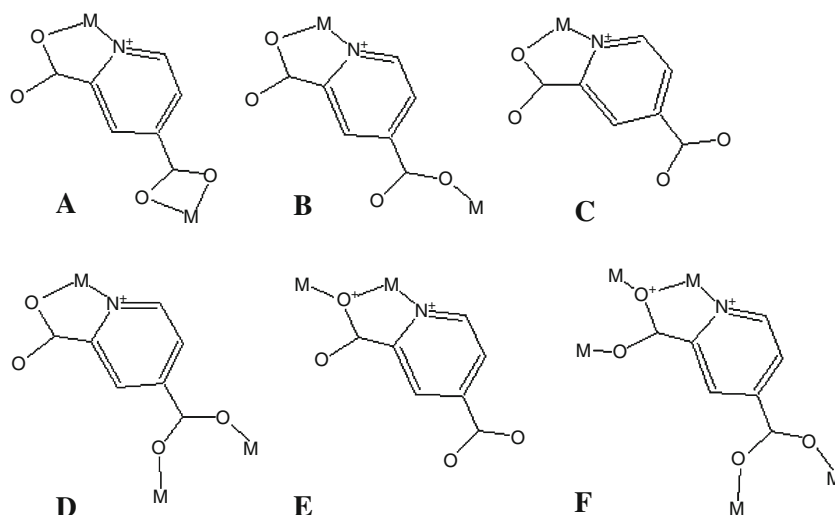
Introduction

Coordination polymers are one of the most common issues in coordination chemistry, which studies were rapidly growing in the last two decades. Many new polymers are synthesized each day which is mainly caused by their wide potential applications required in biochemistry and

pharmacy [1]. Presence of various coordinating atoms like O and N cause that pyridinedicarboxylic acids are ligands which can play an instant role in building crystal architectures. Large number of transition and lanthanide complexes with series of the pyridinedicarboxylic acids, which includes the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-pyridinedicarboxylic isomers, have been reported in the recent two decades. Although there are many publications about their complexes with transition metals [2], there are few papers about compounds formed by 2,4-pydcH₂ ligand. There is a wide range of coordination possibilities among isomers of lutidinic acids (Fig. 1). They form 1:1 and 1:2 metal derivatives with different coordination geometries. Position of coordinating atoms that is oxygen from carboxylate groups and nitrogen determines planar structures that leads to molecular solids among derivatives of 2,6-pyridinedicarboxylates [3, 4] or among 2,4-pyridinedicarboxylates derivatives [5]. Also many deviations from planarity were remarked which form two-dimensional [6] or even three-dimensional [7] structures. The lanthanide (III) coordination takes place through carboxylate groups, which are deprotonated in all complexes. Hence to the high electron density on oxygen atoms of these groups [8] there are many ways of metal ions coordination. Carboxylate group can be chelate [9], bridging, chelate-bridging [10], or monodentate. The geometry of these groups is often different what can be the reason of different ways of metal coordination [11]. Hence to this many different spacial structures can be created. The best way to define the structure of organometallic compound is to obtain a monocrystal. We didn't obtain the right crystal for analysis, though we concentrated on the IR spectra of obtained complexes analysis. IR spectra analysis were presented in this article and many possibilities of lanthanide ions coordination through donor atoms were discussed.

Z. Rzączyńska (✉) · A. Danczowska-Burdon
Department of General and Coordination Chemistry,
Maria Curie-Skłodowska University, M. C. Skłodowskiej SQ 2,
20-031 Lublin, Poland
e-mail: z.rzaczynska@poczta.umcs.lublin.pl

Fig. 1 Schematic representation of possible modes of lutidinic acid



Our aim was to carry out the theoretical IR and Raman investigations based on free acid and its sodium salt and to compare the theoretical results with experimental data. Those results were next compared with experimental IR and Raman data for lanthanide (III) complexes with lutidinic acid. According to the collected data we could assume the possible ways of metal coordination. These kinds of investigations were performed for all six isomers of pyridinedicarboxylic acids and their complexes with light lanthanides. In our previous article we presented results for 2,5-pdca isomer, and now we want to present our latest research for 2,4-pdca isomer and its complexes.

Derivatives of lutidinic acid are biologically active as immune-suppressive and fibro-suppressive compound [12]. It impacts on the growth and floral induction of some plant species [13, 14]. It also play a protection role of some enzymes from *Bacillus subtilis* cells from heat inactivation [15, 16]. The presence of pyridinecarboxylates in biological systems may be also related with metal-transport [17] and cell membrane protection in some microorganisms [18]. Pyridinedicarboxylic acids as the derivatives of benzoic acid and their complexes with metals were also taken into consideration as potential fungicidal and antibacterial compounds [19]. The correlation between the structure of the compound and its biological behavior were also studied by Lewandowski and coworkers and their results soon will be published.

Most complexes of 2,4-pyridinedicarboxylic acid are combinations of two transition metals such like: [CoCu(pydc)₂(H₂O)₄]-2H₂O [20], [ZnCu(pydc)₂(H₂O)₃(DMF)]·DMF [21], Zn₃Pd₂(OH)₂(pydc)₄(H₂O)₄ [22], although there were also reported those containing lanthanides, e.g., Gd₂Cu(pydc)₄(H₂O)₆, Sm₂Cu₃(pydc)₆(H₂O)₆ [23].

This report is continuation of our studies presented on Science and Industry Conference in 2009 in Lublin. Fragments of this study were also presented at 33rd

International Conference on Vacuum, Microbalance and Thermoanalytical Techniques ICVMTT³³ and 3rd Compositum Conference Hybrid Nanocomposites and Their Applications.

Experimental

Materials and methods

All chemicals employed were commercially available from Sigma and Aldrich Company and used without further purification. The purity of used acid was 98%.

The theoretical IR and Raman spectra for 2,4-pdca and its sodium salt were registered by Gaussian 03 W Program with use of Gauss View 4.1.2. graphical overlay. Theoretical calculations were carried out with DFT B3LYP method in 6-311++G** functional base. The experimental IR spectra were recorded with 1725X Perkin Elmer spectrometer at the range of 4000–400 cm⁻¹ using the KBr technique.

Experimental Raman spectra were registered by Renishaw Raman Microscope via Reflex with 10 min exposure time and 785 nm laser edge.

Thermogravimetric analyses were conducted on Setsys 16/18 analyzer in dynamic air atmosphere. Therefore, 7.16–7.63 mg samples are heated in the range of 303–1273 K in ceramic crucibles using a heating rate of 5 K min⁻¹. TG, DTG, and DTA curves were registered.

Elementary analysis was carried out to determine the composition and formulas of the obtained complexes. The analysis was made with use of CHN 2400 Perkin Elmer Analyser. The water content was determined from the thermogravimetric curves of their mass loss and elementary analysis. The metal content was determined from TG curves.

Synthesis

All lanthanide (III) complexes were obtained in double exchange method. To the hot solution of lanthanide chloride (pH 5.5) stoichiometric amount of 0.1 M ammonium salt (pH 5.8) of lutidinic acid was added dropwise. Mixtures of pH about 5.0 were next heated for about 40 min at 338 K. Precipitates were filtered, washed with distilled water to remove ammonium ions and dried in desiccators to the stable mass. Cerium (III) complex was prepared from hexahydrated nitrate (V) with final pH 4.8.

Sodium complex with 2,4-pdca was prepared from 1 M solution of sodium hydroxide into which 20% underflow of stoichiometric amount of 0.5 M 2,4-pyridinedicarboxylic acid solution was added dropwise. pH of final mixture was equal 7. The mixture was left on heater at 333 K for about an hour to remove the excess of solvent. Next the mixture was left at room temperature for slower solvent evaporation and crystallization. After 4 days white, noncrystalline precipitate was dried to the stable mass.

Obtained complexes of lanthanum, europium, and gadolinium were white, samarium was light cream, neodymium was light violet, praseodymium light green, and cerium light yellow.

Results and discussion

Elementary analysis

Carbon, hydrogen, and nitrogen percentage contents determined for the obtained complexes are in agreement with values found (Table 1).

Thermal analysis

Results for thermal analysis confirmed data obtained from elementary analysis. Compounds obtained through the syntheses of lutidinic acid with lanthanide (III) chlorides

are all hydrated with the general formula: $\text{Ln}_2\text{L}_3 \cdot n\text{H}_2\text{O}$. Amount of water molecules is slightly different for each compound, which can be caused by multidimensional porous structures creation into which small water molecules can be captured. As it was shown on representative figures with TG and DTA curves of sodium and neodymium complexes (Figs. 2, 3) all obtained complexes of 2,4-series are hydrated compounds stable at room temperature. Sodium compound was obtained as hexahydrated (Fig. 2). Complexes of lanthanum, praseodymium, and europium contain 8.5 molecules of water, cerium (III), and gadolinium (III) complexes are nonhydrated, while neodymium (III) complex (Fig. 3) is octahydrated and samarium (III) complex contains 7.5 water molecules. Amount of water was determined from thermogravimetric curves. Each complex is stable until 303–313 K (Table 2), next they loose water molecules in one stage dehydration process. This process is connected probably with lost of outersphere water molecules. Tearing out the outersphere water disturbs the structure of hydrated compound which cause fully dehydration process. Anhydrous compounds are created at 443 K (Ce, Nd, Sm) and 453 K (Na, Pr, Eu, Gd), 473 K (La). Their thermal stability is up to about 650 K (Ce, Eu), 660 K (Sm), 670 K (La, Nd), 680 K (Pr, Gd), and 710 K (Na). The range of thermal stability is very important as a main condition for new coordination polymers searching as potential new sorption materials. According to the wide range of thermal stability the 2,4-pdc series with light lanthanides is hopeful for reversible sorption materials creation. Another step in thermal decomposition process is connected with full anhydrous complex degradation through compounds like oxalates, oxocarbonates and carbonates to appropriate lanthanide oxides (La, Nd, Sm, Eu, and Gd). Anhydrous compound of Ce(III) decomposes directly to CeO_2 oxide while Pr(III) compound decomposes through oxocarbonate and Pr_6O_{11} . Values of calculated and found weight loss were given in Table 2.

According to the TG curves and FTIR spectra of gaseous products of neodymium complex we couldn't define weather

Table 1 Results of elementary analysis of 2,4-pyridinedicarboxylates of light lanthanide (III) complexes

Kompleks	C%		H%		N%	
	Calculated	Found	Calculated	Found	Calculated	Found
$\text{La}_2\text{L}_3 \cdot 8.5 \text{H}_2\text{O}$	27.22	26.82	2.81	3.03	4.54	4.44
$\text{Ce}_2\text{L}_3 \cdot 9 \text{H}_2\text{O}$	26.88	26.27	2.88	2.73	4.48	4.42
$\text{Pr}_2\text{L}_3 \cdot 8.5 \text{H}_2\text{O}$	27.10	26.53	2.79	2.89	4.52	4.47
$\text{Nd}_2\text{L}_3 \cdot 8 \text{H}_2\text{O}$	27.17	26.20	2.69	2.81	4.53	4.59
$\text{Sm}_2\text{L}_3 \cdot 7.5 \text{H}_2\text{O}$	27.07	26.70	2.58	2.70	4.51	4.53
$\text{Eu}_2\text{L}_3 \cdot 8.5 \text{H}_2\text{O}$	26.47	25.82	2.73	2.67	4.41	4.39
$\text{Gd}_2\text{L}_3 \cdot 9 \text{H}_2\text{O}$	25.94	25.71	2.77	2.84	4.32	4.23

L C₅H₃N(COO⁻)₂

Fig. 2 TG and DTA decomposition curves of sodium salt

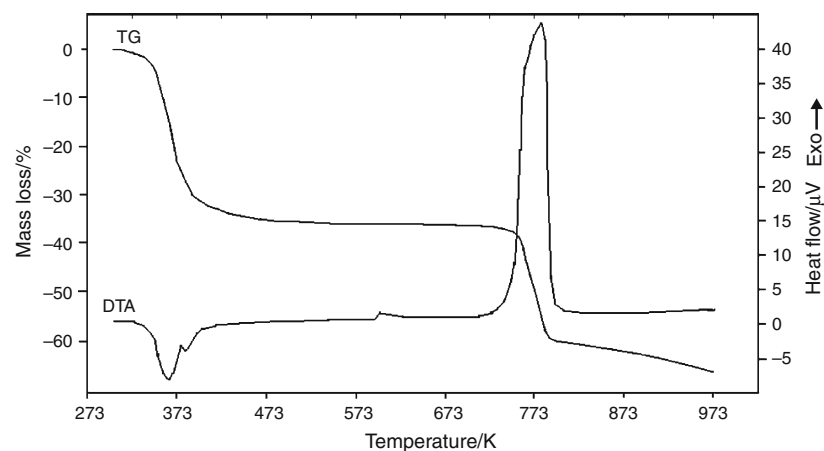
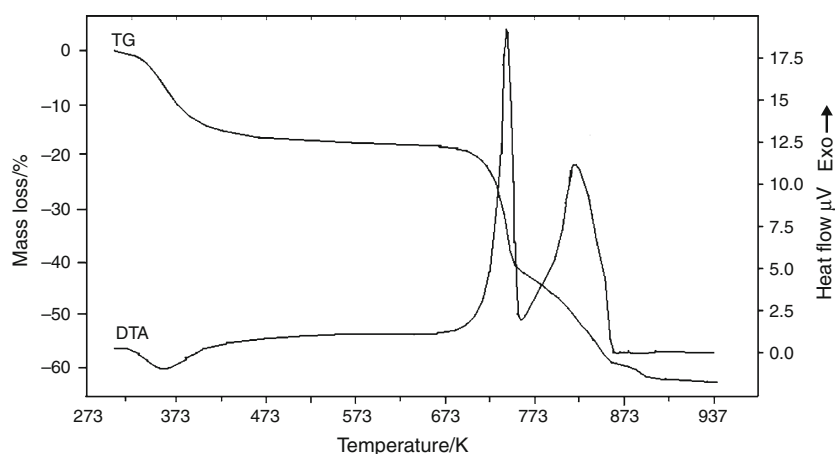


Fig. 3 TG and DTA decomposition curves of Nd(III) complex



water present in compounds is bonded through hydrogen bonding or is coordination type of water. TG curve confirms that only one step of dehydration takes place and only one energetic effect on DTA curve is present for water release. We choose neodymium complex as a representative one for all 2,4-pdc series because it illustrates gaseous and solid phase. FTIR spectrum of gaseous products of Nd(III) complex decomposition (Fig. 4) confirmed the presence of H₂O in the range of lowest decomposition temperatures at 4000–3400 and 1800–1250 cm⁻¹. Bands of CO₂ stretching vibrations appear at 3750–3500 and 2350–2150 cm⁻¹, whereas double bands of CO vibrations appear in the range of 2100–1850 cm⁻¹. Other bands which were registered on FTIR spectrum of gaseous products of Nd(III) complex decomposition were ascribed to CH₃ vibrations at 3000 cm⁻¹ and in the range of 1500–1250 cm⁻¹.

The presence of lone electron pair on the nitrogen atom from the aromatic ring and oxygen atoms from two different carboxylate groups cause the possibility of creation polymeric [24], dimeric [25], and rarely monomeric [26] structures. Lanthanides act as hard Pearson's acids therefore coordination through oxygen atoms from carboxylate groups mainly takes place. There are few examples where

coordination between lanthanide cation and nitrogen atom from pyridine ring takes place. Geometric orientation of donor atoms in neodymium (III) complex with 2,6-pyridinedicarboxylic acid almost force lanthanide-nitrogen bonding [27]. It is mainly caused by the symmetrically spacing of carboxylic groups in 2,6-pyridinedicarboxylic acids. The chance of such lanthanide complexation among the other isomers of pyridinedicarboxylic acid, as well as lutidinic acid, is far lower, mainly due to steric conditions, although we can not exclude such possibility [28].

IR and Raman analysis

Theoretical calculations were collected due to the difficulties with ascribing particular frequencies to bands on infrared spectra. Also these studies were made in order to verify our previous analysis. Bands characteristic for C=N vibrations occurs, according to the literature data at about 1290 and 1120 cm⁻¹ [29] and at 3490–3450 cm⁻¹ [30]. According to the theoretical data we can claim that C=N vibrations do not occur as lone, significant bands, they are always connected with other ring vibrations: stretching or bending in and out of plane of pyridine ring. These C=N

Table 2 Thermal data of light lanthanides (III) complexes and sodium salt with 2,4-pyridinedicarboxylic acid

Compound	Range of decomposition temp/K	Weight loss/%		Stable products of decomposition
		Calculated	Found	
Na ₂ L·6 H ₂ O	303–453	33.85	34.27	Na ₂ L
	723–803	58.00	58.75	Na ₂ Ox
La ₂ L ₃ ·8.5 H ₂ O	313–473	16.39	16.39	La ₂ L ₃
	683–783	41.50	40.20	La ₂ Ox ₃
	818–878	50.57	51.99	La ₂ (CO ₃) ₃
	883–973	64.82	64.10	La ₂ O ₃
Ce ₂ L ₃ ·9 H ₂ O	313–443	17.28	17.51	Ce ₂ L ₃
	663–723	63.285	62.97	CeO ₂
Pr ₂ L ₃ ·8.5 H ₂ O	313–453	16.45	16.19	Pr ₂ L ₃
	693–813	59.81	60.23	Pr ₂ O ₂ CO ₃
	813–848	63.40	63.58	Pr ₆ O ₁₁
Nd ₂ L ₃ ·8 H ₂ O	313–443	15.52	15.75	Nd ₂ L ₃
	683–783	40.45	45.05	Nd ₂ Ox ₃
	788–883	57.92	59.76	Nd ₂ O ₂ CO ₃
	888–943	63.75	63.51	Nd ₂ O ₃
Sm ₂ L ₃ ·7.5 H ₂ O	313–443	14.50	14.53	Sm ₂ L ₃
	673–783	48.37	47.49	Sm ₂ (CO ₃) ₃
	848–948	62.54	62.24	Sm ₂ O ₃
Eu ₂ L ₃ ·8.5 H ₂ O	313–453	16.07	16.11	Eu ₂ L ₃
	663–763	49.18	46.34	Eu ₂ (CO ₃) ₃
	768–923	63.05	62.84	Eu ₂ O ₃
Gd ₂ L ₃ ·9 H ₂ O	313–453	16.67	16.26	Gd ₂ L ₃
	693–783	49.12	47.09	Gd ₂ (CO ₃) ₃
	783–853	58.16	57.39	Gd ₂ O ₂ CO ₃
	873–963	62.70	62.46	Gd ₂ O ₃

bands are present at 1608 and at 1206 cm⁻¹. At higher frequencies they are connected with stretching ring vibrations, whereas at lower with bending OH vibrations.

On theoretical IR acid spectrum (Fig. 5) in the range of highest frequencies there are two similar bands of stretching OH group vibrations from COOH of two and four position, respectively: 3723 and 3748 cm⁻¹. Bands at 1559, 1585, and 1611 cm⁻¹ correspond to valence C=O

vibrations, where values 1559 and 1611 cm⁻¹ were assigned to COOH at four position, and 1585 cm⁻¹ at position two. In addition band at 1559 cm⁻¹ is connected with stretching C=N vibrations. Weak band of C=N vibrations was recorded at 1206 cm⁻¹, it is overlaid onto the band of β(COH) out of plane vibrations. Bands connected with ring vibrations occur below 1000 cm⁻¹, where also at 999 cm⁻¹ ring breathing band vibrations is present. Theoretical Raman spectrum was presented as Fig. 6.

On experimental IR acid spectrum (Fig. 7) in the range of highest frequencies between 3600 and 2200 cm⁻¹ there were two broad, high intensity bands which correspond to stretching νOH vibrations from water molecule present in the structure of commercially available 2,4-pdca. These bands indicate that water molecule takes part in the intermolecular forces creation. Strong, intensive band of νC=O vibrations occurs at 1708 cm⁻¹. Shifting of this band into the lowest frequencies direction confirms that 2,4-pdc acid has a dimeric structure. At 1452 and 1384 cm⁻¹ there are two teared, medium intensity bands of νC=O and βCOH vibrations, respectively. Bands characteristic for C=N vibrations occur at 1288 and 1244 cm⁻¹, although these bands correspond to the pyridine ring vibrations. Also at 1609 cm⁻¹ C=N stretching band vibration is present. In the range 1300 and 200 cm⁻¹ bands of various ring vibrations: stretching, rocking, and wagging are present. Band of breathing ring vibrations occurs at 1012 cm⁻¹. Experimental Raman spectrum was presented in the Fig. 8.

On the theoretical IR spectrum of sodium salt (Fig. 9) at 2986 cm⁻¹ there is weak νC-H vibration present. Bands of asymmetric and symmetric COO⁻ vibrations were registered at 1607 cm⁻¹ (both group in two and four position), 1579 cm⁻¹ (ν_{as}COO⁻ in position two), 1558 cm⁻¹ (ν_{as}COO⁻ in position four), and 1309, 1289 cm⁻¹ (ν_sCOO⁻ in both positions). Asymmetric and symmetric bands distributions Δν were calculated as 270 and 269 cm⁻¹ taking into account the strongest bands.

Band of νC=N vibrations was registered at 1231 cm⁻¹ and it is connected with bending ring vibrations. Very weak band of stretching Me–O vibrations was registered at

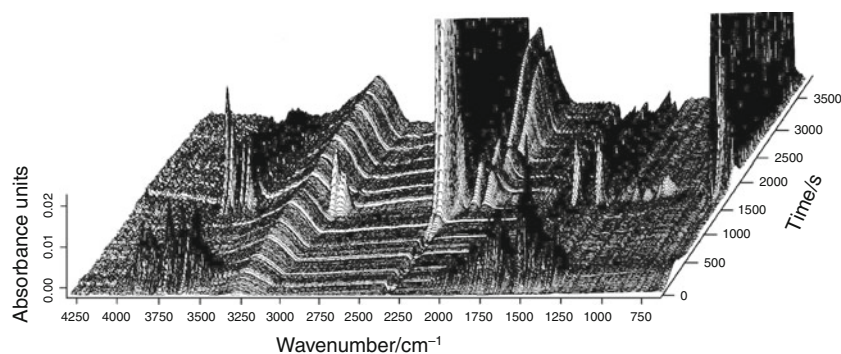
Fig. 4 FTIR spectrum of Nd(III) complex gaseous decomposition products

Fig. 5 Theoretical IR spectrum of lutidinic acid

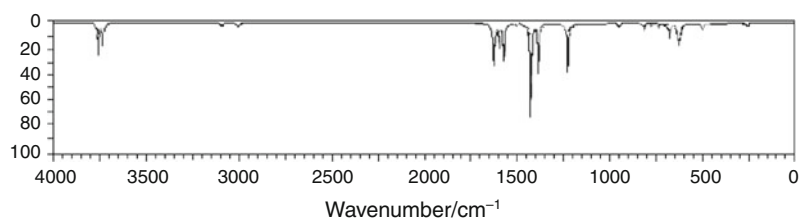


Fig. 6 Theoretical Raman spectrum of 2,4-pyridinedicarboxylic acid

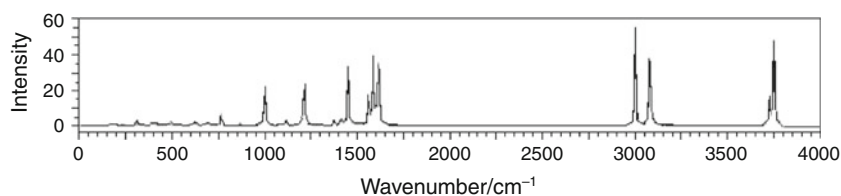


Fig. 7 Experimental IR spectrum of 2,4-pyridinedicarboxylic acid

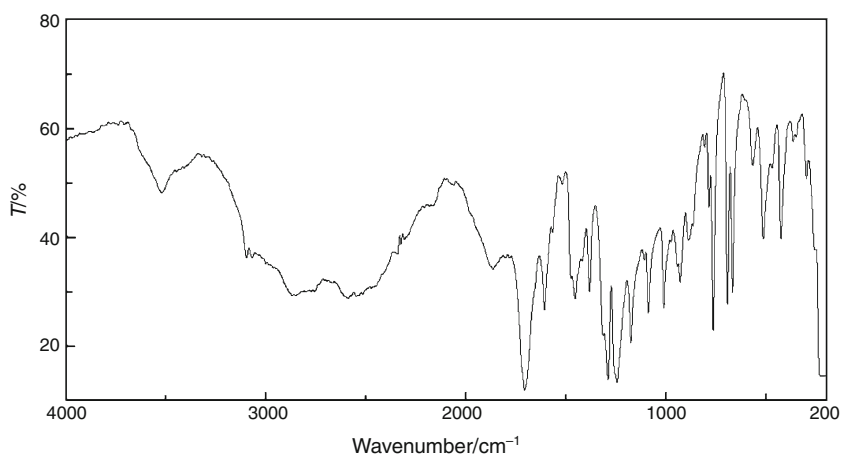


Fig. 8 Experimental Raman spectrum of lutidinic acid

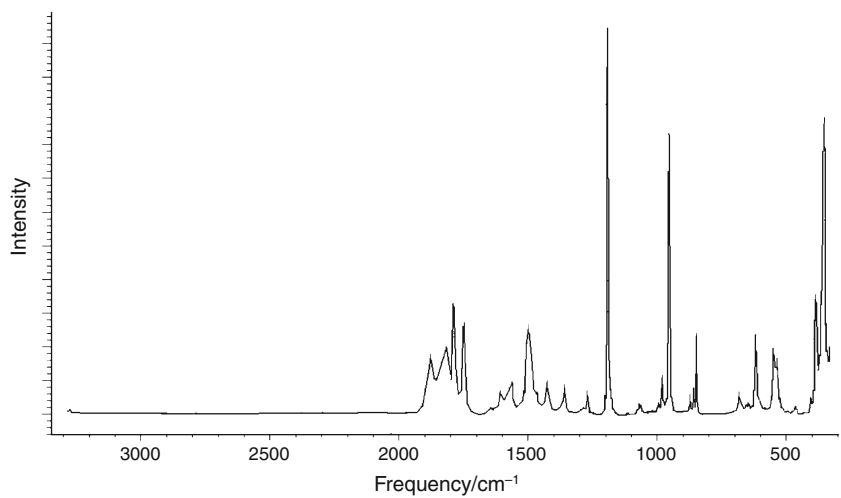


Fig. 9 Theoretical IR spectrum of sodium salt

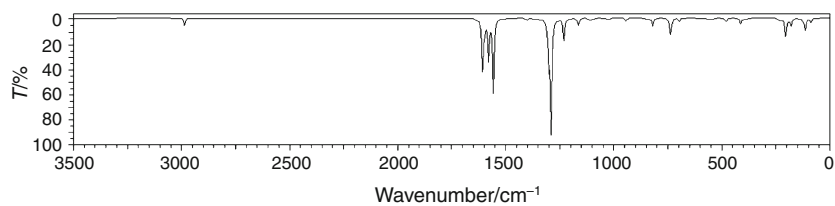


Fig. 10 Theoretical Raman spectrum of sodium salt

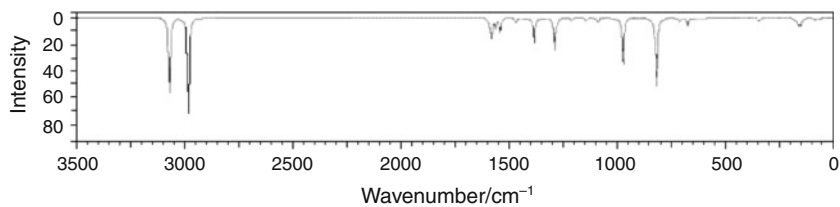


Fig. 11 Experimental IR spectrum of sodium salt

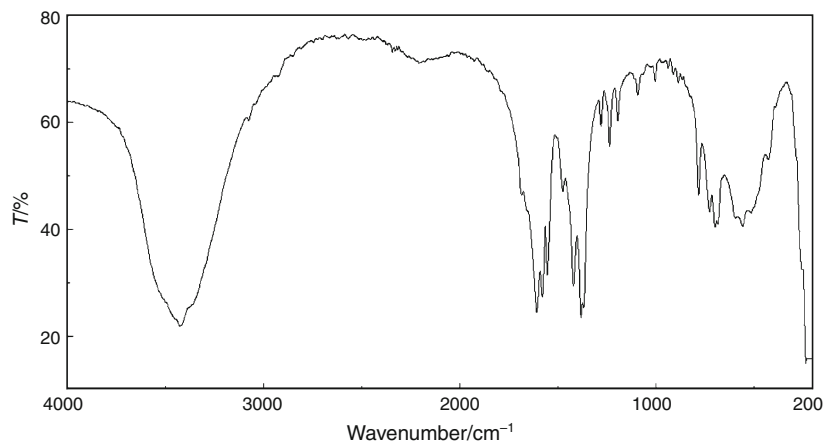


Fig. 12 Experimental Raman spectrum of sodium salt

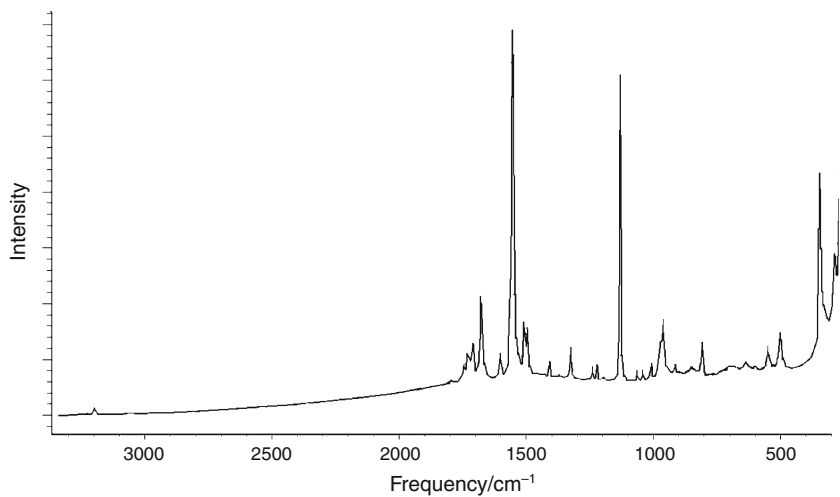
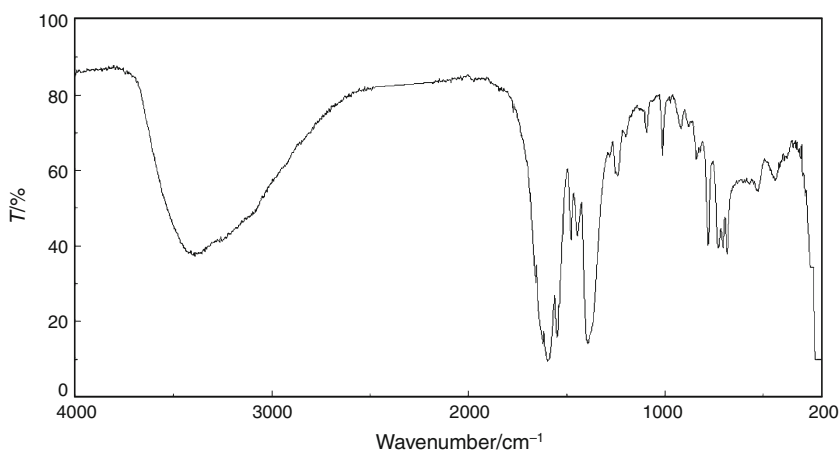


Fig. 13 IR spectrum of Nd(III) complex



480 cm^{-1} . Theoretical Raman spectrum of sodium salt was given in Fig. 10.

Experimental sodium salt was obtained as hexahydrated salt which was confirmed by elementary and thermal analysis. At 3424 cm^{-1} strong, broad band of νOH vibrations from water molecules is present (Fig. 11). Bands at 1604 and 1580 cm^{-1} correspond to the asymmetric carboxylate group vibrations, whereas at 1384 and 1368 cm^{-1} bands of symmetric COO^- vibrations are present. Calculated $\Delta\nu$ distributions were equal 220 and 212 cm^{-1} .

$\Delta\nu$ values for experimental sodium salt are lower than those for theoretical sodium salt which means that both carboxylate groups in this salt have the same bidentate chelate character.

Bands of C=N vibrations are present at 1552 cm^{-1} (connected with asymmetric COO^- vibrations) and at 1236 cm^{-1} (connected with stretching ring vibrations). Below 1004 cm^{-1} there are various pyridine ring vibrations. Me–O band vibration was found at 560 cm^{-1} . Raman spectrum was presented as Fig. 12.

All obtained light lanthanides (III) complexes spectra are similar. In the range of highest frequencies there are strong broad bands corresponding to νOH vibrations from water molecules as all were obtained as hydrated compounds: 3380 cm^{-1} (Ln, Gd), 3400 cm^{-1} (Ce), 3388 cm^{-1} (Pr, Sm, Eu), and 3392 cm^{-1} (Nd) (Fig. 13).

There are any bonds at 1700 cm^{-1} , which indicates that all carboxylic groups in complexes take part in metal coordination. Bands corresponding to the asymmetric COO^- vibrations are present at 1592, 1548 cm^{-1} (La, Ce), and 1596, 1548 cm^{-1} (Pr, Nd, Sm, Eu, Gd), whereas symmetric COO^- vibrations are present at the same wave number for all complexes: 1392 cm^{-1} . Calculated $\Delta\nu$ values are equal 200,156 cm^{-1} for La and Ce compounds and 204, 156 cm^{-1} for the rest of the obtained complexes. These values are lower than those calculated for experimental sodium salt though we can assume bidentate chelate character of carboxylic groups.

Bands of C=N stretching vibrations were registered at 1240 cm^{-1} (La, Ce, Nd, Eu), 1244 cm^{-1} (Pr, Gd), and 1248 cm^{-1} (Sm). In each case these vibrations are connected with stretching pyridine ring vibrations. Stretching and bending ring vibrations bands are present at 1476 and 1444 cm^{-1} for all complexes, while bands of ring breathing vibrations at 1012 cm^{-1} . Bands of weak Me–O vibrations were registered at 524 cm^{-1} (Nd), 525 cm^{-1} (Pr), 528 cm^{-1} (Gd), 532 cm^{-1} (La, Sm), and 536 cm^{-1} (Ce, Eu). Low intensity of these bands can correspond to the bending ring vibrations present in this region of frequencies.

Raman spectra were registered for La, Nd, and Gd complexes. The most intensive bands are present at 1453 cm^{-1} (La) and 1455 cm^{-1} (Gd), which correspond to the stretching C=N and C=C vibrations. For lanthanum and gadolinium complexes another strong bands occur at

1014 cm^{-1} (La) and 1017 cm^{-1} (Gd) and they correspond to the ring breathing vibrations. Both types of vibrations give stronger bands in Raman spectra than in IR. In case of neodymium complex there are only two bands present in the Raman spectrum: 1596 and 1262 cm^{-1} . Both bands correspond to the stretching C=N vibrations connected with stretching COO^- asymmetric vibrations and ring vibrations, respectively.

Conclusions

Sodium and light lanthanide (III) complexes with lutidinic acid have been synthesized by the double exchange method. All compounds are amorphous and differ slightly in water contents which can be caused by special polymers creation bonded through hydrogen bonding. Theoretical and experimental IR and Raman studies were carried out in order to assign bands of C=N vibrations correctly and to investigate way of metal coordination. Coordination probably takes place through both carboxylate groups, hence to the almost unchangeable position of COO^- and C=N bands on IR and Raman spectra.

As it was mentioned in our previous work published in Journal of Thermal Analysis and Calorimetry [31] pyridinedicarboxylic acids, including 2,4-pyridinedicarboxylic acid and its lanthanide complexes, are good potential materials for large microporous compounds synthesis. This is mainly caused by their high thermal stability. Hydrated compounds are stable up to 303–313 K and undergo one step dehydration process in which they loose all water molecules. In case of dehydrated compounds synthesized with lutidinic acid their thermal stability is up to 650–710 K. Their thermal stability is one of the necessary conditions to apply them as microporous compounds.

Theoretical IR and Raman studies allowed us to identify wavenumber regions where C=N bands vibrations are present. Their almost stable position in IR spectra and strictly defined position of COO^- ascertain us that lanthanide coordination take place through oxygens of carboxylate groups.

We compared results obtained for complexes with 2,5-pdca and 2,4-pdca series and stated that both are thermally similar with slight differences. In both series contents of water is similar and all complexes loose water during one step dehydration process. Thermal stability of hydrated compounds is higher 10–20 K for 2,5-pdc series. Anhydrous compounds of 2,5-pdc series are also stable at higher range of temperatures 673–763 K. Decomposition of anhydrous compounds of 2,4-pdc series is more complex because involve not only lanthanides (III) oxocarbonates and carbonates but also lanthanides (III) oxalates emission, while dehydrated compounds of 2,5-pdc series decompose only through oxocarbonates and carbonates. Lanthanides

oxides (III) are final products of decomposition in both series of complexes.

Hence to the theoretical and experimental studies of both series we stated that carboxylate groups in light lanthanides (III) complexes with 2,4-pdc acid have the same bidentate chelating character as carboxylate groups in complexes with 2,5-pdc acid. Therefore, both series of lanthanide (III) complexes are very similar to each other taking into account the thermogravimetric and spectroscopic data. According to obtained data we can assume that in case of these two series of pyridinedicarboxylates nitrogen from the pyridine ring does not take part in lanthanide coordination and that lanthanide metal cations (III) are coordinated only through carboxylate groups.

This stage of our work allowed us to identify the thermal stability and spectroscopic properties of the synthesized complexes. These compounds studies will be continuing in the direction of MOF-like structure obtaining, hydrothermal synthesis, and biological properties studying their influence on particular bacteria behavior.

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