Analytical and thermal investigations of new solid Y(III) and La(III) complexes

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Abstract

New compounds with formulae $\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ (**I**), $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ (**II**), $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ (**III**) and $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ (**IV**) were prepared and characterized by chemical and elemental analysis, IR spectroscopy and powder X-ray diffraction. The thermal properties of compounds in the solid state were studied using TG-DTA techniques under dry air atmosphere. The thermal behavior of investigated compounds was studied in the temperature range 298–1273 K. They are stable up to 323 K. The complexes decompose in several stages, accompanied by endo- and exothermic effects. In all cases, the first step of pyrolysis is partial or total dehydration. When the temperature rises, deamination takes place. The solid final products of decomposition are Y_2O_3 and La_2O_3 , respectively. Additionally, for all complexes mass spectrometry was used to analyze principal volatile thermal decomposition and fragmentation products evolved during pyrolysis under dry air atmosphere.

Keywords Y(III) and La(III) complexes · 2,4'-Bipyridine · TG-DTA · Mass spectra

Introduction

Since many years, large attention is returned to the rare earth element compounds. These classes of complexes have applications in many areas including magnets, catalysts, metal alloys, electronics, glass, ceramics, new materials, medicine and some other high-technology fields. In addition, to their magnetic and physical properties, their medical significance has been proven [1–7]. Although coordination chemistry of the trivalent lanthanide ions has expanded rapidly, the majority of complexes studied have been derived from ligands with nitrogen donor sites. The various types of the coordination may be generated by adjusting the N-donor and the metal ions. 2,4'-Bipyridine (2,4'-bpy) is very interesting organic ligand because of its different possibility to coordinate with central ion. This N-donor may coordinate in two ways: as a monodentate ligand by 4'(N) nitrogen atom [8–13] and bidentate

bridging by both nitrogens as heteronuclear and as bifunctional N-donor [14–17]. The publications with 2,4'-bpy only describe the coordination compounds of d-block elements. In the case of lanthanides, their high coordination numbers and the possibility of bifunctional coordination of 2,4'-bpy could give opportunity to obtain new coordination compounds with potential application in adsorption and catalysis (e.g., as artificial zeolites for removing selected forms from the system). Knowledge of such complexes will allow determining specifically their applicability.

Up to now, in the literature, there are no papers describing yttrium(III) and lanthanides(III) complexes with this N-donor ligand. This work is the beginning of research on such compounds. In this paper, we present preparation and characterization of four new solid complexes of Y(III) and La(III) with 2,4'-bipyridine and chlorides or bromides. Here, we also describe their stoichiometric composition, nature of the metal–organic ligand bond, molar conductivity, thermal decomposition and volatile species emitted during pyrolysis under dry air atmosphere.

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Experimental

Materials, synthesis and analysis

Y_2O_3 , La_2O_3 and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ were obtained from Fluka, HCl and HBr from P. O. Ch. Gliwice, and 2,4'-bipyridine (2,4'-bpy) from Aldrich.

The rare earth salts as hydrated products were prepared by dissolving the appropriate metal(III) oxide (99.9% purity) in concentrated appropriate acid (HCl or HBr). During dissolution, all mixtures were heated until a higher concentration of metal(III) halides was obtained. The compositions of these salts were controlled by determination lanthanide content.

2,4'-Bpy complexes were prepared by mixing 2,4'-bpy in 96% v/v ethanol with the solution of metal halides. The molar ratio of metal(III) to N-donor was 1:2. The reactions were carried out at 343 K for about 15 min. Total mixture volume was 30 mL. Investigated complexes were obtained using the method of slow crystallization from the above-described solutions. The products were filtered off; mixture of EtOH and Et₂O (1:1) was washed. The complexes were dried in air at room temperature.

The contents of N, C and H in prepared compounds were determined by a vario MICRO company Elementar Analysensysteme GmbH; the metal(III) ions in obtained solutions were determined by EDTA titration; content of chlorides and bromides was determined by Volhard method.

Methods and instruments

IR spectra were recorded with an IRTracer-100 Shimadzu Spectrometer (4000–400 cm^{-1} with accuracy of recording 1 cm^{-1}) using KBr pellets. Molar conductance was measured on a conductivity meter of the OK-102/1 type equipped with an OK-902 electrode at 298 ± 0.5 K, using 1×10^{-3} mol L^{-1} solutions of complexes in methanol, dimethylformamide and dimethylsulfoxide. The thermal

properties of complexes in air were studied by TG-DTA techniques in the range of temperature 298–1273 K at a heating rate of 10 K min^{-1} ; TG and DTA curves were recorded on Netzsch TG 209 apparatus under dry air atmosphere $v = 20$ mL min^{-1} using ceramic crucibles which were used as reference material were. The mass spectra were measured on mass spectrometer ThermoStar, Balzers (Germany), in the range of temperature 298–873 K at a heating rate 10 K min^{-1} under dry air atmosphere $v = 20$ mL min^{-1} in ceramic crucibles. The m/z values are given based on ^1H , ^{12}C , ^{16}O , ^{35}Cl , ^{80}Br in the range m/z : 1–90. X-ray powder diffraction data were taken with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) on a PANalytical X'Pert Pro MPD diffractometer ((PANalytical, Almelo, Netherlands) in the Bragg–Brentano reflection geometry. Data were collected in the 2θ range 5–90° with a step of 0.0167° and an exposure per step of 50 s. The samples were spun during data collection to minimize preferred orientation effects. A PANalytical X'Celerator detector based on Real-Time Multiple Strip technology and capable of simultaneously measuring intensities in the 2θ range of 2.122° was used. For structural analysis, the PANalytical High Score Plus software (ver. 3.0e) package was used.

Results and discussion

In the solid state were obtained four new compounds with following formulae $\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ (**I**), $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ (**II**), $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ (**III**) and $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ (**IV**). Table 1 presents results of the elemental and chemical analysis. All complexes do not change their stoichiometric composition in solid state at room temperature.

Molar conductivity

The molar conductivities values (Λ_M) and type of electrolytes in solutions MeOH, DMF and DMSO of isolated complexes are shown in Table 2. Type of electrolytes was

Table 1 Analytical data for synthesized compounds

No.	Compound	Analysis: (found) calculated/%					
		M	C	H	N	Cl^-	Br^-
(I)	$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$	15.50 (15.43)	31.40 (31.32)	4.92 (4.98)	7.32 (7.53)	18.54 (18.30)	–
(II)	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$	16.14 (16.11)	10.90 (11.01)	3.66 (3.69)	2.54 (2.59)	–	43.52 (43.97)
(III)	$\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$	28.26 (28.35)	24.43 (24.32)	3.69 (3.65)	5.70 (5.76)	21.63 (21.45)	–
(IV)	$\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$	19.76 (19.91)	25.63 (25.36)	3.15 (3.11)	5.98 (5.64)	–	34.10 (34.00)

Table 2 Molar conductivity in MeOH, DMF and DMSO for complexes

No.	Compound	$\Lambda_M/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c = 1 \times 10^{-3}/\text{mol L}^{-1}$ (type of electrolyte)		
		MeOH	DMF	DMSO
(I)	$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$	100 (1:1)	160 (2:1)	80 (2:1)
(II)	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$	225 (2:1)	200 (3:1)	120 (3:1)
(III)	$\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$	110 (1:1)	80 (1:1)	65 (2:1)
(IV)	$\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$	190 (2:1)	180 (2:1)	108 (3:1)

Table 3 The frequency of vibrations in the ring of free 2,4'-bpy and obtained complexes in the range of 1650–600 cm^{-1}

2,4'-bpy [19]	$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$	$\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$	$\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$	Assignments
1595	1637, 1608, 1595	1637	1644, 1637, 1606	1637, 1608, 1595	v CN, CC, CC _{ir} 4-sub py
1586	1583 sh	1587	1587	1582 sh	v CN, CC, CC _{ir} 2-sub py
1575	1575	1574	1575	1574	v CN, CC 2-sub py
1553	1560, 1539	1556, 1540	1558, 1540	1538	v CN, CC 4-sub py
1495	1504, 1494	1506, 1494	1508	1506	v CN, CC 4-sub py
1466	1467	1467	1469	1471	v CN, CC 2-sub py
1433	1442	1435	1435	1444	v CN, CC 2-sub py
1405	1417, 1394	1417, 1396	1411, 1396	1417	v CN, CC 4-sub py
1328	1357	1311	1331	1359, 1317	v CN, CC 4-sub py
1040	1056	1052	1060	1059	ring “breathing” 2-sub and 4-sub py
996	987	998	997	998	ring “breathing” 2-sub py
990 sh	1001	1008	1012	1001	ring “breathing” 4-sub py
762 sh	777	775	775	780	γ 2-sub py
670	669	669	669	669	β 2-sub py

sh shoulder, *ir* inter ring, v stretching vibration, β vibration in plane, γ vibration out of plane

determined based on the criteria given by Geary [18]. $\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ in MeOH and $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in MeOH and in DMF are electrolytes type 1 : 1. The compounds: $\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ in DMF and in DMSO, $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ in MeOH, $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in DMSO and $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ in MeOH and in DMF are electrolytes type 2:1. The electrolytes type 3:1 are compounds $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$

(in DMF and in DMSO) and $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ (in DMSO). High Λ_M values are probably due to displacement of inorganic ligands by molecules of solvents. These solvent molecules occupy the place of chlorides or bromides in the inner coordination sphere.

IR spectra

Table 3 presents the absorption bands in the region characteristic for 2,4'-bipyridine. The IR spectra of 2,4'-bpy are the sum of characteristic patterns of 2-substituted (2-sub) and 4-substituted (4-sub) pyridines [19]. When coordination of organic ligand with title metals(III) takes place, the IR spectrum of free 2,4'-bpy changes. The ring vibration modes of 4-substituted pyridine $\nu(\text{CN})$, (CC) , $(\text{CC}_{\text{i.r.}})$ are in uncoordinated 2,4'-bpy at 1595 cm^{-1} . For complexes (I) and (IV), this band practically does not shift, but in the spectra of all the compounds in this region appears new one at 1637 cm^{-1} . In addition, there are new bands at 1608 cm^{-1} for (I) and (IV) and at 1644 cm^{-1} and 1606 cm^{-1} for (III). There are also $\nu(\text{CN})$, (CC) ring vibration modes of free 4-sub pyridine at 1553 cm^{-1} . In the complexes, they are in the range of $1560\text{--}1538\text{ cm}^{-1}$. The bands characteristic for “breathing” deformation modes in ring 4-sub pyridine (990 sh) are changed. Bathochromic shifts of these bands suggest linking N-donor with metal

ions. It is possible to assume that 2,4'-bipyridine coordinates *via* 4'(N) nitrogen atom with metal ions. In the infrared spectra of obtained complexes, there are also bands characteristic for 2-sub pyridine: $\nu(\text{CN})$, (CC) , $(\text{CC}_{\text{i.r.}})$ at 1586 cm^{-1} and all vibrations $\nu(\text{CN})$, (CC) . They are slightly shifted in comparison with free ligand. The ring “breathing” 2-sub and 4-sub pyridines (at 1040 cm^{-1} for free ligand) are noticed for compounds in the range $1060\text{--}1052\text{ cm}^{-1}$. Between 1300 and 900 cm^{-1} , there are also $\beta(\text{CH})$ and $\gamma(\text{CH})$ vibrations of 2-sub and 4-sub pyridines. These bands are slightly shifted toward higher and lower wavenumbers. All these changes in absorption spectra of obtained complexes suggest that 2,4'-bpy can be bonded with metal ions *via* 2(N) nitrogen atom, probably forms polymeric species. This type of coordination has been described by Ming-Liang et al. [12]. Figure 1 presents IR spectra of obtained compounds in the range of vibrations of 2,4'-bipyridine.

In addition, a broad band in the water stretching region (ca $3450\text{--}3350\text{ cm}^{-1}$) appears for all compounds.

Fig. 1 IR spectra of synthesized complexes in the range of vibrations of 2,4'-bipyridine: **a** IR spectra of $\text{Y}(\text{2,4'-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ compound, **b** IR spectra of $\text{Y}(\text{2,4'-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ compound, **c** IR spectra of

$\text{La}(\text{2,4'-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ compound and **d** IR spectra of $\text{La}(\text{2,4'-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ compound

XRD data

Due to the lack of crystals of appropriate quality to determine the crystal structures, the powder X-ray diffraction (PXRD) was utilized as a tool for preliminary structural investigation and characterization of synthesis products. The PXRD analysis revealed the crystalline nature of the studied complexes. When comparing diffraction patterns, more pronounced peaks for bromide than for chloride complexes can be observed. The analysis also confirmed that the synthesis resulted in new products and no peaks from the substrates used for the synthesis were found. The comparison of diffraction patterns for Y(III) and La(III) complexes is shown in Figs. 2 and 3, respectively. The observed diffraction patterns for bromide and chloride complexes are clearly different, which proves that they are not isostructural. The unit lattice parameters were calculated with the help of the PANalytical High Score Plus software and are presented for bromide Y(III) and La(III) complexes in Tables 4 and 5, respectively. Due

to the inferior data quality, the unit cell parameters for chloride complexes have not been determined.

Thermal decomposition

Thermolysis of synthesized complexes in air atmosphere is a multistage process. The steps of thermolysis and the solid products were determined from TG and DTG curves. Intermediate species were verified by mass loss and investigation of the sinters obtained during heating the samples of complexes up to temperature defined from the thermal curves. In the sinters, the presence of chlorides or bromides was identified by qualitative analysis and the presence of bipyridine was identified by IR spectra. The thermal decomposition data are exhibited in Table 6. Figures 4–7 show the TG, DTG and DTA curves of obtained compounds. All complexes are stable up to 323 K. The compound of $\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$ releases 6.5 mol of water in the first step of decomposition (323–448 K); mass found was 20.0% and calculated to be 20.41%. On DTA curve, there are two endothermic peaks at 353 and 393 K.

Fig. 2 The comparison of diffraction patterns for Y(III) complexes

Fig. 3 The comparison of diffraction patterns for La(III) complexes

Table 4 X-ray data for $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ complex

$a = 9.906(5) \text{ \AA}$	$\alpha = 90^\circ$
$b = 13.644(8) \text{ \AA}$	$\beta = 90^\circ$
$c = 8.994(4) \text{ \AA}$	$\gamma = 90^\circ$
Volume = $1215.66(3) \text{ \AA}^3$	
Bravais lattice = P	
Crystal system = orthorhombic	
Figure of merit = 6.03%	
GOF = 1.33	

Table 5 X-ray data for $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ complex

$a = 6.984(6) \text{ \AA}$	$\alpha = 90^\circ$
$b = 16.757(9) \text{ \AA}$	$\beta = 93.11(1)^\circ$
$c = 25.36(2) \text{ \AA}$	$\gamma = 90^\circ$
Volume (V) = $2962.99(2) \text{ \AA}^3$	
Bravais lattice = P	
Crystal system = monoclinic	
Figure of merit = 3.84%	
GOF = 1.73	

In the range of temperature 448–538 K, further dehydration process takes place (two endothermic effects at 463 and 533 K). When the temperature rises, first partial and then total deamination process occurs with the creation of YOCl . These processes connect with exothermic effects on DTA curve at 553 and 613 K. The solid final product of decomposition is Y_2O_3 . It is created between 648 and 948 K. The dehydration process of $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ occurs in four steps. Total recorded water mass loss is 26.0%, and that calculated is 26.16%. On DTA curve appear three endothermic peaks at 393, 433 and 488 K. In the range of temperature 533–603 K, deamination takes place and YBr_3 appears (563 K endothermic and 593 K exothermic peaks). Further elevation of temperature causes formation of YOBr (603–833 K). Above 1048 K, pure Y_2O_3 is observed. Thermolysis of $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ starts with dehydration process, which occurs in two steps. First lanthanum complex loses 3.5 mol of water (323–373 K) and next 1.5 water molecules (373–448 K). On DTA curve, there are two endothermic peaks at 343 and 393 K, respectively. In the interval of temperature 448–648 K, TG curve shows a large mass loss (found 32.0% and calculated 31.74%) as a result of destruction of

Table 6 Thermal decomposition data of obtained compounds

Compound	Range of decomposition/K	DTA peaks/K	Mass loss/%		Intermediate and residue solid products
			Found	Calcd.	
$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$	323–448	353, 393 endo	20.00	20.41	$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3 \cdot 1.5\text{H}_2\text{O}$
	448–538	463, 533 endo	18.00	18.33	$\text{Y}(2,4'\text{-bpy})_{1.5}\text{Cl}_3$
	538–563	553 exo	7.00	6.80	$\text{Y}(2,4'\text{-bpy})_{0.75}\text{Cl}_3$
	563–648	613 exo	30.00	29.99	YOCl
	648–948	653 exo	5.00	4.79	Y_2O_3
$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$	323–418	393 endo	9.50	9.81	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$
	418–468	433 endo	9.50	9.81	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 2\text{H}_2\text{O}$
	468–508	488 endo	3.50	3.27	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot \text{H}_2\text{O}$
	508–533		3.50	3.27	$\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3$
	533–603	563 endo, 593	14.00	14.19	YBr_3
	603–833	663 exo	26.00	26.11	YOBr
	833–1048		13.00	13.05	Y_2O_3
$\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$	323–373	343 endo	12.80	12.83	$\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 1.5\text{H}_2\text{O}$
	373–448	393 endo	6.00	5.50	$\text{La}(2,4'\text{-bpy})\text{Cl}_3$
	448–648	503 endo, 523, 593 exo	32.00	31.74	LaCl_3
	> 648				*
$\text{La}(2,4'\text{-bpy})_{1.5} \text{Br}_3 \cdot 5\text{H}_2\text{O}$	323–373	353 endo	12.50	12.81	$\text{La}(2,4'\text{-bpy})_{1.5} \text{Br}_3$
	373–543	433 endo, 488, 523 exo	32.50	33.33	LaBr_3
	543–728		20.50	20.46	LaOBr
	728–1073		11.00	10.23	La_2O_3

*Very slow transformation to La_2O_3

Fig. 4 TG, DTG and DTA curves of thermal decomposition of $Y(2,4'\text{-bpy})_{1.5}Cl_3 \cdot 8H_2O$ recorded in air atmosphere; mass sample 9.94 mg

Fig. 5 TG, DTG and DTA curves of thermal decomposition of $Y(2,4'\text{-bpy})_{0.5}Br_3 \cdot 8H_2O$ recorded in air atmosphere; mass sample 11.38 mg

2,4'-bipyridine and creation of $LaCl_3$. It connects with one endothermic effect at 503 K and two exothermic peaks at 523 and 593 K, respectively. Found lanthanum chloride very slowly converts to La_2O_3 which is the final solid product of thermal decomposition. Pyrolysis of $La(2,4'\text{-bpy})_{1.5}Br_3 \cdot 5H_2O$ begins at 323 K. On TG curve is recorded a mass loss associated with dehydration process (323–373 K). Increasing temperature (373–543 K) causes decomposition of organic ligand with the formation of $LaBr_3$. These processes are accompanied by endo- and exothermic effects. Between 543 and 728 K, $LaBr_3$ transforms to $LaOBr$. The compound stays stable from 1073 K.

Mass spectrometry

The mass spectrometry was used to analyze the principal volatile products evolved during the thermal decomposition and fragmentation processes. For all synthesized complexes, the principal profiles m/z are very similar, only major maxima of ion currents are slightly shifted. Figure 8 shows, as an example, selected profiles of ion currents for $La(2,4'\text{-bpy})Cl_3 \cdot 5H_2O$ compound. For $Y(2,4'\text{-bpy})_{1.5}Cl_3 \cdot 8H_2O$, the peak characteristic for OH^+ and H_2O^+ ($m/z = 17, 18$) appears as a broad maximum in the range of temperature 353–523 K. It is associated with dehydration process. Signals from CO_2^+ ($m/z = 44$), CH^+ ($m/z = 13$), C^+ ($m/z = 12$) ions were detected in temperature range 583–693 K (with maximum at 643 K). These peaks can connect with the organic ligands destruction and burning of

Fig. 6 TG, DTG and DTA curves of thermal decomposition of $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ recorded in air atmosphere; mass sample 10.49 mg

Fig. 7 TG, DTG and DTA curves of thermal decomposition of $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ recorded in air atmosphere; mass sample 5.60 mg

residues. Additionally, the NO^+ ion signal was observed in the similar temperature range with maximum at 643 K. This suggests that the thermal decomposition of bipyridine and afterburning of organic fragments take place in the temperature range 583–693 K. The species containing chlorine with $m/z = 35$ (Cl^+), 47 (CCl^+) and 70 (Cl_2^+) were also monitored. In the case of $\text{Y}(2,4'\text{-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$ complex, the signals from OH^+ and H_2O^+ ($m/z = 17, 18$) ions were observed in the temperature range 353–503 K, for C^+ ($m/z = 12$) and CO_2^+ ($m/z = 44$) ions between 553 and 753 K with maximum at 603 K. Moreover, the profiles of ion current from CH^+ ($m/z = 13$) were identified at temperature 603 K. The signal from NO^+ ($m/z = 30$) ion was found in the temperature range 573–733 K with maximum at 603 K. All identified peaks indicate the dehydration process first and then thermal decomposition

of bipyridine, where first the breaking of double bonds occurs and next the disconnection of nitrogen and burning of N-donor and residues take place. The signals containing bromide were recorded but with very low intensity. For $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ compound, the signals from OH^+ and H_2O^+ ($m/z = 17, 18$) were recorded between 353 and 423 K. The ions of CO_2^+ (44), C^+ (12) were detected in temperature range 453–723 K with maximum at 523, 553 and 628 K. These peaks can be assigned thermal decomposition of bipyridine and afterburning of organic fragments. Additionally, the NO^+ ($m/z = 30$) ion signal was appeared in the temperature range 473–723 K with maximum at 523, 553 and 628 K, respectively. The mass spectrometer also monitored traces of species containing chlorine: Cl^+ , CCl^+ , Cl_2^+ ($m/z = 35, 47, 70$). In the case of $\text{La}(2,4'\text{-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$, the thermal decomposition is

Fig. 8 Selected ion currents detected by the MS spectra for $\text{La}(\text{2,4'-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ compound in air, mass sample 15.78 mg: (a) m/z : 12 (C^+), 30 (NO^+), 35 (Cl^+), 44 (CO_2^+), 47 (CCl^+), (b) m/z : 13 (CH^+), 35 (Cl^+), 70 (Cl_2^+)

similar to yttrium(III) and lanthanum(III) complexes with 2,4'-bipyridine and halide ions described above. However, the temperature of the principal profiles m/z is shifted to a lower temperature in comparison with $\text{La}(\text{2,4'-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ compound. The profiles for OH^+ and H_2O^+ ($m/z = 17, 18$) from dehydration occur between 333 and 363 K. The signals from C^+ ($m/z = 12$), CO_2^+ ($m/z = 44$) and NO^+ ($m/z = 30$) ions appear in the range 373–623 K. These signals can relate to the thermal decomposition of bipyridine. Signals containing bromine ions were also recorded but with very low intensity.

Conclusions

Four new solid rare earth complexes with 2,4'-bipyridine and chlorides or bromides with formulae $\text{Y}(\text{2,4'-bpy})_{1.5}\text{Cl}_3 \cdot 8\text{H}_2\text{O}$, $\text{Y}(\text{2,4'-bpy})_{0.5}\text{Br}_3 \cdot 8\text{H}_2\text{O}$, $\text{La}(\text{2,4'-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ and $\text{La}(\text{2,4'-bpy})_{1.5}\text{Br}_3 \cdot 5\text{H}_2\text{O}$ were synthesized. IR spectra of the obtained complexes are different from those of the free 2,4'-bipyridine. For 2-sub and 4-sub pyridines, the most characteristic ring vibration modes are changed in comparison with uncoordinated N-donor. These changes indicate the formation of metal–organic ligand bond, probably *via* 2(N) and 4'(N) nitrogen atoms. There is the probability of creating polymeric structures. All obtained compounds are stable up to 323 K. During heating, they decompose

progressively. When the temperature rises, partial and total dehydration take place. The pyrolysis of anhydrous complexes is a multistage process. The final solid products of decomposition are pure metal oxides. In the case of $\text{La}(2,4'\text{-bpy})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ compound, La_2O_3 appears very slowly. The halogen atom (chlorine or bromine) does not affect the thermal stability of the synthesized complexes. Mass spectrometry was used to analyze the principal volatile thermal decomposition and fragmentation products in air atmosphere for all synthesized complexes. MS study also suggests several steps of thermolysis under dry air atmosphere. Volatile thermal decomposition and fragmentation products evolved during pyrolysis are in good agreement with mass losses registered on TG curves. MS profiles for all discussed complexes are very similar. The general recorded signals are from OH^+ , H_2O^+ , C^+ , CH^+ , CO_2^+ , NO^+ with $m/z = 12, 13, 44, 30$ and fragments containing proper halogen.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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