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# Coordination behaviour and thermolysis of some rare-earth complexes with 4,4′-bipyridine and di- or trichloroacetates

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**Abstract** A novel mixed-ligand complexes with empirical formulae: $Dy(4\text{-}bpy)(CCl_2HCOO)_3 \cdot H_2O$ and $Ln(4\text{-}bpy)_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ (where Ln(III) = Ce, Nd) were prepared and characterized by chemical and elemental analysis and IR spectroscopy, conductivity (in methanol, dimethyloformamide and dimethylsulfoxide). Analysis of the diffractograms showed that the obtained complexes are crystalline. Way of metal-ligand coordination discussed. The thermal properties of complexes in the solid state were studied under non-isothermal conditions in air atmosphere. During heating the complexes decompose *via* intermediate products to the oxides: $Ln_2O_3$ (Nd, Dy) and $CeO_2$. TG-MS system was used to analyse principal volatile thermal decomposition and fragmentation products evolved during pyrolysis of $Dy(4\text{-}bpy)(CCl_2HCOO)_3 \cdot H_2O$ in air.

**Keywords** 4,4′-Bipyridine · Dichloroacetate · IR spectra · Mixed-ligand complexes · Thermal decomposition

## Introduction

As a model ligands in our investigation we choose 4,4′-bipyridine (4-bpy) and di- or trichloroacetates. 4,4′-Bipyridine has a huge and versatile use in creating polymeric species [1–4]. In combination with carboxylate groups 4-bpy forms unusual type of structures and properties [5–9]. For many years attention has been focused on lanthanide complexes, because of their applications in diagnostic medicine [10, 11], radiotherapeutic drugs [12], fluoroimmunoassay [13] and in hetero-and homogeneous catalysis [14, 15]. Thermal studies of lanthanide complexes are very important because during elimination of water a macroporous materials with active metal sites is created and during pyrolysis different solid products are formed as important reagents in heterogeneous catalysis [14]. Lanthanide complexes with halogenoacetates have been studied for many years. The crystal structures have been determinated for compounds type: $[\{M(CClH_2COO)\}_3(H_2O)_5]_n$ where M(III) = La, Pr, Nd and Eu [16], $Ln(ClF_2CCOO)_3(H_2O)_3$ where Ln(III) = Gd, Dy, Ho, Er [17], $[\{Nd(CClH_2COO)_3\}_3(H_2O)_5]_n$ [18], $Ln(CCl_2HCOO)_3 \cdot 2H_2O$ where Ln(III) = Pr, Eu [19] and $[Ln_2(CF_3COO)_6(H_2O)_6]$ where Ln(III) = Pr-Lu except Nd and Ho [20]. The complexes: $[Nd_2(CCl_3COO)_6 3H_2O]_n \cdot nH_2O$ and $Nd(CCl_3COO)_3 \cdot 2H_2O$ were synthesized and characterized by EPR investigations [21, 22]. Rohde et al. [23] obtained $Gd(CF_2HCOO)_3(H_2O)_2 \cdot H_2O$ and studied their magnetic properties. Moreover, rare-earth compounds with trifluoroacetates were investigated [24]. In the literature there are also information about thermal decomposition of this type compounds. Thermal decomposition of rare-earth compounds with trifluroacetates is described in [25–27]. According to Logvinenko et al. [28, 29] for compounds type: $Ln(CF_3COO)_3 \cdot 3H_2O$, partially hydrolysis in solid state $[Ln_2(CF_3COO)_3(H_2O)_n] \leftrightarrow [Ln_2(CF_3COO)_5(CF_3COOH)(H_2O)_{n-1}(OH)]$ was observed. Under quasi-equilibrium conditions (in static air atmosphere and linear heating) the first step of thermolysis of $Ln(CF_3COO)_3 \cdot 3H_2O$ (where Ln(III) = La, Gd, Tb) partial dehydration was observed, which was not accompanied by organic ligand decomposition or free acid liberation. Spacu and Antonescu [30] reported thermal stability

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Edyta Koniuszenna participated in experimental part of this work.

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and some properties of complexes $[LnA_3(\text{N-donors})] \cdot nH_2O$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Dy and Er; A = $CClH_2COO^-$,$CCl_2HCOO^-$,$CCl_3COO^-$; N-donors = 1,10-phenanthroline, 2,2′-bipyridine and 4,7-diphenyl-1,10-phenanthroline). Compounds with empirical formula Ln (2-bpy)$(CBrH_2COO)_3$, where: Ln(III) = Nd, Er; 2-bpy = 2,2′-bipyridine (2-bpy) were investigated by thermal studies [31]. John and Urland [32] obtained in solid state $Gd_2(CClH_2COO)_6(2\text{-bpy})_2$. Complexes of Pr(III), Nd(III), Gd(III) and Er(III) with 2-bpy and trichloroacetates [33] also Nd(III) and Er(III) with 2-bpy and dichloroacetaes [34, 35] were isolated. They were structurally characterized by X-ray crystallography and their magnetic properties were determined.

In our recent investigation a novel complexes of Ln (4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ (where: Ln(III) = Y, Ce, Nd, Pr and Eu) [36], $[La(H_2O)(4\text{-bpy})(CCl_2HCOO)_3]_n$ [37] and $[Sm(H_2O)(4\text{-bpy})(CCl_2HCOO)_3]_n$ [5] were obtained. They were characterized by elemental and thermal analysis, IR and conductivity studies. A coupled TG-MS system was used to detect the principal volatile products of thermal decomposition and fragmentation processes for Nd(III), Pr(III) [36] and Sm(III) [5] compounds. Additionally the crystal and molecular structure of La(III) [37] and Sm(III) [5] complexes were determinated.

In this paper we describe the results of our investigations on new mixed-ligand complexes of Dy(III) with 4-bpy and dichloroacetates and Ce(III) and Nd(III) with 4-bpy and trichloroacetates. This report is concerned with their physico-chemical properties and thermal decomposition in air.

## Experimental

### Materials, synthesis and analysis

4,4′-Bipyridine, $CCl_2HCOOH$, $CCl_3COOH$, $Ln_2O_3$ (where Ln(III) = Nd, Dy), $Ce(NO_3)_3 \cdot 6H_2O$, dimethylsulfoxide (DMSO), dimethylformamide (DMF) and methanol (MeOH) (anhydrous) p.a. were obtained from Aldrich and Lab-Scan, respectively. Water solutions of metal(III) di- or trichloroacetates were prepared by adding 2 mol $L^{-1}$ di- or trichloroacetic acid to freshly precipitated $Ln(OH)_3$ (in case of Ce(III) freshly precipitated carbonate) in *ca*. stoichiometric quantities. The contents of M(III) ions in obtained solutions were complexometrically (EDTA) determined. Other chemicals were p.a. products from POCh-Gliwice.

IR spectra were recorded with a Shimadzu spectrometer (4000–400 $cm^{-1}$) using KBr pellets. Molar conductances were measured on a conductivity meter of the OK-102/1 type equipped with an OK 902 electrode at 298 ± 0.5 K. Molar conductivity of complexes was measured using $1 \times 10^{-3}$ mol $L^{-1}$ solutions in MeOH, DMF and DMSO. Thermal studies were performed on a derivatograph Q-1500 under a static air atmosphere. $\alpha$-$Al_2O_3$ served as the reference; mass sample of 100 mg. The system TG-MS under a dynamic atmosphere was used to analysis of the principal volatile products of thermal decomposition and fragmentation of Dy(III) complex. Data were performed by on line connected computer system with commercial (TG/DTA-SETSYS-16/18 apparatus, mass spectrometer QMS-422 model ThermoStar from Balzers) softwere; an ion source of *ca* 423 K by using 70 eV electron impact ionization and flow rate 1 L/h. All thermal investigations were carried out between 293–1273 K at a heating rate 283 K $min^{-1}$. For all complexes X-ray diffractograms (diffractometer D-5000, $CuK_\alpha$, Ni filtered radiation) were done. The measurements were made in the range of $2\theta$ angles 2–80°. Obtained X-ray diffractometric results were analysed using the Powder Diffraction File [38].

4-Bpy complexes were prepared by mixing 9.6 mmol of 4-bpy in 96% v/v ethanol (31.25 mL) with the solution of 4.8 mmol metal di- or trichloroacetates in 8.75 mL of water. During several days the compounds crystallized. The obtained complexes were filtered off; washed with 40% v/v ethanol and then with EtOH and $Et_2O$ mixture (1:1). The products were air dried at room temperature. The carbon, hydrogen and nitrogen contents in the prepared complexes were determined by a Carbo-Erba analyser with $V_2O_5$ as an oxidizing agent. Metal contents of rare-earth elements were mineralized and determined by EDTA titration.

## Results and discussion

Results of the elemental and chemical analyses are listed in Table 1. All complexes were prepared as hydrates. The analysis of the power diffraction patterns of the studied compounds revealed, that they were in the crystalline form. Moreover the crystals formed by the Ce(III) and Nd(III) complexes were not isostructural (see Fig. 1). In the solid state all complexes were stable in air. The observed molar conductivity values in MeOH, DMF and DMSO are given in Table 1. The $Dy(4\text{-bpy})(CCl_2HCOO)_3 \cdot H_2O$ complex in DMF falls within the generally acceptable range for electrolytes 1:2, but in DMSO was characterized as 1:1 electrolyte. All compounds in MeOH display intermediate behaviours between those of non-electrolytes and 1:1 electrolytes. Very low molar conductance value indicated non-electrolytic nature of $Ce(4\text{-bpy})_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ and $Nd(4\text{-bpy})_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ in DMSO and DMF [39].

**Table 1** Analytical data and molar conductivity $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) in MeOH, DMF and DMSO c = $1 \cdot 10^{-3}$ mol L$^{-1}$ at 298 K

| Complex | Analysis: found (calculated) (%) | | | | $\Lambda_M$ | | |
|---|---|---|---|---|---|---|---|
| | M | C | N | H | MeOH | DMF | DMSO |
| Dy(4-bpy)($CCl_2HCOO$)$_3$ · $H_2O$ | 22.75 | 26.49 | 4.19 | 1.80 | 50.5 | 113.1 | 55.5 |
| | (22.55) | (26.67) | (3.89) | (1.82) | | | |
| Ce(4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$ | 15.68 | 28.15 | 4.60 | 1.78 | 68.5 | 12.8 | 10.7$^a$ |
| | (15.61) | (28.10) | (4.68) | (1.80) | | | |
| Nd(4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$ | 16.13 | 28.02 | 4.67 | 1.76 | 66.6 | 15.3 | 3.78$^b$ |
| | (16.00) | (27.97) | (4.66) | (1.79) | | | |

At concentration: $^a$ $-0.4 \times 10^{-3}$ mol L$^{-1}$, $^b$ $-0.6 \times 10^{-3}$ mol L$^{-1}$

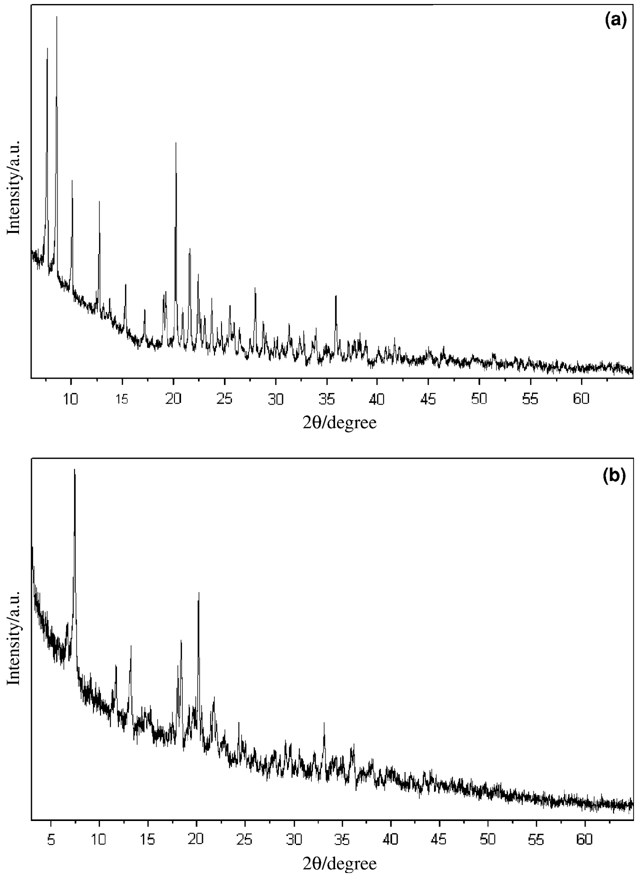

**Fig. 1** X-Ray diffraction patterns for complexes **a** Ce(4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$ and **b** Nd(4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$

## Infrared spectra

IR spectra of the analysed complexes exhibit several absorption bands characteristic for 4-bpy and OCO groups. The fundamental vibration modes of these ligands are summarised in Table 2. The absorption bands were identified in accordance with the literature [40]. In spectra of complexes the bands assigned to ring stretching modes: CC, CN, CC$_{\text{i.r.}}$ ($A_1$ symmetry), CN, CC$_{\text{str.}}$ ($B_1$ symmetry) and ring ‘breathing’ modes are observed in the range of 1608.5–1558.4, 1533 cm$^{-1}$ and 1002.9–1001.0 cm$^{-1}$, respectively. They are shifted in comparison with the free ligand. These shifts of principal absorption bands suggested that 4-bpy and COO$^-$ groups were coordinated to metal ion [40, 41].

The asymmetric $\nu_{as}$(OCO) bands of the carboxylate group in the studied complexes lie between 1703.8–1627.8 cm$^{-1}$ while the bands of symmetric vibrations $\nu_s$(OCO) appear in the range of 1380.0–1367.4 cm$^{-1}$. The separation $\Delta\nu = \nu_{as}(OCO) - \nu_s(OCO)$ characterize the nature of the metal-carboxylate bond. When $\Delta\nu_{Na} > \Delta\nu_{Ln}$ the OCO group is a bidentate-chelating, in case of $\Delta\nu_{Na} < \Delta\nu_{Ln}$ it coordinates as a monodentate ligand and for $\Delta\nu_{Na} \approx \Delta\nu_{Ln}$ acts as a bidentate-bridging donor [42]. The $\nu_{as}$(OCO) of the Dy(III) complex is clearly splitted into two bands. The values of $\Delta\nu$ suggest that carboxylate groups in this compound probably act as monodentate and bidentate-bridging donors. For Ce(4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$ and Nd (4-bpy)$_{1.5}$($CCl_3COO$)$_3$ · $2H_2O$ $\Delta\nu_{Na} > \Delta\nu_{Ln}$. It may suggest, that carboxylate groups in these compounds coordinated as bidentate-chelating ligands. In the case of Ce(III) complex $\nu_{as}$(OCO) is also splitted into two bands (Table 2). Hence, we may suppose that bonds between Ce(III) and carboxylate groups of trichloroacetate ligands are non-completely equivalent [43, 44]. We should not forget, that 4-bpy tends to create polymeric species [6, 9], which may also complicate the structures of the investigated complexes.

In the IR spectra of all complexes there are broad absorption bands with maximum at *ca* 3350–3400 cm$^{-1}$, confirming the presence of water molecules in the compounds.

## Thermal decomposition

Results of thermal analysis indicate that the decomposition of the analysed complexes is a multi-step process. The thermal decomposition data are collected in Table 3. Thermoanalytical curves of decomposed complexes in air are shown in Fig. 2. They reveal that all complexes are

**Table 2** Principal IR bands for 4-bpy and $OCO^-$ group in studied complexes ($cm^{-1}$)

| Assignment of bands | 4-bpy [40] | Nadac [41] | Natac [41] | Complexes of Ln(III) | | |
|---|---|---|---|---|---|---|
| | | | | Dy | Ce | Nd |
| *Coordinated 4,4′-bipyridine modes* | | | | | | |
| $\nu$(CC), $\nu$(CN), $\nu(CC_{i.r})$ | 1588 | – | – | 1608.5 | 1602.7<br>1558.4 | 1600.8 |
| $\nu$(CC), $\nu$(CN) | 1530 | – | – | 1533.3 | 1533.3 | 1533.3 |
| Ring “breathing” | 988 | – | – | 1002.9 | 1001.0 | 1002.9 |
| *Carboxylate group modes* | | | | | | |
| $\nu_{as}$(OCO) | – | 1640 | 1677 | 1703.8<br>1627.8 | 1660.0<br>1645.2 | 1641.3 |
| $\nu_s$(OCO) | – | 1399 | 1353 | 1380.0 | 1369.4 | 1367.4 |
| $\Delta\nu$ | – | 241 | 324 | 376.0<br>247.8 | 290.6<br>275.8 | 273.9 |

*Nadac* $NaCCl_2HCOO$ *Natac* $NaCCl_3COO$, $\Delta\nu = \nu_{as}(OCO) - \nu_s(OCO)$

**Table 3** Thermal decomposition data of obtained complexes in air; mass sample 100 mg

| Complex, intermediate and residue solid products | Ranges of decomposition (K) | Mass loss (%) | | DTA peaks (K) |
|---|---|---|---|---|
| | | Calc. | Found | |
| $Dy(4\text{-}bpy)(CCl_2HCOO)_3 \cdot H_2O$ | | | | |
| ↓ | 353–393 | 2.5 | 3.0[a] | 373 endo |
| $Dy(4\text{-}bpy)(CCl_2HCOO)_3$ | | | | |
| ↓ | 393–553 | 25.67 | 27.0 | 468 exo<br>533 exo |
| $Dy(4\text{-}bpy)(CCl_2HCOO)Cl_2$ | | | | |
| ↓ | 553–1073 | 43.02 | 42.5 | 733 exo<br>853 exo |
| DyOCl | | | | |
| ↓ | 1073–1213 | 2.93 | 2.5 | 1023 exo |
| $Dy_2O_3$ | | | | |
| $Ce(4\text{-}bpy)_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ | | | | |
| ↓ | 363–393 | 2.00 | 2.0 | 393 endo |
| $Ce(4\text{-}bpy)_{1.5}(CCl_3COO)_3 \cdot H_2O$ | | | | |
| ↓ | 393–423 | 2.00 | 2.0 | 413 endo |
| $Ce(4\text{-}bpy)_{1.5}(CCl_3COO)_3$ | | | | |
| ↓ | 423–523 | 42.44 | 41.5 | 473 exo<br>513 exo |
| $Ce(4\text{-}bpy)_{1.5}Cl_3$ | | | | |
| ↓ | 523–873 | 34.39 | 35.0 | 693 exo<br>773 exo |
| $CeO_2$ | | | | |
| $Nd(4\text{-}bpy)_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ | | | | |
| ↓ | 333–353 | 2.00 | 2.5 | 353 endo |
| $Nd(4\text{-}bpy)_{1.5}(CCl_3COO)_3 \cdot H_2O$ | | | | |
| ↓ | 353–373 | 2.00 | 2.5 | |
| $Nd(4\text{-}bpy)_{1.5}(CCl_3COO)_3$ | | | | |
| ↓ | 373–513 | 42.23 | 42.0 | 393 exo<br>473 exo |
| [b]$Nd(4\text{-}bpy)_{1.5}Cl_3$ | | | | |
| ↓ | 513–1133 | 35.11 | 34.5 | 733 exo |
| $Nd_2O_3$ | | | | |

[a] with traces from pyrolysis of organic ligands, [b] probably *via* $NdCl_3$

hydrated, so the pyrolysis starts by the release of water molecules, which is demonstrated by endothermic peaks on DTA curve. $Dy(4\text{-}bpy)(CCl_2HCOO)_3 \cdot H_2O$ is stable up to 353 K. Complexes of Ce(III) and Nd(III) eliminate water molecules in two stages. In the case of anhydrous complex of Dy(III) partial and total decompositions of

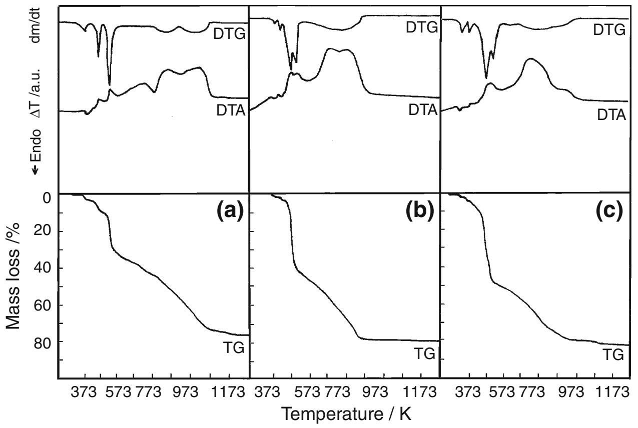

**Fig. 2** Thermoanalytical curves of complexes: **a** Dy(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$, **b** Ce(4-bpy)$_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ and **c** Nd (4-bpy)$_{1.5}$ $(CCl_3COO)_3 \cdot 2H_2O$; mass sample 100 mg

dichloroacetates take place and intermediate compound Dy(4-bpy)$(CCl_2HCOO)Cl_2$ (393–553 K) is formed. DTA curve presents exothermic peaks at 468 and 533 K, respectively. After decomposition of organic ligands (553–1073 K) DyOCl is formed, which next is converted to $Dy_2O_3$. Pyrolysis of complexes of Ce(III) and Nd(III) are very similar. Anhydrous compounds Ln(4-bpy)$_{1.5}$ $(CCl_3COO)_3$ (Ln(III) = Ce, Nd) convert directly to Ln(4-bpy)$_{1.5}Cl_3$. The exothermic peaks on DTA curves are at 473, 513 K for Ce(III) and 393, 473 K in case of Nd(III) complex. Next, further pyrolysis takes place. The final decomposition solid products are $CeO_2$ and $Nd_2O_3$, respectively.

### Mass spectrometry

For Dy(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ a coupled TG-MS system was used to analyse the principal volatile thermal decomposition and fragmentation products. The *m/z* values are given for $^{1}H$, $^{12}C$, $^{14}N$ and $^{16}O$ (additionally $^{13}C$ and $^{18}O$ for $CO_2^+$ which were not interpreted). Generally, many signals of ion currents are observed in the range of *ca* 442–454 and ~963 K. The first peak for $OH^+$ and $H_2O^+$ (*m/z* = 17, 18) occurs at around 373 K. This coincides with elimination of coordinated (or crystalline) water. Maximum rates of forming $H_2O^+$ are observed at 698 K and corresponding to decomposition of organic ligands. The ion signal intensities of $C^+$ and $CO_2^+$ have centers at 442, 647, 768 and 951 K. The first peak of $C^+$ and $CO_2^+$ reveals the partial decomposition of dichloroacetates. The other is connected with the destruction of the organic ligands and the burning of the organic residues. The intensities of major ion signals containing halogen ($Cl^+$, $HCl^+$) appear in the range of 432–541 K. Additionally, there are $CH_3^+$, $CCl^+$, $CHCl^+$, $CH_2Cl^+$ (*m/z* = 15, 47, 48, 49) at 453 K and $CH_3Cl^+$ (*m/z* = 50) at 442 K. These species are produced by decomposition of dichloroacetate ligands. MS measurements present signals of $NO^+$ (or $CH_2O^+$ *m/z* = 30) at 449, 814 and 961 K. Low intensities for ion current with *m/z* = 26, 51, 52, 60 and 84 were monitored. Correlation of selected ion currents and TG curve of Dy(III) complex is presented in Fig. 3.

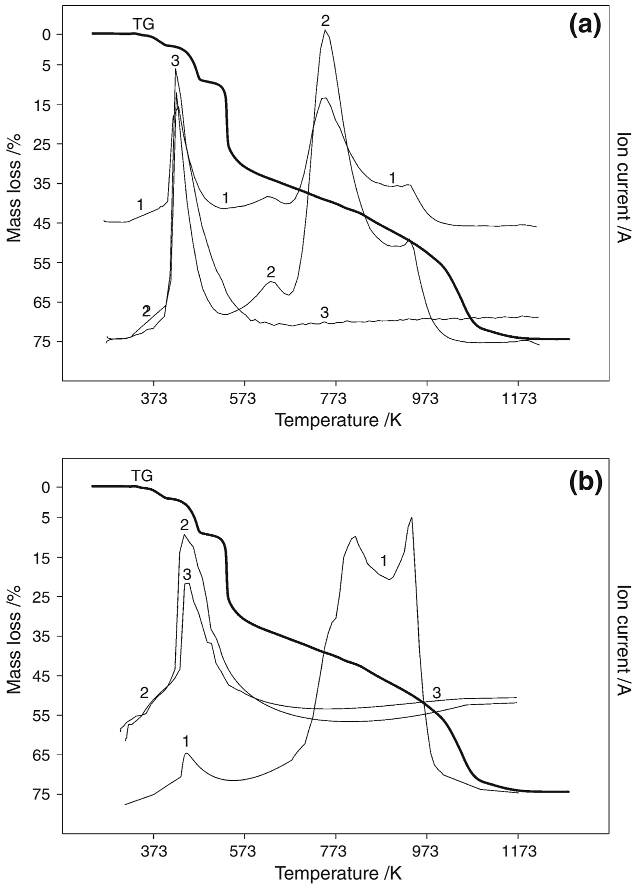

**Fig. 3** TG curve for Dy(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ and ion current detected by MS in air; mass sample 12.39 mg; **a** *m/z*: 1-12, 2–44, 3–50 with sensitivity of ion current: E-11, E-11, E-13, respectively; **b** *m/z*: 1–30, 2–47, 3–49 with sensitivity of ion current: E-12, E-13, E-13, respectively

## Conclusions

This work is a continuation of our earlier work. Previously we described a similar complexes with yttrium and light lanthanides(III) with 4-bpy and dichloroacetates [5, 36, 37]. Now, the new fine-crystalline complexes with the general empirical formulae: Dy(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ and Ln(4-bpy)$_{1.5}(CCl_3COO)_3 \cdot 2H_2O$ (where Ln(III) = Ce, Nd) were isolated. IR spectra of obtained complexes exhibit several absorption bands characteristic for 4-bpy and OCO groups. It indicates that organic ligands coordinate to metal(III) ions. The carboxylate groups, that occur in the title ligands and others, were of special interest because of its different linking types to the cation [5, 36, 37, 45–47]. On the basis of X-ray powder diffraction experiments (carried out immediately after the complexes' synthesis and periodically afterwards) one can state that all of them do not change their crystal structures at room temperature. During heating they decompose progressively. The pyrolysis of all studied complexes starts by the release of water molecules. When the temperature rises partial and total decomposition of organic ligands takes place. The final solid products are the oxides: $Ln_2O_3$ (Ln(III) = Nd, Dy) and $CeO_2$. The thermal decomposition of all obtained complexes is very similar to that we described previously in [5, 36, 37]. On the basis of our results we may compare the stability of all obtained lanthanide complexes with 4,4′-bipyridine and chloroacetates. The most stable hydrated compounds are Ln(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ (where Ln(III): La [37], Sm [5] and Eu [36]). They start to lose water molecules at 373 K. The least stable is Y(4-bpy)$(CCl_2HCOO)_3 \cdot H_2O$ [36], which begins to decompose at 333 K, as Nd(4-bpy)$_{1.5}$ $(CCl_3COO)_3 \cdot 2H_2O$. A coupled TG-MS system was used to analyse the principal volatile thermal decomposition and fragmentation products in air for Dy(4-bpy) $(CCl_2HCOO)_3 \cdot H_2O$. The most species are produced in the range of *ca* 442–454 and ~963 K. The maxima of ion currents are associated with mass decrease observed on TG curve.

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