

CHARACTERIZATION AND TG-MS STUDIES OF LACTATO AND BIPYRIDINE-LACTATO COMPLEXES OF Co(II) AND Ni(II)

D. Czakis-Sulikowska*, A. Malinowska and A. Łuczak

Institute of General and Ecological Chemistry, Technical University of Łódź, Łódź, Poland

Abstract

Two lactates and four new mixed ligand complexes with formulae $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(4\text{-bpy})(\text{lact})_2$, $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$, $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(2,4'\text{-bpy})_2(\text{lact})_2$ (where $4\text{-bpy}=4,4'$ -bipyridine, $2,4'\text{-bpy}=2,4'$ -bipyridine, $\text{lact}=\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$) were isolated and investigated. The thermal behaviour of compounds was studied by thermal analysis (TG, DTG, DTA). In the case of hydrated complexes thermal decomposition starts with the release of water molecules. The compounds decompose at high temperature to metal(II) oxides in air. A coupled TG-MS system was used to analyse the principal volatile products of thermolysis and fragmentation processes of obtained complexes.

Keywords: 2,4'-bipyridine, 4,4'-bipyridine, Co(II) and Ni(II) lactates, TG-MS data, thermal decomposition

Introduction

The present work is a continuation of our previous studies on the synthesis, properties and thermal decomposition of metal complexes with bipyridine isomers and carboxylates [1–8]. Mixed ligand complexes of metal containing anion of biologically active 2-hydroxypropanoic acid (lactic acid) and their thermal behaviour are not well known [9–11]. Only complexes of Cu(II) with lactates and 2,2'-bipyridine (2-bpy) or 4,4'-bipyridine (4-bpy) were prepared and described by Caraballo *et al.* [10, 11]. Lactic acid and its compounds are a subject of considerable interest as a consequence of their application e.g. in the pharmaceutical, agrochemical and food-stuffs industries [9–17].

The complexes of Co(II) and Ni(II) with lactates (*lact*) and 4,4'-bipyridine or 2,4'-bipyridine ($2,4'\text{-bpy}$) described in present paper were obtained in our laboratory. The compounds were characterized by chemical, elemental analysis and molar conductivity. The thermal decomposition of the complexes was studied by TG, DTG and DTA techniques. A coupled TG-MS system was used to investigation of the principal

* Author for correspondence: E-mail: dczakis@p.lodz.pl

gaseous products involved during the pyrolysis or fragmentation of the compounds. All the thermal measurements were carried out in air.

Experimental

Materials

4,4'-Bipyridine, 2,4'-bipyridine, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and methanol (MeOH) (anhydrous) p.a. were obtained from Aldrich and Lab-Scan., respectively. Lactic acid p.a. (85% aqueous solution $d=1.2 \text{ g cm}^{-3}$) and other chemical were p.a. products from POCh-Gliwice.

Measurements

The thermal stabilities of the complexes were studied by means of TG, DTA and DTG techniques. The measurements were made with a Q-1500 Derivatograph, using Al_2O_3 as a standard. Samples of 100 mg were heated in ceramic crucibles in air static atmosphere. All the thermal investigations were carried out in range of temperature 20–1000°C, at heating rate of $10^\circ\text{C min}^{-1}$. A coupled TG-MS system was used to analysis of principal volatile products of thermal decomposition and fragmentation processes of the complexes. Data were performed with using on line connected computer system with commercial software (Derivatograph TG/DTA-SETSIS-16/18, coupled to a Mass Spectrometer QMS-422 model ThermoStart from Balzers); platinum crucible, samples of mass 6–10 mg; dynamic measurements were carried out in air atmosphere (at flow rate of $1 \text{ dm}^3 \text{ h}^{-1}$); an ion source temperature of ca. 150°C by using 70 eV electron impact ionization. The synthesized Co(II) and Ni(II) complexes and solid products of thermal decomposition were characterized by X-ray powder diffraction patterns as previously [2]. Molar conductivity (Λ_M) of complexes was measured using $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ solutions in MeOH, DMSO and DMF. Experimental conditions and apparatus were the same as those described earlier [4].

Synthesis of the compounds

Preparation of Co(II) and Ni(II) lactates

To 20 cm^3 water solution of lactic acid (60 mmol) freshly precipitated carbonates of the metal(II) in ca. stoichiometric quantities were slowly added with stirring. The obtained suspension was heated to ca. 40°C for 1 h. Then the warm mixture was filtered off. The after day the crystalline product was separated, washed with water and dried at room temperature.

Preparation of Co(II) and Ni(II) bipyridine-lactato complexes

4,4'-Bipyridine complexes of Co(II) and Ni(II) were obtained by mixing 6 mmol of 4-bpy (in 23.4 cm^3 of 96% v/v ethanol) with solutions of metal(II) lactates (3 mmol in 6.6 cm^3 of water). 2,4'-Bipyridine complexes of Co(II) and Ni(II) were prepared by

adding 6 mmol of 2,4'-bpy (in 10 cm³ of water with 0.2 cm³ 96% v/v ethanol) to solution of metal(II) lactates (3 mmol in 10 cm³ of water). During the synthesis of all complexes the reaction mixtures were stirred and heated to ca. 40°C for 15 min. After several days solid products were formed and filtered off. They were washed with 40% v/v ethanol (or water for 2,4'-bpy complexes) and then with ethanol and diethyl ether mixture (1:1) and dried at room temperature.

The Co(II) and Ni(II) analyses in obtained compounds were carried out by complexometric titration with EDTA. The contents of C, H and N were determined by elemental analysis with V₂O₅ as oxidizing agent.

Results and discussion

The empirical formulae of the isolated compounds, analytical results and molar conductivities are collected in Table 1. All the complexes are small crystalline solids and air stable. They are fairly soluble in water but insoluble in common organic solvents (e.g. CCl₄, CHCl₃). The molar conductivity values in MeOH, DMSO and DMF (Table 1) show that all complexes behave as non-electrolytes [18], indicating probably coordination of the lactato ligands to metal(II).

Table 1 Analytical data and molar conductivity (Λ_M) in MeOH, DMSO and DMF ($c=1\cdot 10^{-3}$ mol dm⁻³ at 25°C)

Complex (colour)	Analysis found (calculated)/%				Λ_M/Ω^{-1} cm ² mol ⁻¹		
	M	C	N	H	MeOH	DMSO	DMF
(1) Co(lact) ₂ ·2H ₂ O (pink)	21.39 (21.57)	29.93 (30.40)		5.82 (5.95)	24.2	7.2	*
(2) Ni(lact) ₂ ·3H ₂ O (light green)	21.52 (20.18)	25.37 (24.77)		5.40 (5.54)	18.8	5.7	*
(3) Co(4-bpy)(lact) ₂ (light pink)	14.17 (14.99)	48.06 (48.87)	7.52 (7.12)	4.48 (4.61)	22.7	*	28.1
(4) Co(2,4'-bpy) ₂ (lact) ₂ (light pink)	10.90 (10.73)	56.51 (56.86)	10.29 (10.19)	4.80 (4.77)	23.2	11.6	22.7
(5) Ni(4-bpy)(lact) ₂ ·2H ₂ O (light green-blue)	14.16 (13.68)	45.41 (44.79)	6.25 (6.53)	5.09 (5.17)	15.2	11.9	22.2
(6) Ni(2,4'-bpy) ₂ (lact) ₂ (light green-blue)	11.19 (10.69)	57.32 (56.86)	9.99 (10.20)	4.82 (4.77)	18.2	13.1	21.7

*solubility less than 1·10⁻³ mol dm⁻³

Thermal properties of compounds

The thermoanalytical data are given in Table 2. The results of thermal, chemical and X-ray analyses were used to postulate decomposition of the complexes. The thermal profiles (TG, DTA and DTG) of some complexes are presented in Figs 1 and 2. Thermal

Table 2 Thermal decomposition of complexes in air (sample mass 100 mg)

Complex	Ranges of decomposition/°C	DTA peak/°C	Mass loss/%		Intermediates and final solid products
			found	calc.	
(1) Co(lact) ₂ ·2H ₂ O	120–190	160 endo	14.0	13.19	Co(lact) ₂ Co ₃ O ₄
	220–520	305, 380, 460, 490 exo	57.0	57.42	
(2) Ni(lact) ₂ ·3H ₂ O	>900	930 endo	2.0	1.95	CoO Ni(lact) ₂ ·2H ₂ O Ni(lact) ₂ NiO
	50–120	100 endo	6.5 ^a	6.19	
	120–200	180 endo	13.5	12.38	
	280–530	370, 440, 500 exo	55.0	55.74	
(3) Co(4-bpy)(lact) ₂	120–450	220, 400 exo	79.0	79.59	Co ₃ O ₄ CoO
	>900	940 endo	2.0	1.36	
(4) Co(2,4'-bpy) ₂ (lact) ₂	125–450	170, 260, 410 exo	85.0	85.39	Co ₃ O ₄ CoO
	>900	930 endo	1.5	0.97	
(5) Ni(4-bpy)(lact) ₂ ·2H ₂ O	70–210	180 endo	7.5	8.39	Ni(4-bpy)(lact) ₂ NiO
	240–490	310, 440 exo	75.5	74.20	
(6) Ni(2,4'-bpy) ₂ (lact) ₂	140–330	320 exo	64.0		NiO with organic residue NiO
	330–480	440 exo	23.0	86.40	

^aby projecting minimum of DTG curve on TG curve

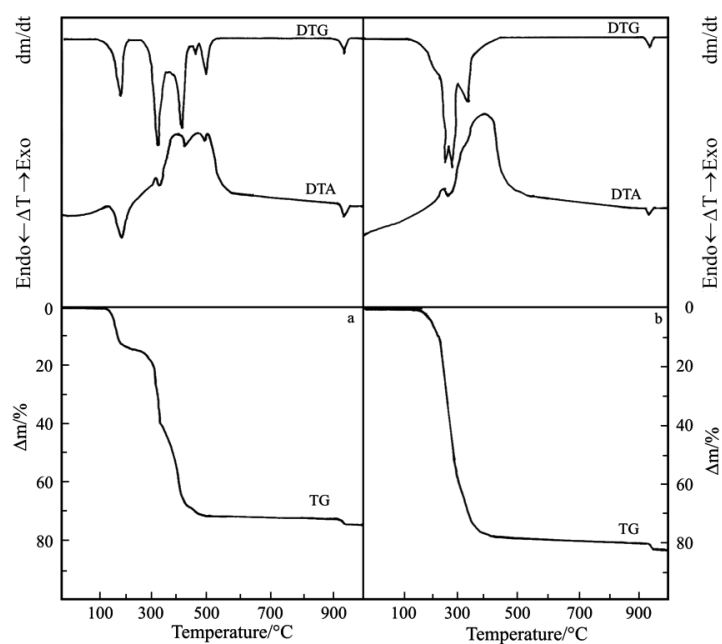


Fig. 1 Thermoanalytical curves for: a – $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$, b – $\text{Co}(4\text{-bpy})(\text{lact})_2$ (mass sample 100 mg)

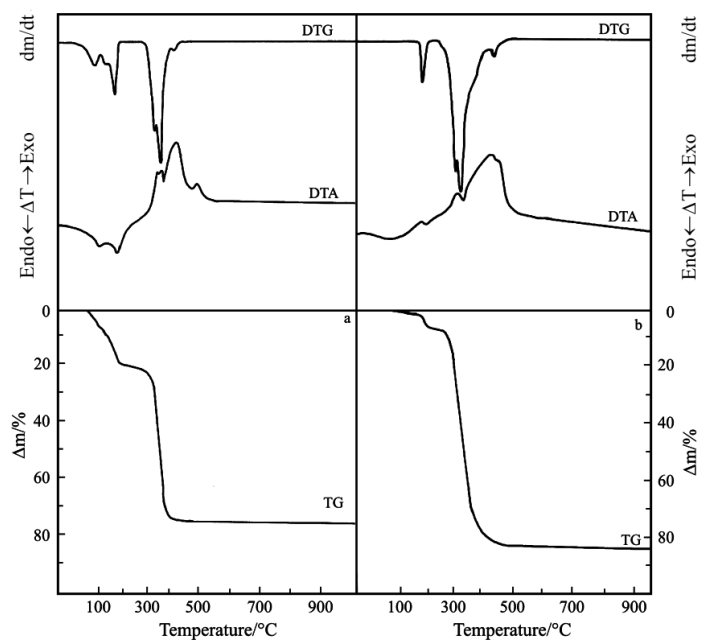


Fig. 2 Thermoanalytical curves for: a – $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$, b – $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ (mass sample 100 mg)

decomposition of $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$ proceeds in three stages. The $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ is stable up to 120°C and then lost water in one step. In contrast to $\text{Co}(\text{II})$ lactate, $\text{Ni}(\text{II})$ lactate is thermally less stable. For $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$ the elimination of water begins at 50°C . According to the DTG curve, molecules of water are lost stepwise in two stages. Dehydration process of these lactates is connected with endothermic effects at 160 and 100°C , 180°C for $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$, respectively. Anhydrous compounds undergo decomposition to appropriate metal oxides. The DTA curves exhibit several exothermic peaks, which are associated with oxidation of organic fragments. The mass loss observed on the TG curves corresponds to the formation of Co_3O_4 and NiO at 520 and 530°C , respectively. The small endothermic peak at 930°C is accompanied with the transformation of Co_3O_4 to CoO .

The thermal decompositions of the complexes $\text{Co}(4\text{-bpy})(\text{lact})_2$, $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$ are similar. In the first step (ca. $120\text{--}450^\circ\text{C}$) the TG curves show a very rapid mass loss, which is connected with decomposition of organic ligands and the formation of Co_3O_4 . X-ray diffractogram of $\text{Co}(4\text{-bpy})(\text{lact})_2$ sintered at 450°C indicates presence of Co_3O_4 (Fig. 3a). Very strong and broad exothermic peaks originating from decomposition and oxidation of organic fragments are observed (Table 2). Apparently in the case of $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$ nature of DTG change shows the stepwise decomposition. However, these processes are not detected on the TG curve. Above 900°C , Co_3O_4 is very slowly converted into CoO (Fig. 3b). This transformation is demonstrated by small endothermic peak at 930°C for both bipyridine-lactato complexes of $\text{Co}(\text{II})$.

The pyrolysis of $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ runs in two steps. The complex is stable up to 70°C , then whole water is eliminated. Dehydration process is characterized by small endothermic effect at 180°C . Next, the decomposition of $\text{Ni}(4\text{-bpy})(\text{lact})_2$ begins at 240°C and is represented in the DTA curve by two broad exothermic peaks with maximum at 310 , 440°C . Pure NiO is the final product of decomposition.

The complex $\text{Ni}(2,4'\text{-bpy})_2(\text{lact})_2$ is more stable than $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$. It starts to decompose at 140°C . In the temperature range $140\text{--}330^\circ\text{C}$, sudden loss of mass occurs on the TG curve. This decrease in mass is connected with sharp DTG peak and exoeffect observed in the DTA curve. The X-ray diffractometric analysis indicates a mixture of organic fragments and NiO in the sinter of $\text{Ni}(2,4'\text{-bpy})_2(\text{lact})_2$ heated up to 330°C (Fig. 4). A strong exothermic peak at 440°C in the DTA curve is associated with combustion of the remaining organic products. A constant mass level for pure NiO begins at 480°C .

TG-MS measurements

Thermal behaviours of complexes also were carried out with a coupled TG-MS system. This method was used to analyse of major gaseous products evolved during the dynamic thermal decomposition and fragmentation processes of investigated complexes in air atmosphere. The m/z values are given based on: ^1H , ^{12}C , ^{14}N and ^{16}O (additionally ^{13}C and ^{18}O in the case of CO_2).

MS data for all the complexes detected several profiles of ion current. As an example, Fig. 5 shows these lines for some m/z detected in mass spectrometer as a func-

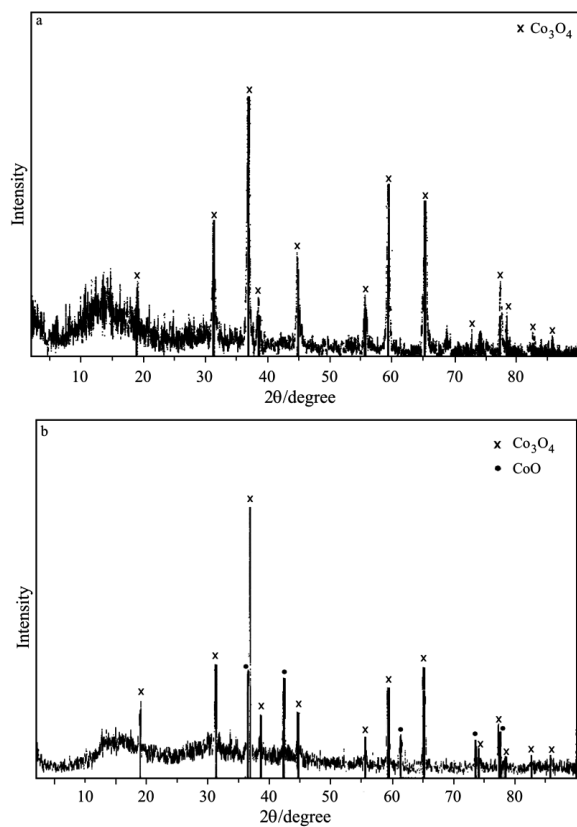


Fig. 3 X-ray diffractograms of $\text{Co}(4\text{-bpy})(\text{lact})_2$ sintered at: a – 450°C; b – 900°C

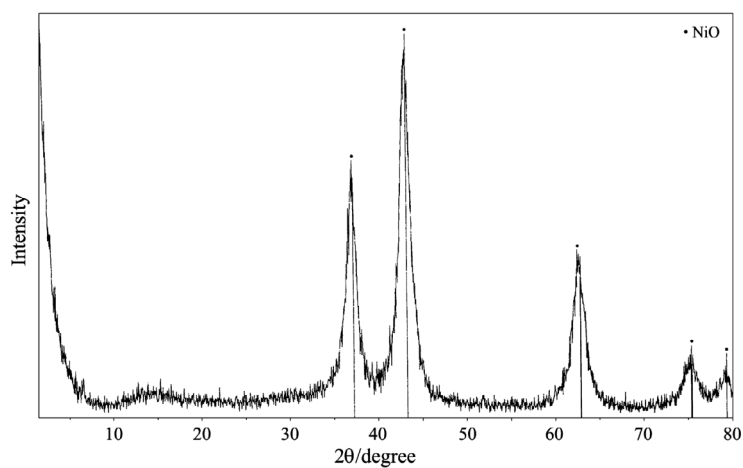


Fig. 4 X-ray diffractogram of $\text{Ni}(2,4'\text{-bpy})_2(\text{lact})_2$ sintered at 330°C

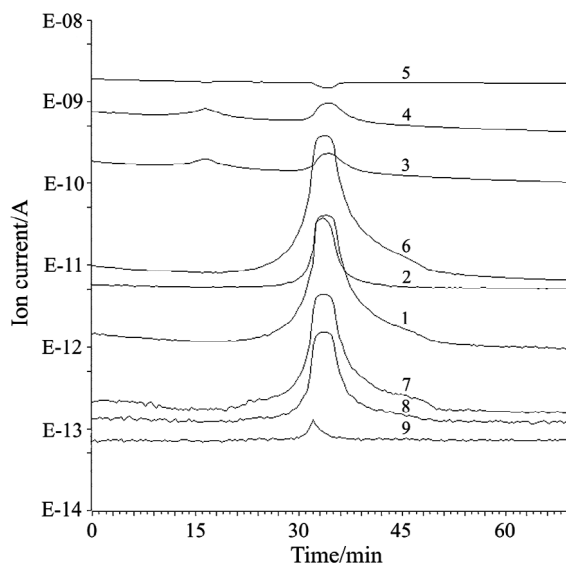


Fig. 5 Ion current detected in the mass spectrometer vs. time for $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$.
Curves for m/z : 1 – 12; 2 – 15; 3 – 17; 4 – 18; 5 – 32; 6 – 44; 7 – 45; 8 – 46;
9 – 60 (mass sample 6.41 mg)

tion of time for $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$. The ion signals of $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{lact})_2 \cdot 3\text{H}_2\text{O}$ are very similar. In the case of $\text{Co}(\text{II})$ lactate the profiles of ion signals are broad. The first peaks of ion current for H_2O^+ and OH^+ ($m/z=18$ and 17) appear at 184 and 177°C for $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ lactates, respectively. They correspond to elimination of crystalline water. Major maxima of ion current are observed in range ca. $280\text{--}380^\circ\text{C}$ for compounds (1) and $330\text{--}370^\circ\text{C}$ for (2). In gaseous pyrolysis products dominate the molecular ion CO_2^+ formed probably by total decomposition of lactate groups. MS peaks with $m/z=44$ (CO_2^+) and low intensity signals for $m/z=45, 46$ (CO_2^+ containing isotope ^{13}C or ^{18}O) appear at 321°C (1) and 354°C (2). The second peaks of H_2O^+ and OH^+ (which are also produced during decomposition of lactates) exist at 322°C (1) and 357°C (2). Additionally low intensities for ion currents with $m/z=1, 12, 15, 26, 29$ and 60 ($\text{H}^+, \text{C}^+, \text{CH}_3^+, \text{C}_2\text{H}_2^+, \text{C}_2\text{H}_5^+$ and $\text{C}_2\text{H}_4\text{O}_2^+$ traces) were monitored. The maxima of ion signals are coincided with mass loss occurred on TG curves. Correlation of selected ion currents and TG curve is presented in Fig. 6 for $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$.

Figures 7a and 7b show the some profiles of ion current detected in mass spectrometer as a function of time for bipyridine-lactato complexes of $\text{Co}(\text{II})$. For complexes $\text{Co}(4\text{-bpy})(\text{lact})_2$, $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(2,4'\text{-bpy})_2(\text{lact})_2$ main MS peaks occur in following range of temperature ca.: $270\text{--}320, 260\text{--}310$ and $290\text{--}340^\circ\text{C}$, respectively. However, all maxima of ion current for $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$ are observed at ca. 210°C and in range $340\text{--}370^\circ\text{C}$. In the case of complexes $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ the first signals for $m/z=18$ and 17 (H_2O^+ and OH^+) appear at ca. 170°C . They are coincided with elimination of coordination (or crystalline) water. MS data for all

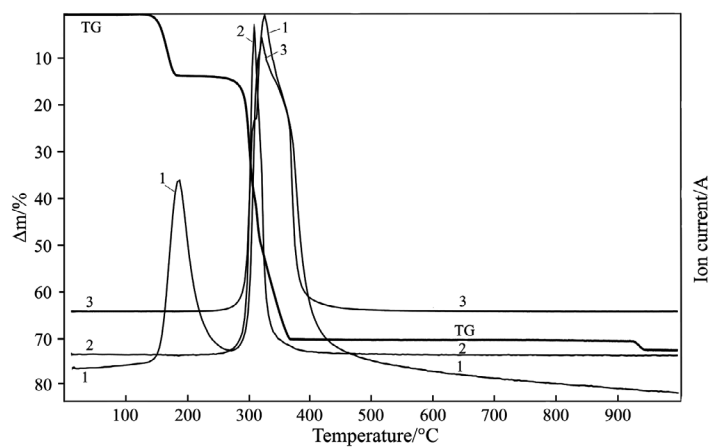


Fig. 6 TG curve and ion current detected in the mass spectrometer for $\text{Co}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$. Curves for m/z : 1 – 15; 2 – 18; 3 – 44 with sensitivity of ion current: E-11, E-10, E-10 A, respectively (mass sample 10.46 mg)

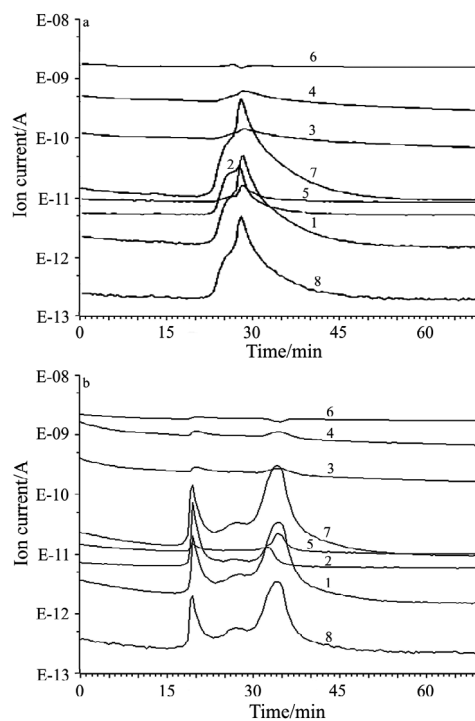


Fig. 7 Ion current detected in the mass spectrometer vs. time for a – $\text{Co}(4\text{-bpy})(\text{lact})_2$ and b – $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$. Curves for m/z : 1 – 12; 2 – 15; 3 – 17; 4 – 18; 5 – 30; 6 – 32; 7 – 44; 8 – 45 (mass sample 9.25 and 8.03 mg for $\text{Co}(4\text{-bpy})(\text{lact})_2$ and $\text{Co}(2,4'\text{-bpy})_2(\text{lact})_2$, respectively)

bipyridine-lactato complexes of Co(II) and Ni(II) indicate that in gaseous pyrolysis products dominate the molecular ions CO_2^+ , H_2O^+ and OH^+ as consequence of decomposition of organic ligands. Very strong CO_2^+ peaks ($m/z=44$) occur at ca. 294°C (3), 210 and 359°C (4), 275°C (5) and 327°C (6). At the same time low intensity ion currents are observed for CO_2^+ ($m/z=45, 46$). The peaks for $m/z=18$ and 17 (H_2O^+ and OH^+) appear at ca.: 300°C (3), 215 and 363°C (4), 272 and 290°C (5) and 300°C (6). The ion for $m/z=1, 12, 15, 26, 29$ (H^+ , C^+ , CH_3^+ , C_2H_2^+ or CN^+ , C_2H_5^+ or CHO^+) at ca. 270–290°C (3), 211 and 340–360°C (4), 270–290°C (5) and 320–325°C (6) were detected. The fragments with $m/z=30$ (correspond probably to CH_2O^+ or NO^+) occur at 297°C (3), 211 and 360°C (4), 267 and 306°C (5) and 329°C (6). The identification of volatile species in appropriate temperature range corresponds exactly to the sudden mass loss presented by TG curve. Figure 8 shows correlation of some profiles of ion current with TG curve for $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$.

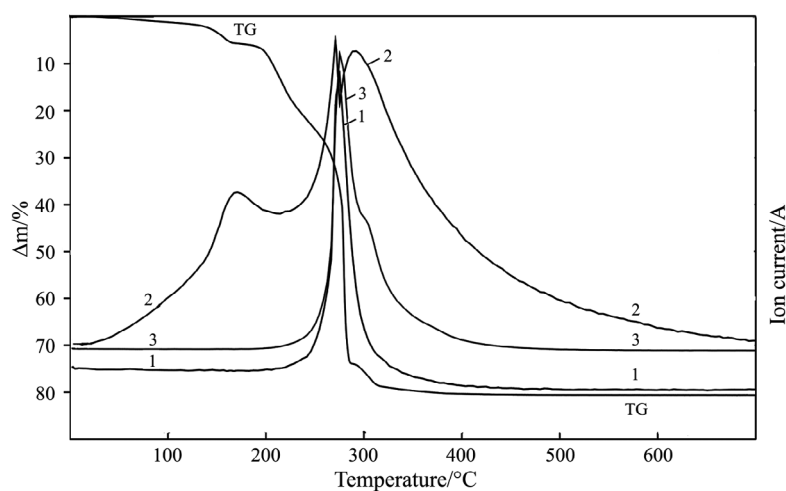


Fig. 8 TG curve and ion current detected in the mass spectrometer for $\text{Ni}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$. Curves for m/z : 1 – 15; 2 – 18; 3 – 44 with sensitivity of ion current: E-11, E-10, E-10 A, respectively (mass sample 8.56 mg)

Conclusions

Thermal decomposition of investigated hydrated compounds begins with the release of water. Generally anhydrous Co(II) and Ni(II) lactates are thermally more stable than corresponding bipyridine-lactato complexes. All the compounds decompose to oxides NiO and CoO, respectively (for Co(II) complexes via Co_3O_4). As it is seen from data obtained by coupled TG-MS system, major volatile species evolved during pyrolysis of Co(II) and Ni(II) lactates and as well as bipyridine-lactato complexes of these metals(II) are produced almost simultaneously. It suggests that steps of decomposition of these compounds are very weakly separated one from another (except dehydration). In bipyridine-lactato complexes elimination and pyrolysis of N-donor ligands (*4-bpy* or

2,4'-bpy) and lactates probably take place at the same time (maxima of ion current for CN^+ , NO^+ and CO_2^+ appear at very similar temperature). These results are in agreement with thermal behaviour of complex $\text{Cu}(2\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ [11].

References

- 1 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, *Pol. J. Chem.*, 77 (2003) 1255.
- 2 J. Radwańska-Doczekalska, D. Czakis-Sulikowska and M. Markiewicz, *J. Thermal Anal.*, 48 (1997) 865.
- 3 T. J. Bartzak, D. Czakis-Sulikowska and J. Kałużna, *J. Coord. Chem.*, 46 (1998) 193.
- 4 D. Czakis-Sulikowska, A. Czyłkowska and J. Radwańska-Doczekalska, *J. Therm. Anal. Cal.*, 63 (2001) 387.
- 5 D. Czakis-Sulikowska, A. Czyłkowska and A. Malinowska, *ibid.*, 65 (2001) 505; *ibid.*, 67 (2001) 667.
- 6 D. Czakis-Sulikowska and A. Malinowska, *Pol. J. Chem.*, 76 (2002) 1047.
- 7 D. Czakis-Sulikowska, A. Malinowska and M. Markiewicz, *ibid.*, 77 (2003) 1363.
- 8 D. Czakis-Sulikowska and A. Czyłkowska, *J. Therm. Anal. Cal.*, 71 (2003) 395; *ibid.*, 74 (2003) 349; *ibid.*, 76 (2004) 543.
- 9 M. Wesołowski and T. Konarski, *Chem. Anal. (Warsaw)*, 41 (1996) 387.
- 10 R. Caraballo, A. Castiñeiras, B. Covelo and E. M. Vázquez-López, *Polyhedron*, 20 (2001) 899.
- 11 R. Caraballo, A. Castiñeiras, S. Balboa, B. Covelo and J. Niclós, *ibid.*, 21 (2002) 2811.
- 12 G. G. Bombi, B. Corain, A. A. Sheikh-Osman and G. C. Valle, *Inorg. Chim. Acta*, 171 (1990) 79.
- 13 G. C. Gunter, R. Craciun, M. S. Tam, J. E. Jackson and D. J. Miller, *J. Catal.*, 164 (1996) 207.
- 14 Z. F. Chen, J. Zhang, R. G. Xiong and X. Z. You, *Inorg. Chem. Comm.*, 3 (2000) 493.
- 15 R. Caraballo, B. Covelo, E. Garcia-Martinez, E. M. Vázquez-López, A. Castiñeiras and J. Niclós, *Polyhedron*, 22 (2003) 1051.
- 16 A. Fischinger, A. Sarapu and A. Companion, *Can. J. Chem.*, 47 (1969) 2629.
- 17 N. Niculescu, N. Vaszilesin, M. Bîrzescu, P. Budrugaec and E. Segal, *J. Therm. Anal. Cal.*, 63 (2001) 181; *ibid.*, 65 (2001) 881.
- 18 W. I. Geary, *Coord. Chem. Rev.*, 7 (1971) 81 and references therein.