

SYNTHESIS AND THERMAL PROPERTIES OF 4,4'-BIPYRIDINE ADDUCTS OF Mn(II), Co(II), Ni(II) AND Cu(II) MONOCHLOROACETATE

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Abstract

The complexes with the empirical formula $M(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot n\text{H}_2\text{O}$ (where: *4-bipy*=4,4'-bipyridine, $L=\text{ClCH}_2\text{COO}^-$, $M(\text{II})=\text{Mn, Co, Ni, Cu}$) were prepared and characterized via the IR and electronic (VIS) spectra and conductivity measurements. Thermal decomposition of these compounds was studied. During heating in air dehydration processes occur. The anhydrous compounds decompose at high temperature to oxides. The principal volatile mass fragments correspond to: H_2O , CO_2 , CH_3Cl , HCl , Cl_2 and other.

Keywords: 4,4'-bipyridine complexes, mass spectrometry, monochloroacetate, thermal decomposition, VIS-IR spectra

Introduction

Whereas the metal(II) compounds of halogenoacetate acid and its mixed complexes containing organic ligands were described by many authors [1–15], the thermal properties of these complexes have not been extensively studied so far. The thermal decomposition of some copper(II) halogenoacetates was carried out by Obier *et al.* [16] and described in other papers [17, 18]. The first decomposition products of the $\text{Cu}(\text{ClCH}_2\text{COO})_2$ detected (MS) were: CO_2 , H_2O , HCl , CH_3Cl and ClCH_2COOH [18]. Thermal properties of zinc(II) monochloroacetate and its complexes with nicotinamide and coffeeine were reported by Zeleňák *et al.* [19].

In paper, we describe the synthesis of new mixed ligand complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 4,4'-bipyridine and monochloroacetic acid. The compounds obtained were characterized by elemental analysis, and by IR-VIS spectroscopic and molar conductivity investigations. The thermal decomposition was studied in air. A coupled TG-MS system was used to analyse the principal gaseous products involved during pyrolysis of the synthesized complexes.

Experimental

Materials and analyses

4,4'-Bipyridine (*m.p.* 69.9°C), ClCH₂COOH p.a. were obtained from Aldrich; methanol (anhydroskan) from Lab-Scan; hydroxyloamine 50% v/v from Fluka; other chemicals were p.a. products from POCh-Gliwice. Solutions of M(ClCH₂COO)₂ were prepared by adding 20 ml 2M ClCH₂COOH to freshly precipitated carbonates of the metal(II) in ca. equimolar ratio. The contents of M(II) ions in obtained solutions were complexometrically determined.

Syntheses of the complexes

A solution of 4-bipy (12.8 mmol) in 96% v/v EtOH (31.3 ml) was added to a solution of M(ClCH₂COO)₂ (4.3 mmol) in water (8.75 ml). During synthesis of manganese(II) complex these mixture containing 1 ml of 10% v/v hydroxyloamine (to stop the oxidation process of Mn(II)). The product was collected, washed with 40% v/v EtOH and then with EtOH-Et₂O (1:1) mixture and dried in open air. The dried complexes were analysed: C, N, H – by elementary analysis with V₂O₅ as oxidizing agent; Mn(II), Cu(II), Co(II) and Ni(II) in mineralized samples were complexometrically determined. The analytical results for obtained complexes are shown in Table 1, together with other characteristic data.

Table 1 Analytical data, solubility S (mol dm⁻³) in water at 21°C and molar conductivity Λ_M (Ω^{-1} cm² mol⁻¹) in methanol (concentration $1 \cdot 10^{-3}$ mol dm⁻³) at 25°C of the complexes, where $L = \text{ClCH}_2\text{COO}^-$

Complex (colour)	Analysis: found (calculated)/%				$S \cdot 10^3$	Λ_M
	M	C	N	H		
Mn(4-bipy)L ₂ ·H ₂ O (white)	13.69 (13.20)	40.83 (40.41)	7.14 (6.73)	3.70 (3.39)	26.9	68.2
Co(4-bipy)L ₂ ·2H ₂ O (light-rose)	13.52 (13.45)	38.06 (38.38)	6.69 (6.39)	3.51 (3.68)	15.2	24.2
Ni(4-bipy)L ₂ ·4H ₂ O (green)	12.90 (12.38)	35.90 (35.48)	6.60 (5.91)	4.38 (4.25)	7.6	64.6
Cu(4-bipy)L ₂ ·4H ₂ O (blue)	14.50 (13.27)	35.48 (35.12)	6.60 (5.85)	4.45 (4.21)	2.2	40.7

Physical measurements

The thermal decomposition processes of the prepared complexes were studied by thermogravimetry (TG, DTG, DTA) and TG/MS techniques. Samples were heated from 25 up to 1000°C with a heating rate of 10°C min⁻¹ in air atmosphere. TG, DTG and DTA curves were recorded by using a derivatograph Q-1500, with the sample mass of 100 mg and $\alpha\text{-Al}_2\text{O}_3$ as reference material. Mass spectrometer was used for

the characterization of volatile thermal decomposition products of the compounds studied. The TG-MS system: derivatograph TG/DTA-SETSIS-16/18, mass spectrometer ThermoStar from Balzers, crucible Pt 100 μl . The other apparatus and measuring conditions were the same as those described in [20, 21].

Results and discussion

The reaction between 4-bipy and $\text{M}(\text{ClCH}_2\text{COO})_2$ afforded compounds of general formula $\text{M}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot n\text{H}_2\text{O}$, where $n=1$ for Mn(II), $n=2$ for Co(II) and $n=4$ for Ni(II) and Cu(II). Diffractogram analysis indicated that the compounds isolated were small crystalline solids. They were air-stable at room temperature. All the complexes dissolved fairly well in water and methanol, decomposed in acid and alkali and were insoluble in most organic solvents (carbon tetrachloride, benzene, acetone, chloroform). The molar conductivity in methanol proved that the $\text{Co}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is a non-electrolyte. The other obtained complexes displayed a behaviour intermediate between those of non-electrolytes and 1:1 electrolytes [22]. Values higher than anticipated Λ_{M} values (*vide infra* IR) are usually due to the displacement of monochloroacetate ligands by solvent molecules. Similar behaviour has previously been observed in metal complexes with bipyridine and other aromatic amines [23–25].

Electronic and IR spectra

The assignments of *d-d* transition bands in the electronic spectra (in Nujol mulls, in the range 26000–12000 cm^{-1}) of the solid Co(II), Ni(II) and Cu(II) complexes are based on the works of Lever [26] and Hathaway [27]. The electronic spectra of these complexes are all consistent with a pseudohedral configuration with tetragonal distortion. The cobalt(II) complexes exhibit band at 21500 cm^{-1} which correspond to the transition ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$. This band is apparently asymmetrical and has a shoulder in the region ca. 20500 cm^{-1} . The ligand field spectra of nickel(II) complex exhibit only one spin allowed band (ca. 16200 cm^{-1}), it is assigned to the ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$ transition. The band due to the ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ transition (ca. 26000 cm^{-1}) is superimposed to intense charge transfer band. The copper(II) complex exhibited single absorption band in the visible region at 15750 cm^{-1} , can be associated with three transitions lying within one broad envelope (${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$, ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{B}_{2\text{g}}$, ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$). The position, as well as and shape, of this band revealed tetragonal distortion of the Cu(II) complex from the one-electron orbital ground state $d_{x^2-y^2}$ [27, 28].

For consistency, only the fundamental vibration modes of 4-bipy and OCO-group for obtained mixed complexes are reported in Table 2. The IR spectrum of free 4-bipy owing to complex formation. The most characteristic ring vibration $\nu(\text{CN})$ and $\nu(\text{CC})$, and pyridine breathing mode are observed in these compounds in the ranges (cm^{-1}): 1600.0–1608.5, 1533.4–1541.0 and 1006.8–1015.0, respectively. These bands are shifted towards higher frequencies in comparison to free 4-bipy [29]. IR spectra of these complexes indicate that 4-bipy is coordinated to metal ion [21, 29]. The absorption bands

arising from asymmetric $\nu_{as}(\text{OCO})$ and symmetric $\nu_s(\text{OCO})$ vibration of OCO-groups appear at 1558.4–1590.0 and 1413.7–1425.3 cm^{-1} , respectively. In the case of Mn(II), Co(II) and Cu(II) complexes the $\nu_{as}(\text{OCO})$ band is splitted into two. The values of the separation of the bands ν_{as} and ν_s ($\Delta\nu = \nu_{as} - \nu_s$) are smaller than those of the sodium salt ($\Delta\nu = 185 \text{ cm}^{-1}$). On this basis one can suppose that the carboxylate groups in obtained mixed-ligand complexes are bonded as bidentate chelating ligands [30–32].

Table 2 Principal IR bands (cm^{-1}) for 4-bipy and OCO^- groups in free ligands and their complexes, where $L = \text{ClCH}_2\text{COO}^-$

Compound	$\nu(\text{CN})$	$\nu(\text{CC})$	γ_r^a	$\nu_{as}(\text{OCO})$	$\nu_s(\text{OCO})$	Δ^b
Na(ClCH ₂ COO) [30]	–	–	–	1603.0	1418.0	185.0
Mn(4-bipy)L ₂ ·H ₂ O	1600.0	1533.4	1008.7	1590.0 1558.4	1425.3	164.7 133.1
Co(4-bipy)L ₂ ·2H ₂ O	1606.6	1537.2	1006.8	1589.2 1569.9	1415.7	173.5 154.2
Ni(4-bipy)L ₂ ·4H ₂ O	1608.5	1537.2	1008.7	1589.2	1413.7	175.5
Cu(4-bipy)L ₂ ·4H ₂ O	1608.5	1541.0	1015.0	1575.0 1558.4	1417.6	157.4 140.8

^a γ_r =ring 'breathing' mode; ^b $\Delta = \nu_{as}(\text{OCO}) - \nu_s(\text{OCO})$

A strong, broad band in the water stretching region (ca. 3400–3500 cm^{-1}) was present in the IR spectra of all new complexes. The M–O stretching modes for coor-

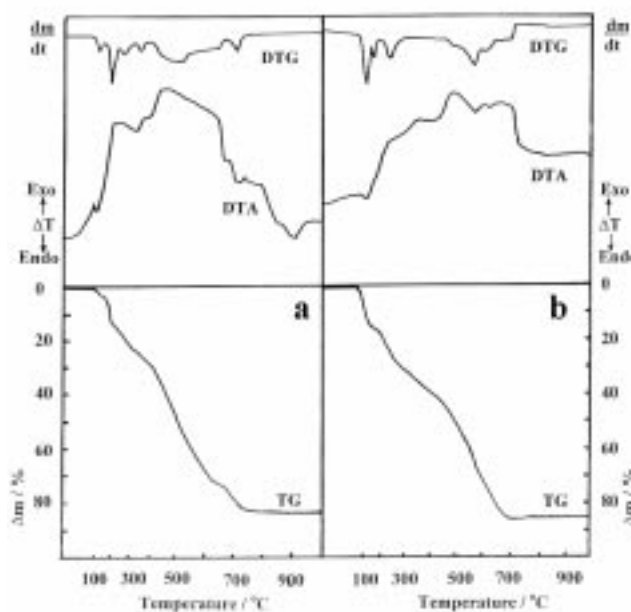


Fig. 1 Thermoanalytical curves of Mn(4-bipy)(ClCH₂COO)₂·H₂O (a), Ni(4-bipy)(ClCH₂COO)₂·4H₂O; (b)

minated water were observed at (cm^{-1}): 489.0 (Cu), 478.3 (Co), 480.2 (Ni) and 472.5 (Mn).

Thermal decomposition

The decomposition solid products obtained during heating of $\text{M}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot n\text{H}_2\text{O}$ complexes were established from thermoanalytical curves and confirmed by chemical analysis together with the X-ray diffraction pattern investigation. The thermal analysis curves of Ni(II) and Mn(II) complexes are presented, as an example, in Fig 1. The results are listed in Table 3. All the complexes decompose progressively.

Table 3 Thermal decomposition data of $\text{M}(4\text{-bipy})\text{L}_2 \cdot n\text{H}_2\text{O}$ ($\text{L}=\text{ClCH}_2\text{COO}^-$; sample mass 100 mg)

Starting material	Ranges of decomposition/ $^{\circ}\text{C}$	Mass loss/%		Intermediates and final solid products
		found	calc.	
$\text{Mn}(4\text{-bipy})\text{L}_2 \cdot \text{H}_2\text{O}$	80–140	4.8	4.3	$\text{Mn}(4\text{-bipy})\text{L}_2$
	140–635	68.2		MnCl_2 with ca. 3% Mn_2O_3
	635–720	9.0	76.7	Mn_2O_3
	>900	0.4	0.6	Mn_3O_4
$\text{Co}(4\text{-bipy})\text{L}_2 \cdot 2\text{H}_2\text{O}$	100–120	8.5	8.2	$\text{Co}(4\text{-bipy})\text{L}_2$
	160–880	75.0	73.5	Co_3O_4 with ca. 1.5% CoO
	>900	~0.8	1.2	CoO
$\text{Ni}(4\text{-bipy})\text{L}_2 \cdot 4\text{H}_2\text{O}$	100–140	15.0	15.2	$\text{Ni}(4\text{-bipy})\text{L}_2$
	140–700	69.0	69.0	NiO
$\text{Cu}(4\text{-bipy})\text{L}_2 \cdot 4\text{H}_2\text{O}$	80–115	7.5	7.5	$\text{Cu}(4\text{-bipy})\text{L}_2 \cdot 2\text{H}_2\text{O}$
	115–150	6.9	7.5	$\text{Cu}(4\text{-bipy})\text{L}_2$
	150–740	72.0	71.7	Cu
	740–800			mixture of $\text{Cu}_2\text{O}+\text{CuO}$

The hydrated complexes $\text{M}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot n\text{H}_2\text{O}$ are stable up to 80–100 $^{\circ}\text{C}$ and then lose all the water (inter or outer) molecules in one step (only $\text{Cu}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in two steps). The TG curves exhibit sufficiently clearly defined mass loss of these steps at the end of the dehydration process. The dehydration processes of Mn(II), Co(II), Ni(II) and Cu(II) complexes are connected with endothermic effects at 100, 110, 118 and 100, 162 $^{\circ}\text{C}$, respectively. The TG curves of $\text{M}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2$ exhibited multiple mass loss steps, from which only some can be defined (Table 3). Anhydrous complexes decompose to oxides with intermediate formation of different products. Compounds of Mn(II), Co(II) and Cu(II) decompose to final products via MnCl_2 , Mn_2O_3 , Co_3O_4 and Cu . The DTA curves are mixtures of several endo and exo peaks. Very strong and broad exothermic effects originating from the oxidation of organic fragments are observed at ca. 440 (Mn), 460 (Co), 490 (Ni) and 350 $^{\circ}\text{C}$ (Cu).

Apart from the chemical and X-ray analysis of the several solid products of decomposition, mass spectrometric analysis of the major gaseous products of decomposition was also carried out. Since the complexes studied here had similar composition, the MS data of these substances are similar. Figure 2 (as an example) presents

the composition of the gaseous mixture above the decomposition sample $\text{Co}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as a function of time (heating rate of $10^\circ\text{C min}^{-1}$). Mass spectrum detected several ions signal intensities. Generally, the first signals are observed at ca. 120°C , and the last strong maxima occur at around 440°C . These MS peaks coincide with the mass decrease appeared on TG. In all cases, when the temperature of the sample raised, the first decomposition products detected were: H_2O ($m/z=18$), CO_2 ($m/z=44, 45, 46, 47$), and fragments with $m/z=12, 15, 17, 26$ and 31 . H_2O is observed in range $100\text{--}160$ and $370\text{--}490^\circ\text{C}$. The first strong maximum (for ion current) in the elimination of H_2O occurs at around 120°C , which coincides with elimination of coordination (or crystalline) water. Next, the H_2O was produced during the decomposition of organic ligands. The profiles observed for $m/z=44, 45, 46,$

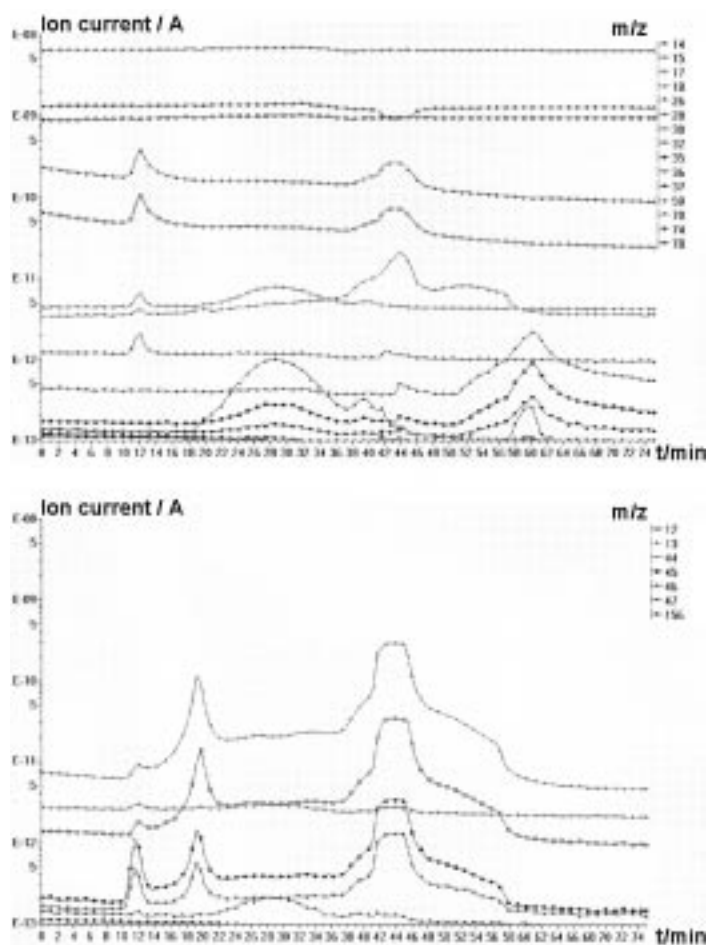


Fig. 2 Ion current for m/z detected in the mass spectrometer vs. time. Complex $\text{Co}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ mass sample 9.02 mg; heating rate $10^\circ\text{C min}^{-1}$, original record

47 (CO_2) are similar to several maxima. Very strong CO_2 peaks appeared at ca. 190 and 440°C. The MS line for $m/z=36$ (O_2 from air atmosphere) exhibits a minimum at 440°C. CH_3Cl ($m/z=50$) starts to be detected at ca. 190°C and reaches a maximum forming rate of CH_3Cl at 285°C. The maximum rate of forming of HCl is observed at 610°C. The MS measurement showed also the presence of a small amount of Cl_2

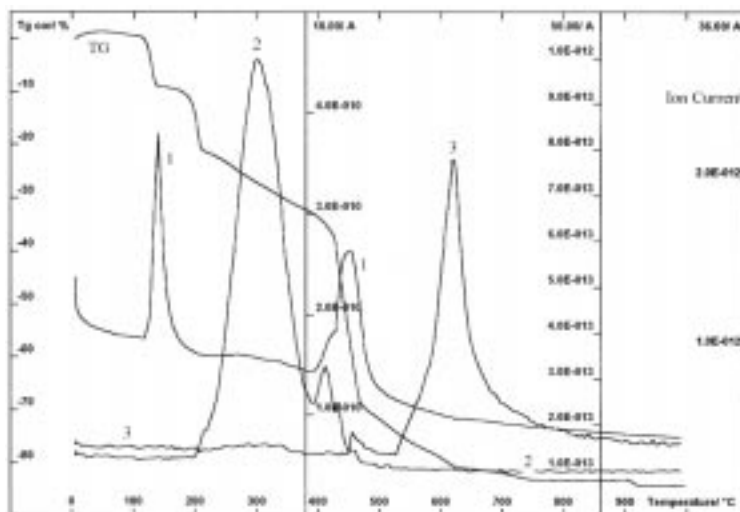


Fig. 3 TG curve for $\text{Co}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and ion current detected by the MS for mass fragments m/z : 1 – 18; 2 – 50; 3 – 36, original record

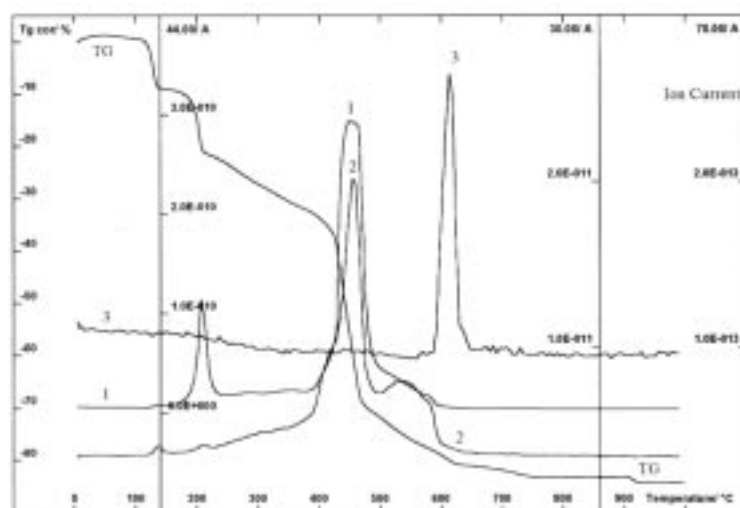


Fig. 4 TG curve for $\text{Co}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and ion current detected by the MS for mass fragments m/z : 1 – 44; 2 – 30; 3 – 70, original record

($m/z=70, 74$) in gaseous products of the decomposition. The fragments with $m/z=30$ correspond probably to CH_2O or NO . They start to be detected at around 360°C and reach a maximum rate of elimination at 440°C . A very low intensity ion current (on measuring error) is observed for 4,4'-bipyridine in the range $200\text{--}500^\circ\text{C}$. CO was not detected. Similar observations have been made for other obtained complexes. TG coupled with MS data for major decomposition products are presented in Figs 3 and 4. According to Lin *et al.* [18] HCl , CH_3Cl , CO_2 and H_2O have been identified in the mass spectra of $\text{Cu}(\text{ClCH}_2\text{COO})_2$ as major decomposition products, while H_2O , CO , CO_2 , CH_2O and ClCH_2CHO were found as the products of thermal decomposition of $\text{Zn}(\text{ClCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ [19].

Conclusions

By means of VIS and IR spectra, thermoanalytical and mass spectrometric measurements, the following information about the coordination of the ligands with $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and the thermal behaviours have been obtained.

The electronic spectra indicated pseudooctahedral environment around the $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$.

The IR spectra of compounds indicate interaction of the 4,4'-bipyridine nitrogen with the metal(II). The values of $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ for complexes correspond to the chelating character of carboxylate groups.

The thermal decomposition of all studied complexes begins by the release of water, bonded as coordinated or crystalline water. Dehydration begins at $80\text{--}100^\circ\text{C}$. The thermal stability of the anhydrous complexes increase in the order: $\text{Mn} < \text{Ni} < \text{Cu} < \text{Co}$. The anhydrous complexes decompose to metal oxides: Mn_3O_4 , CoO , NiO and mixture of $\text{CuO} + \text{Cu}_2\text{O}$.

During the heating of $\text{M}(4\text{-bipy})(\text{ClCH}_2\text{COO})_2$ followed the decomposition of organic ligands. H_2O , CO_2 , CH_2O (or NO), CH_3Cl , HCl , Cl_2 and other fragments were found. As the first major decomposition products were detected H_2O and CO_2 . Next, on increase of the temperature the compounds containing chlorine are released. In air atmosphere CO was not detected.

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