

COPPER(II) ACETATES WITH ALIPHATIC/HETEROCYCLIC AMINES Coupled TG-DTA-EGA study, IR characterization and structure correlation

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Three copper acetate complex compounds, namely $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ (**I**), $\text{Cu}(\text{CH}_3\text{COO})_2(\text{tn})_2$ (**II**) and $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ (**III**) (*en*=ethylenediamine, *tn*=1,3-diaminopropane, *pyz*=pyrazine), were prepared and characterized during heating in argon by thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA) using mass spectrometry (MS). The results of infrared spectroscopy (IR) were evaluated to be used as a spectroscopic criterion for the determination of the carboxylate binding mode in the compounds.

Keywords: copper acetate, 1,3-diaminopropane, DTA, ethylenediamine, evolved gas analysis, IR spectra, pyrazine, structure correlation, thermogravimetry

Introduction

Copper carboxylates attract research interest in the field of catalysis [1], as antifungal agents [2], enzyme models [3], or mainly, in the field of molecular magnetism [4]. The versatile coordination behaviour of carboxylate group leads to the formation of systems of various dimensionalities which exhibit by theory predictable magnetic properties [4–6]. Such systems are prepared by reaction of the corresponding carboxylate salt with bidentate amine (e.g. ethylenediamine) followed by the addition of a salt containing non-coordinating anions [7–9] or, by reaction of metal carboxylate with the organic ligand in a low ligand : metal ratio [10, 11]. The higher ratio of the reactants leads to the synthesis of bis- or tris-chelates. Such chelate compounds, when they are formed by monocarboxylate ligand, have usually mononuclear structure, as it was reported for copper acetate complexes of ethylenediamine or diaminopropane [12]. The dicarboxylate complexes (e.g. oxalate) usually form polymeric compounds [13].

Thermal stability of the copper diamine compounds with various counterions (e.g. chloride, sulphate, perchlorate, nitrate) was studied [14–21]. However, the detailed information concerning the thermal properties of the Cu(II) diamine compounds with carboxylate as counterion are scarce [22, 23]. In the present work we have prepared mixed copper acetate complexes, namely $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2(\text{tn})_2$ and $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ (where

en=ethylenediamine, *tn*=1,3-diaminopropane, *pyz*=pyrazine). The complexes were investigated by means of a coupled TG/DTG-DTA-EGA methods on heating in argon to characterize their thermal stability. Moreover, the correlation of IR spectra of the complex compounds to the structures was made.

Experimental

Ethylenediamine (*en*), 1,3-diaminopropane (*tn*), pyrazine (*pyz*) were supplied from Aldrich and used without further purification. The copper acetate monohydrate was prepared from copper carbonate and acetic acid. The prepared product was recrystallised from water.

Synthesis

Preparation of $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ (compound **I**)

The mass of 0.5 g (2.5 mmol) of the copper acetate monohydrate was dissolved in 50 mL of the water/ethanol mixture (1:1; v/v) and heated to 50°C. Further 1,2-diaminoethane (5 mmol) was added dropwise during stirring. The solution was filtered and the filtrate left for a slow evaporation. After several days the violet crystalline product was recovered. The crystals of the compound were filtered off, washed with ethanol and dried over silica gel. Anal. calc. for

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$C_8H_{26}N_4O_6Cu$: C, 28.5; H, 7.7; N, 16.6; Cu, 18.8%.
Found: C, 28.7; H, 7.7; N, 16.2; Cu, 19.1%.

Preparation of $Cu(CH_3COO)_2(tn)_2$ (compound **II**)

The copper acetate (0.5 g; 2.5 mmol) was dissolved in 50 mL of the water/ethanol mixture (1:1; v/v) and 5 mmol of *tn* was added to the solution while the violet solution was formed. The solution was filtered and left to stand at 50°C. After several days the blue-violet solid $Cu(CH_3COO)_2(tn)_2$ was recovered. The prepared complex compound was highly hygroscopic and therefore was kept in desiccator over silica gel. Anal. Calc. for $C_{10}H_{26}N_4O_4Cu$: C, 36.4; H, 7.9; N, 17.0; Cu, 19.3%. Found: C, 36.2; H, 7.6; N, 16.5; Cu, 18.9%.

Preparation of $Cu_2(CH_3COO)_4(pyiz)$ (compound **III**)

The compound $Cu_2(CH_3COO)_4(pyiz)$ was prepared by mixing the methanol solution (40 mL) of copper acetate (0.5 g, 2.5 mmol) with 20 mL of the methanol solution of pyrazine (0.2 g, 2.5 mmol). The reaction mixture was stirred at the room temperature for several minutes while a green powder precipitated. The powder was filtered off, washed with methanol and dried. Anal. Calc. for $C_{12}H_{16}N_2O_8Cu_2$: C, 32.5; H, 3.6; N, 6.3; Cu, 28.7%. Found: C, 32.1; H, 3.5; N, 6.1; Cu, 28.4%.

Instrumentation

TG/DTG-DTA-EGA measurements were carried out using NETZSCH STA 409 Apparatus equipped with quadrupole-type mass spectrometer BALZERS. The measurements were carried out in flow of argon (75 mL min⁻¹) at the rate 6°C min⁻¹ and with the sample mass 50 mg. To identify the solid products of the thermal decomposition, XRD patterns were recorded with a Micrometa 2 diffractometer using Cr-K α , V-filtered radiation ($\lambda=2.29092$ Å). Elemental analyses were performed with a PerkinElmer 2400 CHN Elemental Analyser. The copper content was determined by complexometric titration using EDTA. Infrared spectra were measured by PerkinElmer 781 spectrophotometer as KBr disc.

Results and discussion

Spectroscopic characterization of the compounds

The IR spectra revealed the presence of the amines as well as the acetates in the compounds **I–III**. The most important spectral bands are listed in Table 1.

The amine moieties in compounds **I** and **II** (*en* and *tn*, respectively) were reflected by the stretching vibrations of the NH₂ groups at 3156 cm⁻¹ for the compound

(**I**) and 3250, 3160 cm⁻¹ for the compound **II**. The band due to the vibrations of the pyrazine ring was observed at 1485 cm⁻¹ in the compound **III**. Moreover, the stretching vibrations of the aromatic C–H groups of the pyrazine were found at 3096 cm⁻¹.

The acetate anions were characterized by carboxylate stretches $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1564 and 1396 cm⁻¹ for compound **I**, 1550 and 1400 cm⁻¹ for compound **II** and 1596 and 1424 cm⁻¹ for the compound **III**. The magnitude of the separation between the stretches ($\Delta=\nu_{as}(COO^-)-\nu_s(COO^-)$) is often used as a spectroscopic criterion for determination of the mode of the carboxylate binding [24–30], including biomolecules [31, 32]. The following order was proposed for Δ values of carboxylate complexes of divalent metal cations [24, 25]:

$\Delta(\text{monodentate}) > \Delta(\text{ionic}) > \Delta(\text{bridging bidentate}) > \Delta(\text{chelating bidentate})$.

This Δ value is about 170 cm⁻¹ for ionic carboxylate group in acetates, i.e. group which does not interact strongly with the metal ion [24]. In monodentate coordination the redistribution of the electron density takes place, the force field around the metal atom changes and consequently the shift in the frequency of $\nu_{as}(COO^-)$ to higher wavenumbers in comparison with ionic group is observed, increasing the value of Δ . On contrary, bidentate coordination shifts the position of the asymmetric carboxylate stretch to lower wavenumbers in comparison with ionic group and thus lowers the value of Δ . In the ‘bridging’ coordination when one divalent metal cation is bound to one of the oxygens in the COO⁻ group and another divalent metal cation to the other oxygen, the $\nu_{as}(COO^-)$ band is located at the same position as that of the ‘ionic’ $\nu_{as}(COO^-)$ band [31].

This criterion is also frequently used in the papers dealing with the thermal properties of the complex compounds. However it has to be applied carefully because sometimes it can be ambiguous or gives misleading results and can be strongly influenced by the presence of the hydrogen bonds [33, 34]. During application of this criterion, the comparison of the proposed mode of the coordination with the structural data within a series of closely related compounds is often useful.

First, the above criteria were applied to the compound **III**, for which the structural data were available [35]. From the single crystal diffraction study it is well known, that the compound **III** forms 1D polymeric chains, in which binuclear paddle-wheel acetate units are connected by the pyrazine bridges [35]. For such paddle wheel structure (one copper(II) cation is bound to one of the two oxygen atoms in the COO⁻ group and another copper(II) cation to the other oxygen) the Δ value should be close to that observed for ionic carboxylate group [31]. The experimental Δ

Table 1 Principal bands in the IR spectra of **(I)**–**(III)** and their assignment

Compound	Wavenumber/cm ⁻¹	Assignment
Cu(CH ₃ COO) ₂ (<i>en</i>) ₂ ·2H ₂ O (I)	3356bs	v(OH)
	3156s	v(NH)
	2960m, 2900m	v(CH)
	1604m	δ(H ₂ O)+δ(NH ₂)
	1564s	v _{as} (COO ⁻)
	1396s	v _s (COO ⁻)
	1330w, 1270m	δ(CH)
	1090s, 1048m, 1008m, 922m	ρ(CH)+ρ(NH)
	706s	δ(COO ⁻)
	Cu(CH ₃ COO) ₂ (<i>tn</i>) ₂ (II)	3250s
3160s		v _s (NH)
3096w		v(CH)
2960m		v(CH)
1550s		v _{as} (COO ⁻)
1400s		v _s (COO ⁻)
1360m, 1310w		δ(CH)
1180m, 1140m, 1060m, 960m		ρ(CH)+ρ(NH)
Cu ₂ (CH ₃ COO) ₄ (<i>pyz</i>) (III)	705s	δ(COO ⁻)
	3096s	v(CH)
	2900m	v(CH)
	1596s	v _{as} (COO ⁻)
	1485m	v(<i>pyz</i>)
	1424s	v _s (COO ⁻)
	1340m, 1060m, 1050m	δ(CH)
	1180m, 1160m	ρ(CH)
	840s	δ(COO ⁻)

Abbreviations: b – broad; s – strong; m – medium; w – weak

value, determined from the IR spectra of the compound **III** (172 cm⁻¹), was in an agreement with this hypothesis. Moreover, based on the knowledge of the X-ray structural data for the compound **III**, the Δ value can be calculated using Eq. (1), proposed and derived by Nara [36] from molecular orbital calculations:

$$\Delta = 1818.1\delta r + 16.47(\theta_{\text{OCO}} - 120) + 66.8 \quad (1)$$

where δr is difference between the two CO bond lengths (Å) and θ_{OCO} is the OCO angle (°) [33, 36]. The calculated Δ value for the complex compound **III** is 170.4 cm⁻¹ and it is in agreement with the experimentally observed value (172 cm⁻¹).

For the complexes **I** and **II**, there is no entry in the Cambridge Structural Database [37]. The value of the separation of the carboxylate stretches, as determined in our study from the IR spectra of compound **I**, is 168 cm⁻¹. This value is close to the value given for ionic or bridging carboxylate group [24, 31]. To verify this possibility, we made a survey of the crystal

structures of the mixed copper ethylenediamine carboxylate compounds. The survey has shown that when the both carboxylate and ethylenediamine are coordinated to copper, the compounds contain usually one *en* molecule e.g. in ethylenediamine-phthalato-copper(II) [38], aqua-(ethylenediamine)-(oxalato)-copper(II) monohydrate [39] or ethylenediamine-bis(2-(methylthio)nicotinato)-copper(II) [40]. Two *en* molecules were found in polymeric bis(oxalato)-bis(1,2-ethylenediamine)-di-copper(II) where each of two carboxylate groups is coordinated monodentately [13]. The Δ values, calculated using Eq. (1) for these complexes differ remarkably from the value observed for the compound **I**. For example the Δ value calculated for oxalate (281 cm⁻¹) is in agreement with the monodentate carboxylate coordination in the compound [13]. The Δ value calculated for 2-(methylthio)nicotinate (155 cm⁻¹) agrees with chelate coordination of the carboxylate in this complex [40].

When two *en* molecules are present in the compounds, carboxylate group is frequently ionic. Such kind of the assembly was found e.g. in aromatic aminosalicylate [41] and isonicotinate [42] or aliphatic N-carboxyglycinate [43]. The observed Δ value in the latter complex, (167 cm^{-1}), formed by the aliphatic carboxylate [43] is similar to the value observed for the compound **I**. The application of Eq. (1) to the structural data of N-carboxyglycinate gives Δ values 177 and 184 cm^{-1} . Therefore the spectral data suggest that in compound **I** 'ionic' acetate group could be present. Such assembly could comprise two ethylenediamine molecules coordinated as chelates and water molecules coordinated to metal ion. The acetate anions could remain uncoordinated, compensating the charge of the copper(II) ion.

For the compound **II**, the value of the separation Δ , as determined from the IR spectra, was 150 cm^{-1} . This value indicates possibility of chelate acetate group [26–28]. Anyway, the survey of the crystal structures of the copper(II) carboxylates with 1,3-diaminopropane has shown, that in the copper carboxylato complexes of the formula $\text{Cu}(tn)_2(\text{carboxylato})_2$, the carboxylate is usually coordinated to copper atom monodentately [44–47]. There is one example of the copper-diaminopropane complex with the "ionic" carboxylate group, but this complex is dihydrate, namely trans-diaqua-(1,3-diaminopropane)-copper(II) 2-nitrobenzoate [48]. The Δ values in nitrobenzoate calculated using Eq. (1) are 184 and 200 cm^{-1} , and the values calculated for the *tn* complexes with the monodentate carboxylate coordination are in the range $123\text{--}225\text{ cm}^{-1}$ [44–47]. Higher Δ values calcu-

lated for ionic nitrobenzoate can be due to hydrogen bonds, formed by the carboxylate oxygen atoms, which influenced the bond lengths and angle in the carboxylate group. Similarly, in the complexes with monodentately bonded carboxylate, the secondary interaction of the non-coordinated carboxylate oxygen atom with the copper probably lowers the values of Δ , in comparison with those, expected for monodentate coordination. Such interaction could also be present in the compound **III** and therefore lower Δ value was observed than that typical for monodentate coordination. However from the IR spectra, the mode of the carboxylate coordination for the compound **III** can not be determined conclusively.

Thermal stability characterization

*Thermal decomposition of $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ (compound **I**)*

The results of TG/DTG, DTA and evolved gas analysis (EGA) obtained for $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ during heating in argon are presented in Fig. 1 and are summarized in Table 2.

The curves are featureless up to the onset of the thermal decomposition at 86°C . Above this temperature, the dehydration of the sample with loss of one water molecule took place in the range $86\text{--}150^\circ\text{C}$. The observed mass loss due to this dehydration was 5.2% (calculated value for one water molecule is 5.3%). The dehydration step was accompanied by an endothermic effect at 120°C . The EGA by mass spectroscopy (MS) detection reflected the process of the

Table 2 Thermal decomposition data of the complexes **I–III**

Complex	Step	Temp. range/ $^\circ\text{C}$	Mass loss/%		DTA peak/ $^\circ\text{C}$	MS ions detected	Product expelled
			Observed	Calculated			
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ (I)	1	86–150	5.2	5.3	120 endo	18	H_2O
	2	150–350	70.5	71.2	179 endo 220 endo	12, 15, 18, 44	$\text{H}_2\text{O}+2\text{en}+$ decomp. of acetate
	3	350–610	24.3	23.5	255 exo	12, 44	CuO
	Solid residue	>610	24.3	23.5	–	–	CuO
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{tn})_2$ (II)	1	136–220	23.5	22.5	158 exo 183 exo	15, 18	<i>tn</i>
	2	220–350	41	40.1	222 exo	12, 15, 44	<i>tn</i> + CH_3COCH_3
	3	350–750	12	13.3	508 exo	12, 15, 44	CO_2
	Solid residue	>750	23.5	24.1	–	–	CuO
$\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ (III)	1	195–510	64.7	64.1	260 endo	12, 15, 18, 44	total pyrolysis of the complex
	Solid residue	>510	35.3	35.9	–	–	2CuO

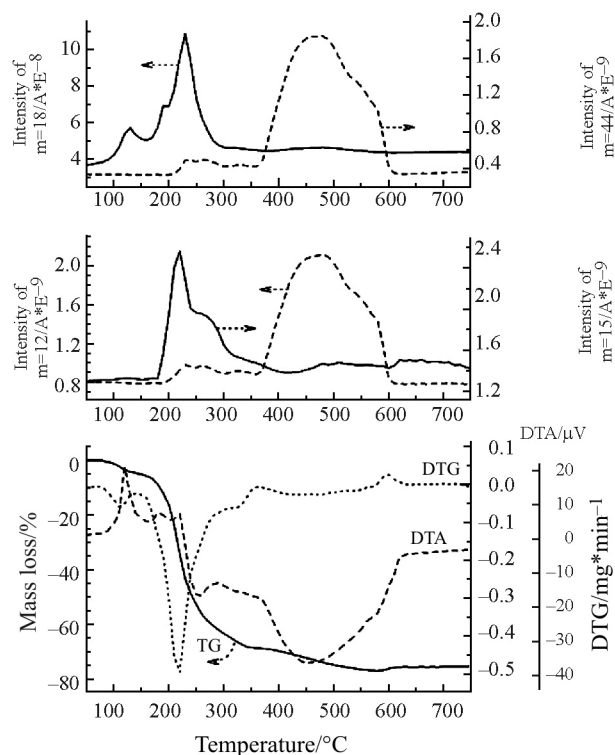


Fig. 1 TG/DTG-DTA-EGA curves of the complex $\text{Cu}(\text{CH}_3\text{COO})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}$ during heating in argon

dehydration by an increase of the intensity of the molecular ion of water ($m/z=18$). The maximal intensity of the release of this ion was observed at 129°C . The second water molecule releases above 150°C . The release is accompanied by a new maximum at 189°C in the MS curve measured for the ion with $m/z=18$ and by endothermic effect at 179°C in the DTA curve.

During further heating deamination and decarboxylation of the sample took place. Both steps coincide in the TG curve, however, the results of MS suggested, that the process of the deamination took place as the first. The increase of the intensity of the fragment ion with $m/z=15$ from 180°C and ion with $m/z=18$ from 195°C was observed in the mass spectrum (Fig. 1), probably due the evolution of the ethylenediamine (ions NH_4^+ , NH^+). It is to mention that the intensity of these fragment ions decreased from about 230°C . However, the decrease of the intensity of the ion with $m/z=15$ was remarkably slowed down at 245°C . This was probably due to the onset of the decarboxylation (i.e. the decomposition of the acetate) and loss of the fragment ion CH_3^+ from the acetone or acetanhydride, which are usually the products of the decomposition of acetates [49]. This is also supported by another maximum observed in the EGA curve for the fragment $m/z=44$ at the temperature of 262°C . On the basis of the EGA curves for the fragments ($m/z=12$, 15 , 44), we supposed that the onset of the decomposition of

acetate was approximately 250°C . The release of the ethylenediamine was reflected in DTA curve by endothermic effect at 220°C . From 270°C the rate of the thermal decomposition was slowed down. The main decomposition product detected in this stage was carbon dioxide ($m/z=44$, 12), formed during the decomposition of the acetate. The DTA curve reflects the decomposition of acetate by exothermic effects at 255 and 452°C , respectively.

The mass loss continued up to 560°C (76.9%). On further heating, in the range 585 – 610°C the small mass increase was observed in the TG curve. We suppose that partial reduction of Cu^{2+} took place during heating to 580°C and above this temperature the re-oxidation to CuO (the mass increase 1.2%) took place. As the thermal decomposition was carried out in the inert atmosphere (Ar, 99.999%), this re-oxidation was probably by carboxylate oxygen atom. The oxidation process was reflected as a shoulder in the exothermic peak at 578°C . The final product of the thermal decomposition, detected by XRD, was CuO (*tenorite*; PDF 45-0937; exp. solid residue 24.3%; calcd. 23.5%).

Thermal decomposition of $\text{Cu}(\text{CH}_3\text{COO})_2(\text{tn})_2$ (compound II)

The TG/DTG, DTA and evolved gas analysis (EGA) results of the complex compound $\text{Cu}(\text{CH}_3\text{COO})_2(\text{tn})_2$ are presented in Fig. 2 and are summarized in Table 2. The mass loss of 1% observed on the sample heating up to 91°C due to the release of water adsorbed as humidity by the sample.

The compound was thermally stable up to 136°C . Above this temperature, the evolution of diaminopropane took place as observed by EGA. In contrast to compound I the deamination in compound II took place in two steps. During the first step, in the range 136 – 220°C , the mass loss 23.5% was observed, corresponding to the loss of one molecule of diaminopropane (calc. mass loss 22.5%). This first step of the deamination was reflected by the increase of the intensity of the fragment ions with $m/z=15$ and 18. The maximal intensity of these ions was observed at about 200°C . In the range 200 – 220°C , the intensity of the ions decreases. This first step of the deamination was accompanied in the DTA curve by the exothermic effects with maximum at 158°C and shoulder at 183°C . Further heating leads to the evolution of the second molecule of diamine as well as simultaneous decomposition of the acetate. This fact was reflected by the increase of the intensity of the ion with $m/z=15$. The intensity of the release of the ion with $m/z=15$ observed at 239°C is higher than the intensity at 200°C , as both NH^+ as well as CH_3^+ contribute to the intensity of this ion (Fig. 2). Moreover, the increase of the intensity of the ions with $m/z=44$ or

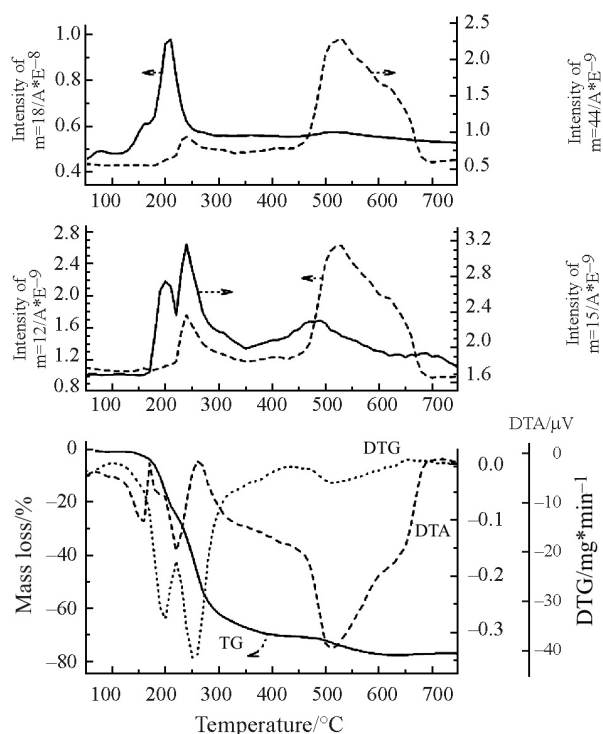


Fig. 2 TG/DTG-DTA-EGA curves of the complex $\text{Cu}(\text{CH}_3\text{COO})_2(m)_2$ during heating in argon

12 was observed above 220°C, due to the decomposition of the acetate. The second step of the decomposition was reflected by the exothermic effect with maximum at 222°C.

The intensity of the MS curves decreases up to 350°C. The total mass loss, observed at this temperature was 64.5%, which may correspond to the loss of the two molecules of diamine and acetone (product of the decomposition of acetate). The calculated mass loss, corresponding to the release of these products is 62.6%. Further heating up to 750°C is characterized by mass decrease of 12%, corresponding release of the carbon dioxide (calculated value 13.3%) and characterized by the ions $m/z=44$ and $m/z=12$ in the MS. This process of the decomposition was accompanied by the exothermic peak with the maximum at 508°C (see DTA results in Fig 2). The solid product of the thermal decomposition, CuO (observed amount, 23.5%; calculated amount, 24.1%), was confirmed by XRD to be *tenorite* (PDF 45-0937).

*Thermal decomposition of $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ (compound **III**)*

TG/DTG, DTA and EGA curves of the thermal decomposition of the compound $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ are presented in Fig. 3 and summarized in Table 2. In contrast to the two previous compounds the decomposition of the compound **III** is an one-step process.

From the results of the X-ray structural analysis [35] it follows, that the structure of the compound **III** is polymeric, with $\text{Cu}_2(\text{CH}_3\text{COO})_4$ units connected by pyrazine ligands to 1D chains. The results of the TG showed, that after attaining of the limit of the stability at 195°C the collapse of the polymeric structure took place and the compound decomposed very rapidly by the steep mass loss (see TG curve in Fig. 3). The process of the decomposition took place in the temperature range 195–360°C and was characterized by the endothermic effect at 260°C in the DTA curve. The total mass loss observed on heating up to 360°C was 67.0%. In the range 390–510°C the small mass increase was observed (2%), probably due to re-oxidation of partially reduced Cu^{2+} to CuO. The amount of the solid residue after the thermal decomposition (35.3% of the initial sample mass) was in a good accordance with the value calculated for two moles of CuO (35.9%). The presence of CuO was confirmed by XRD (*tenorite*; PDF 45-0937).

From the EGA (MS) curves it followed that the maximal intensity of the release of the respective ions was about 275°C. However, the decrease of the intensity of the anions with $m/z=12$ and 44 is slower in comparison to the other, indicating that the kinetics of the decomposition was determined by the decomposition of the acetate.

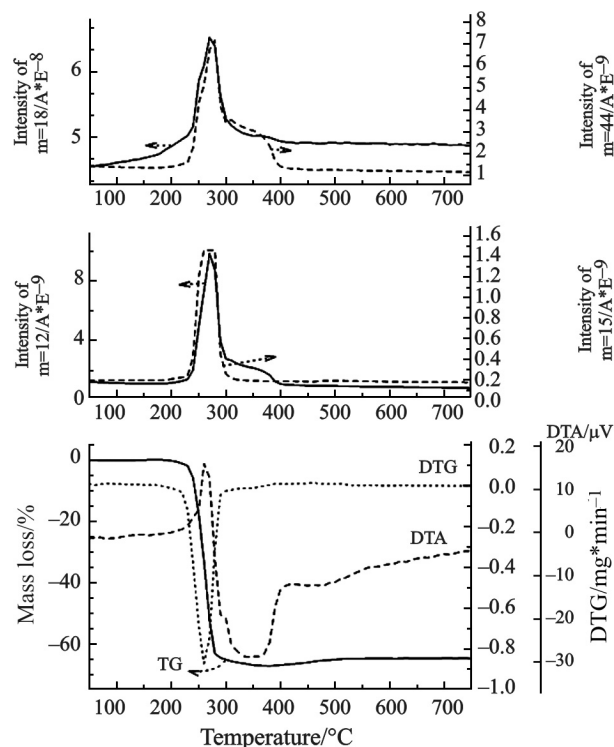


Fig. 3 TG/DTG-DTA-EGA curves of the complex $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{pyz})$ during heating in argon

Conclusion

It was found by simultaneous TG-DTA-EGA techniques that the thermal decomposition of compounds **I** and **II** is a multistep process, involving dehydration, deamination and decarboxylation. During the heating of compound **III** the collapse of the polymeric structure takes place rapidly in one step. The processes of deamination and decarboxylation overlap. However, according to the MS data the deamination takes place first, while the decarboxylation is a slower process.

The values of the separation of the carboxylate stretches (Δ) in the IR spectra of the compounds are frequently used to correlate the IR-spectral data to the molecular structures of the complexes. Indeed this criterion is applied in the papers dealing with the thermal properties of the carboxylates. During the demonstration of the practical application of this spectroscopic criterion it was shown in the present paper that the criterion does not have general validity as it can be influenced by various factors (e.g. hydrogen bonds, non-bonding interactions...). For compounds **I–III**, ionic, monodentate and bridging carboxylate groups were proposed. In accordance with this assumption, compound **III** showed the highest thermal stability. For complexes **I** and **II** the thermal stability was lower and determined by the dehydration and evolution of the amines.

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