

Synthesis, Thermal and Spectral Properties of Cu(II) Complexes with *N,N*-Diethylnicotinamide

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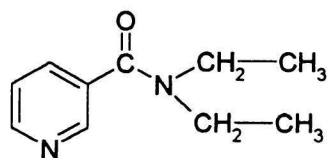
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The thermal decomposition of the complexes $[\text{Cu}(\text{ac})_2 \cdot (\text{Et}_2\text{na})]_2 \cdot \text{Et}_2\text{na} \cdot 2\text{H}_2\text{O}$ (*I*), $\text{Cu}(\text{Clac})_2 \cdot (\text{Et}_2\text{na})_3$ (*II*), and $\text{Cu}(\text{Cl}_2\text{ac})_2 \cdot (\text{Et}_2\text{na})_2 \cdot 2\text{H}_2\text{O}$ (*III*) (where $\text{ac} = \text{CH}_3\text{COO}^-$, $\text{Clac} = \text{ClCH}_2\text{COO}^-$, $\text{Cl}_2\text{ac} = \text{Cl}_2\text{CHCOO}^-$, and $\text{Et}_2\text{na} = N,N$ -diethylnicotinamide) had been investigated in static air in the temperature range 20–1000 °C by means of thermogravimetry (TG) and differential thermal analysis (DTA). The composition of the complexes and the solid state intermediate and resultant products of thermolysis had been identified by means of elemental analysis and compleximetric titration. The possible scheme of destruction of the complexes is suggested. Heating the compounds first results in a release of water molecules. The loss of the volatile ligand (Et_2na) occurs in one step. The thermal stability of the complexes increases in the sequence: *II*, *III*, *I*. The final products of the thermal decomposition were CuO. The IR, EPR, and electronic spectral analyses were used. Et_2na was found to be coordinated to Cu(II) through the nitrogen atom of its heterocyclic ring and EPR data suggest a dimeric structure of compound *I* and monomeric structure of compounds *II* and *III*.

Carboxylatocopper(II) complexes are of interest from both the chemical and biological point of view. Copper(II) carboxylates with nitrogen donor ligands have attracted increasing interest in recent years. This interest largely derives from the discovery that the carboxylate groups possess a pronounced tendency to serve as a bridge between copper(II) atoms with a nitrogen donor ligand in terminal position [1–3]. From our point of view it was challenging to study the interaction between metal ions and heterocyclic nitrogen compounds that occur in living systems and are used as medicaments [4]. It is also well known that heterocyclic compounds play a significant role in many biological systems, especially six-membered ring system being a component of several vitamins and drugs [5, 6]. It is known that some drugs act *via* chelation or *via* the inhibition of metalloenzymes, but little is known about the modification of activity of most drugs when their ligating potential is utilized. The interaction of copper(II) atom, which plays a vital role in a number of quite different biological processes, with therapeutically administered drugs is a subject of considerable interest [7].

The Ni(II), Fe(III), and Cu(II) complexes with nicotinamide have been reviewed earlier [8]. In our previous papers we described the thermoanalytical properties of Mg(II) carboxylates with pyridine and

its derivatives [9–12]. The molecular structure and spectral analysis of Cu(II) flufenamates with *N,N*-diethylnicotinamide known as an important respiration stimulant is described in [13]. In this paper we deal with the results of synthesis, thermal and IR, EPR and electronic spectral analyses of the above-mentioned new copper(II) complexes *I–III*.



N,N-diethylnicotinamide

EXPERIMENTAL

Electronic spectrum in the *T*-region 10–28 kK was measured with a Perkin–Elmer 450 spectrophotometer and IR spectrum in the $\bar{\nu}$ region of 200–4000 cm^{-1} with the Philips analytical PU9800 FTIA spectrometer. In both cases the Nujol suspension technique was used. EPR spectrum of powdered sample was run on a Varian model E 4 spectrometer at room temperature.

Thermal decomposition of the complexes was carried out on Paulik–Paulik–Erdey Derivatograph

Table 1. Analytical Data of the Complexes *I–III*

| Complexes | w_i (calc.)/% w_i (found)/% | | | |
|------------|------------------------------------|------|-------|-------|
| | C | H | N | Cu |
| <i>I</i> | 48.86 | 6.21 | 9.00 | 13.11 |
| | 48.39 | 6.19 | 8.75 | 13.14 |
| <i>II</i> | 52.00 | 5.86 | 10.71 | 8.10 |
| | 51.13 | 6.02 | 11.09 | 8.13 |
| <i>III</i> | 40.48 | 4.78 | 7.87 | 8.93 |
| | 40.47 | 4.71 | 7.89 | 8.95 |

(Type OD 102, MOM Budapest) in air atmosphere by using a platinum crucible with a sample mass of 100 mg in the temperature range 20–1000°C. The rate of temperature increase of 10°C min⁻¹ was chosen for the measurement.

The new copper(II) complexes reported in this paper are soluble in water, ethanol, methanol, acetone, and dimethyl sulfoxide. The content of carbon, nitrogen, and hydrogen was determined by elemental analysis and the content of copper was established by compleximetric titration. The analytical data of the compounds *I–III* reported in Table 1 show a good agreement between the experimental and calculated data.

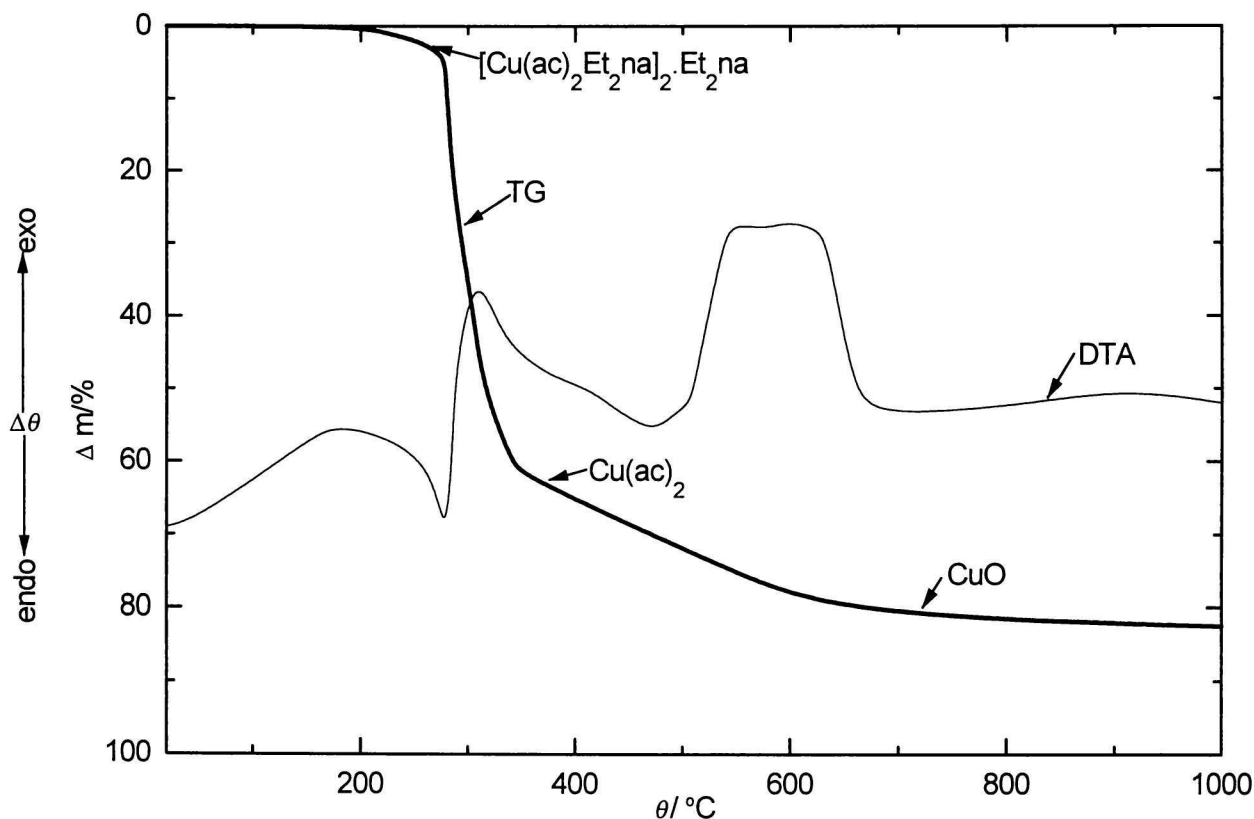
Complexes *I–III*

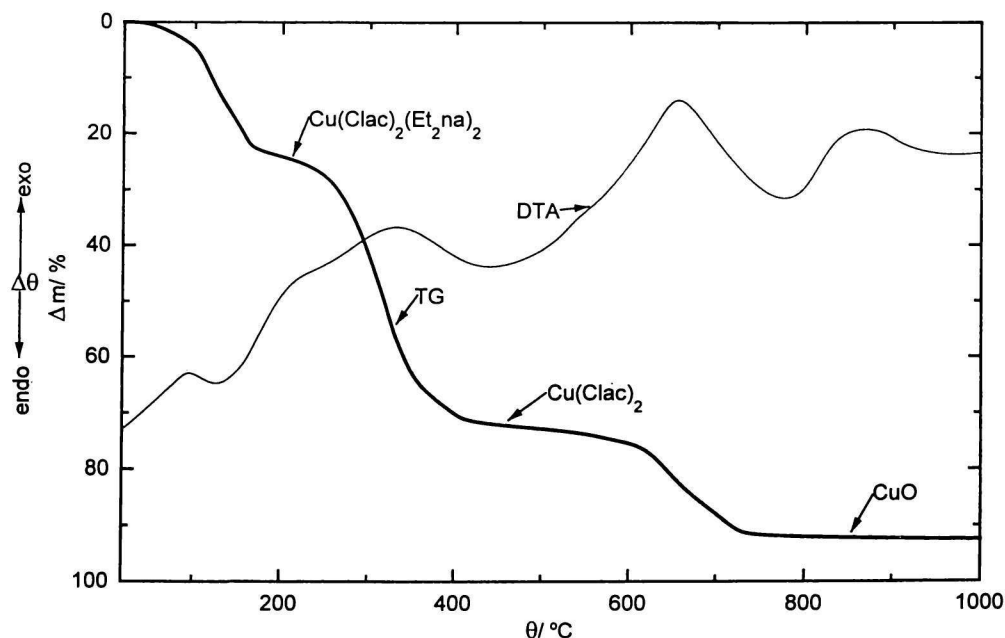
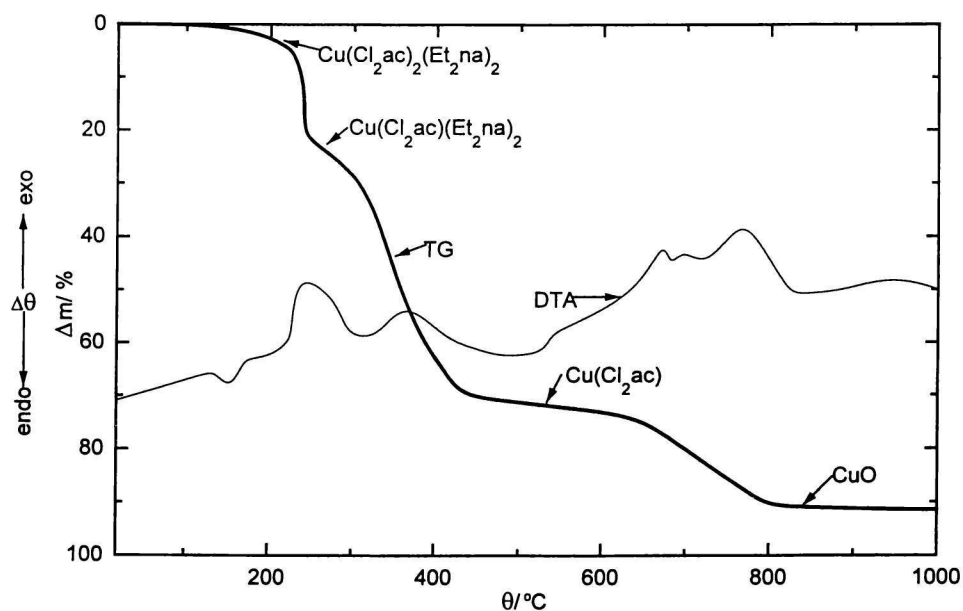
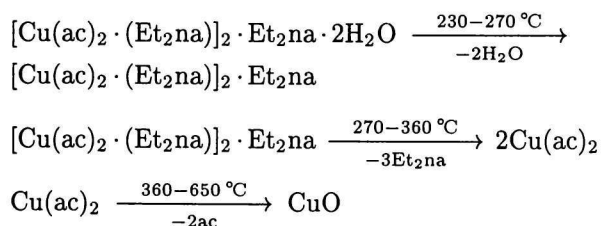
Compounds *I–III* were prepared by dissolving 0.05 mol of appropriate acetato- or halogenoacetato-copper(II) complexes in 100 cm³ of ethanol and by gradually adding (3.56 g, 0.2 mol) Et₂na. The solutions were reduced in volume at room temperature and left to crystallize. The complexes which formed were filtered off, washed with ether, and dried at room temperature.

RESULTS AND DISCUSSION

The TG and DTA curves of the complexes *I–III* are shown in Figs. 1–3. Thermal decomposition of the compounds is the multi-stage process. The subsequent detachment of the ligands was observed. The final product was CuO.

The TG and DTA curves for [Cu(ac)₂·(Et₂na)]₂·Et₂na·2H₂O (*I*) are shown in Fig. 1. The TG curve for that complex indicates that it is stable at temperature up to 230°C, when there begins the slow decomposition to CuO, as to the final product formed at 650°C. The TG curve shows two bendings at 270°C and 360°C. They correspond to the presence of two intermediate decomposition products: [Cu(ac)₂·(Et₂na)]₂·Et₂na and Cu(ac)₂. The most probable thermal decomposition scheme is

**Fig. 1.** TG and DTA curves of *I*.

Fig. 2. TG and DTA curves of *II*.Fig. 3. TG and DTA curves of *III*.

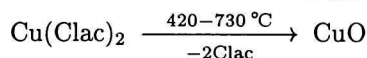
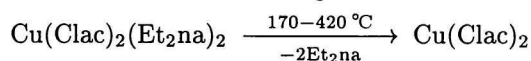
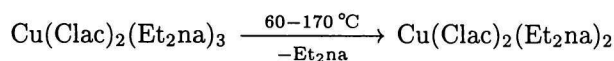
The DTA curve for the complex (Fig. 1) presents an endothermic peak at 250°C corresponding to the loss of 2H₂O and two exothermic processes at 230–450°C and 450–680°C corresponding to decompo-

sition reactions of *N,N*-diethylnicotinamide and acetates, respectively, with simultaneous formation of CuO (Table 2).

The TG and DTA curves for Cu(Clac)₂(Et₂na)₃ (*II*) are shown in Fig. 2. The TG curve for that complex indicates that it is stable at temperature up to 60°C, when there begins the slow decomposition to CuO, as to the final product formed at 730°C. The TG curve shows two bendings at 170°C and 420°C. They correspond to the presence of two intermediate decomposition products: Cu(Clac)₂(Et₂na)₂ and Cu(Clac)₂. The most probable thermal decomposition scheme is

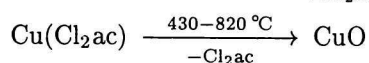
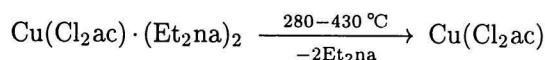
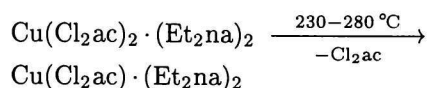
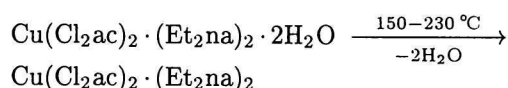
Table 2. Thermal Decomposition Data of the Complexes *I–III*

| Complexes | DTA | | | TG | | |
|---|----------------|-----------------|---------|-----------------|---------------------|---------|
| | Temp. interval | θ_{\max} | Process | Δm % | Released component | Residue |
| | °C | °C | | | | |
| [Cu(ac) ₂ · (Et ₂ na)] ₂ · Et ₂ na · 2H ₂ O (<i>I</i>) | 230–270 | 250 | endo | 3.85 (3.86) | 2H ₂ O | |
| | 270–450 | 300 | exo | 57.20 (57.23) | 3Et ₂ na | |
| | 450–680 | 600 | exo | 25.30 (25.29) | 2ac | CuO |
| Cu(Clac) ₂ (Et ₂ na) ₃ (<i>II</i>) | 50–180 | 120 | endo | 22.70 (22.69) | Et ₂ na | |
| | 180–450 | 320 | exo | 45.40 (45.38) | 2Et ₂ na | |
| | 450–780 | 650 | exo | 23.80 (23.83) | 2Cl ₂ ac | CuO |
| Cu(Cl ₂ ac) ₂ · (Et ₂ na) ₂ · 2H ₂ O (<i>III</i>) | 140–180 | 160 | endo | 5.00 (5.06) | 2H ₂ O | |
| | 180–300 | 240 | exo | 18.00 (17.98) | Cl ₂ ac | |
| | 300–500 | 370 | exo | 50.10 (50.04) | 2Et ₂ na | |
| | 500–830 | 770 | exo | 18.00 (17.98) | Cl ₂ ac | CuO |



The DTA curve for the complex (Fig. 2) presents an endothermic peak at 120°C corresponding to the loss of one *N,N*-diethylnicotinamide molecule and two exothermic processes corresponding to decomposition reactions of remaining two *N,N*-diethylnicotinamide molecules and acetates, respectively, with simultaneous formation of CuO.

The TG and DTA curves for Cu(Cl₂ac)₂ · (Et₂na)₂ · 2H₂O (*III*) are shown in Fig. 3. The TG curve for that complex indicates that it is stable at temperature up to 150°C, when there begins the slow decomposition to CuO, as to the final product formed at 820°C. The TG curve shows three bendings at 230°C, 280°C, and 430°C. They correspond to the presence of three intermediate decomposition products: Cu(Cl₂ac)₂ · (Et₂na)₂, Cu(Cl₂ac) · (Et₂na)₂, and Cu(Cl₂ac). The most probable thermal decomposition scheme is



The DTA curve for the complex (Fig. 3) presents an endothermic peak at 160°C corresponding to the loss of two molecules of water and three exothermic reactions corresponding to decomposition reactions of

one molecule of chloroacetate, two molecules of *N,N*-diethylnicotinamide, and the remaining chloroacetate, respectively, with simultaneous formation of CuO.

The solid state electronic spectra of complexes *I–III* exhibit ligand field bands with maximums at 14.2 kK, 14.7 kK, and 16.0 kK, respectively, which were identified with *d–d* transitions of the Cu(II). Complexes *I* and *III* also exhibit shoulders at 26.5 kK and 12.8 kK, respectively. The shoulder should be the characteristic of the bridging system with the antiferromagnetic interaction [14].

The IR spectra of compounds *I* and *III* show broad absorption bands at $\tilde{\nu} \approx 3660\text{ cm}^{-1}$ and 3332 cm^{-1} , respectively. These frequencies correspond to the $\nu_{\text{s,as}}(\text{OH})$ [15]. These bands clearly confirm the presence of water of crystallization in the compounds. The compounds showed the carboxylate stretching frequencies, $\nu_{\text{s}}(\text{COO}^-)$ in the $\tilde{\nu}$ range $1368\text{--}1489\text{ cm}^{-1}$ and $\nu_{\text{as}}(\text{COO}^-)$ in the $\tilde{\nu}$ range $1622\text{--}1652\text{ cm}^{-1}$. The positions of the bands are characteristic of copper(II) carboxylate compounds [16]. The absorption bands which occur in the $\tilde{\nu}$ range $200\text{--}250\text{ cm}^{-1}$ ($\nu(\text{Cu–N})$) confirm the coordination of *N,N*-diethylnicotinamide through the nitrogen atom of its heterocyclic ring to Cu ion. The absorption bands which occur in the $\tilde{\nu}$ range $602\text{--}609\text{ cm}^{-1}$ and $407\text{--}426\text{ cm}^{-1}$ are due to in-plane ring deformation and out-of-plane ring deformation, respectively, of pyridine ring. The absorption bands which occur in the $\tilde{\nu}$ range $289\text{--}426\text{ cm}^{-1}$ ($\nu(\text{Cu–O})$) confirm the coordination of oxygen to Cu ion.

EPR spectrum of the polycrystalline [Cu(ac)₂ · (Et₂na)]₂ · Et₂na · 2H₂O at room temperature contained the typical absorption bands of an axially symmetric dimeric species [17]. The spectrum can be interpreted by using a spin Hamiltonian for axial symmetry: $H = g_{\parallel}(\beta H_z S_z) + g_{\perp}(H_x S_x + H_y S_y) + D(S_z^2 + 2/3)$, where $S = 1$ for the thermally accessible triplet state and D , the zero-field parameter, and the other symbols have their usual meanings. The values ob-

Table 3. Parameters of EPR Spectra of the Complexes I—III

| Complexes | g_{\parallel} | g_{\perp} | g_{av} | $ D /\text{cm}^{-1}$ |
|--|-----------------|-------------|----------|----------------------|
| $[\text{Cu}(\text{ac})_2 \cdot (\text{Et}_2\text{na})]_2 \cdot \text{Et}_2\text{na} \cdot 2\text{H}_2\text{O}^*$ | 2.32 | 2.07 | 2.16 | 0.342 |
| $\text{Cu}(\text{Clac})_2(\text{Et}_2\text{na})_3$ | 2.24 | 2.01 | 2.09 | — |
| $\text{Cu}(\text{Cl}_2\text{ac})_2 \cdot (\text{Et}_2\text{na})_2 \cdot 2\text{H}_2\text{O}$ | 2.36 | 2.01 | 2.13 | — |

*Dimer.

tained for the spin Hamiltonian parameters are in Table 3. The values are comparable to those found in dimeric copper(II) carboxylates [2, 3]. EPR spectra of $\text{Cu}(\text{Clac})_2(\text{Et}_2\text{na})_3$ and $\text{Cu}(\text{Cl}_2\text{ac})_2 \cdot (\text{Et}_2\text{na})_2 \cdot 2\text{H}_2\text{O}$ contained the typical absorption bands of monomeric species with the g values (Table 3) which are typical for a pseudo-octahedral coordination about Cu(II) atom.

Without X-ray analysis no definite structure can be described for the different components. However, spectroscopic and analytical data available enabled us to remember problems of structures and we could also use thermal decomposition studies to help us.

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