## Preparation, Spectral and Thermal Properties of Mg(II) and Cu(II)Complexes with N,N-Diethylnicotinamide

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The thermal decomposition of the complexes  $Mg(ac)_2 \cdot (Et_2na)_2 \cdot 2H_2O(I)$ ,  $Mg(Cl_3ac)_2 \cdot (Et_2na)_2 \cdot 3H_2O(III)$ , and  $Cu(Cl_3ac)_2 \cdot (Et_2na)_2 \cdot 3H_2O(III)$  (where  $ac = CH_3COO^-$ ,  $Cl_3ac = Cl_3CHCOO^-$ , and  $Et_2na = N, N$ -diethylnicotinamide) had been investigated in 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 complexometric titration. The possible scheme of destruction of the complexes is suggested. Heating the compounds first results if 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 MgO (*I* and *II*) and CuO (*III*). The IR, EPR, and electronic spectral analyses were used.  $Et_2na$  is coordinated to Mg(II) and Cu(II) through the nitrogen atom of its heterocyclic ring. EPR data suggest a dimeric structure of compound *III*.

Carboxylatocopper(II) complexes are of interest from both the chemical and biological points 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]. Therefore, it is not surprising that many authors have investigated heterocyclic compounds, examined them as ligands in coordination complexes of several central atoms and also investigated the thermal properties of these complexes [7-20]. 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 [21].

This work is a continuation of our previously re-

ported studies [22—33] on the Mg(II) complexes with heterocyclic N-donor ligands. The molecular structure and spectral analysis of Cu(II) flufenamates with N,Ndiethylnicotinamide, known as an important respiration stimulant is described in [34]. In this paper we deal with the results of synthesis, thermal and spectral analyses of the above-mentioned new Mg(II) and Cu(II) complexes I—III.

## EXPERIMENTAL

Electronic spectrum in the *T*-region 10—28 kK was measured with a Perkin—Elmer 450 spectrophotometer and IR spectrum in the  $\tilde{\nu}$  region of 200—4000 cm<sup>-1</sup> with the Philips Analytical PU9800 FTIR 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 (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<sup>-1</sup> was chosen for the measurement.

Compounds I, II, and III were prepared by dissolving 0.05 mol of  $Mg(ac)_2 \cdot 2H_2O$ ,  $Mg(Cl_3ac)_2 \cdot 3H_2O$ , and  $Cu(Cl_3ac)_2 \cdot 3H_2O$ , respectively in 100 cm<sup>3</sup> of ethanol and by gradually adding  $\text{Et}_2\text{na}$  (1.78 g, 0.1 mol). The solutions were reduced in volume at room temperature and left to crystallize. The complexes formed were filtered off (*ca.* 70 % yield), washed with ether, and dried at room temperature.

## **RESULTS AND DISCUSSION**

The content of carbon, nitrogen, and hydrogen was determined by elemental analysis and the content of magnesium and copper was established by complexometric titration. The analytical data of the compounds I-III show a good agreement between the experimental and calculated data (variation < 1 %).

The complexes I—III are thermally relatively stable. Thermal decomposition of the compounds is the multistage process. The subsequent detachment of the ligands was observed. The final products were MgO (I, II) and CuO (III). The TG and DTA curves of the complexes I—III are shown in Figs. 1—3.

The TG and DTA curves for  $Mg(ac)_2 \cdot (Et_2na)_2 \cdot 2H_2O(I)$  are shown in Fig. 1. The TG curve for that complex indicates that it is stable at temperature up to 150 °C, when there begins the slow decomposition to MgO, as to the final product formed at 780 °C. The TG curve shows two bendings at 320 °C and 670 °C. They correspond to the presence of two intermediate decomposition products:  $Mg(ac)_2 \cdot (Et_2na)_2$  and  $Mg(ac)_2$ . The most probable thermal decomposition scheme is

$$\begin{array}{c} \mathrm{Mg}(\mathrm{ac})_{2} \cdot (\mathrm{Et}_{2}\mathrm{na})_{2} \cdot 2\mathrm{H}_{2}\mathrm{O} & \xrightarrow{150-320\,^{\circ}\mathrm{C}} \\ & \xrightarrow{150-320\,^{\circ}\mathrm{C}} & \mathrm{Mg}(\mathrm{ac})_{2} \cdot (\mathrm{Et}_{2}\mathrm{na})_{2} + 2\mathrm{H}_{2}\mathrm{O} \\ & \mathrm{Mg}(\mathrm{ac})_{2} \cdot (\mathrm{Et}_{2}\mathrm{na})_{2} & \xrightarrow{320-670\,^{\circ}\mathrm{C}} \\ & \xrightarrow{320-670\,^{\circ}\mathrm{C}} & \mathrm{Mg}(\mathrm{ac})_{2} + 2\mathrm{Et}_{2}\mathrm{na} \\ & \mathrm{Mg}(\mathrm{ac})_{2} & \xrightarrow{670-780\,^{\circ}\mathrm{C}} & \mathrm{MgO} + \mathrm{G. \ products} \end{array}$$

The DTA curve for the complex (Fig. 1) presents two endothermic peaks at 195 °C and 390 °C corresponding to the loss of  $2H_2O$  and N,N-diethylnicotinamide, respectively, and an exothermic process at 700 °C corresponding to decomposition reactions of acetates, with simultaneous formation of MgO.

The TG and DTA curves for  $Mg(Cl_3ac)_2 \cdot (Et_2na)_2 \cdot 3H_2O(II)$  are shown in Fig. 2. The TG curve for that complex indicates that it is stable at temperature up to 155°C, when there begins the slow decomposition to MgO, as to the final product formed at 820°C. The TG curve shows two bendings at 350°C and 640°C. They correspond to the presence of two intermediate decomposition products:  $Mg(Cl_3ac)_2 \cdot (Et_2na)_2$ and  $Mg(Cl_3ac)_2$ . The most probable thermal decomposition scheme is

$$\begin{array}{c} Mg(Cl_3ac)_2 \cdot (Et_2na)_2 \cdot 3H_2O \xrightarrow{155-350^{\circ}C} \\ & \xrightarrow{155-350^{\circ}C} & Mg(Cl_3ac)_2 \cdot (Et_2na)_2 + 3H_2O \end{array}$$



Fig. 1. TG and DTA curves of I.



Fig. 2. TG and DTA curves of II.



Fig. 3. TG and DTA curves of III.

 $\begin{array}{c} \operatorname{Mg(Cl_3ac)}_2 \cdot (\operatorname{Et}_2 \operatorname{na})_2 & \xrightarrow{350-640 \,^{\circ}\!\mathrm{C}} \\ & \xrightarrow{350-640 \,^{\circ}\!\mathrm{C}} & \operatorname{Mg(Cl_3ac)}_2 + 2\operatorname{Et}_2 \operatorname{na} \end{array}$ 

Table 1. Infrared Spectral Data ( $\tilde{\nu}/cm^{-1}$  200–4000) of Complexes I–III

Assignments	$Et_2na$	Ι	II	III
ν(CO)	1636	1637	1640	1638
$\nu(CN)$	1590	1605	1606	1608
$\gamma(CCC)$	644	652	639	642
	617	613	616	618
$\nu_{as}(COO^{-})$		1616	1651	1651
$\nu_{s}(COO^{-})$		1366	1414	1417
$\Delta_{COO}$	943	250	237	234
$\nu(C-C)$		947	949	947
$\nu$ (C—H) <sub>ac</sub>		2851, 918	2847, 919	2853, 920
ν(OH)		3231	3266	3331
Others		652, 710, 824,	762, 822,	669, 754, 770,
$(600 - 1000 \text{ cm}^{-1})$		878, 915	880, 970	795, 824, 880
$\pi(\mathrm{CO}_2)$		539	541	540

as = asymmetric, s = symmetric.

$$Mg(Cl_3ac)_2 \xrightarrow{640-820 \circ C} MgO + G.$$
 products

The DTA curve for the complex (Fig. 2) presents two endothermic peaks at 185 °C and 425 °C corresponding to the loss of  $3H_2O$  and two N,Ndiethylnicotinamide molecules, respectively, and an exothermic process at 725 °C corresponding to decomposition reaction of  $2Cl_3ac$ , with simultaneous formation of MgO.

The TG and DTA curves for  $Cu(Cl_3ac)_2 \cdot (Et_2na)_2 \cdot 3H_2O$  (*III*) are shown in Fig. 3. The TG curve for that complex indicates that it is stable at temperature up to 110°C, when there begins the slow decomposition to CuO, as to the final product formed at 790°C. The TG curve shows two bendings at 230°C and 600°C. They correspond to the presence of two intermediate decomposition products:  $Cu(Cl_3ac)_2 \cdot (Et_2na)_2$ , and  $Cu(Cl_3ac)_2$ . The most probable thermal decomposition scheme is

$$\begin{array}{c} \operatorname{Cu}(\operatorname{Cl}_3\operatorname{ac})_2 \cdot (\operatorname{Et}_2\operatorname{na})_2 \cdot 3\operatorname{H}_2\operatorname{O} & \xrightarrow{110 - 230\, \ensuremath{\mathbb{C}}} \\ & \xrightarrow{110 - 230\, \ensuremath{\mathbb{C}}} & \operatorname{Cu}(\operatorname{Cl}_3\operatorname{ac})_2 \cdot (\operatorname{Et}_2\operatorname{na})_2 + 3\operatorname{H}_2\operatorname{O} \end{array}$$

$$\begin{array}{c} \operatorname{Cu}(\operatorname{Cl}_3\operatorname{ac})_2 \cdot (\operatorname{Et}_2\operatorname{na})_2 \xrightarrow{230 - 600 \, ^{\circ} \mathrm{C}} \\ \xrightarrow{230 - 600 \, ^{\circ} \mathrm{C}} \quad \operatorname{Cu}(\operatorname{Cl}_3\operatorname{ac})_2 + 2\operatorname{Et}_2\operatorname{na} \end{array}$$

$$Cu(Cl_3ac)_2 \xrightarrow{600-790 \circ C} CuO + G.$$
 products

The DTA curve for the complex (Fig. 3) presents an endothermic peak at  $130 \,^{\circ}$ C corresponding to the loss of three molecules of water and two exothermic processes at  $340 \,^{\circ}$ C and  $660 \,^{\circ}$ C corresponding to decomposition reactions of two molecules of N,Ndiethylnicotinamide and  $2Cl_3ac$ , respectively, with simultaneous formation of CuO.

The results of thermal decomposition of the complexes were compared with literature, results of metal complexes with carboxylates and halogenocarboxylates [35—38]. The elimination of  $Et_2na$  is endothermic process in complexes *I* and *II* and exothermic process in complex *III*. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions [39—41].

The solid-state electronic spectrum of  $Cu(Cl_3ac)_2$   $\cdot (Et_2na)_2 \cdot 3H_2O$  exhibits a ligand field band with a maximum at 14500 cm<sup>-1</sup> which was identified with d-d transitions of the Cu(II) and a shoulder at 26000 cm<sup>-1</sup>. The shoulder should be characteristic of the bridging system with the antiferromagnetic interaction [42].

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared spectral data are reported in Table 1. The IR spectra of compounds I-III show broad absorption bands in the  $\tilde{\nu}$  range 3231-3331 cm<sup>-1</sup>. These frequencies correspond to the  $\nu_{s,as}(OH)$  [43]. These bands clearly confirm the presence of water of crystallization in the compounds. The compounds showed the carboxylate stretching frequencies  $\nu_s(\text{COO}^-)$  in the  $\tilde{\nu}$  range 1366—1417 cm<sup>-1</sup> and  $\nu_{\rm as}({\rm COO^-})$  in the  $\tilde{\nu}$ range 1616-1651 cm<sup>-1</sup>. The positions of the bands are characteristic of metal(II) carboxylate compounds [44]. Carboxylate ions can coordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging and there is an evidence of that fact in the IR spectrum. The analysis of COO<sup>-</sup> group bands frequencies allowed the determination of parameter  $\Delta_{\rm COO} = \tilde{\nu}(\nu_{\rm as}({\rm COO^-})) - \tilde{\nu}(\nu_{\rm s}({\rm COO^-})).$ The magnitude of  $\Delta_{COO}$  has been used by Nakamoto as a criterion of the way of carboxylate binding with metal ions. Calculated from the examined spectra values of  $\Delta_{\rm COO}$  are in the  $\tilde{\nu}$  range 234—250 cm<sup>-1</sup>. These values and three bands (COO<sup>-</sup> deformation) at 720— 920 cm<sup>-1</sup> and a strong band ( $\pi$ (CO)<sub>2</sub>) near 540 cm<sup>-1</sup> of complexes *I*—*III* are in good accord with the literature data for unidentately bonded carboxylate structures [43].

The stretching vibration of the C=N in the pyridine ring of N,N-diethylnicotinamide appeared at  $\tilde{\nu}$ = 1590 cm<sup>-1</sup> [45]. Upon complex formation the peak shifts to higher frequencies [46]. The shifts (to about 1605 cm<sup>-1</sup>) may suggest bond formation by the metal with the nitrogen of heterocyclic ring [45].

EPR spectrum of  $\text{Cu}(\text{Cl}_3\text{ac})_2 \cdot (\text{Et}_2\text{na})_2 \cdot 3\text{H}_2\text{O}$  contained the typical absorption band of dimeric species. The spectral feature shows absorption at low and high fields (Hz<sub>1</sub> and Hz<sub>2</sub>, respectively), with an asymmetrical absorption near 4500 G (H<sub>T</sub> 2). The spectrum can be interpreted by a spin Hamiltonian for axial symmetry:  $H = g_{\parallel}\beta H_2 S_2 + g_{\perp}(H_x S_x + H_Y S_Y) + D(S_2^2 + 2/3)$ , where S = 1 for the thermally accessible triple state, D is the zero-field parameter, and the other symbols have their usual meaning. The values obtained for the spin Hamiltonian parameters are:  $g_{\perp} = 2.01$ ;  $g_{\parallel} = 2.23$ ;  $g_{av} = 2.08$ .

Without X-ray analysis no definite structure can be described for the different components. We are not able to get suitable single crystal for the X-ray analysis. However, predictions have been made by using spectroscopic and analytical data and thermal decomposition studies.

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## REFERENCES

- Melník, M., Macášková, Ľ., and Mroziński, J., Polyhedron 7, 1745 (1988).
- 2. Melník, M., Coord. Chem. Rev. 36, 1 (1981).
- 3. Melník, M., Coord. Chem. Rev. 42, 259 (1982).
- Melník, M., Sirota, A., Ondrejkovičová, I., Jóna, E., and Hudecová, D., Progress in Coordination and Organometallic Chemistry, Proc. Int. Conf. Smolenice, Slovakia, p. 215. Slovak University of Technology Press, Bratislava, 1997.
- Jóna, E., Kubranová, M., Šimon, P., and Mroziński, J., J. Therm. Anal. 46, 1325 (1996).
- Jóna, E., Sirota, A., Šimon, P., and Kubranová, M., *Thermochim. Acta* 258, 161 (1995).
- Jóna, E., Sirota, A., Šimon, P., Horváth, I., and Kubranová, M., Progress in Coordination and Organometallic Chemistry, Proc. Int. Conf. Smolenice, Slovakia, p. 297. Slovak University of Technology Press, Bratislava, 1997.
- Papánková, B., Mašlejová, A., and Šimon, P., TER-MANAL '97, Proc. Int. Conf. Belušské Slatiny, Slovakia, p. 48. Slovak University of Technology Press, Bratislava, 1997.
- Skoršepa, J. S., Györyová, K., and Melník, M., J. Therm. Anal. 44, 169 (1995).

- Jóna, E., Hvastijová, M., and Kohut, J., J. Therm. Anal. 41, 161 (1994).
- 11. D'ascenzo, G., Ceipidor, U. B., Cardarelli, E., and Magri, A. D., *Thermochim. Acta* 13, 449 (1975).
- Jóna, E. and Jamnický, M., J. Therm. Anal. 27, 359 (1983).
- Patel, R. N. and Pandeya, K. B., J. Inorg. Biochem. 72, 109 (1998).
- Linert, W., Enamullah, M., Gutmann, V., and Jameson, R. F., Monatsh. Chem. 125, 661 (1994).
- 15. Jóna, E., Horváth, I., and Kubranová, M., Thermochim. Acta 221, 41 (1993).
- Kundu, K. and Miah, M. A. H., Jahangirnagar Univ. J. Sci. 19, 49 (1995).
- 17. Enamullah, M., Jahangirnagar Univ. J. Sci. 19, 55 (1995).
- Jóna, E., Horváth, I., Kubranová, M., and Koman, M., Thermochim. Acta 180, 307 (1991).
- Enamullah, M. and Linert, W., J. Coord. Chem. 35, 325 (1995).
- Patel, R. N. and Pandeya, K. B., Synth. React. Inorg. Met.-Org. Chem. 28, 23 (1998).
- Melník, M., Potočňak, I., Macášková, Ľ., and Mikloš, D., Polyhedron 15, 2159 (1996).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Anal. Appl. Pyrolysis 46, 147 (1998).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Therm. Anal. Cal. 56, 533 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Anal. Appl. Pyrolysis 48, 111 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., Pol. J. Chem. 73, 293 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Therm. Anal. Cal. 56, 541 (1999).
- Mojumdar, S. C., Melník, M., Jóna, E., and Hudecová, D., Chem. Papers 53, 265 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., Chem. Papers 53, 309 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Anal. Appl. Pyrolysis 53, 149 (1999).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Therm. Anal. Cal., in press.
- Mojumdar, S. C., Melník, M., and Jóna, E., Thermochim. Acta, in press.
- Mojumdar, S. C., Hudecová, D., Melník, M., and Jóna, E., Chem. Papers 54, 39 (2000).
- Mojumdar, S. C., Melník, M., and Jóna, E., J. Therm. Anal. Cal., in press.
- 34. Hökelek, T., Acta Crystallogr., Sect C 51, 2020 (1995).
- Allan, J. R. and Gavin, J., J. Therm. Anal. 18, 263 (1980).
- Mroziński, J. and Heyduk, E., Thermochim. Acta 93, 85 (1985).
- Melník, M., Mroziński, J., and Holloway, C. E., J. Coord. Chem. 29, 209 (1993).
- D'ascenzo, G., Ceipidor, U. B., and Angelis, G. D., Thermochim. Acta 58, 175 (1982).
- Šramko, T., Liptay, G., and Jóna, E., J. Therm. Anal. 12, 217 (1977).
- 40. Masuda, Y., Thermochim. Acta 39, 235 (1980).
- Jóna, E., Šramko, T., and Gažo, J., J. Therm. Anal. 16, 213 (1979).

- 42. Dubicki, L. and Martin, R. L., Inorg. Chem. 5, 2203 (1966).
- Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds. 2nd Edition, p. 80. Wiley— Interscience, New York, 1970.
- 44. Nakamoto, K., Morimoto, Y., and Martell, A. E., J. Am. Chem. Soc. 83, 4528 (1961).
- 45. Aslanian, D., Lautic, A., Mantai, Ch., and Baltanski, M., J. Chim. Phys. 72, 1052 (1957).
- 46. Kidani, Y., Noji, M., and Koike, H., Bull. Chem. Soc. Jpn. 48, 239 (1975).

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