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# THERMAL DECOMPOSITION OF Mg(II) COMPLEXES WITH RONICOL

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## Abstract

The thermal decomposition of the complexes $Mg(Clac)_2(ron)_2 \cdot 3H_2O$(**I**), $Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O$(**II**) and $Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O$(**III**), where *Clac*=$ClCH_2COO^-$, *Cl*$_2$*ac*=$Cl_2CHCOO^-$, *Cl*$_3$*ac*=$Cl_3CCOO^-$ and *ron*=3-pyridylcarbinol (ronicol) had been investigated in air atmosphere in temperature range 20–1000°C by means of TG and 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. The final product of the thermal decomposition was MgO. The thermal stability of the complexes can be ordered in the sequence: **I<III<II**. IR data suggest that ronicol was coordinated to Mg(II) through the nitrogen atom of its heterocyclic ring.

**Keywords:** acetate and halogenoacetates, DTA, IR, ronicol and Mg(II) complexes, TG

## Introduction

It is well-documented that heterocyclic compounds play a significant role in many biological systems. Especially six-membered ring systems being a component of several vitamins and drugs [1–2]. It is not surprising, therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms [3–14]. In order to enhance understanding of drug-metal ion interactions, we have been studying the thermal properties of magnesium(II) complexes with ronicol. Ronicol contains pyridine ring and is used in the clinical treatment of analgesics which is believed to act as anti-inflammatory analgesics.

The reveal of the relationship between the structure and thermolysis of metal carboxylate complexes, the study of the influence of metal and ligand nature on the process of thermal decomposition are of certain interest. This work is a continuation of previously reported studies [15–20] on the thermal and spectral properties of mag-

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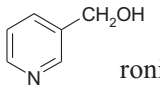
nesium(II) complexes with pyridine and substituted pyridines. But the reported data on thermal decomposition and IR-spectral analysis of halogenoacetato Mg(II) complexes with ronicol are too rare. Therefore, this paper describes the preparation of complexes formed by the mono-, di- and trichloroacetates with ronicol (see scheme), along with thermal analyses and IR spectral investigation of prepared complexes.



ronicol

## Experiment

*Preparation of compounds*

The complexes were prepared by treating ronicol (0.01 M) with appropriate Mg(II) halogenoacetate (0.005 M) in hot ethanol solution. The solution was left to stand at room temperature. The fine microcrystals that precipitated were filtered off, washed with cold ethanol and dried at room temperature.

*Measurements*

Elemental analyses (C, H, N) were carried out by means of a Carlo Erba 1106 analyzer. The infrared spectra were obtained on Philips analytical PU9800 FTIR spectrometer by using Nujol mulls in the range 200–4000 $cm^{-1}$, while thermal decomposition studies were 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 range 20–1000°C. The rate of temperature increase of 10°C $min^{-1}$ was chosen for all measurements.

## Results and discussion

*Analytical results of compounds*

The content of N, C and H was determined by elemental analysis and the content of Mg was established by complexometric titration. The analytical data of the compounds **I–III** reported in Table 1, shows a good agreement between the experimental and calculated data.

**Table 1** Analytical data of compounds

| Complex | Theoretical/% | | | | Experimental/% | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Mg | C | H | N | Mg |
| $Mg(Clac)_2(ron)_2 \cdot 3H_2O$ | 39.73 | 4.96 | 5.79 | 5.03 | 39.75 | 4.93 | 5.75 | 5.05 |
| $Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O$ | 34.77 | 3.98 | 5.07 | 4.40 | 34.70 | 4.08 | 5.12 | 4.42 |
| $Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O$ | 30.91 | 3.22 | 4.51 | 3.91 | 30.89 | 3.20 | 4.42 | 3.90 |

*Thermal behaviour of the compounds*

The thermal decomposition data of the compounds **I–III** are collected in Table 2. The complexes **I–III** are thermally relatively stable. Thermal decomposition of the compounds is the multi-stage process. The subsequent detachment of the ligands was observed. The final product was MgO.

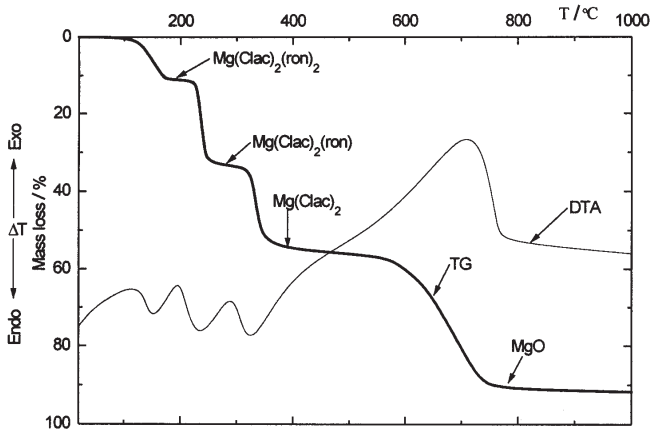



**Fig. 1** TG and DTA curves of $Mg(Clac)_2(ron)_2.3H_2O$

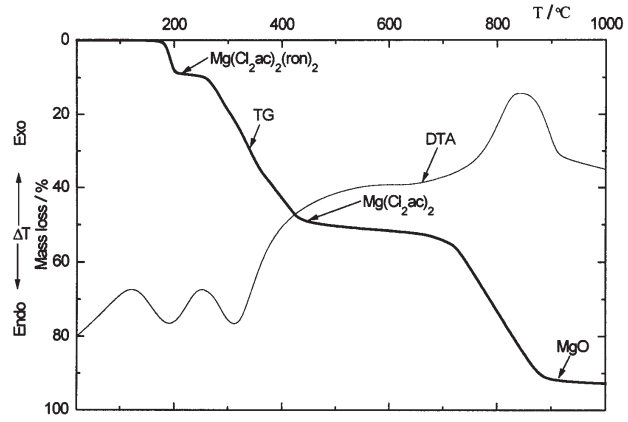



**Fig. 2** TG and DTA curves of $Mg(Cl_2ac)_2(ron)_2.3H_2O$

The TG and DTA curves for $Mg(Clac)_2(ron)_2 \cdot 3H_2O$ is shown in Fig. 1. The TG curve for that complex indicates, that it is stable at temperature up to 105°C, when begins the slow decomposition to MgO, as to the final product formed at 760°C. The TG curve shows three bending at 225, 315 and 570°C. They correspond to the presence of three intermediate decomposition products: $Mg(Clac)_2(ron)_2$, $Mg(Clac)_2(ron)$ and $Mg(Clac)_2$. The most probable thermal decomposition scheme is:

**Table 2** Thermal decomposition data

| Complex | DTA | | | TG | | |
|---|---|---|---|---|---|---|
| | $T_{peaks}$/°C | | $T_{range}$/°C | Mass loss found(calc)/% | Loss of | Composition of the residue found(calc)/% |
| $Mg(Clac)_2(ron)_2 \cdot 3H_2O$ | 150 | endo | 100–195 | 11.20(11.17) | $3H_2O$ | |
| | 240 | endo | 195–290 | 22.60(22.56) | ron | MgO |
| | 340 | endo | 290–500 | 22.50(22.56) | ron | 8.30(8.34) |
| | 710 | exo | 500–800 | decomposition | | |
| $Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O$ | 190 | endo | 115–250 | 9.40(9.42 | $3H_2O$ | |
| | 315 | endo | 250–500 | 39.80(39.84) | 2ron | MgO |
| | 850 | exo | 500–915 | decomposition | | 7.20(7.23) |
| $Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O$ | 140 | endo | 100–160 | 8.60(8.69) | $3H_2O$ | |
| | 245 | endo | 160–300 | 35.20(35.10) | 2ron | MgO |
| | 550 | exo | 300–730 | decomposition | | 6.50(6.49) |

$$Mg(Clac)_2(ron)_2 \cdot 3H_2O \xrightarrow{105-225°C} Mg(Clac)_2(ron)_2$$

$$Mg(Clac)_2(ron)_2 \xrightarrow{225-315°C} Mg(Clac)_2(ron)$$

$$Mg(Clac)_2(ron) \xrightarrow{315-570°C} Mg(Clac)_2$$

$$Mg(Clac)_2 \xrightarrow{570-760°C} MgO$$

The DTA curve for the complex (Fig. 1) presents three endothermic peaks at 150, 240 and 340°C corresponding to the loss of $3H_2O$, ron and ron, respectively and a broad exothermic maximum with center about 710°C corresponding to decomposition reaction of 2Clac with simultaneous formation of MgO.

The TG and DTA curves for $Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O$ is shown in Fig. 2. The TG curve for that complex indicates, that it is stable at temperature up to 175°C, when begins the decomposition to MgO, as to the final product formed at 900°C. The TG curve shows two bending at 250 and 700°C. They correspond to the presence of two intermediate decomposition products: $Mg(Cl_2ac)_2(ron)_2$ and $Mg(Cl_2ac)_2$. The most probable thermal decomposition scheme is:

$$Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O \xrightarrow{175-250°C} Mg(Cl_2ac)_2(ron)_2$$

$$Mg(Cl_2ac)_2(ron)_2 \xrightarrow{250-700°C} Mg(Cl_2ac)_2$$

$$Mg(Cl_2ac)_2 \xrightarrow{700-900°C} MgO$$

The DTA curve for the complex (Fig. 2) presents two endothermic peaks at 190 and 315°C corresponding to the loss of $3H_2O$ and 2ron, respectively and an exothermic maximum with center about 850°C corresponding to decomposition reaction of $2Cl_2ac$ with simultaneous formation of MgO.

The TG and DTA curves for $Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O$ is shown in Fig. 3. The TG curve for that complex indicates, that it is stable at temperature up to 110°C, when begins the decomposition to MgO, as to the final product formed at 630°C.

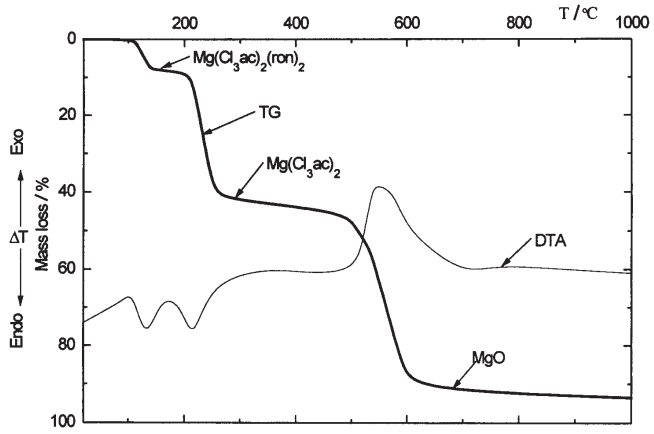



**Fig. 3** TG and DTA curves of $Mg(Cl_3ac)_2(ron)_2.3H_2O$

The TG curve shows two bending at 225 and 485°C. They correspond to the presence of two intermediate decomposition products: $Mg(Cl_3ac)_2(ron)_2$ and $Mg(Cl_3ac)_2$. The most probable thermal decomposition scheme is:

$$Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O \xrightarrow{110-200\,^\circ C} Mg(Cl_3ac)_2(ron)_2$$

$$Mg(Cl_3ac)_2(ron)_2 \xrightarrow{200-485\,^\circ C} Mg(Cl_3ac)_2$$

$$Mg(Cl_3ac)_2 \xrightarrow{485-630\,^\circ C} MgO$$

The DTA curve for the complex (Fig. 3) presents two endothermic peaks at 140 and 245°C corresponding to the loss of $3H_2O$ and 2ron, respectively and an exothermic maximum with center about 550°C corresponding to decomposition reaction of $2Cl_3ac$ with simultaneous formation of MgO.

*IR-spectra*

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared frequencies attributed to the vibrations of the complexes **I–III** are reported in Table 3.

**Table 3** Infrared spectral data (4000–200 $cm^{-1}$) of complexes **I–III**

| Assignments | Ronicol | **I** | **II** | **III** |
|---|---|---|---|---|
| ν(CN) | 1597 | 1598 | 1591 | 1590 |
| γ(CCC) | 640 | 619 | 637 | 646 |
| | 611 | 610 | 610 | 613 |
| ν(C–C) | 953 | 955 | 952 | 949 |
| Mg–N | | 206, 214, 228 | 214, 231 | 203, 212, 230 |
| $\nu COO^-$(as) | | 1684 | 1632 | 1665 |
| $\nu COO^-$(s) | | 1346 | 1462 | 1366 |
| $\Delta_{COO}$ | | 338 | 170 | 299 |
| $\nu(C–H)_{ac}$ | | 2849, 954 | 2845 | 2928, 937 |
| $\nu(C–H)_{ring}$ | 828 | 841 | 824 | 825 |
| ν(OH) | | 3277 | 3366 | 3380 |
| δ(HOH) | | 1637 | 1631 | 1607 |
| Others (650–1000 $cm^{-1}$) | | 694, 770, 816 893, 984 | 772 | 677, 802, 831 938 |
| ν(Mg–O) | | 262, 382 | 310, 377 | 264, 303, 367 |

as=antisymmetric and s=symmetric

The absorption bands ν(OH) and δ(HOH) which occur in the range 3380–3277 and 1637–1607 $cm^{-1}$, respectively confirm the presence of water of crystallization. The absorption bands which occur in the range 1000–600 (Rocking and Wagging stretching) and 382–262 $cm^{-1}$ ν(Mg–O) confirm the pres-

ence of water as coordinated in the complexes [21]. The presence of water as water of crystallization and as coordinated water in the compounds is further borne out by the thermal decomposition data. 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 $COO^-$ group bands frequencies allowed on determination of parameter $\Delta_{COO}$ $=\nu COO^-(as)–COO^-(s)$. The magnitude of $\Delta_{COO}$ has been used by Nakamoto [22] as a criteria of the way of carboxylate binding with metal ions. Calculated from the examined spectra values of $\Delta_{COO}$ of complexes **I** and **III** are 338 and 299 $cm^{-1}$, respectively. These values and three bands (COO deformation ) at 920–720 $cm^{-1}$ in complexes **I** and **III** are in good agreement with the literature data for unidentately bonded acetates structures [23]. In complex **II**, three bands (COO deformation) at 920–720 $cm^{-1}$ are not present and the value of $\Delta_{COO}$=177, which is characteristic of bridging carboxylate structure. The absorption bands which occur in the range 231–206 $cm^{-1}$ $\nu$(Mg–N) confirm the coordination of ronicol to Mg ion through the nitrogen atom of its heterocyclic ring.

## Conclusions

All of the complexes **I–III** are hydrated, stable in air and soluble in water, ethanol, methanol and dimethylsulfoxide. Heating the compounds first results in a release of water molecules. The loss of the volatile ligand (ronicol) occurs (on the TG curves) in two steps(-ron, -ron) in complex **I** and in one step (-2ron) in complexes **II** and **III**. The thermal stability of the complexes can be ordered in the sequence: **I<III<II**. The results reveal that MgO is left as residue at the end of the thermal degradation experiments of the compounds (**I–III**). The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions [24–25]. By means of IR spectral analysis the stereochemistry around Mg(II) atom in the compounds had been studied. Infrared data is in accordance with the literature data for unidentately bonded acetates structures of complexes **I** and **III** and bridging carboxylate structure in complex **II**. Ronicol was coordinated to Mg(II) through the nitrogen atom of its heterocyclic ring in complexes **I**–**III**. The preliminary study has shown that the complexes do have a biological activity. Without X–ray analysis, no definite structure can be described for the different components. However, spectroscopic and analytical data available enable us to predict structures and we can also use thermal decomposition studies to help us.

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## References

1 E. Jóna, M. Kubranová, P. Šimon and J. Mroziński, J. Thermal Anal., 46 (1996) 1325.
2 E. Jóna, A. Sirota, P. Šimon and M. Kubranová, Thermochim. Acta, 258 (1995) 161.

3 E. Jóna, A. Sirota, I. Horvath and M. Kubranová, Progress in Coordination and Organometallic Chemistry, Proc. Int. Conf. Smolenice, Slovakia, June 9-13, 1997, Slovak Technical University Press, Bratislava 1997.
4 B. Papánková, A. Mašlejová and P. Šimon, TERMANAL '97, Proc. Int. Conf. Belušské Slatiny, Slovakia, October 1-3, 1997, CHTF-STU Press, Bratislava 1997.
5 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
6 K. Györyová, V. Balek and V. Zeleňak, Thermochim. Acta, 234 (1994) 221.
7 W. Linert, M. Enamullah, V. Gutmann and R. F. Jameson, Monatsh. Chem., 125 (1994) 661.
8 K. Kundu and M. A. H. Miah, Jahangirnagar Univ. J. Sci., 19 (1995) 49.
9 M. Enamullah and W. Linert, J. Coord. Chem., 35 (1995) 325.
10 R. N. Patel and K. B. Pandeya, Synth. React. Inorg. Met.-Org. Chem., 28 (1998) 23.
11 R. N. Patel and K. B. Pandeya, J. Inorg. Biochem., 72 (1998) 109.
12 E. Jóna, M. Hvastijová and J. Kohut, J. Thermal Anal., 41 (1994) 161.
13 G. D'ascenzo, U. B. Ceipidor, E. Cardarelli and A. D. Magri, Thermochim. Acta, 13 (1975) 449.
14 E. Jóna and M. Jamnický, J. Thermal Anal., 27 (1983) 359.
15 S. C. Mojumdar, M. Melník and E. Jóna, Polish J. Chem., 73 (1999) 293.
16 S. C. Mojumdar, M. Valko and M. Melník, Chem. papers, 52 (1998) 650.
17 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrol., 46 (1998) 147.
18 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrol., 48 (1999) 111.
19 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 533.
20 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 541.
21 G. Deveto, G. Ponticelli and C. Preti, J. Inorg. Nucl. Chem., 37 (1975) 1635.
22 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, J. Wiley, New York 4th edn., 1986.
23 D. Stoilova, G. Nikolov and K. Balarev, Izv. Akad. Nauk SSSR, Ser. Khim., 9 (1976) 371.
24 T. Šramko, G. Liptay and E. Jóna, J. Thermal Anal., 12 (1977) 217.
25 Y. Masuda, Thermochim. Acta, 39 (1980) 235.