

THERMAL BEHAVIOR OF SOME NEW TRIAZOLE DERIVATIVE COMPLEXES

Mihaela Badea^{1*}, Rodica Olar¹, Dana Marinescu¹ and Gina Vasile²

¹University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 90-92 Panduri St., 050663 Sector 5 Bucharest, Romania

²University of Agronomical Sciences and Veterinary Medicine, Department of Agrochemistry, Bd. Marasti 59 Bucharest, Romania

A series of new complexes with mixed ligands of the type $[\text{ML}(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot n\text{H}_2\text{O}$ ((1) $M=\text{Mn}$, $n=1$; (2) $M=\text{Co(II)}$, $n=2$; (3) $M=\text{Ni(II)}$, $n=4$; (4) $M=\text{Cu(II)}$, $n=1.5$; (5) $M=\text{Zn(II)}$, $n=0$; $L=3\text{-amino-1,2,4-triazole}$ and $(\text{C}_3\text{H}_3\text{O}_2)=\text{acrylate anion}$) were synthesized and characterised by chemical analysis and IR data. In all complexes the 3-amino-1,2,4-triazole acts as bridge while the acrylate acts as bidentate ligand except for complex (5) where it is found as unidentate. The thermal behaviour steps were investigated in nitrogen flow. The thermal transformations are complex processes according to TG and DTG curves including dehydration, acrylate ion and 3-amino-1,2,4-triazole degradation respectively. The final products of decomposition are the most stable metal oxides, except for complex (4) that leads to metallic copper.

Keywords: acrylate, 3-amino-1,2,4-triazole, carbonate, complexes, thermal stability

Introduction

Finding new species, with a wide spectrum of biological activity (antimicrobial, antiviral) and also low cytotoxicity represents a very important aspect in the biochemical research area. This is due to the fact that the pathogen agents continuously undergo mutations and also the drugs used to treat the viral diseases develop in time a certain tolerance, while in some cases the use of these can lead to toxic effects.

One of our research directions is to obtain complex species of biocations that possess bioactive ligands and polymerizable functional groups designed to obtain products with antiseptic and anti-infectious activity.

The selection of acrylate ion as ligand was generated by their multiple uses such as excipients for different drugs and for obtaining prosthetic devices used in biomedicine (urinary catheters, central vein catheters, cardiac valves, stomatologic materials) [1–4]. Moreover, the chemistry of 1,2,4-triazole derivatives has also received much attention because of their significant biologic activities [5].

Besides having herbicidal activity [6], 2-amino-1,3,4-triazole has been found as inhibitor for enzymatic processes [7–9]. From coordinative point of view, it has been evidenced that 3-amino-1,2,4-triazole can act as monodentate [10] as well as bridge through the two [11, 12] or three nitrogen atoms of the triazole ring [13] as well as through all nitrogen atoms [14].

In order to modulate biological properties of acrylate complexes, five new complexes with mixed lig-

ands have been synthesized and characterized. These compounds were obtained from the reaction of the metal acrylate with 3-amino-1,2,4-triazole. The complexes were formulated on the basis of analytical and spectral data as: $[\text{ML}(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot n\text{H}_2\text{O}$ ((1) $M=\text{Mn(II)}$, $n=1$; (2) $M=\text{Co(II)}$, $n=2$; (3) $M=\text{Ni(II)}$, $n=4$; (4) $M=\text{Cu(II)}$, $n=1.5$; (5) $M=\text{Zn(II)}$, $n=0$; $L=3\text{-amino-1,2,4-triazole}$ and $(\text{C}_3\text{H}_3\text{O}_2)=\text{acrylate anion}$).

The thermal behaviour provided confirmation of the complexes composition as well as the number and the nature of water molecules and the intervals of thermal stability. The thermal transformations are complex processes according to TG and DTA curves including dehydration, acrylate ion as well as 3-amino-1,2,4-triazole thermolysis. The products of decomposition are the metal oxides except for complex (4) that generates metallic copper.

Experimental

All chemicals were purchased from Aldrich and Merck, reagent grade and were used without further purification.

Synthesis of the complexes

Complex $[\text{MnL}(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot \text{H}_2\text{O}$ (1): 0.197 g of manganese acrylate were dissolved by stirring in a 15 mL mixture water:ethanol (1:2 v/v). To the colourless obtained solution was added under

* Author for correspondence: e_m_badea@yahoo.com, badea.elena@unibuc.ro

continuous stirring 0.084 g of 3-amino-1,2,4-triazole (*L*). There was no colour modification. The reaction mixture was stirred 1 h. The obtained solution was left to stand at room temperature for several days. The white microcrystals obtained were filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Mn, 18.27; C, 32.24; H, 3.87; N, 18.86%; calculated for $\text{MnC}_8\text{H}_{12}\text{N}_4\text{O}_5$: Mn, 18.36; C, 32.12; H, 4.04; N, 18.73%; IR (KBr pellet), cm^{-1} : $\nu_{\text{H}_2\text{O}}$, 3450sh; $\nu_{\text{as}(\text{NH}_2)}$, 3410sh; $\nu_{\text{s}(\text{NH}_2)}$, 3355s; ν_{NH} , 3214sh, 3073m; $\nu_{\text{as}(\text{COO})}$, 1540vs; $\nu_{\text{C}=\text{N}}$, 1646vs; $\nu_{\text{s}(\text{COO})}$, 1363m; $\nu_{\text{C}-\text{N}}$, 1214m; $\nu_{\text{N}-\text{N}}$, 1054m, 986m.

Complex $[\text{CoL}(\text{C}_3\text{H}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$ (**2**): 0.236 g of cobalt acrylate were dissolved under continuous stirring in 15 mL mixture water: ethanol (1:2 *v/v*). To the pale violet solution 0.084 g of 3-amino-1,2,4-triazole (*L*) was added. The colour of the reaction mixture turns rapidly to dark reddish and a precipitate was obtained. The reaction mixture was stirred for 1 h. The reddish precipitate was filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Co, 18.22; C, 29.98; H, 4.25; N, 17.55%; calculated for $\text{CoC}_8\text{H}_{14}\text{N}_4\text{O}_6$: Co, 18.35; C, 29.92; H, 4.39; N, 17.44%; IR (KBr pellet), cm^{-1} : $\nu_{\text{H}_2\text{O}}$, 3460sh; $\nu_{\text{as}(\text{NH}_2)}$, 3420sh; $\nu_{\text{s}(\text{NH}_2)}$, 3333s; ν_{NH} , 3210sh, 3065sh; $\nu_{\text{as}(\text{COO})}$, 1538vs; $\nu_{\text{C}=\text{N}}$, 1620vs; $\nu_{\text{s}(\text{COO})}$, 1361m; $\nu_{\text{C}-\text{N}}$, 1226m; $\nu_{\text{N}-\text{N}}$, 1059m, 993m.

Complex $[\text{NiL}(\text{C}_3\text{H}_3\text{O}_2)] \cdot 4\text{H}_2\text{O}$ (**3**): 0.236 g of nickel acrylate was dissolved by stirring in 15 mL mixture water:ethanol (1:2 *v/v*). At the pale green solution 0.084 g of 3-amino-1,2,4-triazole (*L*) were added and the colour turns in turquoise. The solution was stirred for one hour and was left to stand at room temperature for several days. The obtained pale blue compound was filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Ni, 16.34; C, 26.78; H, 4.88; N, 15.86%; calculated for $\text{NiC}_8\text{H}_{18}\text{N}_4\text{O}_8$: Ni, 16.48; C, 26.92; H, 5.08; N, 15.70%; IR (KBr pellet), cm^{-1} : $\nu_{\text{H}_2\text{O}}$, 3550sh; $\nu_{\text{as}(\text{NH}_2)}$, 3400sh; $\nu_{\text{s}(\text{NH}_2)}$, 3328s; ν_{NH} , 3255sh, 3090sh; $\nu_{\text{C}=\text{N}}$, 1542s; $\nu_{\text{as}(\text{COO})}$, 1546vs; $\nu_{\text{s}(\text{COO})}$, 1362m; $\nu_{\text{C}-\text{N}}$, 1213m; $\nu_{\text{N}-\text{N}}$, 1063m, 990m.

Complex $[\text{CuL}(\text{C}_3\text{H}_3\text{O}_2)] \cdot 1.5\text{H}_2\text{O}$ (**4**): 0.223 g of copper acrylate was dissolved by stirring in 15 mL mixture water:ethanol (1:2 *v/v*). An amount of 0.084 g of 3-amino-1,2,4-triazole (*L*) was added under continuous stirring to the blue copper acrylate solution. The colour of reaction mixture turns rapidly to turquoise. The mixture was stirred for 1 h. The dark green precipitate was filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Cu, 19.87; C, 30.27; H, 4.01; N, 17.75%; calculated for $\text{CuC}_8\text{H}_{13}\text{N}_4\text{O}_{5.5}$: Cu, 20.06; C, 30.33; H, 4.14; N, 17.69%; IR (KBr pellet), cm^{-1} : $\nu_{\text{H}_2\text{O}}$, 3480sh; $\nu_{\text{as}(\text{NH}_2)}$, 3419s; $\nu_{\text{s}(\text{NH}_2)}$, 3340sh; ν_{NH} , 3210sh, 3060sh;

$\nu_{\text{C}=\text{N}}$, 1640s; $\nu_{\text{as}(\text{COO})}$, 1549vs; $\nu_{\text{s}(\text{COO})}$, 1356m; $\nu_{\text{C}-\text{N}}$, 1222m; $\nu_{\text{N}-\text{N}}$, 1065m, 989m.

Complex $[\text{ZnL}(\text{C}_3\text{H}_3\text{O}_2)]$ (**5**): 0.207 g of zinc acrylate was dissolved under continuous stirring in 15 mL mixture water:ethanol (1:2 *v/v*). To the opalescent obtained solution was added 0.084 g of 3-amino-1,2,4-triazole (*L*). It was obtained immediately a white precipitate. The reaction mixture was stirred for 30 min. The precipitate was filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Zn, 22.35; C, 32.82; H, 3.32; N, 19.35%; calculated for $\text{ZnC}_8\text{H}_{10}\text{N}_4\text{O}_4$: Zn, 22.42; C, 32.96; H, 3.46; N, 19.22%; IR (KBr pellet), cm^{-1} : $\nu_{\text{as}(\text{NH}_2)}$, 3400sh; $\nu_{\text{s}(\text{NH}_2)}$, 3365s; ν_{NH} , 3210m, 3050sh; $\nu_{\text{C}=\text{N}}$, 1644s; $\nu_{\text{as}(\text{COO})}$, 1573vs; $\nu_{\text{s}(\text{COO})}$, 1357m; $\nu_{\text{C}-\text{N}}$, 1224m; $\nu_{\text{N}-\text{N}}$, 1069m, 984m.

Methods

The chemical analysis and IR spectral data were used in order to confirm the nature of some intermediates and also the final products. Chemical analysis of carbon and nitrogen has been performed using an EA 1110 analyzer. Manganese, cobalt, nickel and zinc were determined gravimetrically in the laboratories of Inorganic Chemistry Department. Copper was determined volumetrically using the iodometry method. All the chemical analyses were performed on the air-dried compounds without heating to constant mass.

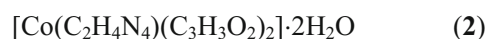
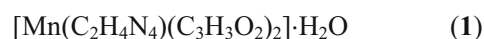
IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the 400–4000 cm^{-1} range.

The heating curves (TG, DTA and DTG) were recorded using a Labsys 1200 Setaram instrument, with a sample mass of 6–27 mg over the temperature range of 20–1000°C, using a heating rate of 10 K min^{-1} . The measurements were carried out in a nitrogen atmosphere (flow rate 20 $\text{cm}^3 \text{min}^{-1}$) by using alumina crucibles.

Results and discussion

Physico-chemical characterization of complexes

In this paper, we report the preparation and physico-chemical characterisation of some complexes with acrylate and 3-amino-1,2,4-triazole. The major goal of this paper was to evidence the thermal behaviour, in nitrogen flow, of these complexes that could be used as intermediate for obtaining some polymer metal containing species. The complexes have been formulated on the basis of chemical analysis and IR spectra as it follows:



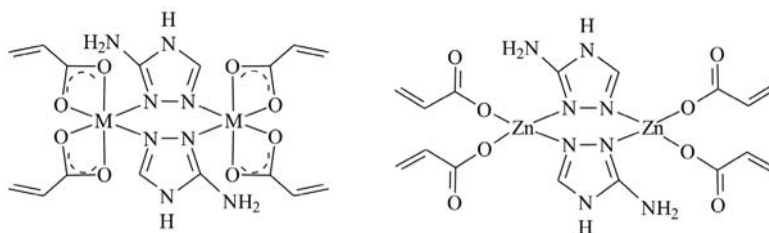
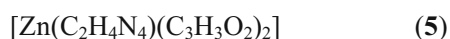
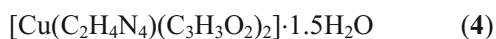
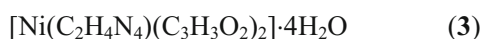


Fig. 1 The proposed coordination for complexes; $M = \text{Mn, Co, Ni, Cu}$



These compounds were obtained from the reaction of the corresponding metal acrylate with 3-amino-1,2,4-triazole. In order to maintain the molar ratio metal ion : amine (1:1), a lower amine quantity was used.

In all complexes the 3-amino-1,2,4-triazole acts as bridge while the acrylate acts as bidentate ligand except for complex (5) where it is found as unidentate.

In the IR spectra of complexes are viewed the characteristic patterns of 3-amino-1,2,4-triazole (experimental part) that generate bands characteristic for amine group in the $3000\text{--}3400\text{ cm}^{-1}$ range. At about 1640 cm^{-1} a very strong band for all complexes is assigned to $\nu_{\text{C}=\text{N}}$ vibrations. In the 3-amino-1,2,4-triazole spectrum two bands appear at 1048 and 969 cm^{-1} assigned to $\nu_{\text{N}=\text{N}}$ vibration mode. For all complexes these bands are shifted to higher wave numbers indicating that this ligand acts as bridge.

The characteristic bands assigned to the acrylate fragment ($\nu_{\text{as}(\text{COO})}$ and $\nu_{\text{s}(\text{COO})}$) can be identified also in all complexes spectra. It is known that the $\Delta = \nu_{\text{as}(\text{COO})} - \nu_{\text{s}(\text{COO})}$ value is an indication of the coordination mode associated with this anion [15]. Thus, the Δ value of 216 cm^{-1} in the case of compound (5) indicates the unidentate coordination mode while the lower difference for other complexes is correlated with the presence of this ligand as bidentate [16]. The presence of water molecule in complexes generates the appearance of a large band about 3500 cm^{-1} assigned to ν_{OH} stretching vibrations [16].

On the basis of the above data the proposed coordination for the complexes is as it follows (Fig. 1):

Thermal behavior of complexes

The main objective of this paper was to analyse the thermal behaviour of the complexes in order to acquire a polymeric fashion for them.

The results concerning the thermal degradation of the new complexes are presented as it follows.

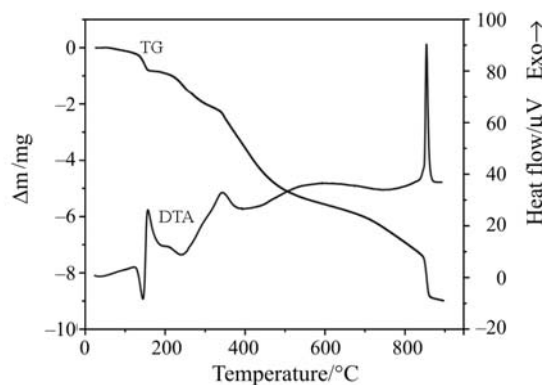


Fig. 2 TG and DTA curves of $[\text{Mn}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot \text{H}_2\text{O}$ (1)

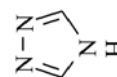
Thermal decomposition of $[\text{Mn}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot \text{H}_2\text{O}$

The TG and DTA curves corresponding to the complex (1) heated in the $20\text{--}900^\circ\text{C}$ temperature range are presented in Fig. 2 and indicate that decomposition follows four steps.

The first step of compound transformation consists in an endothermic elimination of water molecules (Table 1). Considering that the IR spectrum indicates clearly the bidentate nature of acrylate results that the water molecules are uncoordinated. On this basis it is surprising that they are eliminated at so high temperatures. This behaviour could indicate that these molecules are involved in strong hydrogen interactions with the acrylate, as it was also observed in the case of other acrylate complexes previously reported [17, 18]. The second step, endothermic, is not a single one being an overlap of at least two processes as both TG and DTA curves indicate. This step corresponds to the release of the amino group from 3-amino-1,2,4-triazole as well as to acrylate into carbonate transformation. This behaviour at heating of the coordinated 2-amino-1,2,4-triazole was already observed for other complexes bearing this ligand [13]. Next step, endothermic also, corresponds to 1,2,4-triazole ring loss according to TG curve. The resulted intermediate, MnCO_3 , was isolated and characterized using elemental analysis and IR spectrum (Fig. 3). The intermediate at 840°C displays bands characteristic of bidentate carbonate ion: 1605 ($\nu_{1(\text{CO}_3)}$) 1030 ($\nu_{2(\text{CO}_3)}$) and 760 cm^{-1} ($\nu_{3(\text{CO}_3)}$) [16]. Moreover, the chemical

Table 1 Thermal behaviour data (in nitrogen atmosphere) for complexes

| Complex | Step | Thermal effect | Temperature range/°C | $\Delta m_{\text{exp}}/\%$ | $\Delta m_{\text{calc}}/\%$ | The nature of intermediate |
|--|------|----------------|----------------------|----------------------------|-----------------------------|--|
| [Mn(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂]·H ₂ O | 1 | endothermic | 120–165 | 6.12 | 6.02 | [Mn(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂] |
| | 2 | endothermic | 165–470 | 32.26 | 32.46 | Mn(C ₂ H ₂ N ₃)·CO ₃ |
| | 3 | endothermic | 470–845 | 23.16 | 23.08 | MnCO ₃ |
| | 4 | exothermic | 845–900 | 12.15 | 12.04 | Mn ₂ O ₃ |
| [Co(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂]·2H ₂ O | 1 | endothermic | 50–150 | 11.25 | 11.22 | [Co(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂] |
| | 2 | endothermic | 150–470 | 30.18 | 30.24 | Co(C ₂ H ₂ N ₃)*·(CO ₃) |
| | 3 | exothermic | 470–730 | 25.60 | 25.52 | 6CoCO ₃ ·Co ₃ O ₄ |
| | 4 | endothermic | 730–950 | 7.86 | 8.03 | Co ₃ O ₄ |
| [Ni(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂]·4H ₂ O | 1 | endothermic | 55–220 | 20.02 | 20.19 | [Ni(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂] |
| | 2 | endothermic | 220–480 | 46.75 | 46.55 | NiCO ₃ |
| | 3 | exothermic | 480–800 | 12.16 | 12.33 | NiO |
| [Cu(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂]·1.5H ₂ O | 1 | endothermic | 50–150 | 8.40 | 8.53 | [Cu(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂] |
| | 2 | endothermic | 150–395 | 30.72 | 30.65 | Cu(C ₂ H ₂ N ₃)*·(CO ₃) |
| | 3 | exothermic | 395–800 | 40.72 | 40.75 | Cu |
| [Zn(C ₂ H ₄ N ₄)(C ₃ H ₃ O ₂) ₂] | 1 | endothermic | 250–500 | 33.59 | 33.31 | [Zn(C ₂ H ₂ N ₃)*·(CO ₃) |
| | 2 | endothermic | 500–790 | 23.32 | 23.68 | ZnCO ₃ |
| | 3 | exothermic | 790–900 | 14.86 | 15.09 | ZnO |



*

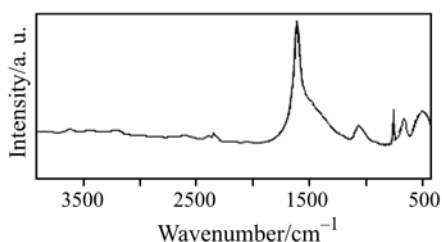


Fig. 3 IR spectrum of the carbonate intermediate resulted at 840°C from thermal degradation of complex (1)

composition corresponds to a minimal formula MnCO_3 (%calc./exp., Mn, 47.79/47.98; C, 10.45/10.24).

MnCO_3 turns in Mn_2O_3 in the last step, process accompanied by a strong exothermic effect (found/calcd. overall mass loss: 73.69/73.60).

Thermal decomposition of $[\text{Co}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$

Complex (2) loses the crystallization water in the 50–150°C range. The second step, similar with that observed for (1) occurs with amino group release and acrylate into carbonate transformation, but the two processes seem to be better evidenced for compound (2). In the third step the complex intermediate leads to $6\text{CoCO}_3 \cdot \text{Co}_3\text{O}_4$ as a result of the triazole ring elimination and partially decomposition of CoCO_3 . The remaining CoCO_3 generates Co_3O_4 as final residue (found/calcd. overall mass loss: 74.89/75.01).

Thermal decomposition of $[\text{Ni}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$

According to the TG profile the decomposition of $[\text{Ni}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$ (3) occurs in three, well-defined steps (found/calcd. overall mass loss: 78.93/79.06). After water loss in the 55–220°C range, the 3-amino-1,2,4-triazole elimination as well as acrylate into carbonate transformation occur in the second step. Unlike the other species of this type for Ni(II) complex the elimination of the amino group and triazole ring respectively are not delimited. The carbonate leads to NiO in the final step according to the mass variation.

Thermal decomposition of $[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_4] \cdot 1.5\text{H}_2\text{O}$

The decomposition of complex (4) comprises also three steps and starts with water elimination, process that also occurs at high temperatures. The anhydrous species releases then the amine group and the acrylate ion turns into carbonate. The next step is a very complex one and consists in triazole ring elimination and carbonate decomposition respectively. The final pro-

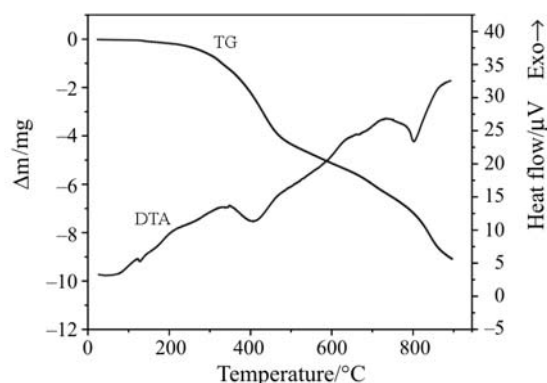


Fig. 4 TG and DTA curves of $[\text{Zn}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_2]$ (5)

duct is metallic copper (found/calcd. overall mass loss: 79.84/79.93).

Thermal decomposition of $[\text{Zn}(\text{C}_2\text{H}_4\text{N}_4)(\text{C}_3\text{H}_3\text{O}_2)_4]$

The anhydrous nature of compound (5) complex is revealed by the fact that decomposition starts up to 250°C. The thermal decomposition (Fig. 4) begins with the amine group release followed by the acrylate degradation. The remaining triazole ring is eliminated in the second step. The third step, exothermic one, corresponds to carbonate transformation into oxide (found/calcd. overall mass loss: 71.77/72.08).

Conclusions

The new complex compounds of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with mixed ligands (3-amino-1,2,4-triazole and acrylate) belong to a class of coordination compounds of current interest having into its composition a ligand which could be involved in polymerisation processes.

Except for complex (5) where acrylate acts as monodentate, for other complexes this ion acts as bidentate according to IR data. The 3-amino-1,2,4-triazole function as bridge for all complexes.

Thermal analysis (TG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules. Except for complex (3) the amino group release was observed in the second step. It was also evidenced the existence of an intermediate step corresponding to the formation of metal carbonates for all compounds.

Acknowledgements

This work was partially supported by the VIASAN grant nr. 142/2006 of the Romanian Ministry of Education and Research.

References

- 1 E. M. Ouriemchi, T. P. Ghosh and J. M. Vergnaud, *Polym. Test.*, 19 (2000) 889.
- 2 G. Schmalz, *J. Dent. Res.*, 81 (2002) 660.
- 3 Y. Yokoyama, H. Iwamoto and A. Y. Amanaka, *J. Artif. Organs*, 9 (2006) 71.
- 4 K. Albrecht and A. Bernkap-Schnürch, *Nanomed.*, 2 (2007) 41.
- 5 B. S. Holla, K. N. Poorjary, B. S. Rao and M. K. Shivananda, *Eur. J. Med. Chem.*, 37 (2002) 511.
- 6 C. C. Kumar and G. Padmanaban, *Biochim. Biophys. Acta*, 607 (1980) 339.
- 7 D. R. Doerge and W. P. Niemczura, *Chem. Res. Toxicol.*, 2 (1989) 100.
- 8 E. A. Havir, *Plant Physiol.*, 99 (1992) 533.
- 9 J. K. Joung, E. I. Ramm and C. O. Pabo, *Proc. Natl. Acad. Sci. USA*, 97 (2000) 7382.
- 10 M. Gabryszewski and B. Wiczorek, *J. Chem.*, 73 (1999) 1925.
- 11 Q. Zhai, C. Lu, Q. Zhang, X. Wu, X. Xu, S. Chen and L. Chen, *Inorg. Chim. Acta*, 359 (2006) 3875.
- 12 L. Antolini, A. C. Fabretti, D. Gatteschi, A. Giusti and R. Sesolli, *Inorg. Chem.*, 30 (1991) 4858.
- 13 Z.-Q. Zheng, C.-W. Liu and B. Lin, *Acta Cryst. E*, 63 (2007) m1252.
- 14 W. Li, H.-P. Jia, Z.-F. Ju and J. Zhang, *Cryst. Growth Des.*, 6 (2006) 2136.
- 15 C. Oldham, *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, Eds, Pergamon Press: Oxford, UK 1987, Vol. 2, p. 435.
- 16 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1986, p. 228.
- 17 M. Badea, R. Olar, D. Marinescu and G. Vasile, *J. Therm. Anal. Cal.*, 85 (2006) 285.
- 18 M. Badea, R. Olar, D. Marinescu, E. Segal and A. Rotaru, *J. Therm. Anal. Cal.*, 88 (2007) 317.

 DOI: 10.1007/s10973-007-8766-4