*Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 205–208*

# THERMAL STABILITY OF NEW COMPLEXES BEARING BOTH ACRYLATE AND ALIPHATIC AMINE AS LIGANDS

*Mihaela Badea*[1*], *Rodica Olar*[1], *Dana Marinescu*[1] *and Gina Vasile*[2]

[1]University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 90-92 Panduri St., 050663 Sector 5 Bucharest, Romania
[2]University of Agronomical Sciences and Veterinary Medicine, Department of Agrochemistry, Bd. Marasti 59, Bucharest, Romania

This paper reports the investigation of the thermal stability of a series of new complexes with mixed ligands of the type $[M(en)(C_3H_3O_2)_2]\cdot nH_2O$ ((**1**) $M$=Ni, $n$=2; (**2**) $M$=Cu, $n$=0; (**3**) $M$=Zn, $n$=2; en=ethylenediamine and $(C_3H_3O_2)$=acrylate anion). The thermal behaviour steps were investigated in a nitrogen flow. The thermal transformations are complex processes according to TG and DTA curves including dehydration, ethylenediamine elimination as well as acrylate thermolysis. The final products of decomposition are the most stable metal oxides except for complex (**2**) that generates metallic copper.

***Keywords:*** *acrylate, carbonate, complexes, ethylenediamine, thermal stability*

## Introduction

The complexes with acrylate ion [1–4] were studied in the last years in order to obtain 'metal-containing monomers', compounds that can be polymerised with different organic monomers in order to obtain metal-containing polymers. It has been shown recently increasing interest in lanthanide acrylates because of their optical properties [5–7]. Complexes with acrylic acid and tetradentate tripodal ligand were also synthesized and structurally characterized [8–10]. Extended studies indicated that some of these complexes display superoxide dismutase-like activity [10]. Complexes bearing acrylate and an aromatic amine (2,2'-bipyridine, 1,10-phenanthroline or 4,4'-bipyridine) were synthesised in order to modulate the biological properties. So far, these species have been studied in detail concerning their thermal behaviour [11–13].

We report here the thermal behaviour of new complexes of the type $[M(en)(C_3H_3O_2)_2]\cdot nH_2O$ ((**1**) $M$=Ni, $n$=2; (**2**) $M$=Cu, $n$=0; (**3**) $M$=Zn, $n$=2; en=ethylenediamine and $(C_3H_3O_2)$=acrylate anion). The study was extended to mixed complexes with ethylenediamine having in view the antimicrobial activity recently evidenced for some Co(III) complexes bearing this ligand [14].

The thermal analysis (TG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules. It was also evidenced the existence of an intermediate step corresponding to the formation of metal carbonate for all compounds. The final residues were the metal(II) oxides, except for copper(II) complex that generates metallic copper as powder X-ray diffraction indicated.

## Experimental

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

### *Synthesis of the complexes*

Complex $[Ni(en)(C_3H_3O_2)_2]\cdot 2H_2O$ (**1**): An aqueous mixture formed from 0.952 g nickel hydroxocarbonate, 1.1 mL acrylic acid and 0.27 mL ethylenediamine was stirred at room temperature for 1 h. The pale green solution obtained was filtered. The filtrate was left to stand at room temperature and after a week 15 mL DMSO was added. After another two weeks the light blue crystals formed, were filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Ni, 19.64; C, 32.27; H, 5.98; N, 9.52%; calculated for $NiC_8H_{18}N_2O_6$: Ni, 19.77; C, 32.36; H, 6.11; N, 9.43%; IR (KBr pellet), $cm^{-1}$: $\nu_{H_2O}$, 3583s; $\nu_{as(NH_2)}$, 3473m; $\nu_{s(NH_2)}$, 3311s; $\delta_{(NH_2)}$, 1646m; $\nu_{as(COO)}$, 1567vs; $\nu_{s(COO)}$, 1397s.

Complex $[Cu(en)(C_3H_3O_2)_2]$ (**2**): To a solution obtained by dissolving 0.896 g copper acrylate in 20 mL water was added 0.27 mL of ethylenediamine under continuous stirring. The color of solution turns immediately to dark blue. The reaction mixture was

---

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

*1388–6150/$20.00*

*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

stirred for one hour. The solution was left to stand at room temperature. The blue crystals obtained after a week were filtered off, washed with ethylic alcohol and air-dried. Analysis, found: Cu, 23.78; C, 36.02; H, 5.22; N, 10.61%; calculated for $CuC_8H_{14}N_2O_4$: Cu, 23.91; C, 36.16; H, 5.31; N, 10.54%; IR (KBr pellet), $cm^{-1}$: $\nu_{as(NH_2)}$, 3438m; $\nu_{s(NH_2)}$, 3311s; $\delta_{NH_2}$, 1650m; $\nu_{as(COO)}$, 1539vs; $\nu_{s(COO)}$, 1368s.

Complex $[Zn(en)(C_3H_3O_2)_2]\cdot 2H_2O$ (**3**): 0.81 g zinc oxide was treated with 1.77 mL acrylic acid in aqueous medium, under continuous stirring, until all quantity of zinc oxide reacted. To this mixture 0.67 mL of ethylenediamine was added and a white precipitate was immediately obtained. The reaction mixture was stirred for 30 min. The precipitate was then filtered off, washed with water and air-dried. Analysis, found: Zn, 21.46; C, 31.58; H, 5.89; N, 9.28%; calculated for $ZnC_8H_{18}N_2O_6$: Zn, 21.53; C, 31.65; H, 5.98; N, 9.23%; IR (KBr pellet), $cm^{-1}$: $\nu_{H_2O}$, 3540sh; $\nu_{as(NH_2)}$, 3481vs; $\nu_{s(NH_2)}$, 3383vs; $\delta_{NH_2}$, 1636m; $\nu_{as(COO)}$, 1538vs; $\nu_{s(COO)}$, 1362s.

### *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. Nickel and zinc were determined gravimetrically in the laboratories of Inorganic Chemistry Department. Copper was determined volumetrically using the thiosulfate method.

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

The heating curves (TG, DTA and DTG) were recorded using a Labsys 1200 Setaram instrument, with a sample mass of 6–20 mg over the temperature range of 20–900°C, using a heating rate of 10 K $min^{-1}$. The measurements were carried out in a nitrogen atmosphere (flow rate 20 $cm^3$ $min^{-1}$) by using alumina crucibles.

## Results and discussion

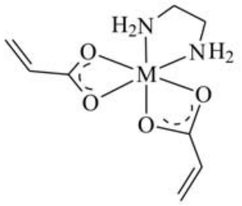
A series of complexes with mixed ligands (ethylenediamine and acrylate) were obtained from the reaction of corresponding metal acrylate and ethylenediamine. Except the copper complex, the other acrylates were obtained in the reaction medium as a first step of synthesis. The purpose of this paper was to evidence the thermal behaviour, in nitrogen flow, of these complexes that could be considered metal containing monomers. The complexes have been formulated on the basis of chemical analysis and IR spectra as it follows:

$$[Ni(C_2H_8N_2)(C_3H_3O_2)_2]\cdot 2H_2O \qquad (1)$$

$$[Cu(C_2H_8N_2)(C_3H_3O_2)_2] \qquad (2)$$

$$[Zn(C_2H_8N_2)(C_3H_3O_2)_2]\cdot 2H_2O \qquad (3)$$

The IR spectra indicates that the ethylenediamine as well as acrylate act as bidentate in all complexes. The characteristic pattern of coordinated ethylenediamine (experimental part) generates the two bands characteristic for amine group in the 3300–3500 $cm^{-1}$ range. At about 1650 $cm^{-1}$ appears a band that can be assigned to $\delta_{NH_2}$ vibration mode characteristic also for ethylenediamine [15]. The acrylate fragment can be identified due $\nu_{as(COO)}$ and $\nu_{s(COO)}$ bands. A $\Delta=\nu_{as(COO)}-\nu_{s(COO)}$ value higher than the ionic one of 203 $cm^{-1}$ observed for sodium acrylate, indicates an unidentate coordination mode while a $\Delta<203$ $cm^{-1}$ value indicates a bidentate (chelation/bridging) coordination mode [16]. The $\nu_{as(COO)}$ and $\nu_{s(COO)}$ bands associated with the acrylate fragment in complexes generate $\Delta$ values about 170 $cm^{-1}$ that indicate a bidentate coordination mode. Except for complex (**2**) the spectra of other complexes display a band around 3500 $cm^{-1}$ assigned to $\nu_{OH}$ stretching vibrations for water molecules [15]. On the basis of the above data the proposed coordination for the complexes is as it follows (Scheme 1):



**Scheme 1** The proposed coordination for complexes; *M*=Ni, Cu, Zn

The results concerning the thermal decomposition of these new complexes in nitrogen atmosphere are presented as follows.

### *Thermal decomposition of $[Ni(C_2H_8N_2)(C_3H_3O_2)_2]\cdot 2H_2O$*

The TG, DTG and DTA curves corresponding to the complex (**1**) heated in the 20–900°C temperature range are presented in Fig. 1.

The thermal decomposition occurs in three, well-defined steps. The first step, which is endothermic, corresponds to water molecules loss. The resulted anhydrous compound is stable over a range larger than 100°C. In Fig. 2 the IR spectra of complex and anhydrous intermediate are presented. The IR spectrum of this residue preserves the pattern observed for complex (**1**) except for the band at 3583 $cm^{-1}$ assigned to $\nu_{OH}$ that disappears. The light

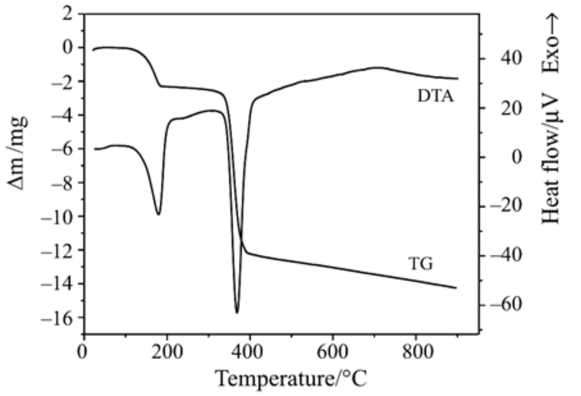


**Fig. 1** TG and DTA curves of $[Ni(C_2H_8N_2)(C_3H_3O_2)_2]{\cdot}2H_2O$

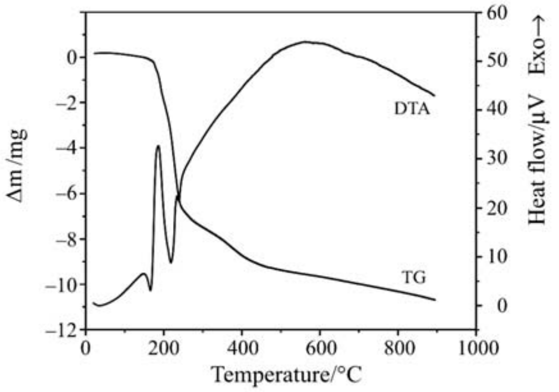


**Fig. 3** TG and DTA curves of $[Cu(C_2H_8N_2)(C_3H_3O_2)_2]$

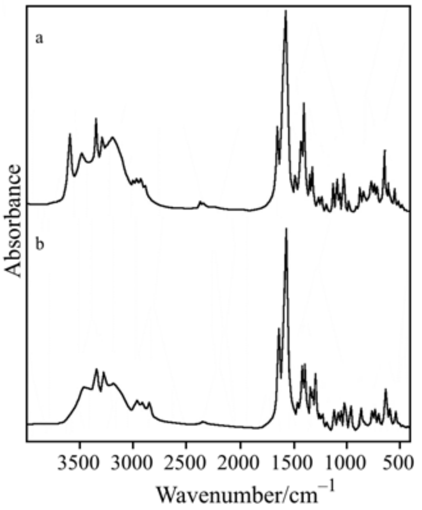


**Fig. 2** IR spectra of the a – $[Ni(C_2H_8N_2)(C_3H_3O_2)_2]{\cdot}2H_2O$ and b – intermediate formed at 200°C

green colour of residue and its electronic spectrum feature indicate that the coordination core remains unchanged after dehydration. These aspects sustain the idea of uncoordinated water, although this species is released at high temperature. This behaviour could indicate that the water molecules are involved in strong hydrogen bonds with the ligands, behaviour observed for other hydrated acrylate complexes [11–13]. The second step corresponds to ethylenediamine elimination as well as acrylate into carbonate transformation. Thermal analysis performed for other ethylenediamine complexes revealed the loss of this species also in the first decomposition step of the anhydrous complex [17–19]. The carbonate decomposition follows as a third step, exothermic one. The result of these processes is nickel(II) oxide (found/calcd. overall mass loss: 74.85/74.84)

### *Thermal decomposition of $[Cu(C_2H_8N_2)(C_3H_3O_2)_2]$*

The complex (**2**) is anhydrous so there is no detectable change in TG curve up to 152°C (Fig. 3).

After melting at 152°C, the decomposition starts immediately and comprises ethylenediamine release and acrylate decomposition, respectively. This step, which is endothermic, is not a single one but consists in at least two processes according to both TG and DTG curves. The next, exothermic step corresponds to carbonate into metallic copper conversion (found/calcd. overall mass loss: 75.97/76.09).

### *Thermal decomposition of $[Zn(C_2H_8N_2)(C_3H_3O_2)_2]{\cdot}2H_2O$*

According to the TG profile the decomposition of complex (**3**) occurs in three steps with zinc(II) oxide as final product (found/calcd. overall mass loss: 73.21/73.15).

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

| Complex | Step | Thermal effect | Temperature range/°C | $\Delta m_{exp}$/% | $\Delta m_{calc}$/% |
|---|---|---|---|---|---|
| $[Ni(C_2H_8N_2)(C_3H_3O_2)_2]{\cdot}2H_2O$ | 1 | endothermic | 90–200 | 12.23 | 12.13 |
| | 2 | endothermic | 315–410 | 48.03 | 47.89 |
| | 3 | exothermic | 410–900 | 14.59 | 14.82 |
| $[Cu(C_2H_8N_2)(C_3H_3O_2)_2]$ | 1 | endothermic | 152* | 0.00 | 0.00 |
| | 2 | endothermic | 152–303 | 53.50 | 53.51 |
| | 3 | exothermic | 303–900 | 22.47 | 22.58 |
| $[Zn(C_2H_8N_2)(C_3H_3O_2)_2]{\cdot}2H_2O$ | 1 | endothermic | 53–180 | 31.49 | 31.62 |
| | 2 | endothermic | 180–510 | 27.24 | 27.04 |
| | 3 | exothermic | 510–900 | 14.48 | 14.49 |

*melting point

In the first step that is not a single one, the water molecules and ethylenediamine elimination occur in three successive processes as both TG and DTA indicate. The second step, also endothermic, is accompanied by a mass loss of 27.24% assigned to zinc(II) acrylate into zinc(II) carbonate transformation. According to the both TG and DTG curves there are at least two processes that take place in this range. Last step, exothermic, corresponds to zinc(II) oxide generation by carbonate decomposition.

## Conclusions

The new complex compounds of Ni(II), Cu(II) and Zn(II) with mixed ligands (ethylenediamine and acrylate) belong to a class of coordination compounds of current interest having into its composition a ligand which allows inclusion of the metallic ions into a polymeric matrix.

Thermal analysis (TG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules. It was also evidenced in all cases the existence of an intermediate step corresponds to the formation of metal carbonates.

In all the cases, the final residue is the most stable metal oxide, except for complex (**2**) that generates metallic copper.

## Acknowledgements

The Romanian Academy Grant no. 55/2007 financially supported this study.

## References

1 Y. Y. Wang, Q. Shi, Q. Z. Shi, Y. C. Gao and Z. Y. Zhou, Polyhedron, 18 (1999) 2009.
2 Y. Y. Wang, Q. Shi, Q. Z. Shi, Y. C. Gao and X. Hou, Polyhedron, 19 (2000) 891.
3 Y. Y. Wang, Q. Shi and Q. Z. Shi, Acta Chim. Sinica, 58 (2000) 675.
4 M. Badea, R. Olar, G. Vasile, A. Emandi, V. Pop and D. Marinescu, J. Therm. Anal. Cal., 81 (2005) 273.
5 V. T. Panyushkin, A. A. Mastakov, N. N.Bukov, A. A. Nikolaenko and M. E. Sokolov, J. Struct. Chem., 45 (2004) 167.
6 F. Ramos-Lara, A. C. Lira, M. O. Ramirez, M. Flores, R. Arroyo and V. Caldino, J. Phys. Condens. Mater., 18 (2006) 7951.
7 M. J. Yang, Q. D. Ling, M. Hiller, X. Z. Fun, L. H. Wang and W. G. Zhang, J. Polym. Sci., Part A: Polym. Chem., 38 (2000) 3405.
8 H. L. Wu, W. Ying, L. Pen, Y. C. Gao and K. B. Yu, Synth. React. Inorg., Met.-Org., Nano-Met. Chem., 34 (2005) 1019.
9 H. L. Wu, Y. C. Gao and K. B. Yu, Trans. Met. Chem., 29 (2004) 175.
10 H. L. Wu and Y. C. Gao, J. Coord. Chem., 59 (2006) 137.
11 M. Badea, R. Olar, D. Marinescu and G. Vasile, J. Therm. Anal. Cal., 80 (2005) 683.
12 M. Badea, R. Olar, D. Marinescu and G. Vasile, J. Therm. Anal. Cal., 85 (2006) 285.
13 M. Badea, R. Olar, D. Marinescu, E. Segal and A. Rotaru, J. Therm. Anal. Cal., 88 (2007) 317.
14 P. Nagababu, J. Naveena Lavanya Latha, P. Pallavi, S. Harish and S. Satyanarayana, Can. J. Microbiol., 52 (2006) 1247.
15 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1986, p. 228.
16 C. Oldham, Comprehensive Coordination Chemistry, G. Wilkinson, R. D. Gillard and J. A. McCleverty, Eds; Pergamon Press, Oxford, UK 1987, Vol. 2, p. 435.
17 L. S. Probhumirashi, G. N. Natu and S. R. Nayak, J. Thermal Anal., 35 (1989) 1105.
18 J. Maslowska and J. Szmich, J. Thermal Anal., 36 (1990) 2701.
19 H. Icbudac, T. K. Yazicilar and V. T. Yilmaz, Thermochim. Acta, 1–2 (1999) 93.

DOI: 10.1007/s10973-007-8765-5