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THERMAL BEHAVIOR OF SOME NEW COMPLEXES BEARING LIGANDS WITH POLYMERISABLE GROUPS*

M. Badea[1**], *R. Olar*[1], *D. Marinescu*[1] *and G. 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 $M(dipy)(C_3H_3O_2)_2(H_2O)_y$ ((**1**) *M*: Mn, *y*=1; (**2**) *M*: Ni, *y*=2; (**3**) *M*: Cu, *y*=1; (**4**) *M*: Zn, *y*=2; dipy: 2,2'-dipyridine and $C_3H_3O_2$ is acrylate anion). The thermal behaviour steps were investigated. The thermal transformations are complex processes according to TG and DTG curves including dehydration, oxidative condensation of acrylate and thermolysis processes. The final products of decomposition are the most stable metal oxides.

Keywords: *acrylate, complexes, formate, thermal stability*

Introduction

The polymeric materials with metals particles or metallic ions have opened up a new research field of current interest due to the practical importance of the obtained products, which exhibit unusual properties. Recent developments in polymer chemistry revealed that complexes with mixed ligands such as aromatic amine and unsaturated polymerisable compounds are suitable for synthesis of these types of materials. The interest for these compounds grew up according with its characteristics such as catalytic activity, unusual magnetic and electro-physical behaviour as well as biological and medical applications for tissue engineering, implantation of medical devices, dentistry, bone repair, etc. [1–3]. Recent studies have evidenced that compounds with polymerisable ligands suffer interesting thermal transformation that generate in the polymeric matrix metal particles with different sizes [4].

This kind of species with biologic activity and polymerisable ligands are studied more and more lately in order to include them into biodegradable nanospheres which allow controlled release, better specificity, greater stability and slower excretion rates of the active agent. Control release of the active agent is made by diffusion from the nanospheres or hydrolytic/enzymatic cleavage from the polymer carrier [5]. For complex compounds with ammine derivatives, the biologic activity such as antimicrobial, antiviral has been already evidenced [6–9].

We succeeded to obtain this type of complexes using acrylate [10] and also with mixed ligands as well [11]. Some complexes behave as inhibitors for different types of microorganisms and also show an interesting thermal behaviour [10–12].

Recently, we have obtained new complexes starting from acrylate and 2,2'-bipyridine [13]. We report here the thermal behaviour of these new complexes of the type $M(dipy)(C_3H_3O_2)_2(H_2O)_y$ that represent the intermediate products in the synthesis of polymeric materials. Thermogravimetric analysis was performed for determining the range of stability of these complexes.

Experimental

All reagents were of commercial analytical quality and have been used without further purification. The new complexes were synthesised and previously characterised by chemical analysis, electronic, IR and EPR spectra. The redox behaviour was characterised by voltammetric study and the biological assay were performed by microdilution method [13]. 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, nitrogen and hydrogen has been performed using an EA 1110 analyzer. Manganese, nickel, copper and zinc were determined gravimetrically in the laboratories of Inorganic Chemistry Department.

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

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

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

The heating curves (TG, DTA and DTG) were recorded in a static air atmosphere using a MOM (Hungary) derivatograph, type Paulik–Paulik–Erdey, with a sample mass of 100 mg over the temperature range of 20–1000ºC, using a heating rate of 10°C min^{-1}.

Results and discussion

The following solid compounds have been studied regarding of their thermal behaviour:

$Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$ (**1**)

$Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$ (**2**)

$Cu(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$ (**3**)

$Zn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$ (**4**)

These compounds were obtained in two steps. First, metallic acrylate from the reaction of metal carbonate with acrylic acid in aqueous solution was obtained and then an ethanolic solution of 2,2'-bipyridine was added.

It is important to mention that the physico-chemical studies had evidenced, that with the Cu(II) exception that adopts a square pyramidal stereochemistry, the other metallic ions have an octahedral surroundings. In all complexes the 2,2'-bipyridine acts as chelate while the acrylate acts as unidentate ligand in all complexes except for complex (**2**) where it is found as chelate. All the compounds contain water molecules as indicated the IR spectra and confirmed the thermal decomposition.

Antibacterial activity of the complexes has been carried out *vs.* Gram positive and Gram negative, reference and clinical strains (*Pseudomonas aeruginosa, Staphylococcus aureus, Salmonella enteridis, Listeria monocytogenes, Candida albicans* and *Escherichia coli*). The values of minimum inhibitory concentration revealed for complex (**1**) a very good activity *vs. Pseudomonas aeruginosa, Staphylococcus aureus, Salmonella enteridis, Listeria monocytogenes* [13].

The main objective of this paper was to analyse the thermal behaviour of the complex species with biologic activity in order to acquire a polymeric fashion for them.

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

TG, DTG and DTA curves corresponding to the complex (**1**) heated in the 20–1000°C temperature range are presented in Fig. 1.

Thermal analysis has confirmed the first step of compound transformation as an endothermic elimination of water molecules. The reaction proceeds with a maximum rate at 135ºC. The second step, which is exothermic, is not a single process (according to DTG curve) but consists in two processes. During this step the oxidative transformation of acrylate ion leads to formate anion, followed by the oxidative degradation of this intermediate leading to MnO_2.

The third step corresponds to the MnO_2 decomposition and Mn_2O_3 formation as the final product.

The thermal decomposition of $Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$ (**2**) occurs in three, well-defined steps. The first step, which is endothermic, corresponds to the loss of water molecules. The resulted anhydrous compound is stable in a wide range of temperature. The second step corresponds to an oxidative condensation of acrylic acid and the degradation of the residual organic part follows as a third step. This step is complex being an overlap of at least three oxidative processes.

The thermal decomposition of $Cu(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$ (**3**) is similar to that of $Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$. TG, DTG and DTA

Table 1 Thermal behaviour data (in static air atmosphere) for the acrylate complexes

Complex	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%
$Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$	1	endothermic	105–160	4.68	4.85
	2	exothermic	160–300	71.56	71.69
	3	endothermic	500–640	2.50	2.15
			residue (Mn_2O_3)	21.26	21.31
$Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	130–200	9.32	9.16
	2	exothermic	200–350	13.14	13.23
	3	endothermic	350–580	58.68	58.54
			residue (NiO)	18.86	19.07
$Cu(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$	1	endothermic	160–215	4.37	4.74
	2	exothermic	265–330	14.06	13.70
	3	endothermic	330–540	60.31	60.61
			residue (CuO)	21.26	20.95
$Zn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	110–150	8.92	9.02
	2	exothermic	150–310	13.32	13.03
	3	endothermic	310–650	57.48	57.64
			residue (ZnO)	20.28	20.30

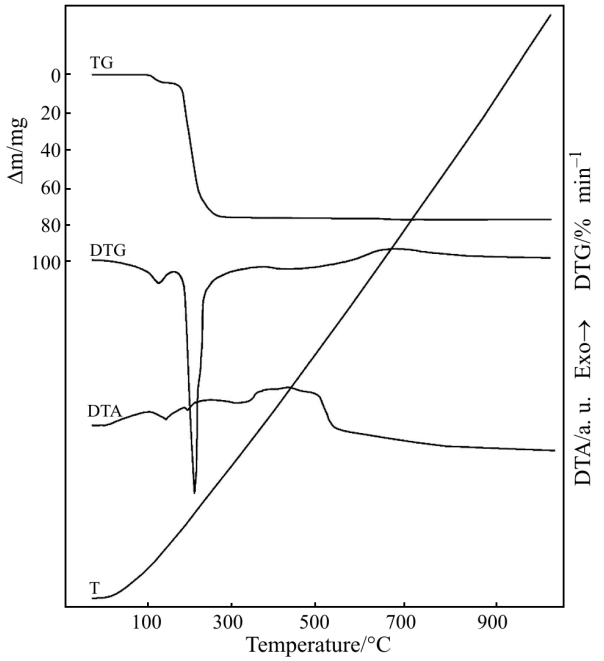

Fig. 1 TG, DTG and DTA curves of $Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$

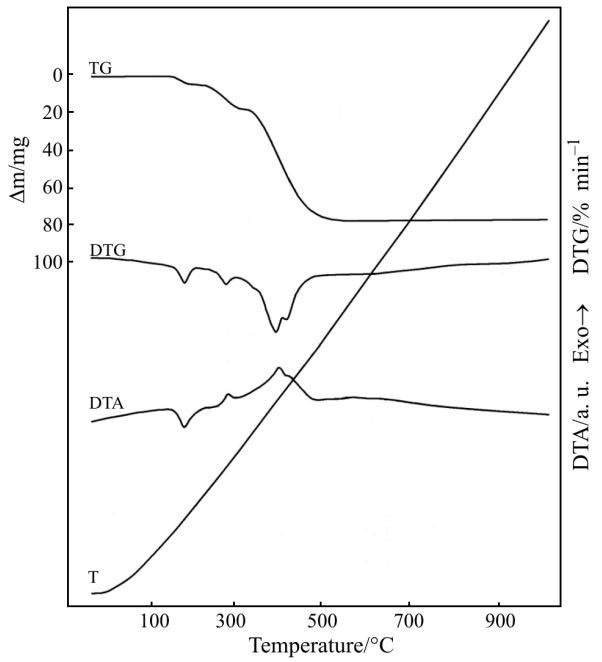

Fig. 2 TG, DTG and DTA curves of $Cu(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)$

curves corresponding to the complex (**3**) heated in the 20–1000°C temperature range are presented in Fig. 2.

During the first step the water molecule loss occurs. Considering the higher temperature corresponding to the dehydration process, it could be assumed that the water molecule is coordinated [14]. The other two exothermic steps correspond to acrylate to formate conversion and to oxidative degradation of the formed compound respectively. The final product at 540ºC is copper oxide.

In the case of complex (**4**) the thermal decomposition occurs similar with (**2**) and (**3**) meaning the complex dehydration followed by the oxidative degradation of organic part. The final residue obtained at 720ºC is zinc oxide.

The formation of complexes with formate at a temperature that decreases following the order: nickel, copper, zinc could be correlated with the increasing preference of the M(II) for tetrahedral stereochemistry.

Conclusions

The new complex compounds of Mn(II), Ni(II), Cu(II) and Zn(II) with mixed ligands (2,2'-dipyridine 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 that, in all cases, the existence of an intermediate step corresponds to the formation of metallic formates.

The formation of the complexes with formate at a temperature that decreases (Ni>Cu>Zn) could be correlated with the increasing preference of the M(II) for tetrahedral stereochemistry.

In all the cases, the final residue is the most stable metallic oxide, as powder X-ray diffraction indicated.

Acknowledgements

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