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SOME NEW ACRYLATE COMPLEXES AS A CRITERION IN THEIR SELECTION FOR FURTHER CO-POLYMERIZATION REACTION

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This paper reports the investigation of the thermal stability of a series of new complexes with mixed ligands of the type $M(phen)(C_3H_3O_2)_2(H_2O)_y$ ((**1**) *M*=Mn, *y*=0; (**2**) *M*=Ni, *y*=2; (**3**) *M*=Cu, *y*=1; (**4**) *M*=Zn, *y*=2; *phen*=phenanthroline 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, fumarate, thermal stability*

Introduction

The interest in the coordination properties of acrylic acid and its homologues was generated by the facile synthesis of the 'metal-containing monomers' (MCM) materials [1, 2]. The presence of metallic ions increases the thermal stability of these species and allows their processing at higher temperature.

These compounds can be polymerised with different organic monomers leading to various metal-containing polymers. Polymeric transformations of MCM have opened up a new research field of current interest due to the practical importance of the obtained products which exhibit unique properties such as high catalytic activity, unusual magnetic, electrophysical, biological activity [3]. Polymers are especially suited for biological applications (tissue engineering, implantation of medical devices, dentistry, bone repair, etc.) because their molecular mass, compositions and architectures may be regulated through controlled reactions [4, 5].

There are a lot of scientific work, which deal with the existence of numerous complexes with acrylate [6–9] and its derivatives [1–3, 6, 10]. So far, these species have not been studied in detail concerning thermal behaviour except our work regarding chromium(III) complexes with acrylate [11]. Thermal transformations of metal-containing monomers have attracted considerable recent attention because they can result in the formation of metal nanoparticles stabilized in the polymer matrix [12, 13].

We report here the thermal behaviour of new complexes of the type $M(phen)(C_3H_3O_2)_2(H_2O)_y$ ((**1**) *M*=Mn, *y*=0; (**2**) *M*=Ni, *y*=2; (**3**) *M*=Cu, *y*=1; (**4**) *M*=Zn, *y*=2; *phen*=phenanthroline and $C_3H_3O_2$ is acrylate anion), that represent the products of a first step in the synthesis of polymeric materials. Thermogravimetric analysis was performed for determining the range of stability for acrylate complexes.

Experimental

The reported complexes were synthesised and previously characterised by chemical analysis, electronic and IR spectra.

The thermal decomposition curves have been recorded using a Shimadzu DTG-TA-51H analyzer, in the temperature range of 20–1000ºC for a heating rate of 10 K min^{-1}.

Results and discussion

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

$$Mn(C_{12}H_8N_2)(C_3H_3O_2)_2 \quad (1)$$

$$Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2 \quad (2)$$

$$Cu(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O) \quad (3)$$

$$Zn(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2 \quad (4)$$

These compounds were obtained in two steps. First, metallic acrylate from the reaction of metal carbonate with acrylic acid in aqueous solution was ob-

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$$MCO_3+CH_2CHCOOH \xrightarrow{H_2O} M(CH_2CHCOOH)_2 \cdot xH_2O \ (M=Mn, Ni, Cu, Zn)$$

$$M(CH_2CHCOOH)_2 \cdot xH_2O+phen \xrightarrow{H_2O/EtOH} Mphen(CH_2CHCOOH)_2(H_2O)_y$$

Scheme 1

tained and then an ethanolic solution of 1,10-phenanthroline was added, as depicted in Scheme 1.

The results concerning the thermal decomposition/degradation of these new complexes are presented as follows in Table 1.

Thermal decomposition of $Mn(C_{12}H_8N_2)(C_3H_3O_2)_2$

Thermal analysis has confirmed the first step of compound transformation as an exothermic oxidation of Mn^{2+} to Mn^{3+}. The reaction proceeds with a maximum rate at 64ºC. The resulted compound after oxidation is very stable in a range greater than 100ºC. This proves that the complex compound is an anhydrous species. The second step, which is exothermic, is not a single process (according to DTG curve) but consists of two processes. It is during this step that the oxidative condensation process of acrylate ion that leads to fumarate ion, occurs. The fumaric acid is a very stable compound (*m.p.*: 300–302ºC). Most probably, the fumarate ion acts as bridge between two metallic ions.

The third step is a complex one corresponding to the oxidative degradation of the organic part and leads to Mn_2O_3 as final product. This step is an overlapping of at least four chemical processes.

Thermal decomposition of $Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

The TG, DTG and DTA curves corresponding to the complex (**2**) heated in the 20–1000°C temperature range are presented in Fig. 1.

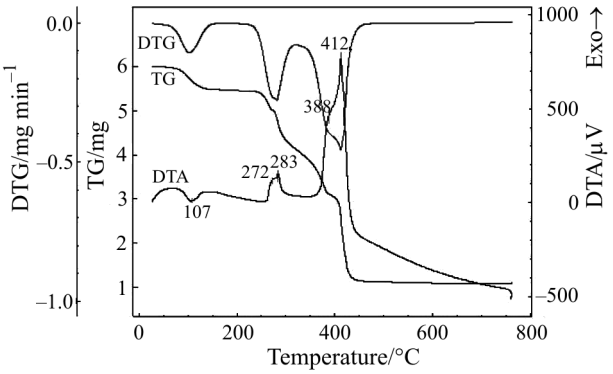

Fig. 1 TG, DTG and DTA curves of $Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

The thermal decomposition occurs in three, well-defined steps. The first step, which is endothermic, corresponds to 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 overlapping of at least three oxidative processes.

Thermal decomposition of $Cu(C_{12}H_8N_2)(C_3H_3O_2)_2 \cdot H_2O$

The thermal decomposition is similar to that of $Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$. During the first step the water molecule is lost. Considering the higher temperature corresponding to the dehydration pro-

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

Complex	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%
$Mn(C_{12}H_8N_2)(C_3H_3O_2)_2$	1	exothermic	33–111	2.24	2.12
	2	exothermic	230–332	7.31	7.42
	3	exothermic	332–630	71.78	71.62
	residue (Mn_2O_3)			18.67	18.84
$Ni(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	55–150	8.66	8.63
	2	exothermic	210–280	6.92	6.71
	3	exothermic	280–450	66.51	66.66
	residue (NiO)			17.91	18.00
$Cu(C_{12}H_8N_2)(C_3H_3O_2)_2 \cdot H_2O$	1	endothermic	95–180	4.54	4.46
	2	exothermic	190–230	6.81	6.93
	3	exothermic	230–630	69.24	68.89
	residue (CuO)			19.41	19.72
$Zn(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	36–103	4.30	4.25
	2	endothermic	103–130	4.10	4.25
	3	endothermic	150 (*m.p.*)	0	0
	4	strong exothermic	200–230	6.49	6.62
	5	exothermic	275–720	65.46	65.72
	residue (ZnO)			19.65	19.16

cess, it could be assumed that the water molecule is coordinated [14]. The other two exothermic steps correspond to acrylate to fumarate conversion and to its oxidative degradation respectively. The final product at 630ºC is copper oxide.

Thermal decomposition of $Zn(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

The TG, DTG and DTA curves corresponding to the complex (**4**) heated in the 20–1000ºC temperature range are presented in Fig. 2.

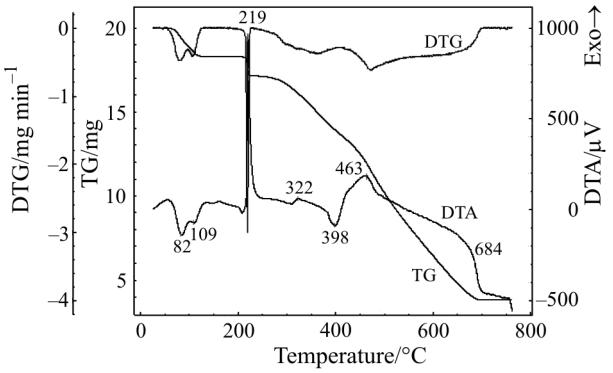

Fig. 2 TG, DTG and DTA curves of $Zn(C_{12}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

The first two endothermic steps correspond to the stepwise elimination of the water molecules. The anhydrous solid compound formed at 130, melts at 150 and remains stable to 200ºC. It is followed by a strong exothermic step that occurs in a narrow range of temperature. With under these conditions an oxidative condensation of acrylate to fumarate occurs. As in the previous cases, the obtained compound is stable over a range of 45ºC and it can be isolated and characterized. The last step occurs in a wide range of temperature and supposes the stepwise oxidative degradation of organic part. According to the DTG curve there are at least three processes that take place. The final residue obtained at 720ºC is zinc oxide.

The formation of complexes with fumarate at a temperature that decreases following the order: Mn, Ni, Cu, Zn 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 (phenanthroline 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 fumarates.

The formation of the complexes with fumarate at a temperature that decreases (Mn>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 indicated by powder X-ray diffraction method.

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