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THERMAL BEHAVIOR OF SOME NEW CHROMIUM COMPLEXES WITH POTENTIAL BIOLOGICAL IMPORTANCE

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This paper reports the investigation of the thermal stability of three new complexes of Cr(III) with acrylate anion, $[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4]$, $[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O$ and $[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O$, respectively. This type of complexes is important in proper carbohydrate and lipid metabolism of mammals. The thermal decomposition steps were evidenced. The thermal transformations are complex processes according to TG and DTG curves including dehydration and oxidative degradation of acrylate ion processes. The final product of decomposition is the chromium(III) oxide.

Keywords: *acrylate anion, chromium(III) complexes, thermal stability*

Introduction

The compounds studied in the present work belong to a class of complexes with immense current interest, the polymers with metallic centres, important in biology, medicine and the science of materials. Two fundamental ways of synthesis are suitable for this kind of polymers: the reaction between the metallic ion and the appropriate polymeric ligand or the reaction between the metallic ion and the monomeric ligand followed by polymerisation. The most used method is the synthesis of an organic polymer that contains one or more functions that can be coordinated to a metallic ion [1]. There are only few references about the syntheses of these compounds based on complexation preceding polymerisation.

Concerning the polymerisable organic component, the literature reports a number of complexes with polyacrylic acid [2–5] but the syntheses of the complexes with acrylic acid or acrylate ion [6–8] followed by its polymerisation were poorly studied.

We report here the thermal behaviour of three new complexes of Cr(III) with acrylate ($C_3H_3O_2$) anion, that represent the products of a first step in the synthesis of polymeric materials. The compounds were formulated $[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4]$ (**1**), $[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O$ (**2**) and $[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O$ (**3**) (Scheme 1), respectively [9].

We have chosen chromium because it is an essential trace element required for normal carbohydrate and lipid metabolism. The biological function of chromium is closely associated with that of insulin. Recently, it was showed that a chromium complex similar with complex (**2**) decreases plasma cholesterol and triglycerides level [10].

Taking into account their intended use, their thermal stability and behaviour are supposed to be clearly known. The thermal study of the coordination compounds was also meant to verify the previously proposed formulation of the new complexes.

Experimental

The compounds (**1**)–(**3**) have been synthesized and previously characterized by chemical analysis, electronic and IR spectra [9].

The thermal decomposition curves have been recorded using a MOM Hungary, Paulik–Paulik–Erdey derivatograph in the temperature range 20–1000ºC for heating rates in the range 2.5–10 K min^{-1}.

Results and discussion

The following solid compounds have been studied from the point of view of their thermal behaviour:

$$[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4] \quad (\mathbf{1})$$

$$[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O \quad (\mathbf{2})$$

$$[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O \quad (\mathbf{3})$$

The results concerning the thermal decomposition/degradation of these new Cr(III) complexes are presented as it follows.

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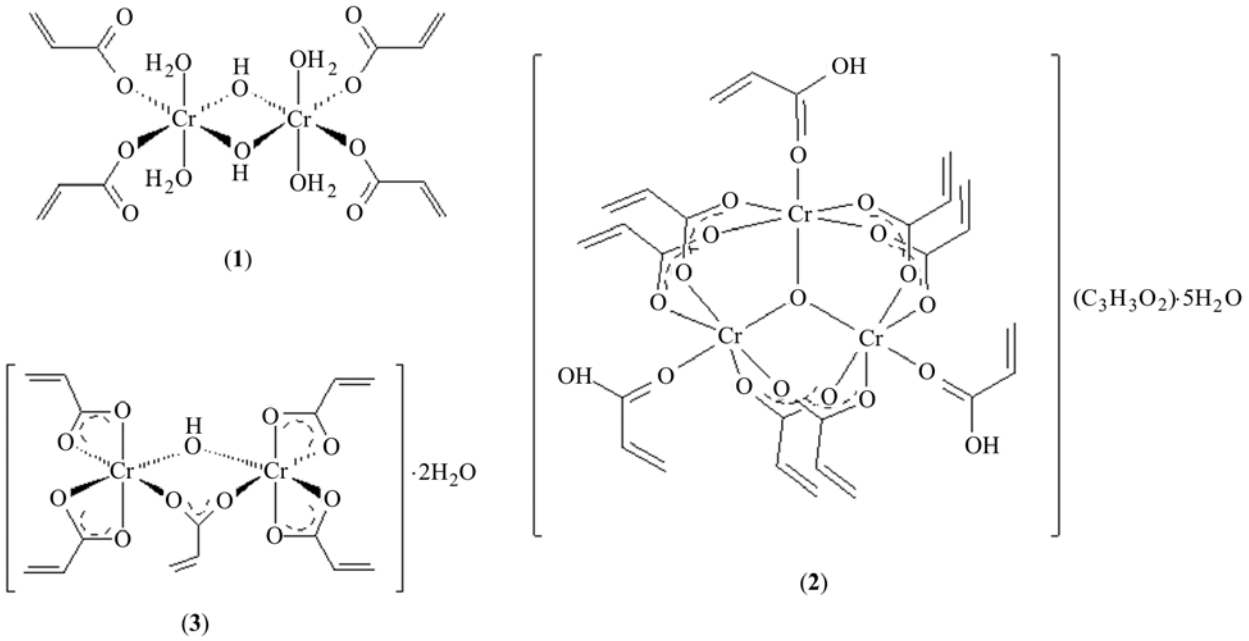

Scheme 1

Thermal decomposition of $[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4]$

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

According to the TG curve at progressive heating, the following decomposition steps have been evidenced:

$$[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4]_{(s)} \rightarrow \rightarrow Cr_2(C_3H_3O_2)_4(OH)_{2(s)} + 4H_2O_{(g)} \quad (1)$$

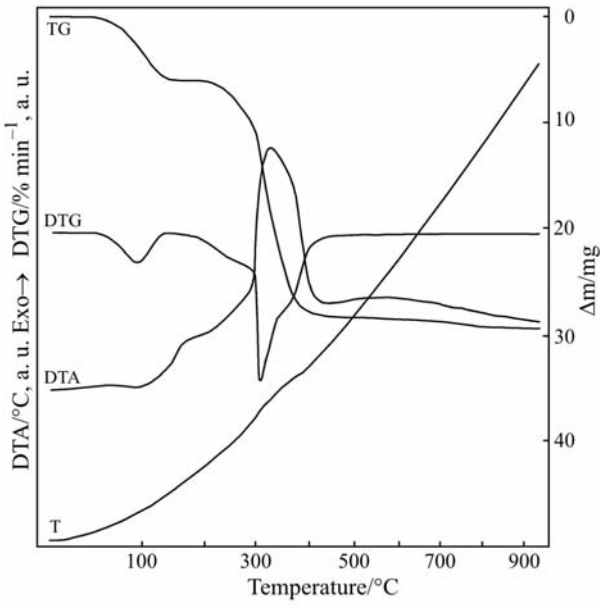

Fig. 1 TG, *T*, DTG and DTA curves of $[Cr_2(C_3H_3O_2)_4(OH)_2(H_2O)_4]$ (sample mass: 42 mg)

$$Cr_2(C_3H_3O_2)_4(OH)_{2(s)} + 12O_{2(g)} \rightarrow \rightarrow Cr_2O_{3(s)} + 12CO_{2(g)} + 7H_2O_{(g)} \quad (2)$$

The thermal decomposition occurs in two well-delimited steps. The first step (occurring in the temperature interval 45–150°C), corresponds to a dehydration process, with a week endothermic effect, having the maximum at 100°C.

The second decomposition step is accompanied by a strong exothermal effect and it corresponds to the oxidative degradation of the dehydrated compound.

Thermal decomposition of $[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O$

The TG and DTG curves indicate that the thermal decomposition occurs through the following steps (Fig. 2):

$$[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O_{(s)} \rightarrow \rightarrow [Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)_{(s)} + 5H_2O_{(g)} \quad (3)$$

$$2[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)_{(s)} + 60O_{2(g)} \rightarrow \rightarrow 3Cr_2O_{3(s)} + 60CO_{2(g)} + 33H_2O_{(g)} \quad (4)$$

The first decomposition step occurs in the 50–150°C temperature range and it is almost similar with the reaction (1). This step also supposes the lost of the water molecules.

The reaction (4) occurs in several steps, difficult to separate; all exhibit an exothermic effect. The weak exothermic effect observed just above 500ºC could be assigned to the formation of a lattice of corundum-type of Cr_2O_3, the final product of the thermal degradation, as the chemical analysis and X-ray diffraction of the residue powder indicates (Fig. 3).

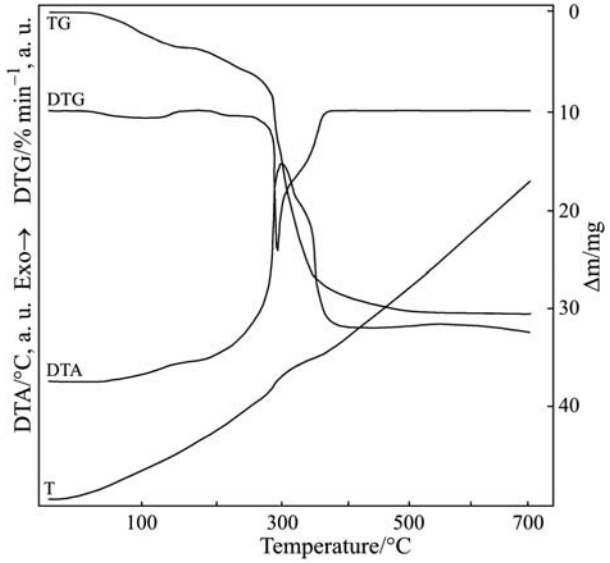

Fig. 2 TG, *T*, DTG and DTA curves of $[Cr_3O(C_3H_3O_2)_6(C_3H_4O_2)_3](C_3H_3O_2)\cdot 5H_2O$ (sample mass: 40 mg)

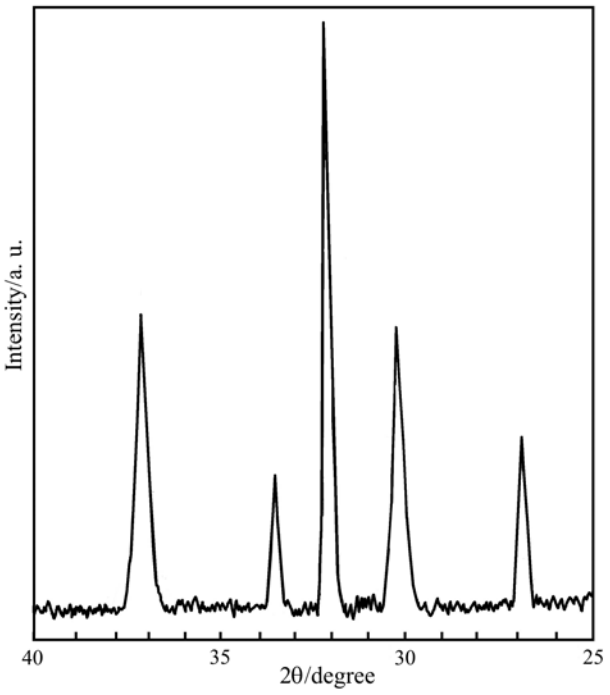

Fig. 3 X-ray diffractogram for the residue obtained at 700°C

Thermal decomposition of $[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O$

The heating curves (Fig. 4) indicate the following thermal degradation steps:

$$[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O_{(s)} \rightarrow \rightarrow [Cr_2(C_3H_3O_2)_5(OH)]_{(s)} + 2H_2O_{(g)} \quad (5)$$

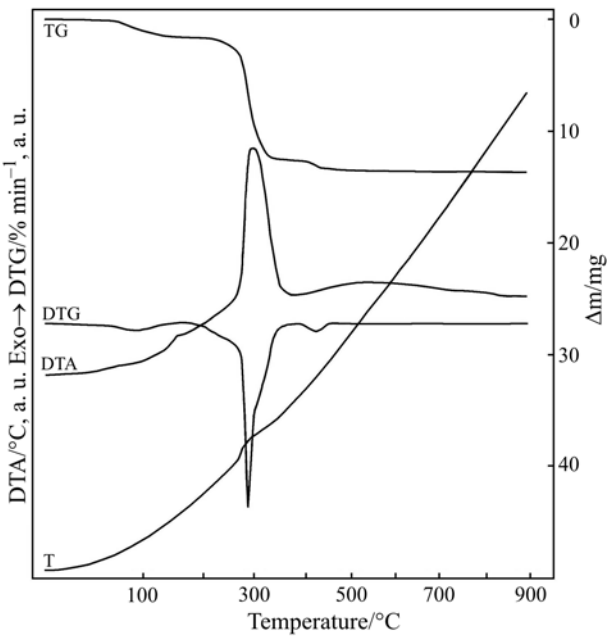

Fig. 4 TG, *T*, DTG and DTA curves of $[Cr_2(C_3H_3O_2)_5(OH)]\cdot 2H_2O$ (sample mass: 19.25 mg)

$$[Cr_2(C_3H_3O_2)_5(OH)]_{(s)} + 15O_{2(g)} \rightarrow \rightarrow 2CrO(OH)_{(s)} + 15CO_{2(g)} + 7H_2O_{(g)} \quad (6)$$

$$2CrO(OH)_{(s)} \rightarrow Cr_2O_{3(s)} + H_2O_{(g)} \quad (7)$$

The thermal decomposition of this coordinated compound occurs with water elimination in the first step.

The second step (reaction (6)) is basically an oxidative degradation and the third could be assigned to a dehydration of the oxo-hydroxide of chromium(III) combined with the formation of a more stable lattice of chromium(III) oxide. As in the case of the previous compound, this last step is associated with an exothermic effect. The powder X-ray diffractogram also reproduces the same pattern.

Conclusions

The compounds studied in the present work were obtained by a method poorly used in the synthesis of a class of complexes with immense current interest, the polymers with metallic centres.

The main decomposition steps of three complexes of Cr(III) with acrylate have been evidenced. In order to confirm the nature of the final residue the X-ray diffractograms and chemical analysis were used.

The thermal analysis (TG, DTG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules.

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