Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 593–597

# THERMAL AND SPECTROSCOPIC INVESTIGATION OF NEW BINUCLEAR Pt(II) COMPLEXES WITH CARBOXYLIC ACIDS

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The thermal decomposition of the binuclear Pt(II) complexes with acetate, propionate, valerate and izovalerate ligands were studied by TG and DTA techniques. The Pt(II) complex with acetic acid (PtAA) was stable up to 343.15 K, Pt(II) complex with propionic acid (PtPrA) was stable up to 323.15 K, Pt(II) complex with valeric acid (PtVA) was stable up to $T$=313.15 K and Pt(II) complex with isovaleric acid (PtIvA) was stable up to 408.15 K. The PtAA complex was investigated again after a year by thermogravimetric analysis. After the thermal decomposition of the Pt(II) complexes with carboxylic acids, only in the PtVA complex and PtAA complex (investigated after a year) the final residue contains only platinum, while in the rest complexes the solid residue was a mixture of platinum and platinum carbides ($PtC_2$, $Pt_2C_3$).

***Keywords:*** *carboxylic acids, Pt(II) complexes, thermal analysis*

## Introduction

Cisplatin is one of most widely used anticancer drugs, effective against several solid tumors such as ovarian, lung, head and neck and bladder cancers [1–3]. Despite the high antitumor activity its clinical application is limited from severe side effects such as nephrotoxicity, cumulative neurotoxicity, ototoxicity and extreme emetogenic potential [2–4]. In recent years, there has been an intense interest in synthesizing new Pt(II) complexes with an aim to reduce the toxicity and/or to achieve a broader antitumor spectrum [5, 6].

Such class of platinum complexes are the compounds containing two, three or four platinum centres with both *cis* and/or *trans* configurations. A representative trinuclear complex BBR3464 has entered a phase II clinical trial and exhibits activity against pancreatic, lung and melanoma cancers [6].

In our previous works [7–11], we reported the synthesis and characterization by physico-chemical methods of new Pt(II) complexes with acetic, propionic, valeric and isovaleric acids. The new Pt(II) complexes were studied pharmacologically and it was found that they exert concentration-dependent cytotoxic effect in a panel of human tumour cell lines. The experimental data retrieved from the cytotoxicity screening program show that all of the novel binuclear platinum complexes, despite of the differences in respect to relative potency, exert antineoplastic activity and since they cause more than 50% inhibition of the malignant cell proliferation, they could be considered as biologically active. On the basis of the $IC_{50}$ values obtained it could be drawn out, that the Pt(II) complex with acetate ligands proved to be the most potent cytotoxic agent with relative potency equal or even exceeding that of the referent drug cisplatin. The increase of the alkyl chain in the organic ligands is invariably related to a pronounced loss of efficacy.

In this paper I present the thermal and spectroscopic behavior of the binuclear Pt(II) complexes with acetate (PtAA) **(1)**, propionate (PtPrA) **(2)**, valerate (PtVA) **(3)** and isovalerate ligands (PtIvA) **(4)**.

## Experimental

The synthesis and the physicochemical methods for the characterization of the new Pt(II) complexes with acetate, propionate, valerate and isovalerate ligands were described in our previous works [7–11]. On the basis of the obtained results, the following most probable schematic formulae of the Pt(II) complexes with some carboxylate ligands were proposed (Fig. 1).

TG and DTA studies were carried out in an air atmosphere and the heating rate was fixed at 5°C $min^{-1}$ on a Q 1500 C Derivatograph (MOM, Hungary) with a simultaneous DTA-TG module. The temperature range employed was 293.15–1173.15 K. The mass of the samples used in this study was 80–345 mg. $\alpha$-$Al_2O_3$ was used as a reference material.

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1388–6150/$20.00

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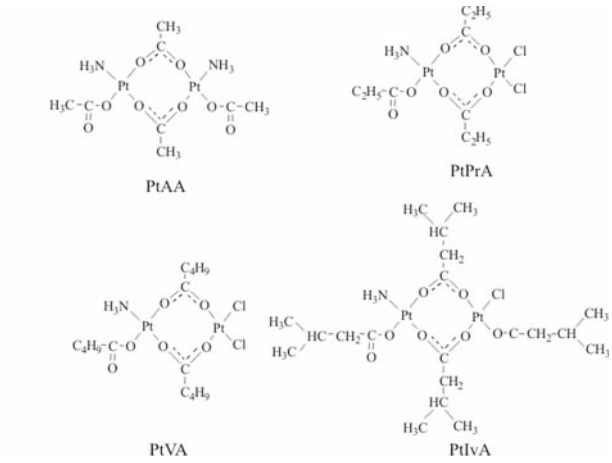


**Fig. 1** Scematic structures of the investigated Pt(II) complexes PtAA, PtPrA, PtVA and PtIvA

The X-ray data are obtained on DRON VM-1 powder diffractometer using $CuK_\alpha$ radiation ($\lambda$=1.5418 Å).

The IR spectra were recorded on IFS 113 v Bruker FTIR spectrophotometer in the range of 4000–400 $cm^{-1}$ in KBr tablets.

## Results and discussion

Thermogravimetric analysis is a very valuable method used for studying the thermal decomposition of solid substances, such as complex compounds [12–14]. The curves obtained depict the decrease in sample mass with linear increase in the treatment temperature.

In the present investigation, the heating rate was fixed at 5°C $min^{-1}$. Depending on the total mass loss within the framework of 593.15–1103.15 K, the sample mass was monitored in the range 80–345 mg during the experimental runs.

A stepped thermal decomposition of the coordination compounds occurred in the range 293.15–1173.15 K. The results of the thermal analysis revealed two distinct steps of mass loss.

*Pt(II) complex with acetic acid – bis(acetato)diammine-bis-*μ*-acetato diplatinum(II) dihydrate –*
*cis-*$[Pt_2(NH_3)_2(CH_3COO)_2(\mu\text{-}CH_3COO)_2]\cdot 2H_2O$ **(1)**

The PtAA complex is stable up to 343.15 K. Its two-stage decomposition begins after this temperature (Fig. 2). The first stage is in the temperature interval 343.15–483.15 K. An initial exothermic effect can be observed in the DTA curve, which overlaps with an endothermic effect in the range 403.15–423.15 K with a maximum at $T$=413.15 K.

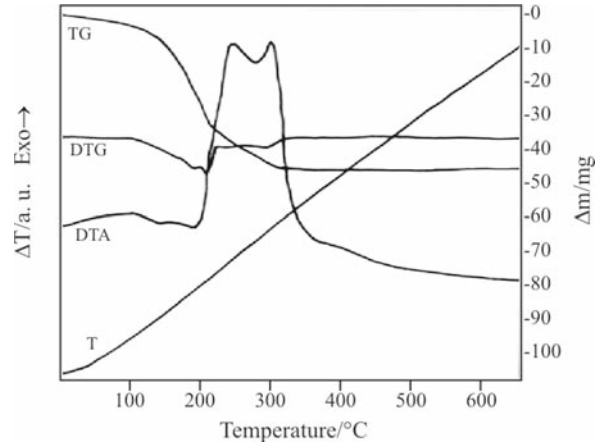


**Fig. 2** TG, DTG and DTA curves of PtAA

This exothermic effect is due to the passing of the complex from one polymorphous form to another. In the TG curve in the range 403.15–423.15 K the mass loss is registered $\Delta m$=7.00%, but the theoretical mass loss is $\Delta m$=7.61%, which may correspond to the disconnection of two molecules of crystal water and one molecule $NH_3$ according to the scheme:

$$cis\text{-}[Pt_2(NH_3)_2(CH_3COO)_4]\cdot 2H_2O \rightarrow$$
$$cis\text{-}[Pt_2(NH_3)(CH_3COO)_4]+2H_2O+NH_3$$

The next endothermic effect in the range 453.15–478.15 K with maximum at $T$=468.15 K includes further break down of the complex and disconnection of further molecule $NH_3$ and four molecules $CO_2$.

$$cis\text{-}[Pt_2(NH_3)(CH_3COO)_4] \rightarrow$$
$$NH_{3(g)}+4CO_{2(g)}+\text{solid residue}$$

The experimental mass loss during the maintenance of these processes in the range 453.15–478.15 K is $\Delta m$=27.50%, while the theoretical mass loss should be $\Delta m$=27.73%. The second stage of the decomposition of the binuclear complex is in the temperature interval 483.15–593.15 K and the mass loss $\Delta m$=55.60%.

Of certain interest is the DTA curve in which after endothermic effect in the range 453.15–478.15 K two successive high exothermic effects in the range 503.15–588.15 K with maximums at 523.15 and 573.15 K were observed. The existence of these two effects is evidence, that except the decomposition process of the compound, new compounds were formed. Pt and platinum carbides were most probably obtained as final residue.

As in a very small temperature interval a lot of successive effects were obtained, it was impossible to separate and identify the different substances at this heating rate 5°C $min^{-1}$. If the final residue was platinum then theoretically $\Delta m$=43.97%. From the TG

curve the registered mass loss of $\Delta m$=55.60%, gives us the reason to suggest that the final residue consists of platinum and platinum carbides [15, 16].

Certain differences were observed at comparing the IR spectra of the PtAA complex when the substance was not heated (at room temperature) and then the same complex was heated at $T$=413.15 K and cooled to room temperature. At room temperature in the IR spectra of the PtAA complex two intensive bands, characteristics for $\gamma^{as}_{(COO^-)}$ and $\gamma^{s}_{(COO^-)}$ at 1569 and 1398 cm$^{-1}$, one quite intensive band at 894 cm$^{-1}$, characteristic for $\rho_{NH_3}$ and one weakly intensive wide band in the range 1300–1021 cm$^{-1}$ were observed, where most probably $\delta^{as}_{(NH_3)}$ and $\delta^{s}_{(NH_3)}$ bands were overlapped. In the IR spectra of the heating complex at $T$=413.15 K, the band at 1569 cm$^{-1}$ was smaller intensive, which was probably due to the changes of the DTA curve at this temperature. Endothermic effect was observed. The shoulder in the range 1300–1021 cm$^{-1}$ disappeared, which was connected with the elimination of one molecule ammonia. Only one weakly intensive band at 875 cm$^{-1}$, characteristic for $\rho_{NH_3}$ and one intensive band at 1375 cm$^{-1}$, characteristic for $\gamma^{s}_{(COO^-)}$ were remained. The results confirm the assumption that the endothermic effect at $T$=413.15 K was connected with the elimination of the molecule ammonia and the change of the structure of the initial complex. In the IR spectra of the heating complex at $T$=573.15 K only one middle intensive band at 1400 cm$^{-1}$ and one weakly intensive band at 875 cm$^{-1}$ were remained. This may be explained with the fact, that the probable new compound with the structure $PtC_2$ was formed.

The same PtAA complex was investigated again after a year by thermogravimetric analysis. At comparing the DTA curve with those made immediately it is evident that the curve followed the analogous movement.

The complex is stable up to $T$=313.15 K (Fig. 3). After this temperature, begins the decomposition in two stages. The first stage is in the temperature interval 313.15–490.15 K and the second stage is – 490.15–593.15 K. At the first stage in the DTA curve two consecutive small endothermic effects in the range 398.15–481.15 K with the maximums at $T$=416.15 and 469.15 K were observed. In the TG curve in the range 398.15–445.15 K the mass loss is registered $\Delta m$=5.68%, but the theoretical mass loss $\Delta m$=5.17%, which may be corresponded to the disconnection of two molecules of crystal water. The second endothermic effect in the range 456.15–481.15 K is connecting with the decomposition of the platinum complex. The experimental mass loss at the TG curve is $\Delta m$=19.6% but the theoretical mass loss $\Delta m$=20.4%, which corresponds to the disconnection of two molecules ammonia, one molecule $CO_2$ and probably one molecule CO.

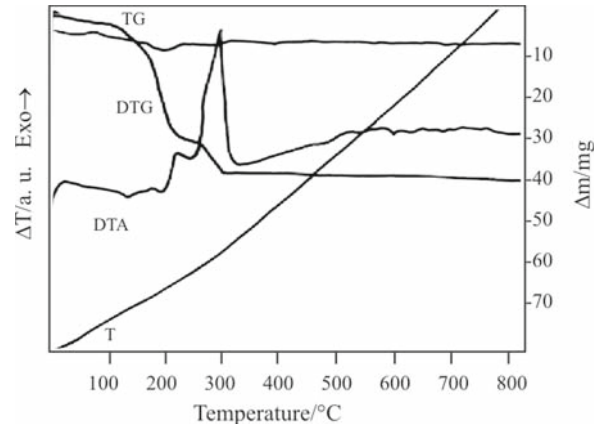


**Fig. 3** TG, DTG and DTA curves of PtAA after a year

The second stage of the decomposition is described with the horizontal part in the TG curve. In the DTA curve in this part one small exothermic effect in the range 490.15–593.15 K is observed which is overlapped with the endothermic effect with maximum at $T$=511.15 K. In this temperature interval the experimental mass loss in the TG curve is $\Delta m$=33.05%, which can be explained with the release of the two molecules $CO_2$. Especially interestingly is the DTA curve in which after endothermic affect with maximum at $T$=511.15 K one strong exothermic effect with maximum at $T$=568.15 K is observed. The availability of this exothermic effect is evidence, that along with the decomposition process of the platinum complex, new compounds have been formed. Platinum is the most probable final residue. This fact is well corresponding to the mass loss $\Delta m$=43.18% of the obtained solid residue. If the final residue is platinum then theoretically $\Delta m$=43.97%. This gives us the reason to suggest that the final residue consists only platinum. These changes in final products of the complex investigated immediately and one year later probably were obliged to variation of the composition.

*Pt(II) complex with propionic acid – potassium dichlorido propionato ammine-bis-*μ*-propionato diplatinate (II) –*
*$K[Pt_2(NH_3)(C_2H_5COO)Cl_2(\mu\text{-}C_2H_5COO)_2]$* **(2)**

The PtPrA complex is stable up to $T$=323.15 K. After this temperature in the DTA curve one pronounced endothermic effect in the temperature interval 453.15–483.15 K with maximum at $T$=473.15 K can be observed which overlaps into exothermic effect because the process gives by burning in air (Fig. 4). At this temperature the experimental mass loss of $\Delta m$=29.00%, which is due to the decomposition of the platinum complex. In this range one molecule $NH_3$, three molecules

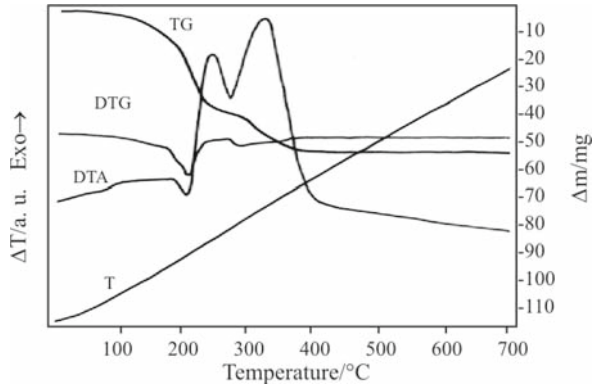


**Fig. 4** TG, DTG and DTA curves of PtPrA

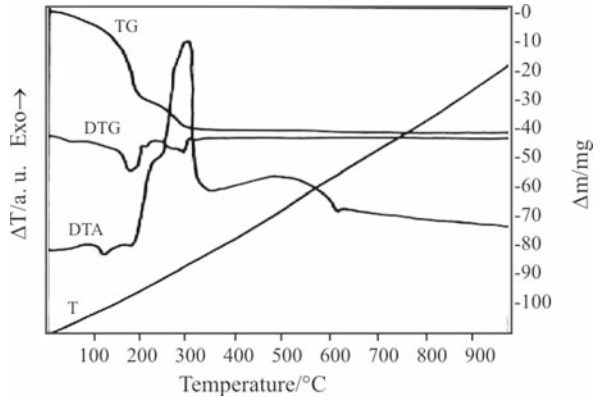


**Fig. 5** TG, DTG and TDA curves of PtVA

carbon dioxide and one molecule chlorine are probably eliminated according to the scheme:

$$cis\text{-}K[Pt_2(NH_3)Cl_2(C_2H_5COO)_3] \rightarrow NH_{3(g)}+3CO_{2(g)}+Cl_{2(g)}+\text{solid residue}$$

The theoretical mass loss is $\Delta m$=29.88%. After this endothermic effect two salient exothermic effects with maximums at $T$=503.15 and 573.15 K were observed.

The availability of these two exothermic effects is due to the fact that except the decomposition process of the platinum complex, new compounds are formed. This fact is well corresponding to the mass loss $\Delta m$=44.04% of the obtained solid residue. If the final residue is platinum then theoretically $\Delta m$=52.99%. This gives us the reason to suggest that the final residue contains platinum and platinum carbides.

*Pt(II) complex with valeric acid – potassium chlorido-*bis*(pentanoato)ammine-bis-*μ*-pentanoato diplatinate(II) –*
*$K[Pt_2(NH_3)(C_4H_9COO)_2Cl(\mu\text{-}C_4H_9COO)_2]$* **(3)**

The PtVA complex is stable up to $T$=313.15 K. Its two-stage decomposition begins after this temperature with pronounced endothermic effect in the range 373.15–413.15 K with a maximum at $T$=393.15 K (Fig. 5). In the TG curve in this range the experimental mass loss is $\Delta m$=9.80%, but the theoretical mass loss is $\Delta m$=9.50%, which corresponds to the disconnection of two molecules $CO_2$. The next endothermic effect in DTA curve is in the range 433.15–453.15 K with maximum at $T$=443.15 K, which is connected with the experimental mass loss $\Delta m$=28.87%, at the theoretical mass loss $\Delta m$=28.12%. This endothermic effect is most probably due to the disconnection of four molecules $CO_2$, one molecule $NH_3$ and two molecules CO.

Of certain interest is the DTA curve after this temperature $T$=443.15 K. It is observed a high exothermic effect overlapping into second exothermic effect in the range 533.15–573.15 K with maximum at 568.15 K. After this temperature third rather wide exothermic effect in the range 613.15–833.15 K is observed. All these exothermic effects are connected with the decrease in mass. The existence of exothermic effects is evidence, that except the decomposition process of the compound, new compounds are formed.

If the final residue is platinum then theoretically $\Delta m$=51.33%. From the TG curve the registered mass loss of $\Delta m$=50.80%, gives us the reason to suggest that the final residue consists of platinum [15, 16].

*Pt(II) complex with isovaleric acid – potassium chlorido-bis(isopentanoato)ammine-bis-*μ*-isopentanoato diplatinate(II) –*
*$K[Pt_2(NH_3)(C_4H_9COO)_2Cl(\mu\text{-}C_4H_9COO)_2]$* **(4)**

The PtIvA complex is stable up to $T$=408.15 K. Its two-stage decomposition begins after this temperature (Fig. 6). The first stage (in the temperature interval $T$=408.15–578.15 K is connected with mass loss of $\Delta m$=49.28%. The second stage is in the temperature interval $T$=408.15–743.15 K and the mass loss $\Delta m$=69.57%.

In the range 393.15–453.15 K two successive exothermic effects with maximums at $T$=416.15 and 443.15 K. The second exothermic effect is connected with the mass loss of $\Delta m$=4.35%. A broad endothermic effect is observed in the DTA curve in the range 478.15–513.15 K where the mass loss of $\Delta m$=24.64%

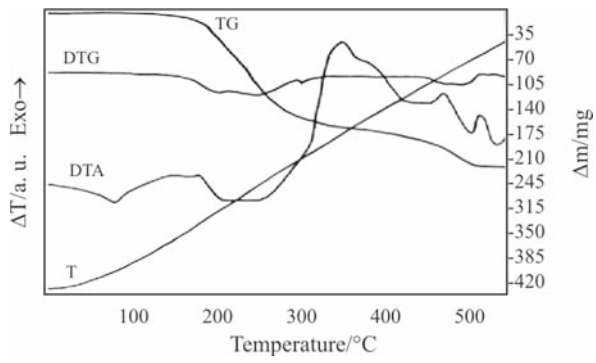


**Fig. 6** TG, DTG and DTA and $T$ curves of PtIvA

and corresponds to the decomposition of the binuclear platinum complex. At this temperature interval one molecule $NH_3$, three molecules $CO_2$ and two molecules CO are most probably disconnected.

The theoretical mass loss of $\Delta m$=24.22%. Of interest is the DTA curve after the last temperature interval. In the DTA curve one marked exothermic effect in the range 578.15–678.15 K with maximum at $T$=613.15 K can be observed, subsequent from one broad endothermic effect in the temperature interval 683.15–703.15 K with maximum at $T$=693.15 K and two small exothermic effects in the range 713.15–763.15 K with maximums at $T$=718.15 and 743.15 K. The availability of these two exothermic effects is proof, that except the decomposition process of the platinum complex, new compounds are formed.

If the final residue is platinum then theoretically $\Delta m$=53.73%. From the TG curve the registered mass loss of $\Delta m$=69.57%, gives us the reason to suggest that the final residue consists of platinum and platinum carbides [15, 16]. In the literature two kinds of platinum carbides are announced – $PtC_2$ and $Pt_2C_3$ [15, 16], but no X-ray data are available for their characterization. There are some data about the existing of PtN [17], but obtained at quite different conditions, then this taking place with the decomposition of the complex.

## Conclusions

The TG/DTA curves of the four binuclear Pt(II) complexes were different in character. There was a two-stage mass loss on heating. The complex PtAA was stable up to 343.15 K, the complex PtPrA was stable up to 323.15 K, the PtVA was stable up to $T$=313.15 K and the PtIvA was stable up to 408.15 K. After the thermal decomposition of the Pt(II) complexes with carboxylic acids, only in the PtVA complex and PtAA complex (investigated after a year) the final residue consisted only platinum, while in the rest complexes the solid residue was a mixture of platinum and platinum carbides ($PtC_2$, $Pt_2C_3$).

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Received: February 20, 2008
Accepted: May 29, 2008
Online First: September 19, 2008

DOI: 10.1007/s10973-008-9069-0