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Thermal Decomposition Study of Platinum(II) and Palladium(II) Thiosaccharinate Complexes With Supporting Diphosphine or Bipyridine Ligands

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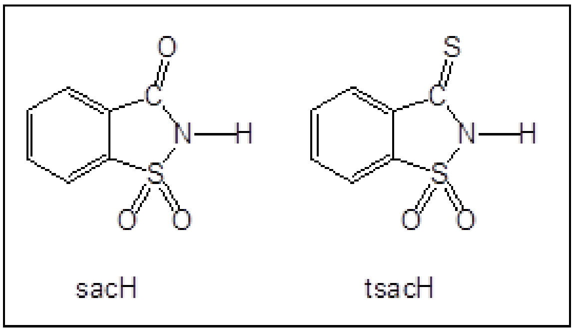
Abstract

The thermal behavior of mixed ligand complexes of platinum (II) and palladium(II) thiosaccharinate (tsac) with diphosphine or bipyridine ligands was studied by thermogravimetry, TG, and differential thermal analysis, DTA. The Platinum complexes showed higher thermal stability than the corresponding palladium complexes. Platinum complexes start decomposition in the molten phase and undergo decomposition in two distinct steps where the tsac ligands are lost first followed by the diphosphine ligand which needed higher temperatures. For the corresponding palladium complexes, the two processes are overlapped. The decomposition was exothermic in general with few exceptions. The coordination of palladium with bipyridine (bpy) ligand gives a unique thermal behavior where only one tsac ligand is lost first followed by half tsac. Such a behavior suggested a dimerization process. The dimer may comprise of two palladium ions with two bpy groups and one tsac group, which finally decomposes into PdO, in a highly exothermic process. The TG data was used for the study of chemical kinetics of the decomposition reactions with the aid of the most recently available formulae. The method is based on plotting a function of the weight loss extent against reciprocal temperature and the plot of the highest correlation coefficient is considered for the optimum reaction order and the activation energy. Both reaction order and the activation energy can be estimated for the studied complexes.

1. Introduction

Over the past two decades there has been significant interest in the chemistry of the metal-bonded saccharinate (sac) and thiosaccharinate (tsac) ligands (chart 1). Saccharin (*o*-sulfobenzimibe; 1,2-benzothiazole-3(2H)-one 1,1-dioxide;(sacH)) is one of the best known and most widely used artificial sweetening agents, its coordination chemistry has been extensively studied [1,2]. Saccharinate can adopt a range of different coordination modes to metal centers being able to bind in a monodentate fashion through either the negatively charged nitrogen atom or an oxygen atom of either the carbonyl or sulfonyl groups. It also has the capacity to bind in a bidentate or even polydentate fashion with participation of both N- and O- donor atoms [1]**.** Replacement of the carbonyl in saccharin by a thiocarbonyl gives thiosaccharin (tsacH), the chemistry of its anion (tsac) has been less extensively explored [3-6]. While the two molecules sacH and tsacH look superficially similar they differ in both their ground state structures and their liginating properties to metal centers. Thus while saccharin (sacH) exist in a single form (amide), thiosaccharine (tsacH) can adopt two tautomeric forms in solution namely amide or thiol (Chart 1). Further upon deprotonation the negative charge remains on nitrogen in saccharinate but is primarily located on sulfur in thiosaccharinate (chart 1) [7,8]. This becomes important for the coordination chemistry of the two amides since the thiosaccharinate (tsac) ligand is expected to bind strongly to *soft* metal centers *via* the carboxylic sulfur atom and consequently the coordination chemistry of the thiosaccharinate [3,6] has been shown to be quite different from that of saccharinate.



(Chart 1)

Thermoanalytical investigations of metal complexes receive increasing interest to establish the mechanisms of the decomposition and studying the thermodynamics and kinetics [9]. The thermal behavior is often correlated with structural and electronic characteristics of the metals and the ligands [10-12]. Kinetic investigations offer supportive evidence about overlapping thermal decomposition reactions [13]. Linear relationship could be established between the *pKb* values of the ligands with the activation energies for decomposition of the complexes [10].

Several authors reported on the thermal decomposition of platinum and palladium complexes [14]. Han-Zhang et al, [15], studied the palladium thioether complexes and showed that they decompose into organic ligands and $PdCl_2$. In his study on palladium and platinum complexes of N-allyl-N'pyrimidin-2ylthiourea, Katib, 2011 [16], could derive practical evidence that Pd and Pt are bound to the S atom in the thiourea. The kinetic parameters are correlated with bonding and structural properties of the complexes. Al Takhin, et al, [12] have shown that platinum and palladium complexes containing phosphine or diene ligands sublime under vacuum. The ligand bonding power to $PtCl_2$ decreases along the series $PPr^i_3 > P(C_6H_{11})_3 > PEt_3 > PPh_3 >$ olefin (in cyclo-octa-1,5-diene). The bond-enthalpy contributions of Pt–X [relative to $\bar{E}$(Pt–Cl)= 290 kJ mol^{-1}] decrease in the series Pt–C* $\sim$ Pt–Cl > Pt–C > Pt–S, where C* and C are trigonal and tetrahedral carbon (in Ph–Pt and CH_3–Pt bonds, respectively). The thermoanalytical study of the monoalkyl [α-(4-benzeneazoanilino)-N-benzyl]phosphonates and their palladium (II) complexes have shown that in the chloro-bridged cyclopalladated complexes ligand de-esterification coupled with dehalogenation is followed by a complex pyrolysis. The decomposition of the mononuclear complexes includes de-esterification and other ligand degradation processes that lead to metallic palladium and P_2O_5 [17]. The mechanism of thermal decomposition for the palladium-imidazole complexes in air involves initial dissociation of H_2O and IMDAH ligands, subsequent dissociation of the chloride atoms to form PdO and finally formation of Pd metal [14]. The thermal behavior of the complexes $Pd_2(dppm)_2Cl_2$, $Pd_2(dppm)_2(SnCl_3)Cl$ and $Pd_2(dppm)_2(SnCl_3)_2$ (dppm = bis[diphenylphos-phino-(methane)], $\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}$ in the solid state resulted in the formation of a mixture of metallic palladium and oxidized species such as PdO, condensed phosphates, SnO_2 and SnP_2O_7 [18]. Naumov et al [19] studied the thermal decomposition of alkali metal saccharinates, while the decomposition behaviors of aqua complexes of the metal (II) saccharinates were studied by Magri et al [20] and Icbudak et al. [21]. Thermal behavior of some transition and non transition metal saccharinates complexes have been reported in literature [22-30].

Although thermal decomposition of saccharine metal complexes have been studied, thermal decomposition of thiosaccharin metal complexes seems to be neglected. We have recently reported the anticancer activity of platinum(II) saccharinate and thiosaccharinate complexes [31]. As part of our research on the synthesis and characterization of metal complexes of tsac with other co-ligands [32-34], we report the thermal behavior of thiosaccharin complexes of the type [M(tsac)$_2$(L-L)], M = Pd or Pt; L-L = dppm. dppe, dpp or 2,2-bipyridine, which we have recently reported in literature [32].

2. **Experimental details**

2.1 Preparation of the complexes:

The metal thiosaccharinate complexes [M(tsac)$_2$(L-L)] or [Pd(tsac)$_2$(μ^1-dppm)$_2$]; M = Pt or Pd; L-L = bis(diphenylphos phino)methane (dppm), bis(diphenylphosphino) ethane (dppe), bis(diphenyl-phosphino)propane (dppp) or 2,2-bipyridine (bpy) were prepared by the method reported earlier [32].

2.2 Measurements

The simultaneous TG, DTG- DTA measurements were carried out on a PerkinElmer SII Diamond TG/DTA thermal analyzer. Samples weighing 5-15 mg of the complexes were placed in the aluminum pans and heated at a rate of 10 ^{o}C min^{-1} between room temperature and 600 ^{o}C under a nitrogen gas flow rate of 100 ml min^{-1}. The complexes were also visually monitored in a melting point apparatus to observe the changes in the phase as well as the evolution of volatile products.

3. Results and Discussion

3.1 Platinum Complexes

The TG curves of platinum complexes are shown superimposed on each other for comparison in Fig 1. The DTG curves that show the rate of weight losses together with the DTA curves are given in Figs. 2-4. For [Pt(tsac)$_2$dppm], a small, but significant, endotherm was noticed (Fig. 2) between 222 and 270 ^{o} with a minimum at 261^o C referring to the melting of the dppm complex.

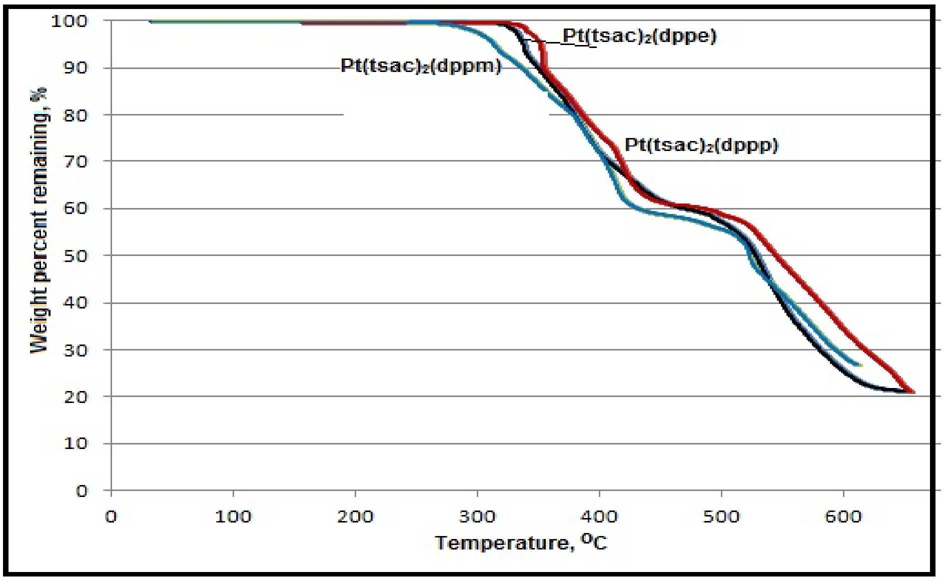


Figure 1: TG curves for the platinum complexes.

The main decomposition process of occurs in the molten phase between 270^o C and 445^o C and resulted in the loss of 40.51%. The DTG curve indicated a multistep weight loss process with complex thermodynamic behavior as indicated by the DTA curve of the complex (Fig. 2). The process starts after melting where an exothermic peak could be noticed between 261 and 327^o C and attains maximum rate at 315^o C losing 8.7%; then an endothermic 9.7% weight loss starts at 328 and ends at 368^o C with a maximum rate at 352^o C. The process goes slightly exothermic after that to end at 395° with a maximum at 390° C and involves a loss of 9.0% and finally proceeds exothermic till 442° C with a max rate at 413° and involves a loss of 13.4% of the weight. The overall weight loss of the process matches the removal of two tsac groups. The next decomposition reaction involves three partially overlapped exothermic steps: 455 – 487° C, losing 2.9%; 487-537° with max at 522° C losing 12.0% and finally between 537 and 650 ° leading to the formation of the metal where the maximum rate of weight loss occurs at 567° C. The overall weight loss agrees with the loss the dppm group.

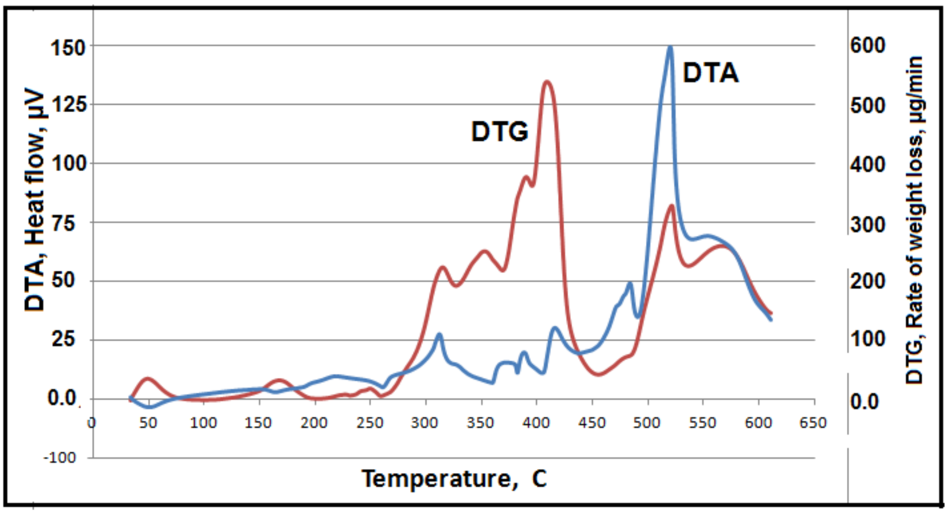


Figure 2: DTA and DTG curves of $[Pt(tsac)_2(dppm)]$.

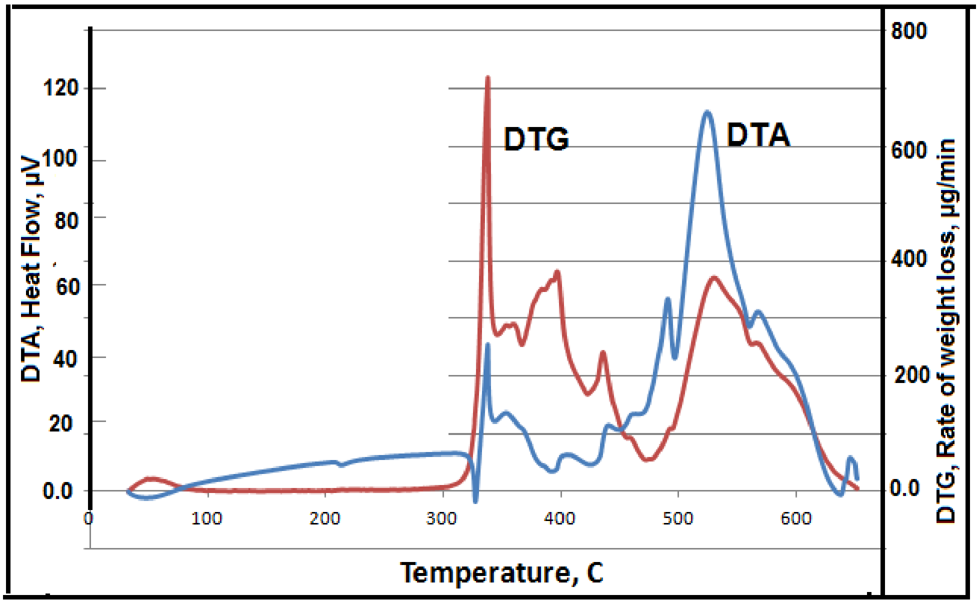


Figure 3: DTA and DTG curves of M81: $[Pt(tsac)_2(dppe)]$.

The main features of the thermal behavior of $[Pt(tsac)_2(dppe)]$ and $[Pt(tsac)_2(dppm)]$ are identical being occurring in the molten state and proceed in two main decomposition reactions. The first reaction starts endothermic where the complex melts at 312° (337 for dppp) prior to decomposition. A slow weight loss step starts at 303° (327° C for dppp) and a slight exothermic behavior can be noticed. The rate of the weight loss significantly increases after 327° due to the improved heat flow through the melt in comparison with the solid. The melting endotherm changes into an exotherm with a maximum at 338° C (352° for dppp) at which the maximum rate of weight loss was recorded and ends at 346° C (368° for dppp) with a loss of 7.2%. The second step is slightly exothermic ends at 367° C with a maximum rate of weight loss at 354° C and resulted in a weight loss of 5.39%. The third step is endothermic and ends at 423 ° C with a maximum rate at 398° C and results in a weight loss of 15.15%. The total weight loss within this step is 40.51% for [Pt(tsac)$_2$(dppm)].

A solid crust is formed on the surface of the materials after the decomposition and this will alter the progress of the decomposition. The evolution of the volatile products will be hindered by the solid crust and hence the weight loss process will be affected significantly.

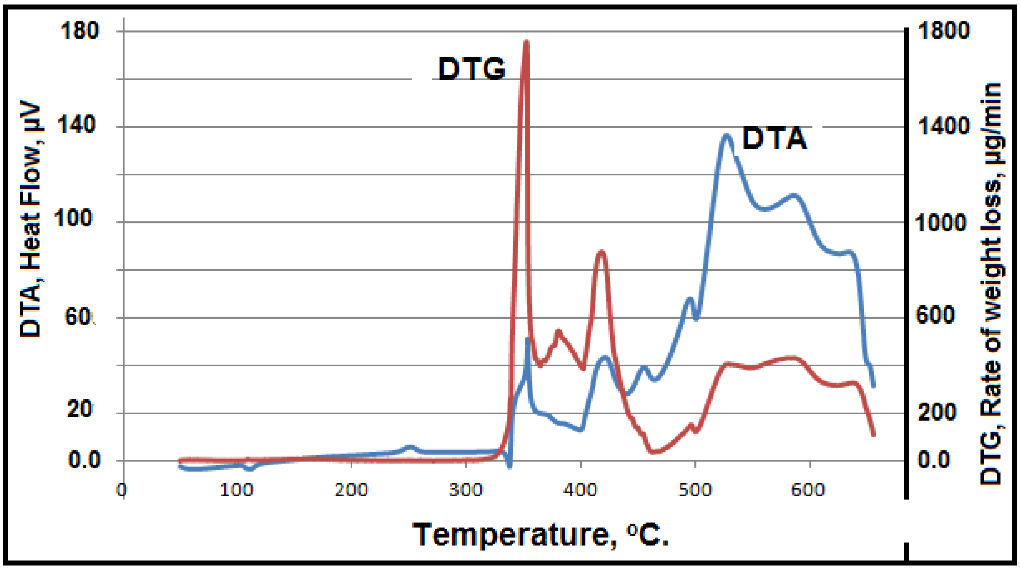


Figure 4: DTA and DTG curves of M132: [Pt(tsac)$_{2(}$dppp)]

The carbon number of the dppp group plays an important role in determining the thermal stability of the complexes. From Fig 1, the TG curves of the three platinum complexes indicate that the initial decomposition temperatures of the Pt complexes were: 265, 317 and 322° C for the dppm, dppe and dppp respectively. Meanwhile the final decomposition temperature was almost the same for the three complexes, 440-443° C. Thus, the Pt bonding to the tsac is weaker than for the Pt to the dpp. The dppp ligand looks more stable when the alkylene group has a higher carbon number and this consequently reflected on the Pt-tsac bonding. Similarly, Al Takhin, et al, [12] have shown that platinum and palladium complexes containing phosphine or diene ligands sublime under vacuum and found that ligand bonding power to $PtCl_2$ decreases along the series PPr^i_3 > $P(C_6H_{11})_3$ > PEt_3 > PPh_3 > olefin (in cyclo-octa-1,5-diene). Weight loss for 132 (dppp) is 36.5% corresponds to the loss of 2 (tsac) groups, *ca*. 38.8%.

The second decomposition process occurred in two steps. The first is between 440 and 471° C, attained a maximum rate of weight loss at 464° with a weight loss of 5.89%. The next step continues up to 649 with a maximum rate at 535° C losing a total of 38.73%.

The kinetics of the decomposition reactions was carried out to evaluate the activation energy and the order. The degree of conversion, ω, was calculated from the TG signals. The kinetic model employed in this work was adapted from several references [35 - 37]. The kinetic treatment of the TG and DTG data by plotting (Ln [(-Ln ω)/T^2]) against (1/T) for the first order reaction, n.

Whereas,

Ln [(1-ω^{1-n})/ (T^2 (1-n))] is plotted versus 1/T for n not equal to 1. The nature of the decomposition and the ease with which the volatile material escapes from the compounds necessitates the movement through the molten phases followed by the formation of the solid crust. The gases will search for defects in the crust to escape. This will disturb the progress of the reaction. Consequently, the kinetics of the reaction is affected and a trend to higher reaction order could be noticed (Table 1). The correlation coefficients of the plots indicate that multi-order reaction is predominant.

Complex	Reaction Order	Temp Range, ^{o}C	Correlation Coefficient, R^2	Activation Energy, J/mol
[Pt(tsac)$_2$(dppm)]	n=1	270-445	0.9203	52.266
	n=2		0.934	86.456
	n=3		0.9431	242.013
[Pt(tsac)$_2$(dppe)]	n=1	313-462	0.9724	66.098
	n=2		0.9378	101.97
	N=3		0.9342	103.02
[Pt(tsac)$_2$(dppp)]	n=1	344-462	0.8959	39.15
	n=2		0.9356	109.78
	n=3		0.9529	132.615

Table 1: Results of kinetic study for the platinum complexes

3.2. Palladium Complexes

The TG curves for [Pd(tsac)$_2$(dppm)] and [Pd(tsac)$_2$(dppe)] superimposed on each other are shown in Fig. 5. The DTG and DTA curves of [Pd(tsac)$_2$(dppm)] and [Pd(tsac)$_2$(dppe)] are shown in Figs. 6 and 7 respectively**.** The initial decomposition temperature of Pddppm and Pd dppe was 238 and 300^o C, respectively and involves an overall weight loss for dppm of 69.6% and the maximum rates of weight loss occur at 258^o C. Thus, Pd-dppe has higher thermal stability than Pd-ppm. For Pd-dppe the maximum rate of weight loss occurred at 328 and the process involved the loss of 58.78% in three successive steps: 18.99%; 7.45%, and 30.80% ending at 479^o C. Further, the two complexes show a lower thermal stability than their corresponding Pt complexes (Fig. 1).

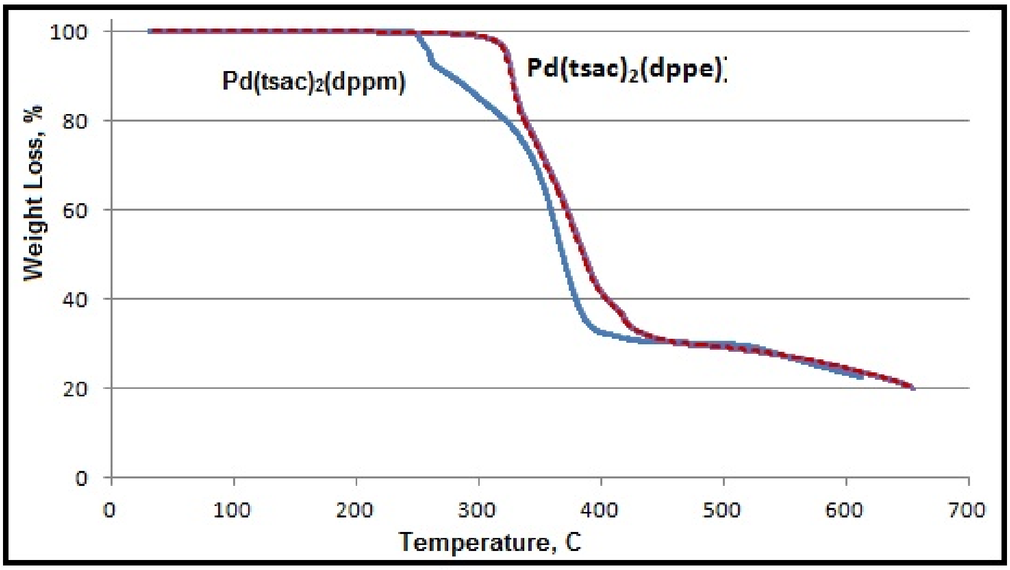


Figure 5: TG curves for [Pd(tsac)$_2$(dppm)] and [Pd(tsac)$_2$(dppe)]

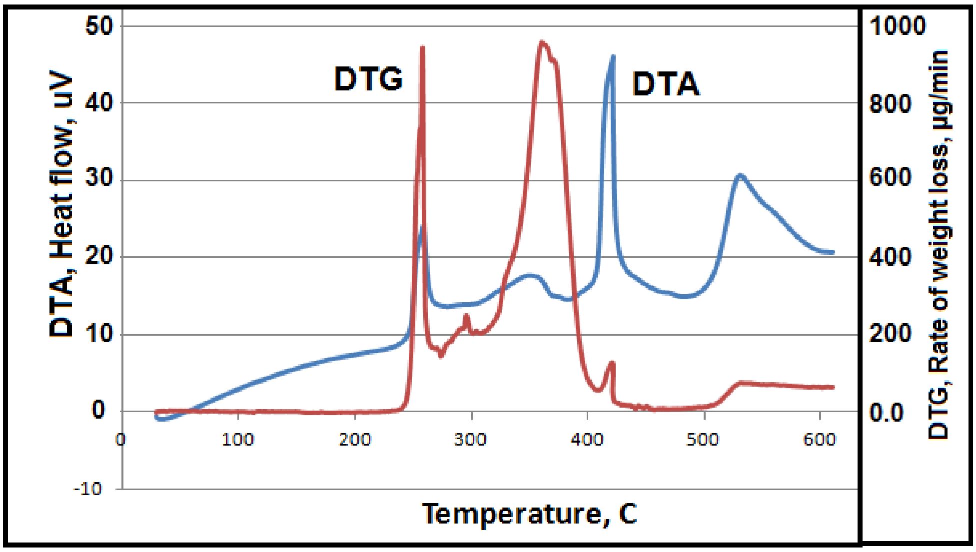


Figure 6: DTA and DTG of [Pd(tsac)$_2$(dppm)]

The results of the kinetic treatment of the reactions are listed in Table 2. Again, the correlation coefficients of the plots indicate that multi-order reaction is predominant (Table 2).

Table 2: Results of kinetic study for palladium complexes

Complex	Reaction order	Temp Range, °C	Correlation Coefficient, R^2	Activation Energy, kJ/mol
[Pd(tsac)$_2$(dppm)] 1st step	n=1	234-265	0.9377	257.13
	n=2		0.9896	406.75
	n=3		0.981	652.44
[Pd(tsac)$_2$(dppm)] 2nd step	n=1	270-410	0,8263	68.70
	n=2		0.9299	98.46
	n=3		0.9666	135.79
1st step Loss of 1 tsac group	n=1	301-336°C	0.9869	234.58
	n=2		0.9301	358.86
	n=3		0.8663	487.89
3rd step ½ tsac + bpy	n=1	396-496	0.8849	80.368
	n=2		0.9728	108.60
	n=3		0.9936	332.489
[Pd(tsac)$_2$(μ^1-dppm)$_2$]	n=1	230-440	0.7974	52.68
	n=2		0.9138	73.35
	n=3		0.9698	101.95
Step 1 20.254% MW Lost 182	n=1	287-338	0.8071	226.12
			0.9529	479.09
			0.9728	797.71

The TG, DTG and DTA curves of [Pd(tsac)$_2$(bpy)] are shown superimposed on each other in Fig. 8.

Three distinct weight loss processes characterizes the thermal behavior of this complex between 268 and 336 ^{o}C, 31.2% weight loss (for one unit of tsac = 30.07%) which is slightly exothermic. The second process was slow and proceeds between 351 and 397^{o} C and involves the loss of 14.8% of the original complex weight. Theoretically this refers to the loss of one half of a tsac group. The third step occurs between 400 and 497^{o} C and involves 35.9% weight loss and end up with PdO. Calculations show that the weight loss corresponds to the removal of one half tsac group, a bpy group and the gain of one oxygen atom from the atmosphere to form PdO, which is only 1.15% more than the practically obtained value (35.90%).

[1/2tsac group (15.03%) + bpy (23.69)] – [O atom (2.4%)] = 36.32%

The last effect was highly exothermic because it involves the oxidation of the metal to end up with a residual material which is 18.4% by weight of the original complex. This is in excellent agreement with the theoretical calculations of PdO which represents 18.59%. Thus, the hypothetical decomposition of the complex may be as follows:

[Pd(tsac)$_2$(bpy)] → [Pd(tsac)(bpy)] → [Pd1/2(tsac).(bpy)] → [PdO]

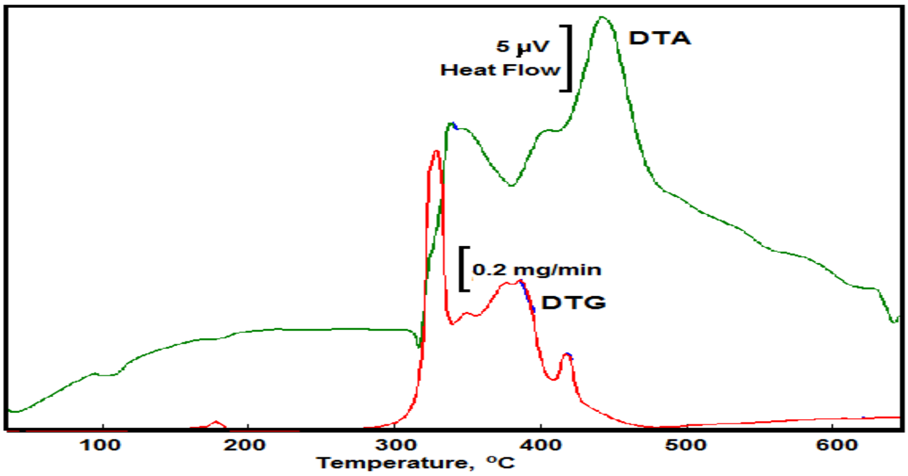


Figure 7: DTA and DTG of [Pd(tsac)$_2$(dppe)]

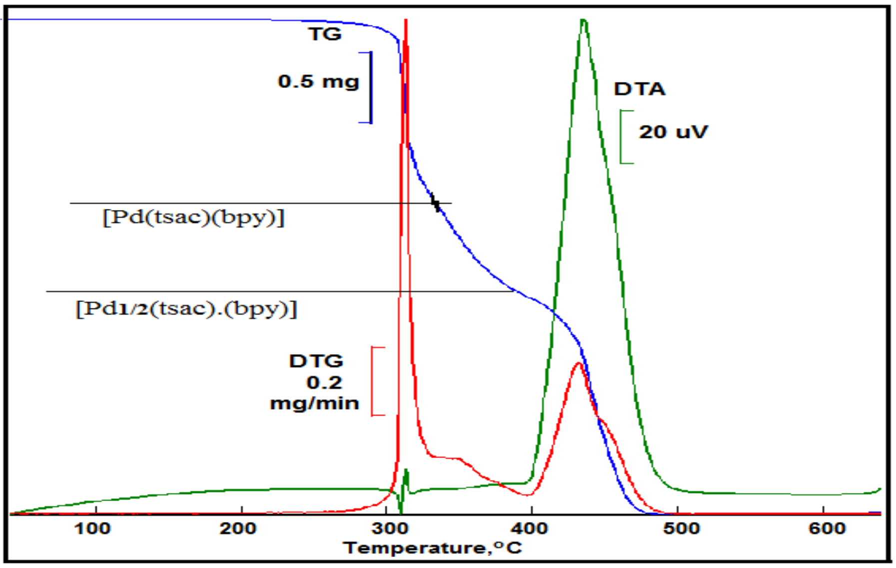


Figure 8: TGA, DTA and DTG of 121 [Pd(tsac)$_2$(bpy)]

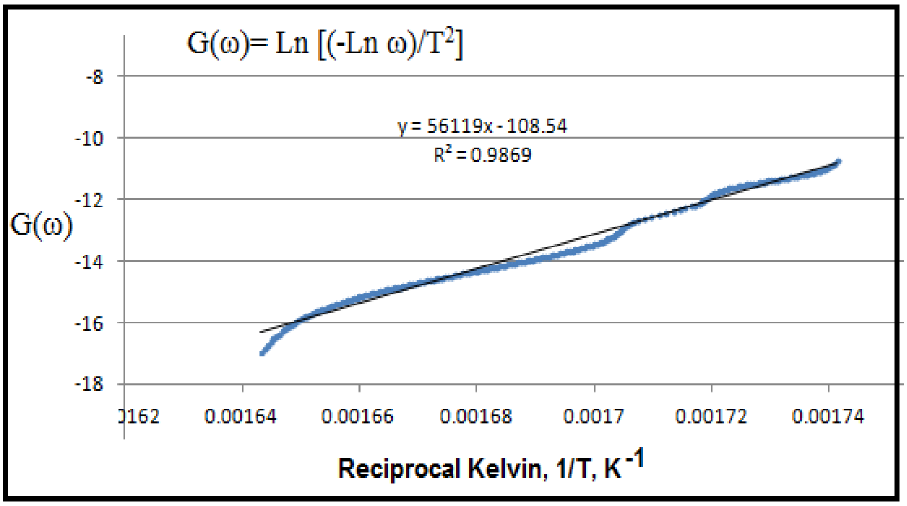


Figure 9: kinetic plot for the first decomposition step of [Pd(tsac)$_2$(bpy)] for reaction order, n = 1.

The kinetic study of the first step (The loss of one tsac group) indicated a first order reaction with activation energy of 234.58 KJ (Fig. 9). Meanwhile, the last reaction was a third order with activation energy of 325.06 KJ, (Fig. 10) because it may involve rearrangement and loss of two groups in addition to abstracting an oxygen atom to form PdO.

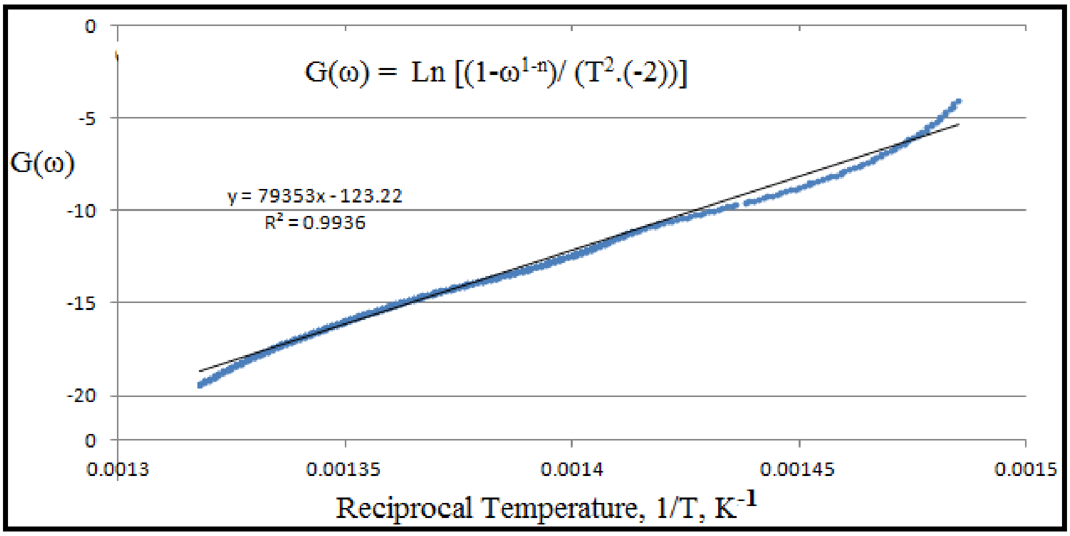


Figure 10: kinetic plot for the third decomposition step of [Pd(tsac)$_2$(bpy)] for reaction order, n = 3.

Conclusions

1. Thermoanalytical investigation is effective as a tool for the description of the thermal decomposition of complexes platinum (II) and palladium(II) thiosaccharinate (tsac) with diphosphine or bipyridine ligands.
2. The complexes melt prior to the decomposition a matter that facilitates the evolution of the volatile products.
3. Conversely, when the molten material decomposes, they result in the formation of a solid crust on the surface.
4. There is also a possibility of the formation of some stable intermediate during the course of decomposition.

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