

Study on the thermal behavior of the complexes of the type [PdX₂(tdmPz)] (X = Cl⁻, Br⁻, I⁻, SCN⁻)

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Abstract Four new mononuclear Pd(II) complexes of the type [PdX₂(tdmPz)] {X = Cl⁻ (**1**); Br⁻ (**2**); I⁻ (**3**); SCN⁻ (**4**); tdmPz = 1-thiocarbamoyl-3,5-dimethylpyrazole} have been synthesized and characterized by elemental analysis, IR spectroscopy, ¹H and ¹³C{¹H}-NMR experiments. The thermal behavior of the complexes **1–4** has been investigated by means of thermogravimetry (TG) and differential thermal analysis (DTA). From the initial decomposition temperatures, the thermal stability of the complexes can be ordered in the sequence: **3** < **4** ≡ **2** < **1**. The final products of the thermal decompositions were characterized as metallic palladium by X-ray powder diffraction.

Keywords Pd(II) complexes · 1-thiocarbamoyl-3,5-dimethylpyrazole · TG and DTA

Introduction

Thiocarbamoylpyrazole ligands have attracted considerable attention in recent years due to their ability to coordinate in neutral S-monodentate [1], neutral N,S-chelating bidentate [2], anionic N,S-bidentate [3], and anionic N,N-bidentate fashions [4].

In particular, a great deal of interest has been devoted to the synthesis of mononuclear Pd(II) compounds containing N,S-chelating 1-thiocarbamoylpyrazole ligands due to their

promising antitumor [5] and antiamoebic activities [6–8]. In our previous article [9, 10], we have reported the synthesis, spectroscopic characterization, and antitumor evaluation of the compounds [PdX₂(tdmPz)] (X = Cl⁻, Br⁻, I⁻, SCN⁻; tdmPz = 1-thiocarbamoyl-3,5-dimethylpyrazole). However, systematic studies on the thermal decomposition of this class of compounds have not been described yet in the literature.

In pursuing our interest on thermal behavior [11–16], structural aspects [17–19], and biological activity of palladium(II) complexes [20–22], we present in this study the thermal investigation of tdmPz and compounds of the type [PdX₂(tdmPz)] by means of thermogravimetry (TG) and differential thermal analysis (DTA).

Experimental

Preparation of the complexes

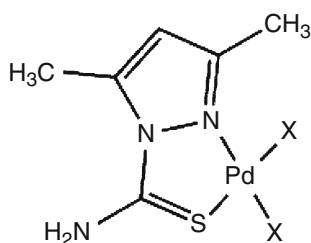
The tdmPz ligand and complexes **1–4** (Scheme 1) were synthesized according to the procedure described in the literature [9, 10].

Instrumentation

Elemental analyses of carbon, nitrogen, and hydrogen were performed on a microanalyser elemental analyser CHN, model 2400 PerkinElmer. Infrared spectra were recorded in KBr pellets on a Nicolet model SX-FT-Impact 400 spectrophotometer in the 4000–400 cm⁻¹ spectral range. The spectra of nuclear magnetic resonance of ¹H and ¹³C were recorded on VARIAN multinuclear spectrometer, model INOVA 500, using dmsd-d₆ for dissolution of samples. Thermal analyses (TG) and differential thermal analyses

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Scheme 1 Proposed structure of the compounds $[\text{PdX}_2(\text{tdmPz})]$ ($\text{X} = \text{Cl}^-$ (**1**), Br^- (**2**), I^- (**3**), SCN^- (**4**); tdmPz = 1-thiocarbamoyl-3,5-dimethylpyrazole)

(DTA) were carried out using a TA Instruments model SDQ 600, under flow of dry synthetic air (50 mL min^{-1}), temperature up to $900 \text{ }^\circ\text{C}$ and at heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ in α -alumina sample holders. The reference substance was pure α -alumina in DTA measurements. X-ray powder diffraction patterns were measured on a Siemens D-5000 X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and setting of 34 kV and 20 mA. The peaks were identified using ICDD bases [23].

Results and discussion

The results of the elemental analyses confirmed the proposed formula for the compounds **1–4** (Table 1).

Spectroscopy

The N,S-chelating coordination of tdmPz ligand was evidenced in the IR spectra of the complexes by the shift to lower frequencies of $\nu\text{C}=\text{S}$ band from 879 cm^{-1} (free ligand) to ca. 866 cm^{-1} (**1–4**) as well as by the appearance of a new IR absorption ($\nu\text{N}-\text{N}$) at 1205 cm^{-1} [10]. The presence of terminal S-bonded thiocyanato groups in **4** was detected by the $\nu_{\text{as}}\text{SCN}$ bands at 2114 and 2098 cm^{-1} [24, 25].

^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra unambiguously showed the formation of the N,S-chelated products. Regarding the ^1H -NMR spectra, signals of the chelating N,S-tdmPz were observed as singlets at ca. 2.60 (3- CH_3), 6.53 (H4), 2.59 (5- CH_3), 9.49 ppm (NH_2). Besides the typical signals of

the pyrazolyl ring, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1–4** also exhibited the $\text{C}=\text{S}$ resonance at $\sim 161 \text{ ppm}$, which was found quasi 18 ppm upfield when compared to the free ligand. This upfield shift clearly indicated the coordination of thiocarbonyl group toward palladium(II) center [9].

Thermal analysis

Table 2 lists the initial and final temperatures ($^\circ\text{C}$), partial mass losses (%) and DTA peaks of the thermal studies on compounds **1–4** together with the assignments of each decomposition stage based on mass calculation. Therefore, the groups indicated at the right column of the Table 2 do not correspond necessarily to the gaseous final products of decomposition. The final residues were characterized by X-ray powder diffraction techniques and the peaks were identified using ICDD bases for Pd^0 (card 05-0681) and PdO (card 06-0515).

The TG and DTA curves of 1-thiocarbamoyl-3,5-dimethylpyrazole are shown in Fig. 1. The TG curve indicated that tdmPz is thermally stable up to $66 \text{ }^\circ\text{C}$. Afterwards, the TG curve showed two consecutive and overlapped weight loss steps up to $242 \text{ }^\circ\text{C}$ and a further progressive mass loss between 242 and $550 \text{ }^\circ\text{C}$. These events are associated with endothermic peaks at $99 \text{ }^\circ\text{C}$ and $194 \text{ }^\circ\text{C}$ and the exothermic signal at $240 \text{ }^\circ\text{C}$, assigned to the oxidation of carbonaceous material.

The TG and DTA curves of complex $[\text{PdCl}_2(\text{tdmPz})]$ (**1**) are depicted in Fig. 2. The TG curve showed that **1** is thermally stable up to $126 \text{ }^\circ\text{C}$, then undergoes the elimination of the tdmPz and Cl^- ligands together with uptake of O_2 in multiple and overlapped mass losses at 126 – $462 \text{ }^\circ\text{C}$. This step is accompanied by 62.34% weight loss (calculated, 63.19%) and associated with the endothermic peak at $225 \text{ }^\circ\text{C}$ and the exothermic signals at $385 \text{ }^\circ\text{C}$ and $443 \text{ }^\circ\text{C}$. A slight and progressive mass gain of +0.58% occurred up to $797 \text{ }^\circ\text{C}$ which is ascribed to the oxidation of the remaining Pd^0 to PdO . The decomposition of PdO to Pd^0 is observed in the last mass loss (5.10%) between 797 and $844 \text{ }^\circ\text{C}$ (calcd. 4.81%), which is accompanied by an endothermic peak at $824 \text{ }^\circ\text{C}$.

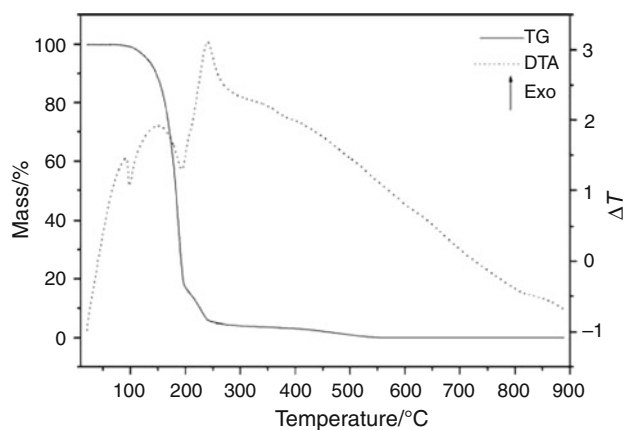
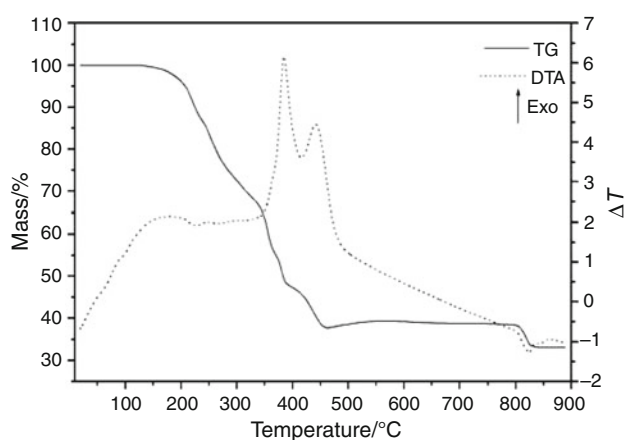
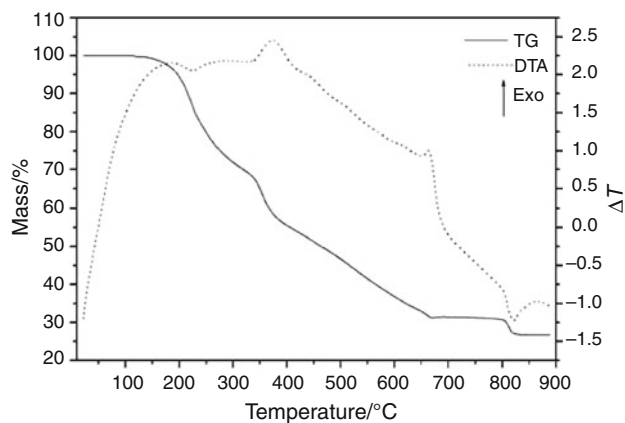
The TG and DTA curves of compound $[\text{PdBr}_2(\text{tdmPz})]$ (**2**) are illustrated by Fig. 3. Compound **2** started to degrade at lower temperature ($101 \text{ }^\circ\text{C}$) than **1**. Afterwards, the release of the tdmPz and Br^- ligands together with uptake of O_2 took place in overlapped mass losses over range 101 – $671 \text{ }^\circ\text{C}$ (calcd. 70.95%; found 68.79%), yielding PdO as residue. In this temperature range, the DTA curve showed an endothermic event at $226 \text{ }^\circ\text{C}$ and two exothermic at 374 and $663 \text{ }^\circ\text{C}$. The last stage (787 – $830 \text{ }^\circ\text{C}$) is characterized by the decomposition of PdO to Pd^0 (calcd. 3.80%; found 4.23%), accompanied by an endothermic signal at $823 \text{ }^\circ\text{C}$.

Table 1 Results of the elemental analyses

Complex	Elemental analysis% calc./obt.		
	C	H	N
1	22.67/22.35	2.93/3.05	13.06/13.19
2	17.40/17.53	2.15/2.28	10.17/10.37
3	13.99/14.25	1.96/2.18	8.65/8.70
4	25.13/24.99	2.40/2.64	18.34/18.05

Table 2 Thermal analysis data of compounds [PdX₂(tdmPz)] {X = Cl (1), Br (2), I (3), SCN (4)}

Compounds	Steps	ΔT/°C	Δm/%		Peaks DTA/°C		Assignment
			Obt.	Calc.	Endo	Exo	
1	1	126–462	-62.34	-63.64	225	385.443	-2Cl ⁻ , -tdmPz, +0.45O ₂
	2	462–797	+0.58	+0.48	-	-	+0.05 O ₂
	3	797–844	-5.10	-4.81	824	-	-0.5O ₂
2	Residue		33.10	32.00			Pd ⁰
	1	101–671	-68.79	-70.95	226	374.663	-2Br ⁻ , -tdmPz, +0.5O ₂
3	2	787–830	-4.23	-3.8	823	-	-0.5O ₂
	Residue		26.78	25.25			Pd ⁰
4	1	71–530	-75.43	-76.25	202	386.464	-2I ⁻ , -tdmPz, +0.5O ₂
	2	804–860	-3.31	-3.10	834	-	-0.5O ₂
4	Residue		21.00	20.65			Pd ⁰
	1	101–530	-66.44	-67.60	210	482	-2SCN ⁻ , -tdmPz, +0.5O ₂
4	2	788–830	-3.88	-4.23	813	-	-0.5O ₂
	Residue		29.68	28.17			Pd ⁰

**Fig. 1** TG and DTA curves of the tdmPz**Fig. 2** TG and DTA curves of the [PdCl₂(tdmPz)]**Fig. 3** TG and DTA curves of the [PdBr₂(tdmPz)]

The TG and DTA curves of compound [PdI₂(tdmPz)] (3) are depicted in Fig. 4. The first step (71–530 °C) is associated with two overlapped decomposition stages (calcd. 76.25%; found 75.43%) assigned to the elimination of the tdmPz and two iodide ligands and uptake of 0.5 O₂,

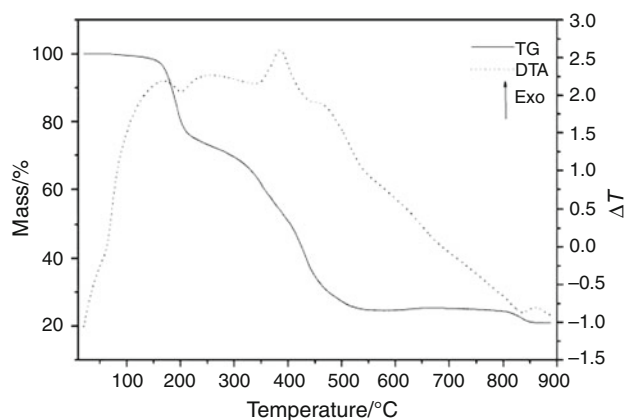


Fig. 4 TG and DTA curves of the $[\text{PdI}_2(\text{tdmPz})]$

affording PdO as residue. This process is related to one endothermic peak at 202 °C and two exothermic peaks at 386 and 464 °C. The decomposition of PdO to Pd⁰ is observed by the mass loss of 3.31% between 804 and 860 °C (calcd. 3.10%), which is accompanied by one endothermic peak centered at 813 °C.

According to TG and DTA curves, complex **4**, $[\text{Pd}(\text{SCN})_2(\text{tdmPz})]$ decomposed into PdO by two consecutive weight losses (calcd. 67.60%; found 66.44%) between 101 and 530 °C, attributed to the elimination of thiocyanato and tdmPz ligands, and the uptake of oxygen required for oxidation of Pd⁰ to PdO. These events are associated with an endothermic peak at 210 °C and an exothermic signal at 482 °C. In the range of 788–830 °C, the PdO decomposes into Pd⁰ (weight loss calcd. 4.23%; found 3.88%) (Fig. 5).

Considering the initial decomposition temperature, the thermal stability of the complexes **1–4** varies in the sequence **3** < **4** ≈ **2** < **1**. From the inspection of TG and DTA curves, it became clear that the anionic ligand plays an important role in the thermal behavior of the $[\text{PdX}_2(\text{tdmPz})]$ complexes. The chloro-complex **1** displayed the highest

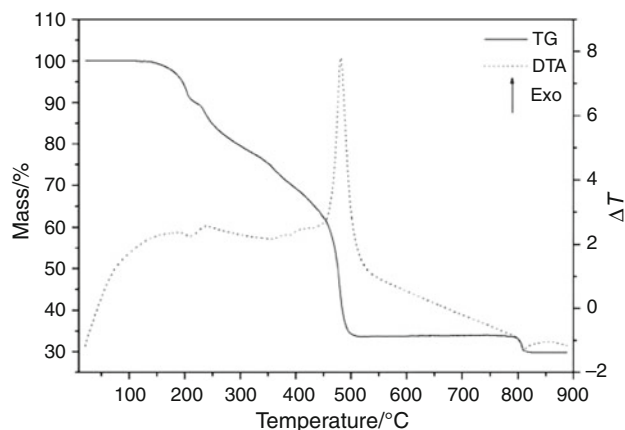


Fig. 5 TG and DTA curves of the $[\text{Pd}(\text{SCN})_2(\text{tdmPz})]$

thermal stability being in accordance with the previous thermal studies on pyrazolyl Pd(II) compounds [11–13]. Compound **3** started to decompose at the lowest temperature probably due to the steric hindrance introduced by *cis* iodo ligands.

Conclusions

The thermal behavior of complexes of general formula $[\text{PdX}_2(\text{tdmPz})]$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , SCN^- ; $\text{tdmPz} = 1$ -thiocarbamoyl-3,5-dimethylpyrazole) has been described in this study. The TG and DTA curves showed that the nature of the anionic ligand in $[\text{PdX}_2(\text{tdmPz})]$ compounds strongly affects their thermal stability. The steric hindrance introduced by *cis*-related iodide groups may be responsible for the lowest thermal stability found for compound **3**.

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