Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 339–342

THERMAL DECOMPOSITION OF PALLADIUM(II) PYRAZOLYL COMPLEXES
Part II[*]

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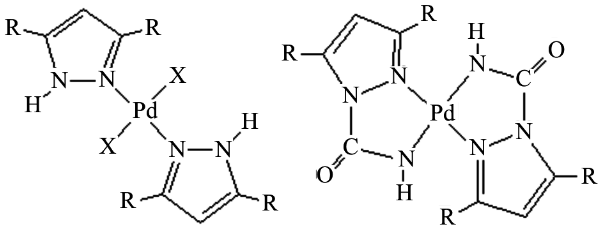
Thermal behavior of pyrazolyl complexes $[PdCl_2(HPz)_2]$ (**1**), $[PdCl_2(HdmPz)_2]$ (**2**), $[Pd(SCN)_2(HPz)_2]$ (**3**), $[Pd(SCN)_2(HdmPz)_2]$ (**4**), $[Pd(N_3)_2(HdmPz)_2]$ (**5**), $[Pd(PzNHCO)_2]$ (**6**) and $[Pd(dmPzNHCO)_2]$ (**7**) (*HPz*=pyrazole, *HdmPz*=3,5-dimethylpyrazole) has been studied by TG and DTA. In general, the thermal stability of $[PdX_2(HL)_2]$ (*HL=HPz*, *HdmPz*) compounds varies in the following order: *HdmPz>HPz* as well, according to the trends $X=Cl^->SCN^->NNN^-$. Except for **5**, the $[PdX_2(HL)_2]$ complexes showed higher thermal stability than the **6** and **7** chelates. No stable intermediates were isolated during the thermal decompositions because of the overlapping degradation processes. The final products of the thermal decompositions were identified as metallic palladium by X-ray powder diffraction.

Keywords: *DTA, palladium(II), pseudohalides, pyrazoles, TG*

Introduction

The coordination chemistry of pyrazoles has been the subject of intense researches in recent years due to their versatility of bonding modes, yielding compounds with large structural diversity and peculiar properties [2, 3]. Particularly, mononuclear complexes of the $[PdCl_2(HL)_2]$ (*HL*=pyrazolyl ligands) type have received considerable interest due to their potential use as olefin polymerization catalysts [4] and liquid crystals [5]. These facts have inspired us to investigate the chemistry of Pd(II) pyrazolyl systems containing pseudohalides [6–9] including their thermal behavior. The thermal decomposition of the complexes $[PdCl_2(HPz)_2]$ (**1**), $[PdCl_2(HdmPz)_2]$ (**2**), $[Pd(SCN)_2(HPz)_2]$ (**3**), $[Pd(SCN)_2(HdmPz)_2]$ (**4**), $[Pd(N_3)_2(HdmPz)_2]$ (**5**), $[Pd(PzNHCO)_2]$ (**6**) and $[Pd(dmPzNHCO)_2]$ (**7**) (*HPz*=pyrazole, *HdmPz*=3,5-dimethylpyrazole) (Scheme 1) using TG and DTA are described in this present study.



Complex	R	X	Complex	R
1	H	Cl^-	**6**	H
2	CH_3	Cl^-	**7**	CH_3
3	H	SCN^-		
4	CH_3	SCN^-		
5	CH_3	N_3^-		

Scheme 1

Experimental

Preparation of the complexes

The complexes $[PdCl_2(HPz)_2]$ (**1**), $[Pd(SCN)_2(HPz)_2]$ (**3**), $[Pd(SCN)_2(HdmPz)_2]$ (**4**) and $[Pd(N_3)_2(HdmPz)_2]$ (**5**) were prepared according to the methods found in the literature [7, 9, 10]. The $[PdCl_2(HdmPz)_2]$ (**2**) compound was prepared as follows: 3,5-dimethylpyrazole (157 mg; 1.61 mmols) in 2 mL of CH_3OH was added to an orange solution of $[PdCl_2(MeCN)_2]$ (200 mg; 0.77 mmols) in 10 mL of CH_3OH, resulting a yellow suspension. The solid was isolated by filtration, washed with cold CH_3OH, and dried under vacuum (yield 70%). Compounds $[Pd(PzNHCO)_2]$ (**6**) and $[Pd(dmPzNHCO)_2]$ (**7**) were prepared in a differ-

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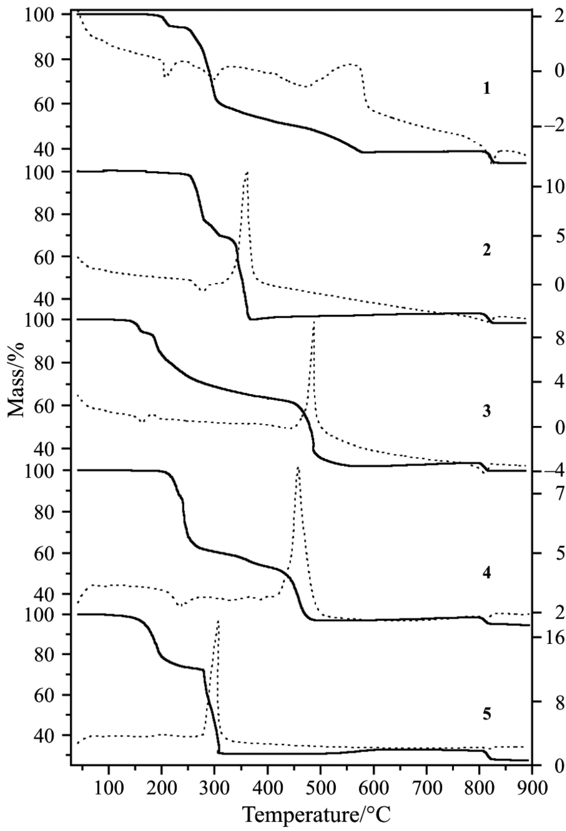

Fig. 1 —– TG and ··· – DTA curves for the complexes $[PdCl_2(HPz)_2]$ (**1**), $[PdCl_2(HdmPz)_2]$ (**2**), $[Pd(SCN)_2(HPz)_2]$ (**3**), $[Pd(SCN)_2(HdmPz)_2]$ (**4**) and $[Pd(N_3)_2(HdmPz)_2]$ (**5**)

ent way from that reported by Hvastijová *et al.* [11]. To an orange solution of $[PdCl_2(MeCN)_2]$ (200 mg; 0.77 mmols) in 10 mL of CH_3OH was added 1.61 mmols of the respective pyrazolyl ligand {110 mg of *HPz* (**6**); 155 mg of *HdmPz* (**7**)}. After stirring the mixture for 5 min, KNCO (131 mg; 1.61 mmols), dissolved in 2 mL of H_2O, was added dropwise, yielding a clear suspension. The solid was isolated from the suspension by filtration, washed with CH_3OH, and dried under vacuum. (Yield 75% (**6**), 70% (**7**)}.

Instrumentation

Melting points were determined using a Mettler FP-2 microscope. Elemental analysis of carbon, nitrogen, and hydrogen were performed on a CE Instruments microanalyser, model EA 1110 – CHNS-O. Infrared spectra were recorded in KBr pellets using a Nicolet FTIR-Impact 400 spectrophotometer in the range of 4000–400 cm^{-1}. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a TA instrument model SDT 2960, under a dry synthetic air flow (100 mL min^{-1}), temperature up to 900°C and heating rate of 20°C min^{-1}, in α-alumina sample holders. The reference substance was pure α-alumina for DTA measurements. X-ray powder diffraction patterns of the residues were obtained using a Zeiss HGZ4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg–Bretano arrangement was adopted using CuK_α radiation (λ=1.541 Å) and setting of 34 kV and 20 mA. The peaks were identified using ICDD bases [12].

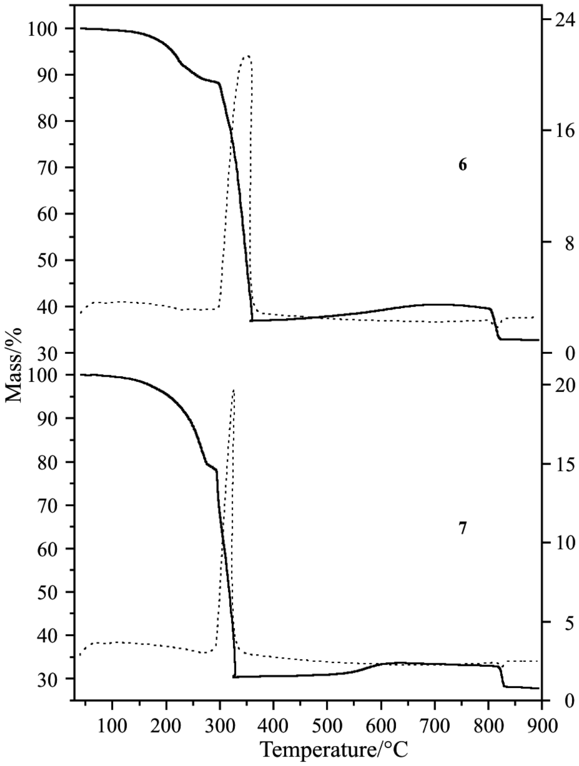

Fig. 2 —– TG and ··· – DTA curves for the complexes $[Pd(PzNHCO)_2]$ (**6**) and $[Pd(dmPzNHCO)_2]$ (**7**)

Results and discussion

The elemental analyses and thermogravimetric data, together with IR spectroscopy results, confirmed the proposed formula for the obtained compounds. The results of the analyses and melting points are summarized in Table 1.

Infrared spectra

The neutral monodentate coordination of pyrazolyl ligands in **1**–**5** was evidenced by the presence of intense νNH bands in ca. 3100 cm^{-1} as well by the shift of the ring breathing bands to lower frequencies (1579–1516 cm^{-1}) when compared to those ones of the free ligands (1595–1558 cm^{-1}) [8]. The existence of

Table 1 Results of elemental analyses and melting points of the compounds **1**–**7**

Complex	*m.p.*/°C	Carbon/%		Nitrogen/%		Hydrogen/%	
		found	calc.	found	calc.	found	calc.
1	203–204	23.14	22.99	17.82	17.87	2.87	2.57
2	>250	32.34	32.50	14.93	15.16	4.40	4.36
3	149–150	26.60	26.78	23.50	23.43	2.12	2.25
4	206–207	34.42	34.74	19.92	20.26	4.13	3.89
5	>250	31.42	31.38	36.41	36.59	4.55	4.21
6	>250	29.02	29.42	25.35	25.73	2.73	2.47
7	>250	37.84	37.66	22.20	21.96	4.10	4.21

Table 2 Thermal analysis data for compounds **1**–**7**

Complex	Step	ΔT/°C	Δm/%		DTA peaks/°C		Assignment
			obt.	calc.	endo	exo	
1	1	181–359	–44.36	–44.33	206, 214, 300	–	$-2Cl^{-}$, –*HPz*
	2	359–584	–17.31	–17.13	–	563	–*HPz*, $0.45O_2$
	3	584–805	0.46	0.51	–	–	$0.05O_2$
	4	805–842	–5.20	–5.10	826	–	$-0.50O_2$
	residue		*33.59*	*33.95*			
2	1	238–372	–69.72	–69.91	279	362	$-2Cl^{-}$, –2*HdmPz*, $0.15O_2$
	2	372–784	2.75	3.03	–	–	$0.35O_2$
	3	784–845	–4.45	–4.33	814	–	$-0.50O_2$
	residue		*28.58*	*28.79*			
3	1	132–371	–35.27	–35.17	164	183	$-SCN^{-}$, –*HPz*
	2	371–578	–33.05	–33.39	–	488	$-SCN^{-}$, –*HPz*, $0.2O_2$
	3	578–794	1.64	1.78	–	–	$0.3O_2$
	4	794–840	–3.72	–3.56	811	–	$-0.5O_2$
	residue		*29.60*	*29.66*			
4	1	188–275	–37.87	–37.18	236, 247	–	$-SCN^{-}$, –*HdmPz*
	2	275–436	–12.70	–14.00	–	–	$-SCN^{-}$
	3	436–496	–22.16	–21.63	–	458	–*HdmPz*, $0.2O_2$
	4	496–792	1.48	1.54		–	$0.3O_2$
	5	792–831	–3.21	–3.08	813		$-0.5O_2$
	residue		*25.54*	*25.65*			
5	1	121–253	–26.65	–25.12	–	200	–*HdmPz*
	2	253–332	–42.70	–44.15	–	308	–*HdmPz*,$-2N_3^{-}$, $0.35O_2$
	3	332–803	1.56	1.25	–	–	$0.15O_2$
	4	803–845	–4.55	–4.18	819	–	$-0.50O_2$
	residue		*27.66*	*27.80*			
6	1	129–299	–11.80	–13.18	–	–	–HNCO
	2	299–363	–51.31	–51.79	–	353	–*Pz*$^{-}$, $-PzNHCO^{-}$, $0.25O_2$
	3	363–803	2.58	2.44	–	–	$0.25O_2$
	4	803–852	–6.67	–4.89	817	–	$-0.50O_2$
	residue		*32.80*	*32.58*			
7	1	90–333	–69.58	–70.10	–	329	$-2dmPzNHCO^{-}$, $0.25O_2$
	2	333–815	2.49	2.08	–	–	$0.25O_2$
	3	815–847	–4.83	–4.18	827	–	$-0.50O_2$
	residue		*28.08*	*27.80*			

terminal S-bonded thiocyanato groups in **3** and **4** was detected by the ν_{as}SCN bands at 2117 and 2112 cm^{-1} [7, 9], respectively, whereas the terminal coordination of azido ligand in **5** was inferred on basis of the ν_{as}NNN band at 2044 cm^{-1} [9]. The formation of the 1-carbamoylpyrazole and 1-carbamoyl-3,5-dimethylpyrazole ligands in the chelates **6** and **7**, originated from the 1,3-dipolar cycloaddition reaction between the Pd(HL) moiety and NCO group, was confirmed by the presence of a strong νCO band at ca. 1710 cm^{-1} [10]. The disappearance of the usual ν_{as}NCO absorption in the 2250–2200 cm^{-1} range, characteristic of terminally coordinated NCO group [13], gave further evidence to the formation of the chelated addition products **6** and **7**.

Thermal analysis

The TG and DTA curves for the compounds **1–5** and **6–7** are shown in Figs 1 and 2, respectively. Table 2 lists the results of the thermal studies of these complexes together with the assignments of each decomposition step. The TG curves of these compounds showed a similar thermal degradation pattern in which the ligands are initially released in 1, 2 or 3 stages, together with uptake of O_2, leading to a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [12]. The slight mass increase up to ca. 800°C is ascribed to the oxidation of the remaining Pd to PdO. Finally, the decomposition of PdO to Pd (ASTM 05-0681) is completed at ca. 840°C.

From the inspection of TG curves some interesting trends can be observed. The thermal stability of the complexes **1–4** varies in the sequence of *HdmPz>HPz*, probably due to packing effects. In fact, the crystal structures of **2** and **4** showed that intermolecular hydrogen bonds held the monomers together within the crystal whereas such interactions are absent in the crystal packing of **3** [7, 9, 14]. Therefore, hydrogen bonding is supposed to play an important role in the thermal stability in this class of compounds. On the other hand, the stability also varies according to the anionic groups, following the order $Cl^- > SCN^- > NNN^-$, as can be seen in the TG curves of $[PdX_2(HPz)_2]$ {$X=Cl^-$ (**1**); SCN^- (**3**)} and $[PdX_2(HdmPz)_2]$ {$X=Cl^-$ (**2**); SCN^- (**4**); NNN^- (**5**)}. Such behavior was similar to those observed in our previous studies on the thermal stability of $[PdX_2(phmPz)_2]$ complexes ($X=Cl^-$, SCN^-, NNN^-; *phmPz*=1-phenyl-3-methylpyrazole) [1] that also showed the low stability of the azido-complex probably due to the known explosive nature of inorganic azides [13]. TG/DTA curves of the $[Pd(LNHCO)_2]$ (*L=Pz*, *dmPz*) series revealed a lower thermal stability than those of the $[PdX_2(HL)_2]$ family.

Conclusions

The thermal behavior of $[PdCl_2(HPz)_2]$ (**1**), $[PdCl_2(HdmPz)_2]$ (**2**), $[Pd(SCN)_2(HPz)_2]$ (**3**), $[Pd(SCN)_2(HdmPz)_2]$ (**4**), $[Pd(N_3)_2(HdmPz)_2]$ (**5**), $[Pd(PzNHCO)_2]$ (**6**) and $[Pd(dmPzNHCO)_2]$ (**7**) has been described in this work. TG studies showed increased thermal stability for $[PdX_2(HL)_2]$ complexes in the order *HdmPz>HPz* and $X=Cl^- > SCN^- > NNN^-$. In general, the $[PdX_2(HL)_2]$ type complexes showed higher thermal stability than the chelates $[Pd(LNHCO)_2]$ (*L=Pz*, *dmPz*). The thermoanalytical results presented in this work will be important for further investigations dealing with the application of these compounds in catalytic systems and as antitumor agents.

Acknowledgments

The authors are thankful to CNPq, CAPES and FAPESP for their financial support.

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