

Synthesis, characterization, and thermal behavior of palladium(II) coordination compounds containing isonicotinamide

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Abstract Palladium(II) coordination compounds of general formula *trans*-[PdX₂(isn)₂], X = Cl[−] (**1**), N₃[−] (**2**), SCN[−] (**3**), NCO[−] (**4**), isn = isonicotinamide; were synthesized and characterized in solid state by elemental analysis, infrared spectroscopy, and simultaneous TG–DTA. TG experiments reveal that the compounds **1–4** undergo thermal decomposition in three or four stages, yielding Pd⁰ as final residue, according to calculus and identification by X-ray powder diffraction.

Keywords Palladium(II) · Isonicotinamide · TG–DTA · IR spectroscopy

Introduction

Recently, transition metal-based compounds with structures that violate the empirical structure–activity relationships of platinum-based complexes, such as transplatin derivatives, have been developed in order to discover non-classical drugs that can act in a different way from cisplatin [1]. In particular, *trans*-palladium(II) complexes containing pyridine type-ligands have received considerable interest due to their attractive antitumor properties [2, 3].

As a part of our ongoing studies on the biological properties [4–6], structure determinations [7–9], and

thermal behavior [10–13] of Pd(II) compounds bearing *N*-based ligands, we report herein the synthesis, spectroscopic characterization and thermal studies on the complexes *trans*-[PdCl₂(isn)₂] (**1**), [Pd(N₃)₂(isn)₂] (**2**), [Pd(SCN)₂(isn)₂] (**3**), and [Pd(NCO)₂(isn)₂] (**4**), where isn = isonicotinamide (Scheme 1).

Experimental

Instrumentation

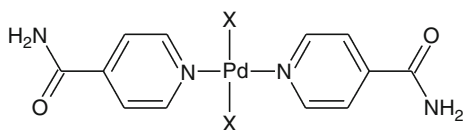
Analyses of C, H, and N were performed using a Perkin Elmer model 2400 CHN elemental analyzer. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer in the 4000–400 cm^{−1} spectral range, using KBr pellets. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained simultaneously with the same modulus on a TA Instruments SDT Q600 equipment under dynamic air atmosphere, flow 100 mL min^{−1}, from 35 to 1000 °C and heating rate of 20 °C min^{−1}, using α -Al₂O₃ sample holders. An amount of 10.0–10.5 mg of the sample was used in this study. The reference substance was pure α -Al₂O₃ for DTA measurements. X-ray diffraction patterns of the residues were obtained on a Siemens D-5000 diffractometer, with Cu K α radiation ($\lambda = 1.541 \text{ \AA}$), monochromatized by a graphite monochromator.

Preparation of the compounds *trans*-[PdX₂(isn)₂], X = Cl[−] (**1**), N₃[−] (**2**), SCN[−] (**3**), NCO[−] (**4**)

All reagents of p.a. grade were obtained from commercial suppliers and used without further purification. All the

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Scheme 1 Structural representation of the *trans*-[PdX₂(isn)₂] complexes {isn = isonicotinamide; X = Cl⁻ (**1**), N₃⁻ (**2**), SCN⁻ (**3**), NCO⁻ (**4**)}

syntheses have been carried out at room temperature. The starting complex [PdCl₂(CH₃CN)₂] was synthesized as previously described [14].

The compounds were prepared according to the literature procedure [6]. Briefly, the complex *trans*-[PdCl₂(isn)₂] (**1**) was prepared by the addition of 0.098 g (8.09 × 10⁻⁴ mol) of the isonicotinamide ligand, previously dissolved in 5 mL of CHCl₃/CH₃OH (1:1 v/v), to 20 mL of a CHCl₃ solution containing 0.100 g (3.85 × 10⁻⁴ mol) of precursor complex [PdCl₂(CH₃CN)₂]. After magnetic stirring of the mixture for 1 h, the solvents were evaporated and the solid formed was washed with H₂O, CH₃OH, and pentane, filtered, and dried under vacuum. The yield was 80%.

For the compounds **2–4**, was followed the same procedures of **1**, with addition in the next step of 8.09 × 10⁻⁴ mol of the corresponding pseudohalide salt (NaN₃, NaSCN, and KNCO, respectively), dissolved in 7 mL of a CH₃OH/H₂O (1:1 v/v) solution. After magnetic stirring for 1 h, the resulting suspensions were filtered off and the obtained solids were washed with H₂O, CH₃OH, and pentane, and then dried in vacuum. The yields were 85% (for **2**) and 90% (for **3** and **4**).

Results and discussion

The elemental analyses and thermogravimetric data, together with IR spectroscopic results confirmed the proposed formulae. The analytical results are summarized in Table 1.

Infrared spectra

Isonicotinamide is a pyridine derivative with an amide group in the *para* position of the aromatic ring. As a ligand, isonicotinamide displays the ability to coordinate via pyridinic nitrogen atom and/or through amide group.

The coordination via pyridinic N atom was clearly detected in the IR spectra of **1–4** by the shift of the absorption band attributed to the ring breathing vibrational mode (Φ) to higher frequency (ca. 1062 cm⁻¹) when compared to that one of the free ligand (993 cm⁻¹) [15]. The bands at 3412–3186 cm⁻¹ and 1707–1670 cm⁻¹ were attributed to ν N–H and ν C=O modes, respectively. The most significant IR frequency bands of the complexes with their assignments are presented in Table 2.

The terminal coordination of azide group in **2** was suggested by the $\nu_{as}NNN$ band at 2008 cm⁻¹ [16], whereas the presence of terminal *S*-thiocyanate ligand in **3** was evidenced by the appearance of a strong $\nu_{as}SCN$ band at 2118 cm⁻¹ [17, 18]. Concerning the IR spectrum of **4**, the presence of the $\nu_{as}NCO$ absorption at 2258 cm⁻¹ indicated the existence of *N*-cyanate groups coordinated in a terminal fashion [9].

Table 1 Analytical data for the compounds *trans*-[PdX₂(isn)₂], X = Cl⁻ (**1**), N₃⁻ (**2**), SCN⁻ (**3**), NCO⁻ (**4**), isn = isonicotinamide

Complex	Color	Decomposition/°C	Carbon/%		Nitrogen/%		Hydrogen/%	
			Found	Calc.	Found	Calc.	Found	Calc.
1	Yellow	>300.0	34.05	34.19	13.03	13.29	2.72	2.87
2	Dark yellow	≥205.0	33.17	33.16	32.22	31.99	2.74	2.78
3	Orange	≥270.0	35.89	36.02	17.91	18.00	2.40	2.59
4	Light yellow	≥240.0	38.26	38.68	19.68	19.33	2.59	2.78

Table 2 Main vibrational modes (cm⁻¹) for the palladium(II)-isonicotinamide compounds

Complex	ν (NH ₂)	ν_{as} (NXY)	ν (C=O)	Φ (ring breathing)
<i>trans</i> -[PdCl ₂ (isn) ₂] (1)	3412–3186	–	1705	1063
<i>trans</i> -[Pd(N ₃) ₂ (isn) ₂] (2)	3406–3207	2008	1670	1063
<i>trans</i> -[Pd(SCN) ₂ (isn) ₂] (3)	3369–3205	2118	1674	1061
<i>trans</i> -[Pd(NCO) ₂ (isn) ₂] (4)	3381–3186	2258	1707	1061

X = Y = N for **2**, X = C and Y = S for **3**, and X = C and Y = O for **4**

Thermogravimetry

TG–DTA curves for complexes **1–4** are illustrated in Fig. 1 and Table 3 lists the results of the thermal investigation of these compounds.

The TG curve showed that **1** is thermally stable up to 305 °C, then undergoes the oxidation of the ligands together with uptake of O₂ in two overlapped mass losses at 305–442 °C, yielding a mixture of Pd⁰ (ASTM 05-0681) and PdO (ASTM 06-0515) [19], according to the analysis of XRD powder. This step is associated with a weak endothermic peak at 373 °C and an intense exothermic signal at 434 °C. A slight and progressive mass gain of +2.14% occurred up to 729 °C which is ascribed to the oxidation of the remaining Pd⁰ to PdO. The decomposition of PdO to Pd⁰ (ASTM 05-0681) [19] is observed in the last mass loss (−3.70%) between 729 and 830 °C, which is accompanied by an endothermic peak at 825 °C.

Compound **2** started to degrade at lower temperature (203 °C) than **1**. Afterwards, the elimination of the isn and N₃[−] ligands together with uptake of O₂ took place in two abrupt and overlapped mass losses over range 203–242 °C which is accompanied with an intense exothermic peak at 239 °C. A progressive mass loss of 9.17% took place over the range 242–468 °C, affording a mixture of Pd⁰ (ASTM 05-0681) and PdO (ASTM 06-0515) [19]. In this temperature range, the DTA curve showed an exothermic event at 450 °C. A slight mass increase of 1.28% (468–797 °C) is ascribed to the oxidation of Pd⁰ to PdO which further degraded to Pd⁰ (ASTM 05-0681) [19] in the last mass loss (−3.57%) at 797–835 °C, accompanied by an endothermic peak at 829 °C.

Compound **3** started to decompose at 267 °C. A further heating to 319 °C resulted in an abrupt mass loss of 55.54% which is accompanied by an endothermic signal at 282 °C. The next step is characterized by a mass loss

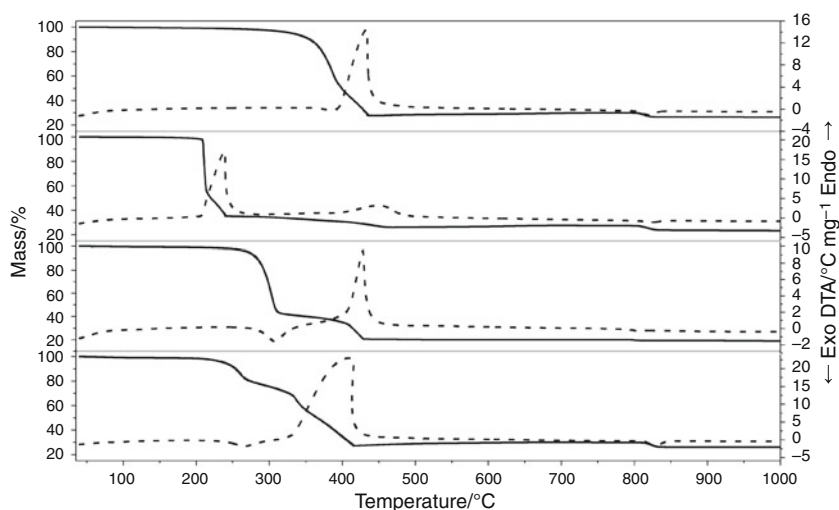
Table 3 Thermal analysis data for compounds *trans*-[PdX₂(isn)₂], X = Cl[−] (**1**), N₃[−] (**2**), SCN[−] (**3**), NCO[−] (**4**), isn = isonicotinamide

Complex	Step	$\Delta T/^\circ\text{C}$	$\Delta m/\%$	DTA/ $^\circ\text{C}$	
				Endo	Exo
1	1	305–442	−71.62	373	434
	2	442–729	+2.14		
	3	729–830	−3.70	825	
	Residue		26.82 (calcd. 27.05)		
2	1	203–242	−64.68		239
	2	242–468	−9.17		450
	3	468–797	+1.28		
	4	797–835	−3.57	829	
	Residue		23.86 (calcd. 24.48)		
3	1	267–319	−55.54	282	
	2	319–517	−21.36		428
	3	786–820	−0.77	793	
	Residue		22.33 (calcd. 22.80)		
4	1	208–273	−20.19	265	
	2	273–415	−54.28		409
	3	415–804	+2.90		
	4	804–845	−3.79	829	
	Residue		24.64 (calcd. 24.48)		

($\Delta m = -21.36\%$) between 319 and 517 °C associated with an intense exothermic event at 428 °C attributed to the oxidation of the ligands, affording a mixture of Pd⁰ + PdO. The decomposition of PdO to Pd⁰ (ASTM 05-0681) [19] is noticed in the last mass loss (−0.77%) between 786 and 820 °C, being associated with an endothermic peak at 793 °C.

With regard to the thermal behavior of **4**, the first stage (208–273 °C) is characterized by a mass loss of 20.19% which is associated with an endothermic signal at 265 °C. A further heating to 415 °C resulted in two overlapped

Fig. 1 TG (solid line) and DTA (dashed line) curves for the complexes **1–4**



mass losses ($\Delta m = -54.28\%$), giving rise to a mixture of Pd⁰ (ASTM 05-0681) and PdO (ASTM 06-0515) [19] as residue. This step is accompanied with an intense exothermic signal at 409 °C, probably due to the oxidation of organic matter. The formation of PdO is noticed by a progressive mass gain of 2.90% observed at 415–804 °C. The decomposition of PdO to Pd⁰ (ASTM 05-0681) [19] is observed in the last step between 804 and 845 °C, being associated with an endothermic signal at 829 °C.

From the inspection of the initial decomposition temperatures, it was noticed that the thermal stability varies according to the anionic groups, following the trend $\text{Cl}^- > \text{SCN}^- > \text{NCO}^- > \text{NNN}^-$, as can be observed in the TG curves of *trans*-[PdX₂(isn)₂], X = Cl⁻ (**1**), N₃⁻ (**2**), SCN⁻ (**3**), NCO⁻ (**4**). Such behavior agrees well with those evidenced in our previous studies on the thermal stability of [PdX₂L₂] complexes, X = Cl⁻, SCN⁻, NNN⁻, L = pyrazoles [10] which also revealed that the low thermal stability of the azido-complex is probably associated to the known explosive nature of inorganic azides.

Conclusions

This work describes the synthesis, IR spectroscopic characterization and thermal studies of the compounds *trans*-[PdCl₂(isn)₂] (**1**), *trans*-[Pd(N₃)₂(isn)₂] (**2**), *trans*-[Pd(SCN)₂(isn)₂] (**3**), and *trans*-[Pd(NCO)₂(isn)₂] (**4**). The results showed that the thermal decompositions into Pd⁰ occurred in three steps for **1** and **3**, whereas for **2** and **4** occurred in four stages. Furthermore, taking into account the initial decomposition temperature, it was possible to establish the following thermal stability order: **1** > **3** > **4** > **2**. The lowest thermal stability of **2** is probably ascribed to the known explosive nature of inorganic azides.

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