

Thermal study of mononuclear Pd(II) complexes of the type [Pd(X)₂(Rtu)(PPh₃)] (X = Cl, SCN; Rtu = *N*-methylthiourea, *N*-phenylthiourea)

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Abstract The synthesis, spectroscopic characterization, and thermal analysis of the compounds [Pd(X)₂(mtu)(PPh₃)] (X = Cl[−] (**1**), SCN[−] (**2**); mtu = *N*-methylthiourea; PPh₃ = triphenylphosphine) and [Pd(X)₂(phtu)(PPh₃)] (X = Cl[−] (**3**), SCN[−] (**4**); phtu = *N*-phenylthiourea) are described. The thermal decomposition of the compounds occurs in two, three, or four stages and the final decomposition products were identified as Pd⁰ by X-ray powder diffraction. The thermal stability order of the complexes is **4** > **3** > **2** > **1**.

Keywords Palladium (II) compounds · Thioureas · Pseudohalides · Thermal analysis

Introduction

Palladium(II) compounds have been used as pathways to new products in organic synthesis [1], as catalysts [1], antitumor drugs [2–4], and for the design of metallomesogens [5]. On the other hand, the chemistry of thiourea (tu) and substituted tu derivatives has attracted attention because of their potential use as reagents for the separation of metal ions [5] and in biological applications such as their employment as antitumor and antimycobacterial agents [2–4]. In addition to their uses, the ligands are of interest as they possess various donor sites: the sulfur atom of the C–S group and the nitrogen atom of the NH or NHR moieties

(R = alkyl or aryl groups). Thus, thiourea-type ligands represent a good choice for designing new structures sustained by coordinate [2, 6, 7] and hydrogen bonds [7]. In particular, complexes containing thiolates and phosphines (such as PPh₃) ligands have received considerable attention because of their prominent therapeutic activity in the rheumatoid arthritis treatment [8]. Another important S-based group is the thiocyanate ion (SCN[−]) which possesses a rich coordination chemistry because of its ambidentate character [9]. It can coordinate through either the nitrogen or the sulfur atom, or both, giving rise to linkage isomers or polymers [10–12].

Extending our interest in the spectroscopic, biological evaluation, and thermogravimetric studies on complexes containing halides and pseudohalides as co-ligands [13–17], we wish to report the synthesis, characterization, and thermal behavior of the compounds [PdCl₂(mtu)(PPh₃)] (**1**), [Pd(SCN)₂(mtu)(PPh₃)] (**2**), [PdCl₂(phtu)(PPh₃)] (**3**), and [Pd(SCN)₂(phtu)(PPh₃)] (**4**).

Experimental

General comments

All the syntheses have been carried out at room temperature. All reagents were obtained from commercial suppliers. The starting complex [PdCl₂(CH₃CN)₂] was prepared as previously described [18].

Preparation of the complexes

[PdCl₂(mtu)(PPh₃)] (**1**) and [PdCl₂(phtu)(PPh₃)] (**3**) were prepared by adding a mixture containing 0.38 mmol of the thiourea derivative (34 mg of mtu or 58 mg of phtu) and

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triphenylphosphine (100 mg; 0.38 mmol) dissolved in 15 mL of $\text{CH}_3\text{COCH}_3/\text{CH}_3\text{OH}$ (1:1) to an orange solution of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (100 mg; 0.38 mmol) in 15 mL of CH_3COCH_3 . The mixtures were stirred magnetically for 1 h, the solvent was removed under reduced pressure and the yellow solids obtained were recrystallized from $\text{CHCl}_3/n\text{-C}_5\text{H}_{12}$ and dried in vacuum. The yields were 80% for (**1**) and 85% for (**3**).

In the synthesis of $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**) and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**), the KSCN salt (35 mg; 0.36 mmol) was dissolved in 5 mL of CH_3OH , and then was added to a solution containing 0.18 mmol of the appropriate chloro-compounds (95 mg of **1** or 106 mg of **3**) dissolved in 7 mL of CH_3COCH_3 . The resulting solutions were stirred for 1 h, the solvent was removed under reduced pressure and the yellow (**2**) and orange (**4**) solids obtained were recrystallized from $\text{CHCl}_3/n\text{-C}_5\text{H}_{12}$ and dried in vacuum. The yields were 70% for (**2**) and 75% for (**4**).

Instrumentation

Melting points were determined on a Microquímica apparatus. Elemental analyses of carbon, nitrogen, and hydrogen were performed on a microanalyzer elemental analyzer CHN, model 2400 PerkinElmer. Infrared spectra (IR) were recorded on a Nicolet Impact 400 spectrophotometer in the spectral range $4000\text{--}400\text{ cm}^{-1}$ in KBr pellets. Simultaneous thermal analyses (TG-DTA) were carried out using a SDT 2960 system from TA Instruments, under dynamic flow of dry synthetic air (100 mL min^{-1}) at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ using α -alumina open crucibles for sample and reference. The X-ray powder diffractograms were obtained in a Siemens D5000 diffractometer, using CuK_α radiation ($\lambda = 1.541\text{ \AA}$) and setting of 40 kV and 30 mA. The residues (Pd^0 and PdO) were identified using ICDD bases [19, 20].

Results and discussion

In previous investigations, we have successfully developed a procedure for the synthesis of *cis*- $[\text{PdCl}_2(\text{tu})(\text{PPh}_3)]$ (tu = thiourea; PPh_3 = triphenylphosphine) whose structure was determined by single-crystal X-ray diffraction [7]. The results derived from *cis*- $[\text{PdCl}_2(\text{tu})(\text{PPh}_3)]$ have prompted us to investigate the reactions of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with substituted thioureas and PPh_3 ligands in order to generate compounds $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**) and $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**). The complexes $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**) and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**) were obtained by reactions between the suitable chloro-derivative precursors and KSCN in the 1:2 molar ratio. In this context, the results of the elemental analyses and the thermogravimetric data

together with infrared spectroscopy data, confirmed the proposed formulae for the compounds **1–4**. The results of the analyses and melting points are shown in Table 1.

Infrared spectra

In the IR spectra of **1–4**, recorded as KBr pellets, some characteristic bands of coordinated PPh_3 were observed at $3057\text{--}3067\text{ cm}^{-1}$ (νCH) and $1479\text{--}1491$, 1433 , 997 cm^{-1} (νring). Other important band frequencies observed in the IR spectra of the complexes along with their assignments are presented in Table 2. Concerning the thiourea-type ligands, the band at $1538\text{--}1578\text{ cm}^{-1}$ (νCN) in IR spectra of **1–4** was found shifted to a higher wavenumber when compared to that observed for the free ligands. These results are consistent with S-monodentate coordination of *N*-methylthiourea or *N*-phenylthiourea to Pd(II), as observed in other similar complexes [2, 6, 7]. Regarding to the SCN ligand, the presence of the terminal S-bonded thiocyanato group in **2** and **4** was evidenced by the νCN bands at 2106 cm^{-1} and a very sharp band at 2107 cm^{-1} , respectively [10]. The analytical and IR results obtained for compounds **1–4** suggest a square planar environment around the Pd atom whose coordination sites are occupied by one thiourea-type ligand, one triphenylphosphine molecule and two anionic X^- groups ($\text{X} = \text{Cl}^-, \text{SCN}^-$). The *cis* configuration is attributed

Table 1 Elemental analyses and melting points for complexes $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**), $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**), $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**), and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**)

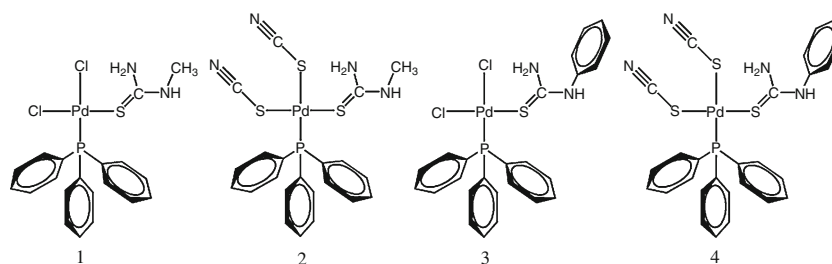
Complex	Melting point/ $^\circ\text{C}$	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calc.	Found	Calc.	Found	Calc.
1	104 (dec.)	45.19	45.34	3.88	4.00	5.07	5.29
2	111 (dec.)	45.90	45.95	3.49	3.69	9.22	9.75
3	131–132	50.26	50.73	3.74	3.92	4.61	4.73
4	150–151	50.45	50.90	3.86	3.65	8.74	8.80

Table 2 Selected IR data for $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**), $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**), $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**) and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**)

Complex	$\bar{\nu}/\text{cm}^{-1}$			
	Rtu (R = methyl or phenyl)			SCN
	νNH	δNH_2	νCN	νCN
1	3400 sh, 3100 s	1618 s	1572 vs, 1298 w	–
2	3313 s, 3155 s	1623 s	1578 s, 1296 w	2106 vs
3	3352 w, 3165 vs	1620 vs	1548 w	–
4	3174 w	1617 s	1538 w	2107 vs

sh shoulder, s strong, w weak, vs very strong are the abbreviations used for bands

Fig. 1 Suggested structures for compounds $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**), $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**), $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**), and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**)



to these complexes on basis of the known X-ray structure of the *cis*- $[\text{PdCl}_2(\text{tu})(\text{PPh}_3)]$ (tu = thiourea; PPh_3 = triphenylphosphine) [7] (see Fig. 1).

Thermogravimetry

The TG and DTA curves for the mononuclear compounds **1–4** are shown in Fig. 2. Table 3 presents the thermal studies data of these complexes.

Compound $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**) started to decompose at 75 °C. A further heating to 372 °C resulted in an abrupt mass loss of 70.14% which is accompanied by an exothermic signal at 327 °C. The next step is characterized by a progressive mass loss from 372 to 855 °C attributed to the decomposition of the carbonaceous matter and formation of PdO (ICDD 41–1107) [19], followed by the decomposition of PdO to Pd⁰ (ICDD 05–0681) [20] which is associated with an endothermic peak at 815 °C.

Compound $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**) started to degrade at higher temperature (101 °C) than $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**). Afterward, the elimination of the ligands together with uptake of O₂ took place in one abrupt mass loss of 58.58% over range 101–327 °C. The second step (327–470 °C) is characterized by two consecutive and overlapped mass losses of 17.09% accompanied with an intense exothermic peak at 389 °C which is attributed to the oxidation of the organic matter. A progressive mass loss of 1.94% took place over the range 470–809 °C, affording PdO (ICDD 41–1107) as residue [19] which

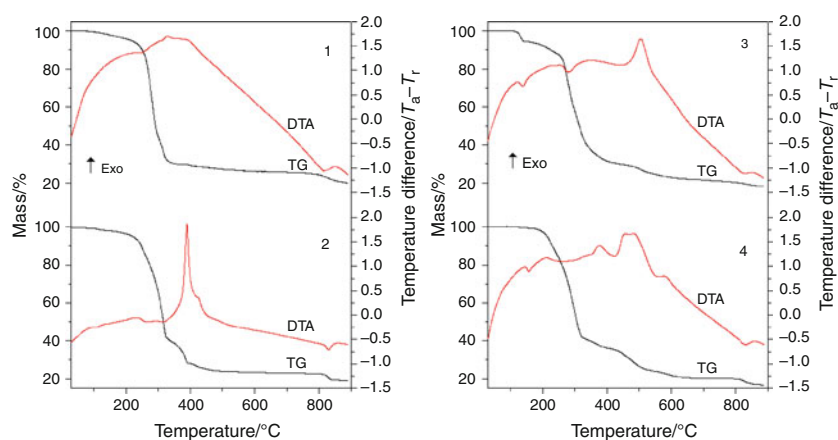
further degraded to Pd⁰ (ICDD 05–0681) [20] in the last mass loss ($\Delta m = -3.11\%$) at 809–855 °C, accompanied by an endothermic peak at 830 °C.

Table 3 Thermal analysis data for compounds $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**), $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**), $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**), and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**)

Complex	Step	$\Delta T/^\circ\text{C}$	$\Delta m/\%$	DTA peak/ $^\circ\text{C}$	
				Endo	Exo
1	1	75–372	-70.14	-	327
	2	372–855	-8.85	815	-
	Residue		21.01		
2	1	101–327	-58.58	-	-
	2	327–470	-17.09	-	389
	3	470–809	-1.94	-	-
	4	809–855	-3.11	830	-
	Residue		19.28		
3	1	110–147	-5.45	138	-
	2	147–430	-64.35	281	-
	3	430–879	-11.99	830	505
	Residue		18.21		
4	1	136–333	-59.05	158	-
	2	333–538	-16.74	-	376, 458, 483
	3	538–787	-4.06	-	580
	4	787–864	-3.12	833	-
	Residue		17.03		

m_{initial} : (**1–4**) \cong 5.000 mg

Fig. 2 TG and DTA curves for complexes $[\text{PdCl}_2(\text{mtu})(\text{PPh}_3)]$ (**1**), $[\text{Pd}(\text{SCN})_2(\text{mtu})(\text{PPh}_3)]$ (**2**), $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**), and $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**)



The TG curve showed that $[\text{PdCl}_2(\text{phtu})(\text{PPh}_3)]$ (**3**) is thermally stable up to 110 °C. A further heating to 147 °C caused a mass loss of 5.45% associated with a weak endothermic signal at 138 °C which is ascribed to a melting process followed by decomposition. Over the temperature range of 147–430 °C, it is observed a mass loss of –64.35% accompanied by an endothermic peak at 281 °C. The third stage of decomposition (430–879 °C) is characterized by a progressive mass loss of –11.99% associated with an exothermic event at 505 °C and an endothermic peak at 830 °C, attributed to the oxidation of organic matter with formation of PdO, followed by generation of Pd⁰ as final residue (ICDD 05-0681) [20].

Regarding the thermal behavior of $[\text{Pd}(\text{SCN})_2(\text{phtu})(\text{PPh}_3)]$ (**4**), the first stage (136–333 °C) is characterized by a mass loss of 59.05% associated with an endothermic signal at 158 °C, being attributed to a melting process followed by decomposition. A further heating to 538 °C resulted in a mass loss of 16.74%. This step is accompanied by exothermic peaks at 376, 458, and 483 °C, ascribed to the oxidation of organic matter. The third step (538–787 °C) is characterized by a mass loss of 4.06% associated with a weak exothermic signal at 580 °C, yielding PdO as residue (ICDD 41-1107) [19]. The decomposition of PdO to Pd⁰ (ICDD 05-0681) [20] is observed in the last mass loss ($\Delta m = -3.12\%$) between 787 and 864 °C, accompanied by an endothermic signal at 833 °C.

Taking into account the initial decomposition temperatures, the following thermal stability order can be established: **4** > **3** > **2** > **1**. The thermal stability of the complexes **1–4** varies in the sequence of phtu > mtu, probably due to packing effects. On the other hand, the thermal stability also varies according to the anionic groups, following the order $\text{SCN}^- > \text{Cl}^-$, as can be observed in the TG curves of $[\text{PdX}_2(\text{mtu})(\text{PPh}_3)]$ {X = Cl⁻ (**1**); SCN⁻ (**2**)} and $[\text{PdX}_2(\text{phtu})(\text{PPh}_3)]$ {X = Cl⁻ (**3**); SCN⁻ (**4**)}. The fact that thiocyanato-compounds are more thermally stable than their respective chloro analogous agrees well with our earlier study [21], in which the highest thermal stability for thiocyanato-derivatives of Pd(II) was verified. On the other hand, we have also obtained experimental evidences on Pd(II) compounds which indicated the opposite order of thermal stability, i.e., Cl⁻ > SCN⁻ [22–24]. Therefore, further studies are required in order to rationalize the influence of the anionic ligand on the thermal stability of palladium(II) compounds.

Conclusions

The results of this investigation showed that the mononuclear compounds $[\text{PdX}_2(\text{mtu})(\text{PPh}_3)]$ (X = Cl⁻ (**1**), SCN⁻

(**2**)) and $[\text{PdX}_2(\text{phtu})(\text{PPh}_3)]$ (X = Cl⁻ (**3**), SCN⁻ (**4**)) were obtained in excellent yields. The IR data of **1–4** are consistent with monodentate coordination of the organic and inorganic groups to Pd(II) atom. The thermoanalytical results showed that the thermal stability of compounds **1–4** varies in the sequence **4** > **3** > **2** > **1**. TG studies indicated increased thermal stability for $[\text{PdX}_2(\text{L})(\text{PPh}_3)]$ complexes in the order L = phtu > mtu and X = SCN⁻ > Cl⁻.

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