

Thermal behavior study of palladium(II) complexes containing the iminic ligand *N*,*N*'-bis(3,4-dimethoxybenzaldehyde) ethane-1,2-diamine

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Abstract

This study describes the synthesis, characterization and thermal behavior study of the Schiff base *N*,*N*'-bis(3,4-dimethoxybenzaldehyde)ethane-1,2-diamine (**C.1**) and four new compounds of palladium(II) *N*,*N*-chelate coordination, with the general formula $[Pd(X_1)(X_2)(3,4dm-1,2am)]$ where 3,4dm-1,2am=*N*,*N*'-bis(3,4-dimethoxybenzaldehyde)ethane-1,2-diamine, $X_1 = X_2 = Cl^-$ (**C.2**), $X_1 = X_2 = Cl^-$ and Br⁻ (**C.3**), $X_1 = X_2 = N_3^-$ (**C.4**) and $X_1 = X_2 = NCO^-$ (**C.5**). The compounds were characterized by elemental analysis, infrared vibrational spectroscopy (IR) and nuclear magnetic resonance (NMR) ¹H and ¹³C. The TG/DTA curves showed that the thermal decomposition of the **C2–C.5** complexes occurred in steps that involve the removal of both inorganic and organic ligand, and palladium oxidation steps forming palladium(II) oxide followed by the reduction of PdO into Pd(0), this being the constituent of the residual mass observed at the end of the TG curves, which have values consistent with the expected ones. The formed compounds can be ordered according to thermal stability considering the initial decomposition temperature (**C.5** > **C.2** > **C.3** > **C.4**).

Keywords Pd(II) complexes · Iminic ligand · IR and NMR spectroscopy · TG-DTA

Introduction

For some time, transition metal complexes, especially cisplatin, have been investigated due to their antineoplastic and trypanocidal activities [1]. There are several studies in the literature that seek to exploit the properties of palladium complexes, such as cancer cells anti-proliferative activity [2], anti-inflammatory activity [3], bactericidal activity [4, 5] applications in catalytic processes [6, 7], nanotechnology [8] and nucleation studies [9].

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As a study material, we have palladium(II) compounds, first synthesizing the organic ligand in order to turn the action of this metal ion more specific. Palladium(II) compounds show ligand-exchange kinetics 10⁵ times greater than the platinum(II) analogous, which may facilitate the hydrolysis of the leaving groups that dissociate readily in solution, before the complex reaches the pharmacological target. To overcome their high lability, chelating ligands have been used to afford high thermodynamically stable and kinetically inert palladium(II) complexes [10, 11]. Therefore, it is extremely important to search for ligands that optimize its performance. The N,N'-bis(3,4dimethoxybenzaldehyde)ethane-1,2-diamine (3.4dm-1,2am) C.1 ligand is a Schiff base and has its synthesis and characterization reported in literature [12–14]. We investigated the thermal behavior of a new series of coordination compounds [Pd(Cl)₂(3,4dm-1,2am)] C.2, [PdBrCl(3,4dm-1.2am)] C.3. $[Pd(N_3)_2(3,4dm-1,2am)]$ **C.4** and $[Pd(NCO)_2(3,4dm-1,2am)]$ C.5. The compounds were characterized by elemental and thermogravimetric analyses, as well as infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies ¹³C and ¹H.

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Experimental

Instrumentation

Elemental analysis of carbon, nitrogen and hydrogen was performed using a Leco Instruments Ltda, model TruSpec CHNS-O instrument. Infrared spectra were recorded as KBr pellets on a Shimadzu-IR-Prestige-21 spectrophotometer in the spectral range $400-4000 \text{ cm}^{-1}$. NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz (¹H) and 75 MHz (¹³C), using CDCl₃ as solvent for C.1 and C.4 or DMSO-d₆ for C.2, C.3 and C.5 for dissolution of samples. The melting point (mp), C.1, or decomposition temperatures, C.2-C.5, were obtained using the MARTE (PFM II) equipment. The curves of thermogravimetric analysis (TG) and differential thermal analysis (DTA) were obtained from TA Instruments equipment-Q 600, under dry air synthetic or nitrogen flow (100 mL min⁻¹), mass sample approximately 10 mg, alumina crucible and heating rate of 20 K min⁻¹ from room temperature to 1373 K. The reference substance was pure *a*-alumina in DTA measurements. The patterns of powder X-ray diffraction (XRD) were obtained by Rigaku Ultima IX equipment using KaCu wavelength $(\lambda = 1.5418 \text{ Å})$ setting of 34 kV and 20 mA.

Synthesis of Schiff base C.1

A solution of ethylenediamine (0.80 mL; 11.84 mmol) in methanol (10.0 mL) was added to a solution of 3,4-dimethoxybenzaldehyde (3.7257 g; 22.42 mmol) in methanol (30.0 mL). The mixture was stirred at room temperature (approximately 298 K) for 1 h. The white precipitate was separated by filtration, washed with water, ethyl ether and dried in vacuum. Yield 92%.

Synthesis of C.2

The **C.2** compound was prepared under an inert and anhydrous atmosphere. A dichloromethane (10.0 mL) solution of **C.1** (0.4134 g; 1.16 mmol) in dichloromethane (30.0 mL) was added to a stirred dichloromethane (30.0 mL) solution of $[PdCl_2(CH_3CN)_2]$ (0.300 g; 1.16 mmol). The mixture was stirred at room temperature (approximately 298 K). After a magnetic stirring of the mixture for 20 h, the solvents were evaporated and the **C.2** compound was precipitated by adding pentane. The precipitate was separated by filtration, washed with ethyl ether and dried in vacuum. Literature procedures were followed for the synthesis of $[PdCl_2(CH_3CN)_2]$ using $PdCl_2$ [15]. Yield 80%.

Synthesis of C.3, C.4 and C.5

For the C.3–C.5 compounds, the same atmosphere conditions were followed. To a stirred dichloromethane (30.0 mL) solution of C.2 (about: 0.300 g; 0.56 mmol) was added (about 1.12 mmol) the corresponding halide/pseudohalide salt (KBr, NaN₃ and KCNO, respectively). After magnetic stirring of mixture for 2 h, the solvent was evaporated and the C.3–C.5 compounds were precipitated by adding pentane. The precipitate was separated by filtration, washed with ethyl ether and dried in vacuum. The yields were 53% (for C.3), 60% (for C.4) and 72% (for C.5).

Results and discussion

The analytical results confirmed the proposed formulae for the synthesized compounds. The results of the analyses are presented in Table 1. The proposed structures for the **C.1**– **C.5** compounds are shown in Fig. 1.

Infrared spectra

The IR spectrum of synthesized ligand **C.1** exhibits the v(N=C) band at 1637 cm⁻¹, indicating their formation. Compared with the spectrum of the starting primary amine, the absence of the bands corresponding to the characteristic asymmetric (~ 3300 cm⁻¹) and symmetric (~ 3200 cm⁻¹) stretching (N–H) bond is observed. Furthermore, when compared with the spectrum of the precursor aldehyde, there is the disappearance of the intense stretching band characteristic of the v(C=O) bond of the aromatic aldehyde (~ 1700 cm⁻¹). These spectra data indicate the formation of a Schiff base from the starting materials [16–19].

By analyzing the IR spectra of compound C.2 can be observed the presence of the main bands of C.1, besides the absence of the bands at 2328, 446 and 409 cm⁻¹ assigned to the C=N precursor [PdCl₂(CH₃CN)₂], that indicates the

Table 1 Results of chemical analyses of the compounds C.1-C.5

Compound	Carbon/%		Hydrogen/%		Nitrogen/%	
	Found	Calc.	Found	Calc.	Found	Calc.
C.1	67.7	67.4	6.9	6.8	7.9	7.9
C.2	45.3	45.0	5.0	4.6	5.3	5.3
C.3	42.5	41.6	4.0	4.2	5.2	4.9
C.4	44.1	43.9	4.9	4.5	20.6	20.5
C.5	48.6	48.3	4.8	4.5	9.8	10.2



Fig. 1 Proposed structures of the C.1-C.5 compound

formation of the [PdCl₂(3,4dm-1,2am)] compound [20, 21]. However, there was a shift in v(N=C) band to lower frequency (1626 cm^{-1}). It can be explained by the interaction between the metal and the Schiff base binding site (nitrogen atoms), where an electronic relocation occurs in this bond [22]. The replacement of a Cl⁻ by Br⁻ halide caused no distinction in the IV spectrum of the C.3 compound. The terminal coordination of azide group in C.4 was suggested by the v_{as} NNN band at 2019 cm⁻¹ [22, 23]. Concerning the IR spectrum of C.5, the presence of the v_{as} NCO absorption at 2172 cm⁻¹ indicated the existence of *N*-cyanate groups coordinated in a terminal mode [22, 24]. The bands frequencies observed in the IR spectra for the novel complexes and the irrespective assignments are presented in Table 2, which allowed the elucidation of the molecular structures.

¹H and ¹³C NMR spectra

Chemical shifts (δ) and coupling constants (*J*) observed in ¹H NMR spectra, Fig. 2, of the **C.1** ligand and the **C.2–C.5** complexes, are shown in Table 3, where the values in bold correspond to the more intense signals related to the compounds with more stable *E*/*Z* conformation and, therefore, the major product. In the 8–10 ppm region for **C.1**, a strong signal is noted in 8.19 ppm referring to the

proton (-HC=N-) in *E* conformation, whereas the sign in 9.85 ppm refers to the same proton but in *Z* conformation, related to the ligand's (HC=N) connections. The chemical shifts of iminic hydrogens are sensitive to conformation effects, due to other effects such as charge density and magnetic anisotropy. For Schiff bases of *N*-benzylidene type, the chemical shift of iminic hydrogen can range from 7.56 to 9.78 ppm [25].

Forming coordination compounds, palladium shifts its electron density to form a coordinative binding deshielding even more the nearby nuclei and causing an increase in the chemical shift of the proton (-HC=N-) from 8.19 to 8.62 ppm in the C.2, C.3 compounds and 8.39 ppm in C.4, which have low intensities in relation to the 9.82 ppm signals observed for C.2, C.3 and C.5 and to 9.86 ppm for **C.4**. The fact that these signals $\simeq 9.8$ ppm are more intense than the signals at 9.62 and 9.39 ppm also confirms the formation of the coordination compound, as the geometry of the palladium(II) atom is a square planar, leaving it in a position very close to the aromatic rings, which makes the products containing the ligand in the ZZ and EZ conformations more stable. This is different from the zinc and mercury compounds, that are found in the literature with signals between 8.22 and 8.40 ppm [19, 26], and that contain the same C.1 ligand and halides (Br⁻ and I⁻), but which have tetrahedral geometry and retain the most stable conformation EE of the ligand, because in these geometrics the steric effects are minimized. The spectra for the C.2 and C.3 compounds are very similar in relation to the chemical shifts of protons. However, the changes in the coupling constants (J) in both the aromatic hydrogens and the methylenic hydrogens support the proposal of replacing one of the chlorides by a bromide, since the chemical environment of such protons is slightly modified. The substitution of chloride ions by azide ions generates small changes in the chemical shifts of the protons, referring to the imines; from 8.62 to 8.39 ppm and from 9.82 to 9.86 ppm, which refer, respectively, to the protons of the imine (-HC=N-) in the E and Z conformations in the ligand. Unlike the others, C.5 has a spectrum with a number of signals considerably smaller. The absences of signals related to protons, assigned to the ligand with *E* conformation, are consistent with the replacement of the chloride ions by the cyanate ions, since due to the introduction of this large group, the major product exhibited a structure having the ligand in ZZ conformation. In the aromatic H region (6.8–7.6 ppm) also, we can see signals at different intensities, which indicate the formation of products with different conformations and are shown in Table 3. Products with different conformations are observed due to the weakening of (C=N) bindings, when palladium is coordinated with the ligand, which results in an increase in rotation freedom [16].

Table 2Assignments of theprincipal bands presents in IRspectrum of C.1–C.5compounds

Assignments	Wavenumber/cm ⁻¹								
	C.1	C.2	C.3	C.4	C.5				
v(C–H) Aryl C(sp ²)	3003 (w)	2999 (w)	3003 (w)	2999 (w)	2999 (w)				
$v_{as}(C-H) C(sp^3)$	2945 (w)	2956 (w)	2957 (w)	2957 (w)	2957 (w)				
$v_{as}(C-H) (-CH_2-)$	2912 (w)	2936 (w)	2933 (w)	2934 (w)	2936 (w)				
$v_{\rm s}({\rm C-H}) \ {\rm C}({\rm sp}^3)$	2894 (w)	_	_	_	-				
v _s (C–H) (–CH ₂ –)	2833 (w)	2837 (w)	2835 (w)	2838 (w)	2837 (w)				
$v_{\rm as}(\rm NNN)$	_	_	_	2019 (s)					
$v_{as}(NCO)$	_	_	_	_	2172 (w)				
v(C=N) Arylimine	1637 (s)	1626 (m)	1628 (m)	1626 (m)	1632 (m)				
v(C=C) Aryl	1583 (s)	1595 (s)	1595 (s)	1593 (s)	1593 (s)				
v(C=C) Aryl	1458 (s)	1458 (m)	1460 (m)	1460 (m)	1460 (m)				
	1421 (s)	1421 (m)	1421 (m)	1421 (m)	1421 (m)				
$v_{as}(C-O-C)$	1267 (s)	1273 (s)	1273 (s)	1273 (s)	1275 (s)				
$v_{\rm s}(\rm C-O-C)$	1022 (s)	1018 (s)	1018 (s)	1016 (s)	1018 (s)				
$\delta_{s}\gamma$ (C–H) Aryl	874 (w)	854 (w)	854 (w)	854 (w)	854 (w)				
	810 (m)	810 (m)	808 (m)	808 (m)	810 (m)				

(s) strong, (m) medium, (w) weak, *s* symmetric, *as* asymmetric, *v* axial deformation, δ angular deformation, γ out-of-plane deformation



Fig. 2 ¹H NMR spectra for compounds C.1 and C.4 in CDCl₃ and C.2, C.3 and C.5 in DMSO-d₆

The data for the NMR spectra of the ¹³C to C.1–C.5, Fig. 3, indicate the formation of coordination compounds. In the 162–192 ppm region, the signal appears at 162.19 ppm in C.1, shifting to 168.95 ppm (C.2), 168.95 and 170.07 ppm (C.3), 167.29 ppm (C.5), with very low intensities that are referring to the (–HC=N–) C in the *E* conformation, and the most intense signals in 191.85 ppm (C.2, C.3 and C.5) 190.93 ppm (C.4) assigned to the iminic carbons in the Z conformation. The ¹³C NMR spectrum shows many signals close to the values assigned to the ligand **C.1**, Table 4, in the aromatic carbons region and the 45–65 ppm region, referring to the carbons (–O–CH₃) and (–NCH₂–) groups, which contribute to the interpretation of mixtures of products with different conformations (*EE*, *ZZ*, *ZE*). Thus, as it is shown in Fig. 3, there are signals, in the **C.2**, **C.3** compounds, related to the

Table 3	'H NMR data (ppm)
for com	pounds C.1 and C.4 in
CDCl ₃	C.2, C.3 and C.5 in
DMSO-	d_6 , given as δ (ppm) and
multiplie	city-J (Hz)

Assignment	C.1		C.2		C.3	
	δ /ppm	J/Hz	δ /ppm	J/Hz	δ/ppm	J/Hz
–O–CH ₃ (A)	3.90	S	3.85	S	3.85	S
–NCH ₂ – (B)	3.93	dd-13.9; 6.1	3.81	t-4.36	3.81	t-3.82
Ar–H (C)	6.85	<i>d</i> -8.3	7.09	<i>d</i> -8.46	7.09	<i>d</i> -8.42
Ar–H (D)	7.08	dd-1.9; 8.2	7.28	dd-1.45; 8.30;	7.28	dd-1.69; 8.42;
Ar–H (E)	7.38	<i>d</i> -1.86	7.22	<i>d</i> -1.46	7.22	1.68
-HC=N- (F)	8.18	S	8.62	S	8.62	S
Ar–H (C')	6.98	d-8.15	7.15	d-8.25	7.15	d-8.25
Ar–H (D')	7.46	dd-1.87; 8.15;	7.53	dd-1.82; 8.22;	7.54	dd-1.89; 8.25;
Ar–H (E')	7.40	<i>d</i> -1.94	7.36	<i>d</i> -1.74	7.37	<i>d</i> -1.84
-HC=N- (F')	9.84	S	9.82	S	9.82	S
Assignment	C.4		C.5		Conformation	ns (EE. ZZ e ZE)
	δ /ppm	J/Hz	δ/ppm	J/Hz		
-O-CH ₃ (A)	3.96	m	3.83	m	Б Б	B F
$-NCH_2-(B)$					A E	E /A
Ar–H (C)	6.92	<i>d</i> -8.45	-	-	D	D
Ar–H (D)	7.12	dd-1.92; 8.28;	-	-	Â	Â
Ar– \mathbf{H} (E)	7.02	<i>d</i> -1.96	-	-	A,	A
- H C=N- (F)	8.39	S	_	-	°C`	C.
Ar– \mathbf{H} (C')	6.98	<i>d</i> -8.17	7.15	<i>d</i> -8.23	A D' E	
Ar– \mathbf{H} (D')	7.46	dd-1.90; 8.17;	7.54	dd-1.86; 8.23;	E` F`	γ≡∕ E F`
Ar– \mathbf{H} (E')	7.41	<i>d</i> -1.85	7.37	<i>d</i> -1.86	A/ C	
- H C=N- (F')	9.86	S	9.82	S		B F D D
						C A

The values in bold correspond to the more intense signals that can be observed in Fig. 2

¹H nuclei of the ($-NCH_2-$) group, more shielded, compared to the same cores in the **C.1** and **C.4** compounds, in Fig. 3 also, we can observe more shielded signals $\simeq 47$ ppm related to the ¹³C nuclei of this group ($-NCH_2-$).

Thermal analysis

TG curve of organic compound **C.1** shows that it is thermally stable up to 449 K. After this temperature is exceeded, the compound begins to decompose, occurring mass lost up to 1060 K. Being an organic compound, no formation of residue is observed. It is possible to identify an endothermic peak of 433 K in the DTA curve, typical to the physical phenomenon, which corresponds to the melting point of the compound that is why we did not observe any mass change. These data are consistent with the values obtained from the melting point equipment (\sim 428 K). A relationship between TG curves and DTA peaks was observed, respectively.

As it can be observed from the TG curve shown in Fig. 4, the **C.2** compound is thermally stable up to 396 K. Within the range from 396 to 817 K, a mass loss is observed, referring to the elimination of 3,4dm-1,2am and Cl⁻ ligands. The DTA curve shows three exothermic peaks, at 571, 645 and 794 K, related to this loss. However, before the elimination of the ligands is finished, the oxidizing of Pd⁰ to PdO is starting, causing a mass gain up to 1082 K, concerning the incorporation of 0.5 O₂ (396–1082 K experimental Δm : 73.72%/calculated Δm : - 77.06%). The mass loss of 3.37% initiated at 1082 K shown in the TG curve (Δm calculated: - 3.00%), together with an endothermic peak at 1101 K shown in the DTA curve, indicates the reduction in palladium(II) oxide in metallic palladium (PdO \rightarrow Pd⁰) eliminating 0.5 O₂.



Fig. 3 NMR spectra for compounds C.1–C.5: (a) ${}^{13}C{}^{1}H$ of C.1 in CDCl₃; (b) ${}^{13}C/DEPT$ -135 of C.1 in CDCl₃; (c) ${}^{13}C/DEPT$ -90 of C.1 in CDCl₃; (d) ${}^{13}C{}^{1}H$ of C.2 in DMSO-d₆; (e) ${}^{13}C/DEPT-135$ of C.2

in DMSO-d₆; (f) ¹³C/DEPT-90 of C.2 in DMSO-d₆; (g) ¹³C{¹H} of **C.3** in DMSO-d₆; (h) ${}^{13}C{}^{1}H{}$ of **C.4** in CDCl₃ e; (i) ${}^{13}C{}^{1}H{}$ of **C.5** in DMSO-d₆

Table 4 ¹³ C/DEPT NMR data (ppm) for compound C.1 in CDCl ₃ , given as δ (ppm)	Carbon	¹³ C δ/ppm	¹³ C/DEPT-135	¹³ C/DEPT-90	Assignment
	a	55.91	55.91		ьb.
	b	64.64	64.64 (invert)		
	c or d	108.66	108.66	108.66	$a = a \xrightarrow{c} f \qquad f \xrightarrow{c} a$
		110.35	110.35	110.35	$e e e^{3}$
	e	123.06	123.06	123.06	h d d
	f	129.41			
	g	149.27			a a
	h	151.30			
	i	162.19	162.19	162.19	

This thermal behavior is repeated in compounds C.3, C.4 and C.5, with variations in the initial and final decomposition temperatures, in the mass variation in each step and in the final residue percentage. These final residues were analyzed by X-ray diffraction powder, and peaks were identified on the basis of ICDD to metallic palladium (05-0681) and palladium(II) oxide (06-0515) [27]. The data obtained in the TG/DTA curves are in Table 5.

On analyzing the TG curves of all synthesized complexes (Fig. 5), the C.2, C.3 and C.5 compounds show very similar decomposition patterns. The relative ease of interesting to note that the substitution of Cl ions by Br and pseudohalides (N₃ and NCO) caused a change in the final decomposition temperature: **C.3** (904 K) > C.2(817 K) > C.5 (789 K) > C.4 (771 K). Compound C.3 showed higher final temperature. This may be explained by the higher affinity of the Br ion for Pd(II), according to the theory of acidity and basicity of Pearson [28], resulting in a greater bond stability, thereby increasing the final temperature of the decomposition step. In TG curves of the

decomposition of the azide ion is one of the factors that

may justify the differences in the TG curve of C.4. It is



Fig. 4 TG e DTA curves of the complex C.2

complexes, a very slight initial mass loss is observed, most possible due to solvent evaporation.

The DTA curves of the synthesized palladium complexes, shown in Fig. 6, offer data that agree with TG curves. The amount of energy released in the C.4 decomposition was higher than that of the other. This thermal behavior similar to that observed for other Pd(II) compounds containing coordinated azide exhibits inherent tendency of highly exothermic decomposition, yielding Pd and/or PdO and gaseous products, such as N₂. In some cases, these compounds are potential explosives [29, 30].

Analyzing the TG and DTA curves of all the compounds that contain palladium, we can see the presence of mass

 Table 5 Thermal analysis data of compounds C.2–C.5 and PdCl₂

gain, concerning the oxidation of palladium, that occurs simultaneously with the losses referring to the elimination of organic compounds, halides and pseudohalides, and afterward, a mass loss above 1073 K which is accompanied by an endothermic peak in the DTA, due to the formation of palladium(II) oxide followed by their reduction into metallic palladium.

The TG and DTA curves of the PdCl₂ compound, supplied by Vetec[®], are shown in Fig. 7, where we can see a similar behavior. The thermal decomposition starts at approximately 820 K. In the range from 820 to 1079 K, there is a mass loss of 32.82% equivalent to the elimination of the chloride ligands and the capture of $0.5 O_2$ due to the formation of palladium(II) oxide (calculated Δm : -31.64%). Note that, in this case, the 0.5 O₂ incorporation occurs completely simultaneously with the 2 Cl⁻elimination, because the PdCl₂ compound decomposes at higher temperatures compared to the C.2-C.5 compounds. In the range from 1079 to 1176 K, another mass loss occurs with a value of 8.14% equivalent to the reduction of the formed palladium(II) oxide (calculated Δm : - 8.36%). The 58.76% existing residue is within the instrumental error of \pm 3% (calculated 60.01%). The data of the TG and DTA curves of $PdCl_2$ are also in Table 5.

The formation of solid oxides, through heating, that contain platinum group metals has been studied for several years; Bayler and Wiedemann published a study in 1975 [31] in which they confirm the palladium(II) oxide formation and its thermal decomposition during the heating

Compounds	Step	$\Delta T/\mathrm{K}$	$\Delta m/\%$		DTA peaks/K		Assignment
			Obt.	Calc.	Exo.	End.	
C.2	1	396-1082	- 73.72	- 77.06	571		- 2Cl ⁻ , -(3,4dm-1,2am)
					645/794		$+ 0.5 O_2$
	2	1082-1351	- 3.37	- 3.00		1101	- 0.5 O ₂
	Residue		22.44	19.94			Pd ⁰
C.3	1	391-1070	- 74.96	- 78.84	575/701/869		$-Br^{-}$, $-Cl^{-}$, $-(3,4dm-1,2am)$, + 0.5 O ₂
	2	1070-1355	- 2.89	- 2.75		1093	- 0.5 O ₂
	Residue		21.49	18.41			Pd ⁰
C.4	1	371-1081	- 76.23	- 77.58	500/667		$-2(N_3^{-}), -(3,4dm-1,2am)$
					744		$+ 0.5 O_2$
	2	1081-1446	- 3.00	- 2.93		1096	- 0.5 O ₂
	Residue		20.58	19.46			Pd ⁰
C.5	1	397-1088	- 74.53	- 77.6	574/644/767		$- 2$ CNO ⁻ , $-(3,4$ dm-1,2am), $+ 0.5 O_2$
	2	1088-1350	- 3.35	- 2.03		1104	- 0.5 O ₂
	Residue		21.30	19.46			Pd ⁰
PdCl ₂	1	820-1079	- 32.82	- 31.64		691/961	$-2Cl^{-}, +0.5 O_{2}$
	2	1079–1176	- 8.14	- 8.36		1102	- 0.5 O ₂
	Residue		58.76	60.01			Pd^0



Fig. 5 TG curves of the complex C.2-C.5



Fig. 6 DTA curves of the complex C.2-C.5



Fig. 7 TG e DTA curves of the complex PdCl₂

treatment of palladium metallic samples. The first traces of palladium(II) oxide are formed at 473 K, the oxidation is complete at about 973 K, and its decomposition follows in the range from 1093 to 1123 K. Moreover, they concluded that the temperatures at which these events occur will vary according to the grain size of the metallic powder, the β and the ovens atmosphere.

In the present work, the thermal analysis for metallic palladium, supplied by Sigma-Aldrich[®], was carried out under the same β (20 K min⁻¹) and atmosphere (synthetic air) conditions as those performed for the obtained **C.2–C.5** compounds, as well as in nitrogen atmosphere. These data are shown in Fig. 8. As expected, and according to data from literature [28], the TG and DTA curves of metallic palladium in synthetic air show a mass gain, indicating that part of the metallic palladium had oxidized and then reduced, according to its mass loss at temperatures around 1073 K, as well as the presence of the endothermic peak at 1091 K in the DTA. These events are not observed in the metallic palladium TG and DTA curves in the N₂ atmosphere, since without the presence of O₂, palladium(II) oxide formation is not possible.

Conclusions

The 3,4dm-1,2am ligand **C.1** and the $[Pd(Cl)_2(3,4dm-1,2am)]$ (**C2**), [PdBrCl(3,4dm-1,2am)] (**C.3**), $[Pd(N_3)_2(3,4dm-1,2am)]$ (**C.4**) and $[Pd(NCO)_2(3,4dm-1,2am)]$ (**C.5**) compounds were synthesized and characterized by elemental and thermal analysis and IR spectrometry as well as by ¹H and ¹³C NMR. These data complement each other and agree with the presented structures. The **C.3** compound, despite being synthesized as the others, in molar ratios (1:2, **C.2/KBr**), the elemental



Fig. 8 TG e DTA curves of the Pd⁰ in synthetic air and nitrogen

and thermal analyses show consistent results with the replacement of only one Cl⁻. From the final decomposition temperatures, the thermal stability of the complexes can be ordered in the following sequence: C.3 > C.2 > C.5 > C.4. Thermal analysis data also showed that occurs formation of palladium (II) oxide with heat treatment for all C.2–C.5 compounds, including PdCl₂ reagent and palladium metal, occurs and reducion to palladium metalic at temperatures close to of 1093 K.

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