

MONO- AND DINUCLEAR PALLADIUM(II) COMPOUNDS CONTAINING N,S DONOR LIGANDS

Synthesis, characterization and thermal behavior

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Synthesis, spectroscopic characterization and thermal analysis of the compounds [Pd₂(dmba)₂(μ-NCO)(μ-2-qnS)] (**1**), [Pd₂(dmba)₂(μ-NCO)(μ-8-qnS)] (**2**), [Pd(2-qnS)₂] (**3**) and [Pd(8-qnS)₂] (**4**) (dmba=N,N-dimethylbenzylamine; 2-qnS=2-quinoline-thiolate; 8-qnS=8-quinolinethiolate) are described. The thermal decomposition of these compounds occurs in four consecutive steps and the final decomposition products were identified as Pd(0) by X-ray powder diffraction. The thermal stability order of the complexes is **4**>**3**>**1**>**2**.

Keywords: chelates, cyclopalladated compounds, quinolinethiol, thermal analysis

Introduction

Benzylamines, such as N,N-dimethylbenzylamine (dmba), are C,N donor ligands and good candidates to the synthesis of cyclometallated species [1–5], which constitute an important class of compounds within the organometallic chemistry, whose preparation and uses are currently under investigation in many laboratories [1, 2]. Cyclopalladated compounds, for example, have been used as pathways to new products in organic synthesis [6], as catalysts [7], anti-tumor drugs [8], in photochemistry [7] and for the design of metallomesogens [9].

On the other hand, heterocyclic thiols attract considerable attention because of their relevance in biological systems [10]. Moreover, reactions between cyclometallated compounds and 2-quinolinethiol (2-qnSH) [1, 10] have been explored due to the ability of this ligand to form stable compounds with several transition metals [11, 12]. This thioligand exists predominantly in the quinolinethione form and coordinates through the sulfur atom in the most common S-monodentate coordination mode [13]. In addition, the versatility of the conjugate anion qnS⁻ has been demonstrated in a large number of complexes, yielding a variety of coordination compounds with great structural diversity: S-monodentate [13]; N,S-chelating [12] and μ-N,S-bridging [10]. This behavior is analogous to the dominant coordination chemistry of pyridinethiolate [14, 15]. Previously, we had been interested in the spectroscopic and thermogravimetric studies of cyclopalladated compounds [1–5]. As a part of our research program in this area, we report in the present study the synthesis, char-

acterization and thermal behavior of the compounds [Pd₂(dmba)₂(μ-NCO)(μ-2-qnS)] (**1**), [Pd₂(dmba)₂(μ-NCO)(μ-8-qnS)] (**2**), [Pd(2-qnS)₂] (**3**) and [Pd(8-qnS)₂] (**4**).

Experimental

Preparation of the complexes

All the syntheses were carried out at room temperature. All reagents were obtained from commercial suppliers and used without further purification. The starting materials [Pd(dmba)(μ-NCO)]₂ and [PdCl₂(CH₃CN)₂] were prepared as previously described [3, 16].

[Pd₂(dmba)₂(μ-NCO)(μ-2-qnS)] (**1**) and [Pd₂(dmba)₂(μ-NCO)(μ-8-qnS)] (**2**) were prepared by the addition of 0.030 g (0.18 mmol) of the thioligand to a dichloromethane solution containing 0.10 g (0.18 mmol) of [Pd(dmba)(μ-NCO)]₂. The mixtures were stirred for 1 h, the solvent was removed under reduced pressure and the red (**1**) and yellow (**2**) solids obtained were recrystallized from CHCl₃/n-C₅H₁₂ and dried in vacuum. The yield was 71% in each case.

[Pd(2-qnS)₂] (**3**) and [Pd(8-qnS)₂] (**4**) were synthesized by the addition of 0.12 g (0.76 mmol) of the thioligand and 0.031 g (0.76 mmol) of NaOH to an acetone solution containing 0.10 g (0.38 mmol) of [PdCl₂(CH₃CN)₂]. The resulting suspensions were stirred for 1 h and the orange (**3**) and red (**4**) solids were filtered, washed with water, acetone, pentane and then dried in vacuum. The yields were 55% for (**3**) and 80% for (**4**).

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Instrumentation

Elemental analyses of carbon, nitrogen and hydrogen were performed on an EAGER-200 CHNSO-CE equipment. Infrared spectra (IR) were recorded on an Nicolet Impact 400 spectrophotometer in the 4000–400 cm^{-1} spectral range as KBr pellets.

Simultaneous thermal analyses (TG-DTA) were carried out using a SDT 2960 system (TA Instruments Co.) under dynamic flow of dry synthetic air (50 mL min^{-1}) at a heating rate of $20^\circ\text{C min}^{-1}$ using α -alumina open crucibles for sample and reference. The X-ray powder diffractograms were obtained in a HGZ4/B horizontal diffractometer (G.D.R) equipped with a proportional counter and pulse height discriminator. The Bragg–Bentano arrangement was adopted using $\text{CuK}\alpha$ radiation ($\lambda=1.541 \text{ \AA}$) and setting of 34 kV and 20 mA. The residues (Pd, PdO) were identified using ICDD bases [17].

Results and discussion

Elemental analyses for the synthesized compounds are in agreement with the proposed formulae and are given in Table 1 together with the melting points. In dichloromethane solutions, the reactions between $[\text{Pd}(\text{dmba})(\mu\text{-NCO})]_2$ and 2- and 8-quinolinethiol in the 1:1 molar ratio occurred readily, leading to the species $[\text{Pd}_2(\text{dmba})_2(\mu\text{-NCO})(\mu\text{-2-qnS})]$ (**1**) and $[\text{Pd}_2(\text{dmba})_2(\mu\text{-NCO})(\mu\text{-8-qnS})]$ (**2**). These complexes are more soluble than the starting compounds in organic solvents. The mononuclear compounds $[\text{Pd}(2\text{-qnS})_2]$ (**3**) and $[\text{Pd}(8\text{-qnS})_2]$ (**4**) were obtained by reactions between $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ and 2- and 8-qnS in the 1:2 molar ratio. The infrared and thermogravimetric data of the complexes **1–4** are discussed as follows.

Infrared spectra

The characteristic bands of the cyclometallated ring at $3041\text{--}3047 \text{ cm}^{-1}$ ($\nu_{\text{CH}_{\text{ring}}}$), $2910\text{--}2972 \text{ cm}^{-1}$ (ν_{CH_3}) and $2727\text{--}2854 \text{ cm}^{-1}$ (ν_{CH_2}) in the infrared spectra of (**1**) and (**2**) were found unchanged when compared to those observed for the precursor [3]. Therefore, the interaction between 2-qnS and 8-qnS ligands and the start-

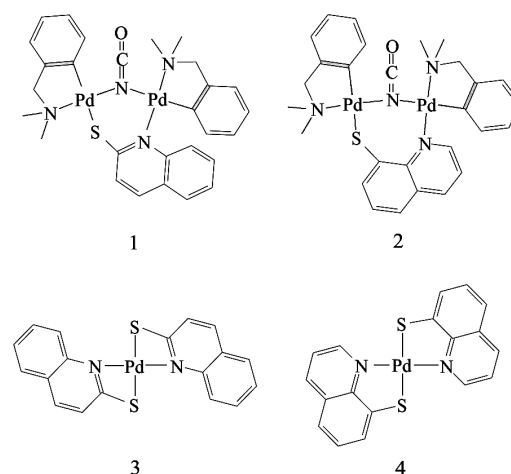


Fig. 1 Suggested structures for compounds **1–4**

ing compound did not affect the integrity of the orthometallated ring. Concerning the NCO ligand, the presence of the N-bridging cyanato group in (**1**) and (**2**) was evidenced by the ν_{CN} band at 2172 and 2197 cm^{-1} , respectively [3, 18]. The bidentate coordination of 2-qnS and 8-qnS between $[\text{Pd}(\text{dmba})]$ moieties in (**1**) and (**2**) was clearly evidenced by the appearance of additional IR bands at $1494\text{--}1495 \text{ cm}^{-1}$ ($\nu_{\text{CN}_{\text{ring}}}$), and $1071\text{--}1102 \text{ cm}^{-1}$ (ν_{CS}). Regarding to the IR spectra of (**3**) and (**4**), the coordination of the 2-qnS and 8-qnS ligands was detected by the disappearance of the bands at 2329 cm^{-1} , attributed to the ν_{CN} of the acetonitrile molecules, and of the ones at 3100 and 2500 cm^{-1} (ν_{NH} and ν_{SH} , respectively), characteristics of the neutral thioligands [1], as well as by the presence of bands at $1543\text{--}1557 \text{ cm}^{-1}$ (ν_{CC}) and $1076\text{--}1088 \text{ cm}^{-1}$ (ν_{CS}). The proposed molecular structures for compounds **1–4** are shown in Fig. 1.

Thermogravimetric analysis

At this point it is worthy to note that thermal analysis has been scarcely employed for the study of cyclometallated compounds, despite its large use for other classes of metal complexes [1–4]. In the present paper, the main objectives of the thermogravimetry studies (TG) is to enlight the influence of the thioligands on the initial decomposition temperature of the complexes, as well as to propose decomposi-

Table 1 Elemental analyses and melting points for compounds **1–4**

Complex	Melting point/ $^\circ\text{C}$	Carbon/%		Nitrogen/%		Hydrogen/%	
		found	calc.	found	calc.	found	calc.
1	119 (dec.)	49.0	49.2	8.24	8.20	4.41	4.42
2	108 (dec.)	49.6	49.2	7.98	8.20	4.35	4.42
3	215 (dec.)	50.1	50.6	6.40	6.56	2.60	2.84
4	242 (dec.)	50.3	50.6	6.70	6.56	2.94	2.84

tion steps. The TG/DTG and DTA curves for the dinuclear (**1** and **2**) and mononuclear compounds (**3** and **4**) are shown in Fig. 2. Table 2 presents the representative thermal data of complexes **1–4**, together with the assignments for each decomposition step.

In the 100–480°C temperature range, compounds (**1**) and (**2**) lose the organic (qnS and dmbs) and inorganic (NCO) ligands, with uptake of O₂, in

two consecutive steps, yielding a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [17]. Afterwards, the TG curves also exhibit a progressive mass gain up to 790°C due to the partial oxidation of the Pd to PdO. The last mass loss is characterized by the decomposition of the remaining PdO to Pd (ASTM 05-0681) at 900°C. The ligands of the compounds (**3**) and (**4**) are eliminated in the

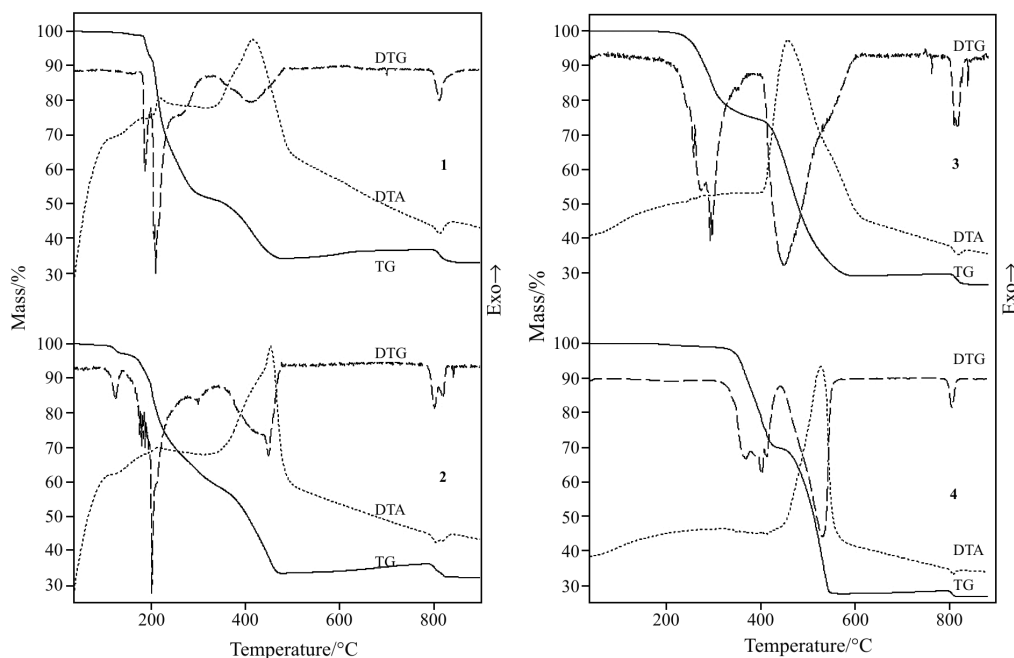


Fig. 2 TG/DTG and DTA curves of **1–4** complexes

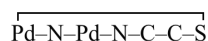
Table 2 Thermal analysis data for compounds **1–4**

Complex	Step	$\Delta T/^\circ\text{C}$	$\Delta m/\%$		DTA peak/ $^\circ\text{C}$		Assignment
			found	calc.	endo	exo	
1	1	111–295	–47.7	–48.0	189	218	–NCO–dmbs–(2–qnS)+1/4O ₂
	2	295–480	–19.4	–19.6	–	416	–dmbs
	3	480–790	+2.72	+2.34	–	–	+1/2O ₂
	4	790–900	–3.98	–3.51	812	–	–3/4O ₂
	residue		31.6	31.1	–	–	
2	1	100–360	–43.7	–44.2	–	–	–NCO–2dmbs+1/4O ₂
	2	360–475	–24.0	–23.4	–	453	–(8–qnS)
	3	475–780	+2.76	+2.34	–	–	+1/2O ₂
	4	780–900	–3.98	–3.51	804	–	–3/4O ₂
	residue		31.1	31.1	–	–	
3	1	200–350	–23.9	–23.5	–	–	–2C ₄ H ₂
	2	350–600	–48.5	–50.6	–	456	–2C ₃ H ₄ NS+1/8O ₂
	3	600–800	+0.6	+0.9	–	–	+1/8O ₂
	4	800–900	–3.20	–1.93	822	–	–1/4O ₂
	residue		25.2	24.9	–	–	
4	1	230–430	–30.4	–30.0	–	–	–C ₁₀ H ₈
	2	430–560	–43.5	–43.2	–	513	–C ₈ H ₄ N ₂ S ₂ +1/8O ₂
	3	560–795	+0.80	+0.89	–	–	+1/8O ₂
	4	795–900	–1.62	–1.88	809	–	–1/4O ₂
	residue		25.3	24.9	–	–	

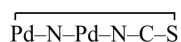
m*_{initial}: (1**) – 5.223 mg; (**2**) – 4.820 mg; (**3**) – 5.164 mg; (**4**) – 5.181 mg.

range 200–600°C, with uptake of O₂, affording a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515). In the 600–800°C range the partial oxidation of Pd to PdO is observed. The last step corresponds to the decomposition of the remaining PdO to Pd (ASTM 05-0681) at 800–900°C.

Taking into account the initial decomposition temperatures, the following thermal stability order can be established: **4**>**3**>**1**>**2**. It is suggested that the lower thermal stability of (**2**) can be the result of the less stable seven-membered ring formed by the metal and the ligands,



in comparison with the six-membered ring,



observed in (**1**). Finally, compound (**4**) is the stablest one, as expected for a complex containing two five-membered rings formed by the metallic centre and 8-qnS.

Conclusions

The results of the present investigation showed that the compounds [Pd(dmmba)(μ-NCO)]₂ and [PdCl₂(CH₃CN)₂] are cleaved by the N,S donor ligands giving products that are easily isolated. For the cyclopalladated species [Pd₂(dmmba)₂(μ-NCO)(μ-2-qnS)] (**1**) and [Pd₂(dmmba)₂(μ-NCO)(μ-8-qnS)] (**2**), both cyanate and qnS groups act as bridging ligands between two [Pd(dmmba)] moieties. For compounds [Pd(2-qnS)₂] (**3**) and [Pd(8-qnS)₂] (**4**), the thioligands are coordinated to the palladium atom in the chelating mode. The thermoanalytical data showed that the thermal stability of compounds **1–4** varies in the **4**>**3**>**1**>**2** sequence. Complex (**2**) is less stable than (**1**) probably due to the small stability conferred by the seven membered ring formed by the metal and the ligands in comparison with the six-membered ring observed in (**1**). The greater stability of (**4**) can be explained by the less tensioned five-membered ring formed between the metallic centre and 8-qnS.

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