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THERMAL STUDY OF CYCLOPALLADATED COMPLEXES OF THE TYPE $[Pd_2(dmba)_2X_2(bpe)]$ (X=NO_3^-, Cl^-, N_3^-, NCO^-, NCS^-; bpe=*trans*-1,2-bis(4-pyridyl)ethylene)

E. T. de Almeida[1,2], *A. M. Santana*[1], *A. V. G. Netto*[1], *Claudia Torres*[1] *and A. E. Mauro*[1*]

[1]Instituto de Química de Araraquara-UNESP-C.P. 355, 14801-970 Araraquara-SP, Brazil
[2]Centro de Ciências da Educação e de Humanidades, CCEH, Universidade Católica de Brasília, UCB, EPCT–QS-07–Lote 1, Águas Claras, 71966-700 Brasília-DF, Brazil

The synthesis, characterization and thermal analysis of the novel cyclometallated compounds $[Pd_2(dmba)_2Cl_2(\mu\text{-bpe})]$ (**1**), $[Pd_2(dmba)_2(N_3)_2(\mu\text{-bpe})]$ (**2**), $[Pd_2(dmba)_2(NCO)_2(\mu\text{-bpe})]$ (**3**), $[Pd_2(dmba)_2(SCN)_2(\mu\text{-bpe})]$ (**4**), $[Pd_2(dmba)_2(NO_3)_2(\mu\text{-bpe})]$ (**5**) (bpe=*trans*-1,2-bis(4-pyridyl)ethylene; dmba=N,N-dimethylbenzylamine) are described. The thermal stability of $[Pd_2(dmba)_2X_2(\mu\text{-bpe})]$ complexes varies in the sequence **1**>**4**>**3**>**2**>**5**. The final residues of the thermal decompositions were characterized as metallic palladium by X-ray powder diffraction.

Keywords: *cyclopalladated complexes, DTA, pseudohalides, TG*

Introduction

In the past few years, the cyclopalladated chemistry have undergone spectacular advances mainly due to their potential uses as technologically relevant materials (e.g. liquid crystals) [1], catalysts [2, 3], and antitumoral drugs [4]. Despite the increased attention on the cyclopalladated compounds, less attention appears to have been paid to their derivatives containing linear pyridyl-donor ligands. Of particular interest is to use pyrazine, 4,4'-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene) as bridges between metals, yielding binuclear species as well supramolecular architectures [5, 6]. We reasoned that unusual bimetallic compounds could be generated by the cleavage of orthopalladated compounds of the type $[Pd(dmba)(\mu\text{-}X)]_2$ (X=bridging anionic group; dmba=N,N-dimethylbenzylamine) by the desired linear exobidentate ligand such as *trans*-1,2-bis(4-pyridyl)ethylene (bpe). In the framework of our current research on cyclometallated compounds [7–12] as well in the coordination and supramolecular chemistry of pseudohalides [13, 14], we report herein the synthesis, characterization and thermal study of novel binuclear cyclopalladated species of general formulae $[Pd_2(dmba)_2X_2(\mu\text{-bpe})]$ (X=Cl^- (**1**), N_3^- (**2**), NCO^- (**3**), SCN^- (**4**), NO_3^- (**5**); bpe=*trans*-1,2-bis(4-pyridyl)ethylene; dmba=N,N-dimethylbenzylamine).

Experimental

Preparation of the complexes

The complexes $[Pd(dmba)(\mu\text{-}X)]_2$ (X=Cl^-, N_3^-, NCO^-, NCS^-) and $[Pd(dmba)(CH_3CN)_2](NO_3)$ were prepared as previously described [4, 7, 8].

$[Pd_2(dmba)_2X_2(\mu\text{-bpe})]$ (X=Cl^- (**1**), N_3^- (**2**), NCO^- (**3**), NCS^- (**4**)) were synthesized for the first time by adding a solution containing 0.354 mmol of *trans*-1,2-bis(4-pyridyl)ethylene in CH_2Cl_2 to the respective $[Pd(dmba)(\mu\text{-}X)]_2$ precursors (0.354 mmol) dissolved in 15 mL of CH_2Cl_2. $[Pd_2(dmba)_2(NO_3)_2(\mu\text{-bpe})]$ (**5**) was prepared as mentioned above but using the $[Pd(dmba)(CH_3CN)_2](NO_3)$ precursor. The resulting clear suspensions were stirred for 1 h and filtered off. The pale yellow powders obtained were washed with CH_2Cl_2 and pentane and dried in vacuum. All compounds showed poor solubility in most common solvents. Yields: 80–90%.

Instrumentation

Melting points were determined on a Mettler FP-2 microscope. Elemental analyses of carbon, nitrogen, and hydrogen were performed on a microanalyser CE Instruments, model EA 1110 – CHNS-O. Infrared spectra were recorded as KBr pellets on a Nicolet FTIR-Impact 400 spectrophotometer in the spectral range 4000–400 cm^{-1}. Simultaneous thermal analysis (TG-DTA) were carried out using a TA system model SDT 2960, under flow of dry synthetic air

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[*] Author for correspondence: mauro@iq.unesp.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Results of chemical analyses and melting points of the compounds **1**–**5**

Complex	*m. p.*/°C	Carbon/%		Nitrogen/%		Hydrogen/%	
		found	calc.	found	calc.	found	calc.
1	195.2 (dec.)	49.1	49.1	7.3	7.6	4.7	4.7
2	164.4 (dec.)	48.1	48.2	18.3	18.7	4.5	4.6
3	174.0 (dec.)	51.4	51.4	11.2	11.2	4.6	4.6
4	189.5 (dec.)	49.3	49.3	10.8	10.8	4.1	4.4
5	147.1 (dec.)	45.1	45.8	10.3	10.7	4.4	4.3

Table 2 IR spectral data (4000–400 cm^{-1}) for compounds [Pd$_2$(dmba)$_2$$X_2$(μ-bpe)] ($X$=Cl$^-$ (**1**), N$_3^-$ (**2**), NCO$^-$ (**3**), SCN$^-$ (**4**), NO$_3^-$ (**5**))

Complex	$\bar{\nu}$/cm^{-1}						
	dmba			bpe		*X*	
	νCH	νCH$_3$	νCH$_2$	νCH	ν$_{ring}$	ν	δ
1	3047 w	2907 m	2872 m	2984 w	1594 s	–	–
2	3050 w	2912 m	2844 w	2999 w	1606 s	2036 s (ν$_{as}$), 1351 w (ν$_s$)	–
3	3051 m	2907 w	2835 w	2987 w	1605 s	2203 s (ν$_{as}$), 1316 w (ν$_s$)	581 w
4	3046 m	2885 m	2792 w	2978 m	1573 m	2134 s (ν$_{as}$)	472 w
5	3045 m	2905 m	2840 w	2999 m	1604 s	1369 s	836 s

(100 mL min^{-1}), temperature up to 1000°C and heating rate of 10°C min^{-1}, in α-alumina sample holders. The reference substance was pure α-alumina in DTA measurements. X-ray powder patterns of the residues were obtained with a Zeiss HGZ4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg–Brentano scheme was adopted using CuK$_\alpha$ radiation (λ=1.541 Å) and setting of 34 kV and 20 mA. The residues (Pd, PdO) were identified using ICDD bases [15].

Results and discussion

The elemental analyses results and thermogravimetric data, together with IR spectroscopy data, confirmed the proposed binuclear formulae for the synthesized compounds. The results of the analyses and melting points are presented in Table 1.

Infrared spectra

The most important bands frequencies observed in the IR spectra of the complexes along with their assignments are presented in Table 2.

Comparison of the IR spectra of the precursors [4, 7, 8] and **1**–**5** allowed us to gain some insight about the molecular structures of these novel species. The characteristic bands of the cyclometallated ring (dmba) at 3045–3050 cm^{-1} (νCH), 2885–2912 cm^{-1} (νCH$_3$), and 2792–2844 cm^{-1} (νCH$_2$) in IR spectra of **1**–**5** were found unchanged when compared to those observed for the precursors. Therefore, the interaction between bpe ligand and the precursors did not affect the integrity of orthometallatted ring. Concerning to the anionic ligands (*X*), the presence of terminal azide in (**2**) was evidenced by the ν$_{as}$NNN band at 2036 cm^{-1} [13] whereas the terminal N-bonded cyanato ligand in (**3**) was inferred on basis of the ν$_{as}$NCO absorption at 2203 cm^{-1} [16]. Compounds (**4**) and (**5**) are characterized by the existence of terminal *S*-bonded thiocyanato (2134 cm^{-1}, ν$_{as}$SCN) [13] and unidentate *O*-nitrato groups (1369 cm^{-1}, ν$_s$NO$_2$) [8], respectively. The bidentate coordination of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) in **1**–**5** was clearly evidenced by the appearance of additional IR bands at 2978–2999 cm^{-1} (νCH), and 1573–1606 cm^{-1} (ν$_{ring}$). Taking into account the discussion of the IR data, the adjacent coordination sites of the resulting *cis*-protected fragment (dmba)Pd are occupied by one terminal anionic group (*X*) and one 4-pyridyl ring from the bidentate bpe ligand which acts as a bridge between two metallic centers. The proposed molecular structure for compounds **1**–**5** is shown in Fig. 1.

Thermogravimetric analysis

TG and DTA curves for the compounds **1**–**5** are depicted in Fig. 2. Table 3 presents the results of the thermal studies of these complexes together with the assignments of each decomposition step.

In the range 165–459°C, the compounds **1**–**4** lose their organic (i.e. bpe and dmba) and inorganic (*X*) lig-

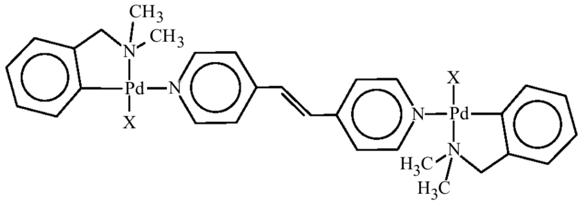

Fig. 1 Proposed structure of the compounds **1**–**5** (*X*=Cl^-, N_3^-, NCO^-, SCN^-, NO_3^-)

ands, with uptake of O_2, in 2–3 steps, yielding a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [15]. Afterwards, the TG curves of **1**–**4** also exhibited a progressive mass gain up to ca. 800°C due to the oxidation of the remaining Pd to PdO. The last mass loss is characterized by the decomposition of PdO to Pd (ASTM 05-0681) at ca. 840°C. The ligands of the compound (**5**) are eliminated in the 147–473°C range, affording pure PdO (ASTM 06-0515). After that, no mass change in the TG curve of (**5**) was observed in the range 473–803°C. The PdO further decomposed into Pd (ASTM 05-0681) in the last mass loss of (**5**) at 803–841°C.

Taking into account the initial decomposition temperatures, the thermal stability of the complexes [$Pd_2(dmba)_2X_2(\mu\text{-bpe})$] varies in the sequence *X*=**1**>**4**>**3**>**2**>**5**. These thermoanalytical results agree well with our previous studies [17], in which the highest thermal stability for chloro and thiocyanato-derivatives of palladium was verified. The lowest stability of (**5**) deserves further comments. According to HSAB principle [18], soft Lewis acid forms more stable coordination compounds with soft bases. As expected for a complex composed by a hard base (NO_3^- and a soft acid Pd(II)), the thermal decompostion of (**5**) begins at the lowest temperature among those of the compounds investigated. Finally, the known explosive characteristic of azide contributes to the low thermal stability of (**2**), as evidenced in our previous studies [17].

Table 3 Thermal analysis data for compounds **1**–**5**

Complex	Step	Δ*T*/°C	Δm/%		DTA peak/°C		Assignment
m_{initial}			found	calculated	endo	exo	
1 10.4976 mg	1	195–281	–35.18	–36.72	–	233	–2dmba
	2	281–332	–8.32	–9.63	–	–	–2Cl
	3	332–459	–27.01	–23.88	–	383	–1bpe, $+0.2O_2$
	4	459–787	3.36	3.47	–	–	$+0.8O_2$
	5	787–830	–3.83	–4.34	818	–	$–1.0O_2$
	residue		29.02	28.90			
2 8.28618 mg	1	165–238	–5.22	–5.61	–	–	$–1N_3$
	2	238–248	–43.19	–41.68	–	249	–2dmba, $–1N_3$
	3	248–428	–21.70	–23.03	–	416	–1bpe, $+0.3O_2$
	4	428–800	3.10	2.99	830	–	$+0.7O_2$
	5	800–845	–3.99	–4.27	–	–	$–1.0O_2$
	residue		29.00	28.40			
3 8.26233 mg	1	174–277	–36.38	–36.08	–	–	–2dmba
	2	277–326	–25.36	–24.31	–	320	–1bpe
	3	326–435	–8.26	–9.50	–	381	–2NCO, $+0.4O_2$
	4	435–790	2.72	2.56	–	–	$+0.6O_2$
	5	790–829	–4.09	–4.27	822	–	$–1.0O_2$
	residue		28.63	28.39			
4 5.46025 mg	1	189–266	–40.96	–42.03	–	–	–2dmba, –1NCS
	2	266–334	–30.62	–29.51	–	332	–1bpe, –1NCS, $+0.3O_2$
	3	334–813	4.52	2.86	–	–	$+0.7O_2$
	4	813–833	–5.32	–4.10	821	–	$–1.0O_2$
	residue		27.62	27.22			
5 6.70398 mg	1	147–323	–57.23	–57.33	–	245	–2dmba, –1bpe
	2	323–473	–10.95	–11.66	–	335	$–1N_2O_4$
	3	473–803	0.00	0.00	–	–	–
	4	803–841	–4.55	–4.05	821	–	$–1.0O_2$
	residue		27.27	26.96			

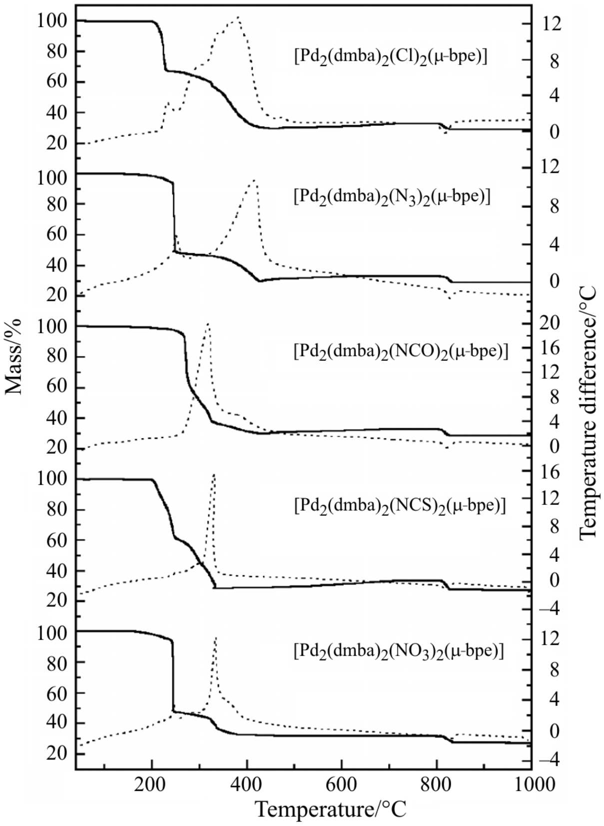

Fig. 2 —– TG and ··· – DTA curves for the complexes $[Pd_2(dmba)_2X_2(\mu\text{-}bpe)]$ (X=Cl^- (**1**), N_3^- (**2**), NCO^- (**3**), SCN^- (**4**), NO_3^- (**5**)

Conclusions

The synthesis, characterization and thermal behavior of the binuclear cyclometallated compounds $[Pd_2(dmba)_2X_2(\mu\text{-}bpe)]$ (X=Cl^- (**1**), N_3^- (**2**), NCO^- (**3**), SCN^- (**4**), NO_3^- (**5**) (bpe=*trans*-1,2-bis(4-pyridyl)ethylene; dmba=N,N-dimethylbenzylamine) has been described in this work. The thermoanalytical data showed the thermal stability of $[Pd_2(dmba)_2X_2(\mu\text{-}bpe)]$ compounds varies in the sequence X=Cl^->SCN^->NCO^->N_3^->NO_3^-. Further studies involving the use of cyclometallated as precursors for the construction of peculiar metallosupramolecular structures are in progress in our laboratories.

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