J Therm Anal Calorim (2009) 97:153–156
DOI 10.1007/s10973-009-0249-3

Synthesis, spectral and thermal studies on dicarboxylate-bridged palladium(II) coordination polymers. Part II

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ICTAC2008 Conference

Abstract The synthesis and thermal behavior of the new $[Pd(fum)(bipy)]_n \cdot 2nH_2O$ (**1**), $[Pd(fum)(bpe)]_n \cdot nH_2O$ (**2**) and $[Pd(fum)(pz)]_n \cdot 3nH_2O$ (**3**) {bipy = 4,4′-bipyridine, bpe = 1, 2-bis(4-pyridyl)ethene and pz = pyrazine} fumarate complexes are described in this work as well their characterization by IR and ^{13}C CPMAS NMR spectroscopies. TG curves showed that the compounds released organic ligands and lattice water molecules in the temperature range of 46–491 °C. In all the cases, metallic palladium was identified as the final residue.

Keywords Palladium(II) · Fumarate · N-based linear spacers · Thermal studies · Coordination polymers

Introduction

Research on metal-directed supramolecular compounds has rapidly been expanding duo to their interesting topologies and potential applications as functional materials [1, 2]. Recently the use of organic spacers, particularly the dicarboxylic acid, as superexchange pathways between the metal ions is of growing interest in the field of catalysis [3], gas sorption and desorption [4–6], opto-electronic devices [7], and molecular magnetism [8].

In the present study, we describe the synthesis, spectroscopic characterization and thermal studies on the polymeric species $[Pd(fum)(bipy)]_n \cdot 2nH_2O$ (**1**), $[Pd(fum)(bpe)]_n \cdot nH_2O$ (**2**) and $[Pd(fum)(pz)]_n \cdot 3nH_2O$ (**3**) {fum = fumarate, bipy = 4,4′-bipyridine, bpe = 1,2-bis(4-pyridyl)ethane, pz = pyrazine} as a part of our ongoing research interest in thermal behavior of palladium-based compounds [9].

Experimental

Preparation of the complexes

Compounds **1**–**3** were synthesized from the dropwise addition of a methanolic mixture containing the appropriate amounts of the N-based ligand (76.8 mmols) and sodium fumarate (61.6 mg, 38.5 mmol) to a solution of the precursor $[PdCl_2(CH_3CN)_2]$ (100 mg, 38.5 mmols) in methanol. Yellow suspensions were obtained, filtered off and the solids were washed with water, methanol and dried in vacuum.

Methods

The elemental analysis (carbon, nitrogen and hydrogen) were performed on a CE Instruments, model EA 1110-CHNS-O microanalyser.

Infrared spectra were recorded on a Nicolet FTIR-Impact 400 spectrophotometer in the 4000–400 cm^{-1} spectral range using KBr pellets.

The ^{13}C CP NMR spectra were obtained on a Varian Unity INOVA spectrometer operating at 300 MHz for carbon. Samples were packed in a silicon nitride rotor (OD = 7 mm). Chemical shift values were referenced externally to tetramethylsilane at 0 ppm.

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TG experiments were carried out using a Shimadzu system model TGA-50. The TG curves were recorded in dry synthetic air flow (100 mL min^{-1}), with temperature up to 900 °C and at a heating rate of 20 °C min^{-1} in platinum sample holders.

X-ray powder diffraction patterns of the residues were measured using SIEMENS D-5000 diffractometer equipped with a proportional counter and pulse height discriminator. The Bragg–Bretano arrangement was adopted using CuK_α radiation ($\lambda = 1.541$ Å) and setting of 34 kV and 20 mA. The peaks were identified using PDF bases [10].

Results and discussion

The fumarate-bridged palladium polymers **1–3** were characterized through elemental analyses, thermogravimetric data, IR and ^{13}C CPMAS NMR spectroscopies, leading us to suggest the formulae illustrated in the Fig. 1 to the isostructural compounds. The analytical data are presented in Table 1.

Infrared spectra

The principal IR data of the complexes are presented in Table 2. The bis-monodentate coordination mode of the fumarate ligand was evidenced in the IR spectra of **1–3** by the appearance of its characteristic bands at 1640–1650 cm^{-1} (ν_{as}COO$^-$) and 1375–1385 cm^{-1} (ν_sCOO$^-$) [11]. Infrared vibrational studies also revealed the coordination of the linear spacers in these compounds by the presence of the typical νCN absorptions at 1423–1416 cm^{-1} and δCH bands at 815–833 cm^{-1} [12, 13].

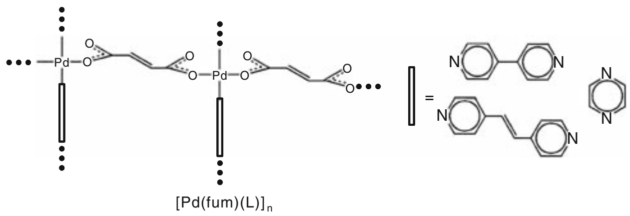


Fig. 1 Proposed structural formulae for the complexes **1–3**

Table 2 Selected vibrational data (cm^{-1}) of the palladium(II) complexes **1–3**

$\bar{\nu}$/cm^{-1}			
1	**2**	**3**	Assignment
3446s	3425s	3454s	ν(OH)
3090w	3092w	3091w	ν(CH)$_{ar}$
1610ms	1605ms	–	ν(CC)
1416m	1423m	1423m	ν(CN)
815m	833m	817m	δ(CH)
–	–	–	ν(Pd–O)
1647ms	1643ms	1643ms	ν_{as}(COO$^-$)
1382m	1376m	1382m	ν_s(COO$^-$)
–	–	–	δ(O–C–O)

m medium, *s* strong, *ms* medium–strong, *w* weak

^{13}C CPMAS NMR spectra

Table 3 lists the ^{13}C CPMAS NMR results obtained to **1–3**. The presence of coordinated fumarate in **1** and **2** is inferred due to the existence of ^{13}C=O signal at 185.72 and 187.83 ppm, respectively [14]. The ^{13}C signals at 153.60 (C$_A$, C$_{A'}$), 147.37 (C$_q$), and 124.47 ppm (C$_B$, C$_{B'}$) agree well with the presence of 4,4′-bipyridine in **1** (see numbering scheme in Table 3). For the compound **2**, the

Table 3 ^{13}C CPMAS NMR data (ppm) for compounds **1** and **2**

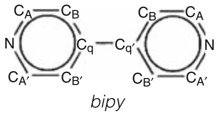
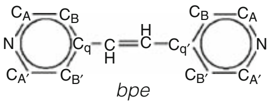
Numbering scheme	Compound	Chemical shift/ppm	Assignment
	**1**	185.72	C=O
		153.36	C$_A$, C$_{A'}$
		147.37	C$_q$, C$_{q'}$
		133.54	–CH=CH–
		124.47	C$_B$, C$_{B'}$
	**2**	187.83	C=O
		150.93	C$_A$, C$_{A'}$
		144.78	C$_q$, C$_{q'}$
		132.48	–CH = CH–
		125.53	C$_B$, C$_{B'}$

Table 1 Results of elemental analysis of the compounds **1–3**

Compound	Color	Formula	Carbon/%		Nitrogen/%		Hydrogen/%	
			Found	Calc.	Found	Calc.	Found	Calc.
[Pd(μ-fum)(μ-4,4′-bipy)]$_n$·2nH$_2$O **1**	Yellow	$C_{14}H_{10}N_2O_4Pd$	40.2	40.6	7.0	6.8	3.6	3.6
[Pd(μ-fum)(μ-bpe)]$_n$·nH$_2$O **2**	Yellow	$C_{16}H_{12}N_2O_4Pd$	45.5	45.6	7.3	6.6	3.9	3.6
[Pd(μ-fum)(μ-pz)]$_n$·3nH$_2$O **3**	Yellow	$C_8H_6N_2O_4Pd$	27.4	27.0	7.1	7.9	3.0	3.7

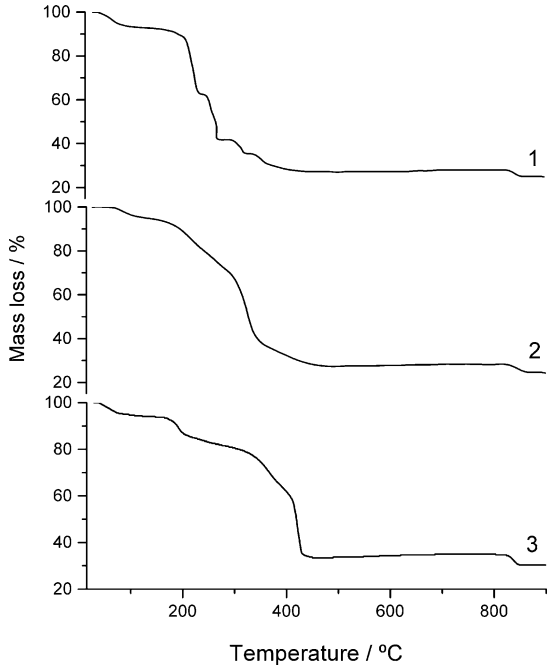


Fig. 2 TG curves for the complexes **1**–**3**

Table 4 Thermal analysis data for compounds **1**–**3**

Complex	Step	ΔT/°C	Δm/%		Assignment
			Obt.	Calc.	
1	1	46–462	*−72.74*	*−72.28*	-2 H_2O; −1 bipy; −1 fum
	2	462–818	*+0.66*	*+1.94*	+0.25 O_2
	3	818–864	*−2.92*	*−3.87*	−0.50 O_2
	Residue		*25.00*	*25.79*	Pd
2	1	70–491	*−70.91*	*−72.81*	−1 H_2O; −1 bpe; −1 fum
	2	491–819	*+0.97*	*+1.91*	+0.25 O_2
	3	819–876	*−3.64*	*−3.18*	−0.50 O_2
	Residue		*26.42*	*25.92*	Pd
3	1	50–450	*−66.55*	*−67.69*	−3 H_2O; −1 pz; −1 fum
	2	450–818	*+1.55*	*+2.26*	+0.25 O_2
	3	818–860	*−4.68*	*−4.52*	−0.50 O_2
	Residue		*30.51*	*30.05*	Pd

coordination of 1,2-bis(4-pyridyl)ethane (bpe) is evidenced by the aromatic signals at 150.93 (C_A, $C_{A'}$), 144.78 (C_q), and 125.53 ppm (C_B, $C_{B'}$) as well the resonance of –CH=CH– moiety at 132.48 ppm [15]. The ^{13}C CPMAS NMR spectrum of **3** could not be registered due to its lower yield synthesis.

Thermogravimetric analysis

The TG curves for **1**–**3** are illustrated in Fig. 2. Table 4 shows the results of the thermal investigations in dry synthetic air atmosphere of these compounds together with the assignments of each decomposition stage based on mass calculation.

Compound **1** undergoes decomposition to Pd^0 by a gradual elimination started at 46 °C followed by an abrupt mass loss completed at 462 °C, associated to the elimination of bipy, fum and H_2O molecules and uptake of O_2, yielding a mixture of Pd^0 (05-0681) and PdO (ASTM 06-0515) [10]. The formation of additional PdO is noticed by a slight progressive mass loss up to 818 °C. The decomposition of PdO to Pd^0 is observed in the last mass loss between 818 and 864 °C.

Compound **2** started to degrade at higher temperature (70 °C) than **1**. Afterwards, a mass change of 70.91% is caused by the thermal breakdown of the main chain, leading to a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [10] at 491 °C. A progressive mass gain of 0.97% up to 819 °C is ascribed to the formation of additional PdO which further decomposed into Pd (Calcd. 25.92%, Found 26.42%) over the range 819–876 °C.

The coordination polymer **3** started to decompose at 50 °C. A further heating to 450 °C resulted in a mass loss of 66.55% associated with the degradation of the main polymeric chain and elimination of H_2O molecules, yielding a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [10] as residue. A slight mass gain of 1.55%, between 450 and 818 °C, is ascribed to the oxidation of Pd^0 to PdO. The decomposition of PdO to metallic palladium is observed in the last mass loss (4.68%) between 818 and 860 °C (Calcd. 4.52%).

Conclusions

The novel coordination polymers $[Pd(fum)(bipy)]_n \cdot 2nH_2O$ (**1**), $[Pd(fum)(bpe)]_n \cdot nH_2O$ (**2**) and $[Pd(fum)(pz)]_n \cdot 3nH_2O$ (**3**) are described in this work. TG curves showed that the thermal degradation pattern of **1**–**3** consists of the elimination of solvent occlusion (water) during the initial decomposition step. Further increase temperature resulted in the degradation of linear bridging ligand and fumarate group.

TG studies also showed that the nature of the N-based linear spacers does not affect significantly their thermal stability of the coordination polymers. After the release of water molecules, the dehydrated form of polymer **1** is stable up to 205 °C whereas the decomposition of the main polymeric chain started at about 181 °C and 179 °C for the dehydrated compounds **2** and **3**, respectively.

Acknowledgements The authors acknowledge CNPq, FAPESP and CAPES for financial support.

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