J Therm Anal Calorim (2009) 97:123–126
DOI 10.1007/s10973-009-0252-8

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

**R. L. Fernandes · P. M. Takahashi · R. C. G. Frem ·
A. V. G. Netto · A. E. Mauro · J. R. Matos**

ICTAC2008 Conference

Abstract This work describes the synthesis, IR and ^{13}C CPMAS NMR spectroscopic as well the thermal characterization of the new dicarboxylate complexes $[Pd_2(ox)_2(4,4'\text{-bipy})]n$ (**1**), $[Pd_2(ox)_2(bpe)]_n$ (**2**) and $[Pd_2(ox)_2(pz)]_n$ (**3**) {ox = oxalate, bipy = 4,4′-bipyridine, bpe = 1,2-bis(4-pyridyl)ethane, pz = pyrazine}. TG experiments reveal that compounds **1**–**3** undergo thermal decomposition in three steps. Metal palladium was the final product of the thermal decompositions, which was identified by X-ray powder diffraction.

Keywords ^{13}C CPMAS NMR · IR · Oxalate · Palladium(II) · Thermal behavior

Introduction

Research on metal-organic frameworks (MOFs) has rapidly been expanding due to their interesting topologies and potential applications as functional materials in catalysis and gas adsorption [1, 2]. Particularly, dicarboxylic acids and linear ligands bearing nitrogen (for instance 4,4′-bipyridine) have been used successfully as building blocks in the construction of such interesting architectures due to their ability to act as linkers between metals [3]. Concerning the oxalate group, the main reasons for the extensive use of this old but evergreen ligand are: (a) its remarkable ability to mediate electronic effects between metal centers affording compounds with a wide range of magnetic properties [4, 5] and (b) the prevalence of its rigid bis-bidentate mode providing some degree of predictability with regard to the structural characteristics of the resulting metal-oxalato networks.

Following up our interest in supramolecular systems involving transition metals and *N*-based-ligands as well in their thermal behavior [6, 7] we describe in the present study the synthesis, spectroscopic characterization and thermal studies on the series of palladium(II) oxalate compounds $[Pd_2(ox)_2(4,4'\text{-bipy})]_n$ (**1**), $[Pd_2(ox)_2(bpe)]_n$ (**2**), and $[Pd_2(ox)_2(pz)]_n$ (**3**) {ox = oxalate, bipy = 4,4'-bipyridine, bpe = 1,2-bis(4-pyridyl)ethane, pz = pyrazine}.

Experimental

Synthesis of the complexes

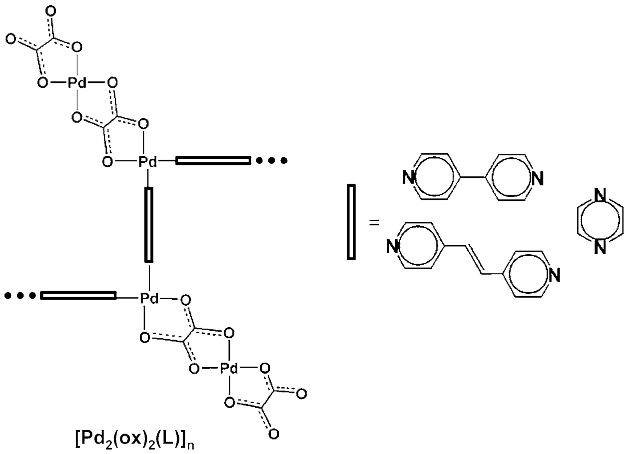
Compounds **1**–**3** were synthesized as follows: 3 mL of a methanolic mixture containing the appropriate amount of pyridil ligand (76.8 mmols) and sodium oxalate (51.6 mg, 38.5 mmol) was added dropwise to a deep orange solution of $[PdCl_2(CH_3CN)_2]$ (100 mg, 38.5 mmols) in 10 mL of MeOH. Yellow suspensions were obtained, filtered off and the solids were washed with water, methanol and dried in vacuum.

Methods

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

R. L. Fernandes · P. M. Takahashi · R. C. G. Frem (✉) ·
A. V. G. Netto · A. E. Mauro
Instituto de Química de Araraquara, UNESP, P.O. Box 355,
Araraquara 14801-970, SP, Brazil
e-mail: rcgfrem@iq.unesp.br

J. R. Matos
Instituto de Química-USP-SP, P.O. Box 26077, São Paulo, SP,
Brazil



Scheme 1 Representation of the probable structural formulae of the coordination polymers $[Pd_2(ox)_2(L)]n$ (L = 4,4′-bipyridine; 1,2-bis(4-pyridyl)ethane; pyrazine)

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.

TG experiments were carried out using a Shimadzu system model TGA-50. The TG curves were registered under flow of dry synthetic air (100 mL min^{-1}), temperature up to 500 °C and 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 [8].

Results and discussion

Reactions of the $[PdCl_2(MeCN)_2]$ precursor with pyridyl-type ligands in the presence of oxalate groups lead to the air stable dicarboxylate-bridged palladium solids **1**–**3**. The elemental analyses and thermogravimetric data, together with IR spectroscopy and ^{13}C CPMAS NMR results confirmed the proposed formula for the synthesized compounds (see Scheme 1). The polymeric nature of the obtained compounds was inferred by their intractability and amorphous nature. The analytical data are presented in Table 1.

Infrared spectra

The most significant bands of the complexes with their tentative assignments are presented in Table 2. The bis-chelating coordination mode of the oxalate ligand was clearly detected in the IR spectra of **1**–**3** via the presence of the characteristic bands at 1635–1645 cm^{-1} ($\nu_{as}COO^-$), 1315–1325 cm^{-1} ($\nu_s COO^-$) and 775–780 cm^{-1} (δO–C–O) [9, 10]. IR experiments also revealed the coordination of the linear bridging ligands in these complexes by the appearance of the typical νCN and δCH bands at 1431–1411 cm^{-1} and 815–833 cm^{-1}, respectively [11, 12].

^{13}C CPMAS NMR spectra

The ^{13}C CPMAS NMR results are given in Table 3. The ^{13}C CPMAS NMR spectra of **1** and **2** clearly indicate the coordination of oxalate ligand by the appearance of its typical signal at 166.13 and 165.96 ppm, respectively [13].

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

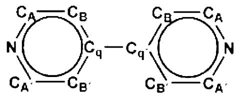
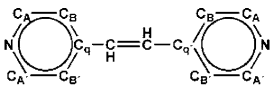
$(\bar{\nu}/\mathrm{cm}^{-1})$			
1	2	3	Assignment
3409w	3415w	3440w	ν(OH)
3043w	3045w	3038w	$\nu(CH)_{ar}$
1606ms	1605ms	–	ν(CC)
1411s	1431m	1421s	ν(CN)
815s	833m	815m	δ(CH)
513m	518m	518m	ν(Pd–O)
1636ms	1643s	1642ms	$\nu_{as}(COO^-)$
1321s	1321m	1319F	$\nu_s(COO^-)$
776m	775m	776m	δ(O–C–O)

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

Table 1 Results of chemical analysis and melting points of compounds **1**–**3**

Compound	Color	Formula	Carbon/%		Nitrogen/%		Hydrogen/%	
			Found	Calc.	Found	Calc.	Found	Calc.
$[Pd_2(ox)_2(4,4'bipy)]_n$ **1**	Yellow	$C_{14}H_8N_2O_8Pd_2$	30.3	30.85	4.9	5.14	2.2	1.48
$[Pd_2(ox)_2(bpe)]_n$ **2**	Yellow	$C_{16}H_{10}N_2O_8Pd_2$	32.9	33.65	4.8	4.91	2.1	1.76
$[Pd_2(ox)_2(pz)]_n$ **3**	Yellow	$C_8H_4N_2O_8Pd_2$	20.6	20.49	6.0	5.97	0.9	0.86

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

Numbering scheme	Compound	Chemical (shift/ppm)	Assignment
 *bipy*	**1**	166.13	C=O
		153.02	C_A, $C_{A'}$
		147.76	C_q, $C_{q'}$
		126.40, 122.51	C_B, $C_{B'}$
 *bpe*	**2**	165.96	C=O
		153.10	C_A, $C_{A'}$
		146.38	C_q, $C_{q'}$
		131.25	–CH=CH–
		120.89	C_B, $C_{B'}$

The ^{13}C signals at 153.02 (C_A, $C_{A'}$), 147.76 (C_q), 126.40 and 122.51 ppm (C_B, $C_{B'}$) agree well with the presence of 4,4′-bipyridine in **1** (see numbering scheme in Table 3). For the complex **2**, the coordination of 1,2-bis(4-pyridyl)ethane (bpe) is evidenced by the aromatic signals at 153.10 (C_A, $C_{A'}$), 146.38 (C_q), and 120.89 ppm (C_B, $C_{B'}$) as well the resonance of –CH=CH– moiety at 131.25 ppm [14]. The ^{13}C CPMAS NMR spectrum of **3** could not be registered due to its lower yield synthesis.

Thermogravimetric analysis

The TG curves for the complexes **1**–**3** are illustrated in Fig. 1. Table 4 lists the results of the thermal studies of these compounds together with the assignments of each decomposition stage based on mass calculation. Therefore, the groups indicated at the right column of the Table 2 do not correspond necessarily to the gaseous final products of decomposition.

The TG curve of **1** indicates that this compound is thermally stable up to 167 °C, then undergoes two mass losses y oxidative thermal breakdown of the polymer backbone, giving rise to Pd^0 (ASTM 05-0681) [8] as residue at 444 °C. A slight mass increase of 2.8%, between 444 and 835 °C is ascribed to the partial oxidation of Pd^0 to PdO which further degrades to metallic palladium in the last mass loss (3.3%) at 835–867 °C. The final mass percent residue of 39.30% agrees well with the calculated amount of Pd (39.05%).

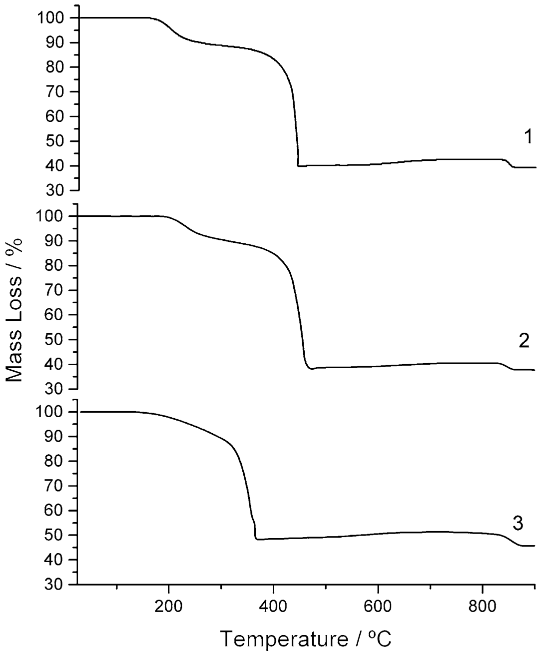


Fig. 1 TG curves for the complexes **1**–**3**

Compound **2** showed a similar thermal behavior to **1**. The first step between 191 and 474 °C is accompanied by two mass losses which are attributed to the elimination of oxalate and bpe ligands, yielding Pd^0 as residue (ASTM 05-0681) [8]. The increase of mass (2.3%) observed at 474–824 °C is probably due to the partial oxidation of Pd^0 to PdO by uptake of O_2. The decomposition of PdO to metallic Pd is noticed in the last mass loss (2.6%) between 824 and 873 °C (Calcd. 2.77%).

Compound **3** decomposed faster than the coordination polymers **1** and **2**. The TG curve indicates that **3** is thermally stable up to 130 °C, then decomposes into Pd^0 in three steps. The first step between 130 and 373 °C is accompanied by 51.7% mass loss, which is attributed to the elimination of oxalate and pirazine ligands and uptake of O_2 (Calcd. 51.21%) yielding a mixture of Pd^0 (05-0681) and PdO (ASTM 06-0515) [8]. A progressive mass gain of 3.1% up to 724 °C is ascribed to the formation of additional PdO which further decomposed into Pd (Calcd. 45.38%, Found 45.7%) at 724–883 °C.

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

Complex	Step	ΔT (°C)	Δm (%)		Assignment
			Obt.	Calc.	
1	1	167–444	*−60.2*	*−60.9*	−1 bipy; −2 ox
	2	444–835	*+2.8*	*+3.2*	+0.5 O_2
	3	835–867	*−3.3*	*−3.2*	−0.5 O_2
	Residue		*39.3*	*39.1*	Pd
2	1	191–474	*−61.9*	*−63.0*	−1 bpe; −2 ox
	2	474–824	*+2.3*	*+2.8*	+0.5 O_2
	3	824–873	*−2.6*	*−2.8*	−0.5 O_2
	Residue		*37.8*	*37.0*	Pd
3	1	130–373	*−51.7*	*−51.2*	−1 pz; −2 ox
	2	373–717	*+3.1*	*+3.4*	+0.5 O_2
	3	717–887	*−5.7*	*−6.8*	−1 O_2
	Residue		*45.7*	*45.4*	Pd

Conclusions

This work describes the synthesis, spectroscopic characterization and thermal studies of the new palladium(II) dicarboxylate complexes $[Pd_2(ox)_2(4,4'\text{-bipy})]_n$ (**1**), $[Pd_2(ox)_2(bpe)]_n$ (**2**) and $[Pd_2(ox)_2(pz)]_n$ (**3**). From the inspection of TG curves of these neutral $[Pd_2(ox)_2(L)]_n$ complexes, it is noticed that the stability varies according to the linear bridging groups, following the order bpe $\geq$ 4,4′-bipy $>$ pz.

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

References

1. Mori W, Sato T, Ohmura T, Kato CN, Takei T. Functional microporous materials of metal carboxylate: gas-occlusion properties and catalytic activities. J Solid State Chem. 2005;178:2555–73.
2. Chen B, Ma S, Zapata F, Fronczek FR, Lobkovsky EB, Zhou H-C. Rationally designed micropores within a metal−organic framework for selective sorption of gas molecules. Inorg Chem. 2007;46:1233–6.
3. Eddaoudi M, Moler DB, Li H, Chen B, Reineke TM, O′Keeffe M, et al. Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal−organic carboxylate frameworks. Acc Chem Res. 2001;34:319–30.
4. Zhang B, Zhang Y, Kurmoo M. Preparation, crystal structure and magnetic property of a binuclear oxalate-bridged iron(III) compound: $Fe_2(C_2O_4)Cl_4(DMF)_4$ (DMF = dimethylformamide). Inorg Chim Acta. 2007;360:2513–7.
5. Garcia-Couceiro U, Castillo O, Luque A, García-Terán JP, Beobide G, Román P. Rational design of 2D magnetic metal−organic coordination polymers assembled from oxalato and dipyridyl spacers. Cryst Growth Des. 2006;6:1839–47.
6. Netto AVG, Frem RCG, Mauro AE, Crespi MS, Zorel HE Jr. Synthesis, spectral and thermal studies on pyrazolate bridged palladium(II) coordination polymers. J Therm Anal Calorim. 2007;87:789–92.
7. Netto AVG, Santana AM, Mauro AE, Frem RCG, De Almeida ET, Crespi MS, et al. Thermal decomposition of palladium(II) pyrazolyl complexes. Part II. J Therm Anal Calorim. 2005;79:339–42.
8. Powder Diffraction File of the Joint Committee on Powder Diffraction Standards. Set 1-32. Swarthmore, PA 19081, USA: Published by the International Center of Diffraction Data; 1982.
9. Castillo O, Luque A, Julve M, Lloret F, Román P. One-dimensional oxalato-bridged copper(II) complexes with 3-hydroxypyridine and 2-amino-4-methylpyridine. Inorg Chim Acta. 2001;315:9–17.
10. Xia S-Q, Hu S-M, Dai J-C, Wu X-T, Fu Z-Y, Zhang J-J, et al. Syntheses and structures of 1D, 2D, 3D cadmium(II) coordination polymers with oxalate and aromatic co-ligands. Polyhedron. 2004;23:1003–9.
11. Tong M-L, Ye B-H, Cai J-H, Chen X-M, Ng SW. Clathration of two-dimensional coordination polymers: synthesis and structures of $[M(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ and $[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2Bpy)$ (M = CdII, ZnII and bpy = bipyridine). Inorg Chem. 1998;37:2645–50.
12. Huang SD, Xiong R-G. Molecular recognition of organic chromophores by coordination polymers: design and construction of nonlinear optical supramolecular assemblies. Polyhedron. 1997;16:3929–39.
13. Loiseau T, Ferey G, Haouas M, Taulelle F. Structural analysis of F/OH distribution in a hybrid open-framework fluorinated gallium oxalate−phosphate templated by 1,3-diaminopropane (MIL-90). Chem Mater. 2004;16:5318–26.
14. Mathers NJ, Xu Z. Solid-state ^{13}C NMR spectroscopy: characterization of soil organic matter under two contrasting residue management regimes in a 2-year-old pine plantation of subtropical Australia. Geoderma. 2003;114:19–31.