

SYNTHESIS, SPECTRAL AND THERMAL STUDIES ON PYRAZOLATE-BRIDGED PALLADIUM(II) COORDINATION POLYMERS

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Synthesis, spectroscopic characterization and thermal behavior of pyrazolate-bridged palladium complexes $[\text{Pd}(\mu\text{-Pz})_2]_n$ (**1**), $[\text{Pd}(\mu\text{-mPz})_2]_n$ (**2**), $[\text{Pd}(\mu\text{-dmPz})_2]_n$ (**3**), $[\text{Pd}(\mu\text{-IPz})_2]_n$ (**4**) {pyrazolate (Pz⁻), 4-methylpyrazolate (mPz⁻), 3,5-dimethylpyrazolate (dmPz⁻), 4-iodopyrazolate (IPz⁻)} have been described in this work. The exobidentate coordination mode of pyrazolate ligands in **1–4** was inferred on basis of IR spectroscopic evidences. TG investigations indicated that the introduction of substituents at the 4 position in the pyrazolyl moiety into coordination polymers do not affect significantly their thermal stability, whereas at the 3 and 5 position reduced the stability of the main chain. Metal palladium was the final product of the thermal decompositions, which was identified by X-ray powder diffraction.

Keywords: coordination polymers, DTA, palladium(II), pyrazolates, TG

Introduction

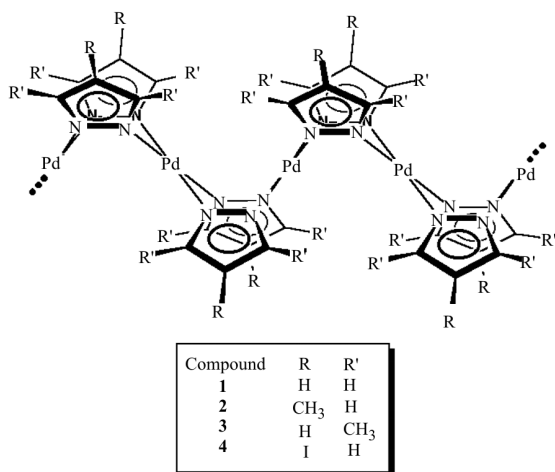
A large area of coordination and supramolecular chemistry has been develop around with pyrazolate anions. In particular, homoleptic pyrazolate complexes are attracting interest in the recent years since they exhibit a rich structural diversity (trimers, tetramers, hexamers or coordination polymers may result depending on the reaction conditions, the side chains at the pyrazolate ligand and the geometry at the metal centres) [1–3], their potential use as liquid crystals [4], antimicrobial drugs [5], olefin cyclopropanation catalysts [6], phosphorescent materials [7, 8] and CVD source reagents [9].

Following up our interest in mono and polynuclear systems involving transition metals and pyrazolyl-type ligands [10–13] as well in their thermal behavior [14–16], we describe in the present study the synthesis, spectroscopic characterization and thermal studies by TG and DTA on a series of palladium(II) pyrazolate compounds $[\text{Pd}(\mu\text{-Pz})_2]_n$ (**1**), $[\text{Pd}(\mu\text{-mPz})_2]_n$ (**2**), $[\text{Pd}(\mu\text{-dmPz})_2]_n$ (**3**), $[\text{Pd}(\mu\text{-IPz})_2]_n$ (**4**) {pyrazolate (Pz⁻), 4-methylpyrazolate (mPz⁻), 3,5-dimethylpyrazolate (dmPz⁻), 4-iodopyrazolate (IPz⁻)} (Scheme 1).

Experimental

Preparation of the complexes

Compounds **1–4** were synthesized as follows: 2 mL of a methanolic mixture containing the appropriate amounts of pyrazolyl ligand (0.61 mmols) and triethylamine (0.1 mL, 0.61 mmols) was added dropwise to a deep orange solution of $[\text{PdCl}_2(\text{meCN})_2]$ (75 mg, 0.29 mmols) in 10 mL of MeOH affording a clear suspension. The solids were separated by filtration, washed vigorously with MeOH and dried under vacuum. This procedure, which differs from that previously reported by Minghetti *et al.* [17] and Ardizzoia *et al.* [18], allowed the separation of the insoluble fine powders of the polymers. It is well known that soluble cyclic trinuclear species of general formulae $[\text{Pd}_3(\mu\text{-L})_6]_3$ (L=pyrazolate ligand) are also formed in the reaction media [19].



Scheme 1

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Instrumentation

Elemental analysis of 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. Thermal analyses (TG, DTA) were carried out using a TA SDT 2960 model, under dry synthetic air (flow rate: 100 mL min^{-1}) temperature up to 900°C and at heating rate of 10°C min^{-1} in α -alumina sample holders. The reference substance was pure α -alumina in the DTA measurements. X-ray powder diffraction patterns of the residues were obtained using Zeiss HGZ4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg–Bretano arrangement was adopted using $\text{CuK}\alpha$ radiation ($\lambda=1.541 \text{ \AA}$) and setting of 34 kV and 20 mA. The peaks were identified using ICDD bases [20].

Results and discussion

Reactions of the $[\text{PdCl}_2(\text{MeCN})_2]$ precursor with pyrazole-type ligands in the presence of the non-coordinating weak triethylamine base lead to the pyrazolate-bridged palladium coordination polymers **1–4**, as intractable and air stable solids. The elemental analyses and

thermogravimetric data together with the IR spectroscopy results confirmed the proposed formulas of the synthesized compounds. The polymeric nature of the obtained compounds was inferred by their intractability, high stability and amorphous nature. The analytical data are presented in Table 1.

Infrared spectra

The most significant band of the complexes with their tentative assignments are presented in Table 2. The exobidentate coordination mode of the pyrazolate ligands was clearly detected in the IR spectra of **1–4**. Firstly, the absence of the strong and broad ν_{NH} band at ca. 3400–3200 cm^{-1} is an indication of the deprotonation of the pyrazolyl ligands. Secondly, the shift of the absorption band attributed to the ring breathing mode to lower frequency (1491–1530 cm^{-1}) when compared with that one of the free ligand (1533–1596 cm^{-1}) is characteristic of exobidentate coordination mode [10]. Thirdly, the appearance of the expected two γ_{CH} bands at 868 and 744 cm^{-1} for **1** agrees well with the exobidentate character of pyrazole instead of three ones for monodentate pyrazole complexes [10]. Taking into account that two γ_{CH} bands are expected for monodentate 4-substituted-pyrazolyl derivatives [10], the presence of only one γ_{CH} absorption in the spectra of **2** (818 cm^{-1}) and **4** (825 cm^{-1}) also supports the exobidentate coordination.

Table 1 Results of chemical analyses of the compounds **1–4**

Compound	Color	Formula	Carbon/%		Nitrogen/%		Hydrogen/%	
			found	calc.	found	calc.	found	calc.
$[\text{Pd}(\mu\text{-Pz})_2]_n$ 1	white	$\text{C}_6\text{H}_6\text{N}_4\text{Pd}$	30.10	29.96	23.49	23.29	2.49	2.51
$[\text{Pd}(\mu\text{-mPz})_2]_n$ 2	white	$\text{C}_8\text{H}_{10}\text{N}_4\text{Pd}$	35.96	35.77	21.05	20.86	3.58	3.75
$[\text{Pd}(\mu\text{-dmPz})_2]_n$ 3	pale yellow	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{Pd}$	40.25	40.49	19.01	18.88	4.94	4.76
$[\text{Pd}(\mu\text{-IPz})_2]_n$ 4	white	$\text{C}_6\text{H}_4\text{N}_4\text{I}_2\text{Pd}$	14.56	14.64	11.42	11.38	0.88	0.82

Table 2 Selected vibrational data (cm^{-1}) of pyrazolate-bridged palladium(II) coordination polymers **1–4**

ν/cm^{-1}				Assignment
$[\text{Pd}(\mu\text{-Pz})_2]_n$ (1)	$[\text{Pd}(\mu\text{-mPz})_2]_n$ (2)	$[\text{Pd}(\mu\text{-dmPz})_2]_n$ (3)	$[\text{Pd}(\mu\text{-IPz})_2]_n$ (4)	
3130w	3128w	3128sh	3124mw	ν_{CH}
1491mw	–	1530m	1490w	ring breathing
–	1463mw	1443sh	–	$\delta_{\text{as}(\text{CH}_3)}$
1385m	1381s	1420s, 1379m	1378m	$\nu_{\text{ring}}+\beta_{\text{ring}}$
–	1323ms	1349ms	–	$\nu_{\text{anel}}+\beta_{\text{CH}}$
1288mw	–	–	1299m	$\beta_{\text{CH}}+\nu_{\text{ring}}$
1184m	1177m	1152mw	1165m	$\nu_{\text{ring}}+\beta_{\text{CH}}$
1062s	1084s	1053m	1066s	β_{CH}
–	1015mw	–	943m	β_{ring}
868w, 744s	818s	763ms	825s	γ_{CH}
624mw	626m	651w	612m	γ_{ring}

Thermal analysis

TG and DTA curves obtained for compounds **1–4** are shown in Fig. 1 and the results of the thermal investigations are listed in Table 3.

The TG curves showed that the amorphous solids **1–4** decomposed without melting. Compound **1** is thermally stable up to 301°C, then undergoes a subsequent mass loss caused by the oxidative thermal break-

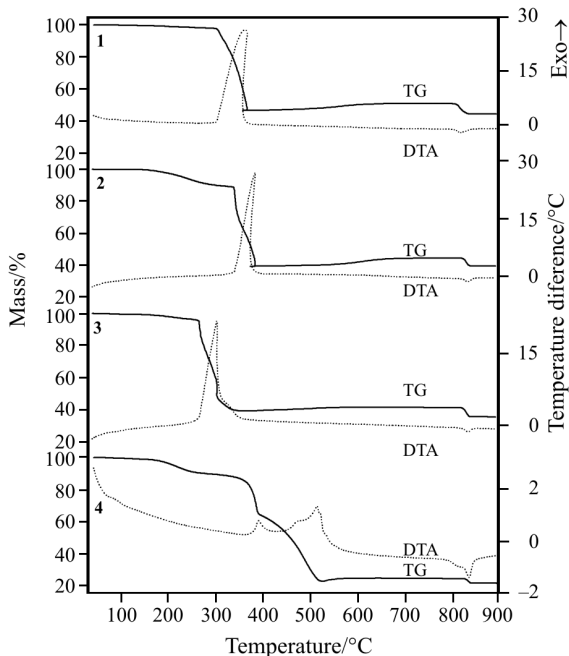


Fig. 1 — — TG and ... — DTA curves of the 1 — $[\text{Pd}(\mu\text{-Pz})_2]_n$, 2 — $[\text{Pd}(\mu\text{-mPz})_2]_n$, 3 — $[\text{Pd}(\mu\text{-dmPz})_2]_n$, 4 — $[\text{Pd}(\mu\text{-IPz})_2]_n$ complexes

down of the polymer backbone affording a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [20]. A slight mass increase of 4.03% between 371–799°C is ascribed to the formation of additional PdO which further degrades to Pd (ASTM 05-0681) in the last mass loss (6.33%) at 799–847°C. The final residue of 44.60% agrees well with the calculated amount of Pd (44.23%).

The TG-DTA curves for compound **2** indicated that the first step (125–336°C) is accompanied by 11.15% mass loss assigned to the decomposition of the methyl side chains (calcd. 11.20%). Such elimination of methyl substituents does not affect the stability of the main chain until 336°C, because the mass loss is only ca. 11% at this temperature, indicating that the polymer backbone of **2** is very stable below 336°C. A further heating to 406°C resulted in an abrupt mass loss of 49.22% associated to the degradation of the main polymeric chain, yielding Pd as a residue (calcd. 39.61%, found 39.70%).

Compound **3** started to degrade at lower temperature (256°C) than **1**. Afterwards, a mass loss of 60.84% is caused by the thermal breakdown of the main chain, leading to a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [20]. A progressive mass gain of 2.15% up to 813°C is ascribed to the formation of additional PdO which further decomposed to Pd (calcd. 35.87%, found 35.52%) at 813–859°C.

Compound **4** decomposed more slowly than the other coordination polymers. A small mass loss of 10.37% upon heating of the sample in the range of 114–298°C is attributed to the partial release of iodine at the 4 position on the pyrazolyl ring. Similarly to the thermal behavior of **2**, the main chain of **4** remains stable until 298°C. A further increase in the temperature

Table 3 Representative thermoanalytical data of compounds **1–4**

Complex	Step	$\Delta T/^\circ\text{C}$	$\Delta m/\%$		DTA peaks/ $^\circ\text{C}$		Assignment
			obt.	calc.	endo	exo	
1	1	301–371	–53.10	–53.11	–	362	–2Pz, +0.2O ₂
	2	371–799	+4.03	+3.99	–	–	+0.3O ₂
	3	799–847	–6.33	–6.65	817	–	–0.5O ₂
	residue		44.60	44.23			
2	1	125–336	–11.15	–11.20	–	–	–2CH ₃
	2	336–406	–49.22	–49.19	–	383	–2Pz
	3	406–817	+5.92	+5.96	–	–	+0.5O ₂
	4	817–854	–5.85	–5.96	832	–	–0.5O ₂
	residue		39.70	39.61			
3	1	256–364	–60.84	–60.90	–	302	–2dmPz, +0.3O ₂
	2	364–813	+2.15	+2.16	–	–	+0.2O ₂
	3	813–859	–5.79	–5.39	832	–	–0.5O ₂
	residue		35.52	35.87			
4	1	114–298	–10.37	–10.36	–	–	–0.2I ₂
	2	298–525	–66.77	–66.73	–	390, 513	–2Pz [–] , –0.8I ₂ , +0.2O ₂
	3	525–822	+1.67	+1.61	–	–	+0.25O ₂
	4	822–852	–2.79	–2.93	834	–	–0.45O ₂
	residue		21.74	21.61			

to 525°C resulted in the breakdown of the polymer backbone caused by a considerable mass loss of 66.77%, affording a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [20]. The partial oxidation of the Pd content in the mixture is related to the slight mass gain of 1.67% between 525–822°C. The decomposition of PdO to Pd (calcd. 21.61%, found 21.74%) occurred at 822–852°C.

Conclusions

Synthesis, characterization and thermal behavior of [Pd(μ -Pz)₂]_n (**1**), [Pd(μ -mPz)₂]_n (**2**), [Pd(μ -dmPz)₂]_n (**3**), [Pd(μ -IPz)₂]_n (**4**) have been described in this work. TG studies showed that the introduction of substituents at the 4 position on the pyrazolyl moiety into coordination polymers does not affect significantly their thermal stability. While the unsubstituted polymer **1** is stable up to 301°C the decomposition of the main polymeric chain started at about 336°C (**2**) and 298°C (**4**) when methyl groups and iodine, respectively, are attached to these polymers. On the other hand, the coordination polymer **3** started to degrade at a temperature lower than the other species, probably due to the steric hindrance introduced by methyl groups at 3 and 5 position, adjacent to the coordination sites of the pyrazolyl ring.

Acknowledgements

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