STUDIES ON THE THERMAL BEHAVIOR OF POLYNUCLEAR PALLADIUM(II) COMPOUNDS CONTAINING PYRAZOLATO LIGANDS

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ABSTRACT

The synthesis, spectroscopic characterization and thermal behavior of the pyrazolate-bridged palladium complexes $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-Pz})_5]_n$ (1), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-mPz})_5]_n$ (2), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-IPz})_5]_n$ (3), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-mPz})_5]_n$ (4), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-dmPz})_5]_n$ (5) and $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-IPz})_5]_n$ (6) {pyrazolate (Pz⁻), 4-methylpyrazolate (mPz⁻), 3,5-dimethylpyrazolate (dmPz⁻), 4-iodopyrazolate (IPz⁻)} have been described in this work. The thermal decomposition of the compounds occurs in four or five stages and the final decomposition residues were identified as metallic palladium using X-ray powder diffraction method. TG studies showed that the introduction of substituted pyrazolato groups in the composition of the polynuclear compounds affect significantly their thermal stability. It can be concluded that the presence of pyrazolato ligands containing methyl or iodine groups at the 4 position has a crucial effect on the thermal stability of the polynuclear compounds described in this work.

Introduction

The design of one-, two- or three-dimensional metallosupramolecular species with fascinating topologies and desired functions [1], such as optical [2], porous [3],

magnetic [4-5] and electrochemical [6] molecular materials, represents one of the most exciting and challenging research topics in current chemistry [7-8]. Among the *N*-donor bridging ligands employed in the self-assembly

reactions [9], pyrazolato groups have emerged as promising 60° angular building blocks [10]. Homoleptic pyrazolate metallocsupramolecules exhibit a rich structural diversity (e.g. triangles, tetramers, polynuclear compounds) which is dependent on the reaction conditions, the side chains at the pyrazolate ligand and the geometry at the metal centres [11-13]. Similarly to their binary counterparts, heteroleptic pyrazolate derivatives are well-known to possess also unusual structures and peculiar properties. For instance, the compound $[\text{Cu}(\mu\text{-dmPz})(\mu\text{-OH})]_8$ [14], a discrete octameric molecule with a cyclic planar system of copper(II) atoms bridged by OH and 3,5-dimethylpyrazolato (dmpz) ligands, acts as catalyst in the oxidation reactions of a variety of organic substrates. Raptiset *al.* have reported that metallacycles complexes of general formulae $[\{cis\text{-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_n]$ ($n = 6, 8, 9, 12$ and 14) are self-assembled with their lipophilic pyrazolates (Pz) oriented towards the outer surface and their hydrophilic OH groups towards an encapsulated anion at the inner cavity of the assembly [15]. These copper metallacrowns possess the ability to bind anions through the cooperative H bonding to all bridging OH groups due to their inward oriented oxygen electron lone pairs.

Some years ago, we have described the spontaneous formation of polynuclear compounds from the reaction among $[\text{PdCl}_2(\text{MeCN})_2]$, neutral pyrazoles (HPz) and

azide ions [16-17]. These amorphous compounds were characterized as $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-Pz})_5]_n$ (**1**), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-mPz})_5]_n$ (**2**), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-IPz})_5]_n$ (**3**), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-mPz})_5]_n$ (**4**), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-dmPz})_5]_n$ (**5**) and $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-IPz})_5]_n$ (**6**) {pyrazolate (Pz⁻), 4-methylpyrazolate (mPz⁻), 3,5-dimethylpyrazolate (dmPz⁻), 4-iodopyrazolate (IPz⁻)} according to the results obtained from elemental analysis, vapor phase osmometry, infrared (IR), ultraviolet-visible (UV-Vis) and nuclear magnetic resonance (NMR) spectroscopies. An interesting property of these polynuclear compounds is their good ability to form thin films by spin coating using chloroform solutions, which could be useful for new uses of such species. Particularly, metal azido complexes are of technological interest since they can be employed as forerunners for the photolithography of metallic films [18]. To achieve such goal, it is desirable that the photolysis of the azido compounds gives rise to thermally unstable intermediates which further decompose into the metallic form. In this sense, the thermal stability of azido complexes is an important parameter to be investigated. As a part of our ongoing studies on the structure and properties of palladium(II) compounds [19–28], we describe herein an investigation of the thermal behavior of the polynuclear complexes **1–6** by means of thermogravimetry (TG) and Differential Thermal Analysis (DTA), as depicted in Figure 1–2.

Figure 1. Proposed structure of the compounds of the type $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-L})_5]_n$ $\{\text{L} = \text{Pz}^- \text{ (1)}, \text{mPz}^- \text{ (2)}, \text{IPz}^- \text{ (3)}\}$

Figure 2. Proposed structure of the compounds of the type $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-L})_5]_n$ $\{\text{L} = \text{mPz}^- \text{ (4)}, \text{dmPz}^- \text{ (5)}, \text{IPz}^- \text{ (6)}\}$

Materials and methods

General comments

All the synthesis have been carried out at room temperature. All reagents were obtained from commercial suppliers. The starting complex $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ was prepared as previously described [29].

Synthesis

Synthesis of the complexes 1–3 [16–17]

Briefly, to a deep orange solution of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.39 mmol) in 10 mL of MeOH, the appropriate pyrazolyl ligand (0.81 mmol) dissolved in 2 mL of methanol was added dropwise. After stirring the resulting mixture for 5 min, NaN_3 (0.81 mmol) dissolved in 2 mL of water was added dropwise yielding a yellow suspension, which was filtered off and the obtained solid was washed with methanol and dried under vacuum. Yield 75 %. *Anal.* Calcd. For **1** ($\text{C}_{165}\text{H}_{167}\text{N}_{143}\text{Pd}_{32}$) %: C, 26.2; N 26.5; H, 2.2. Found: C, 25.9; N 26.2; H, 2.2, for **2** ($\text{C}_{220}\text{H}_{277}\text{N}_{143}\text{Pd}_{32}$) %: C, 31.7; N 23.4; H, 4.0. Found: C, 31.9; N 23.4; H, 4.1, and **3** ($\text{C}_{165}\text{H}_{112}\text{N}_{143}\text{I}_{55}\text{Pd}_{32}$) %: C, 13.7; N 13.6; H, 0.8. Found: C, 13.5; N 13.5; H, 0.9.

Synthesis of the complexes 4–6 [16]

Briefly, pyrazole (0.43 mmol) and corresponding substituted pyrazolyl ligand (0.43 mmol), dissolved in 2 mL of methanol, were added dropwise to a deep orange solution of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.39 mmol) in 10 mL of MeOH. After stirring the resulting mixture for 5 min, NaN_3 (0.81 mmol) dissolved in 2 mL of water was added affording a yellow suspension, which was filtered off and the obtained solid was washed with methanol and dried under vacuum. Yield 70 %. *Anal.* Calc. For **4** ($\text{C}_{367}\text{H}_{421}\text{N}_{273}\text{Pd}_{62}$) %: C, 28.9; N

25.1; H, 2.8. Found: C, 29.3; N 24.9; H, 3.0, for **5** ($C_{419}H_{525}N_{273}Pd_{62}$) %: C, 31.5; N 23.6; H, 3.6. Found: C, 31.6; N 23.9; H, 3.5, and **6** ($C_{315}H_{262}N_{273}I_{52}Pd_{62}$) %: C, 18.0; N 18.1; H, 1.3. Found: C, 17.9; N 17.8; H, 1.3.

Instrumentation

Elemental analysis of carbon, nitrogen and hydrogen were performed on a microanalyser elemental analyser CHN, model 1112 FLASH EA. Infrared spectra were recorded in KBr pellets on a Nicolet model SX-FT-Impact 400 spectrophotometer in the 4000–400 cm^{-1} spectral range. Melting points were determined on a MAPFQ apparatus. Thermal analyses (TG) and differential thermal analysis (DTA) were carried out using a TA Instruments model SDQ 600, under flow of dry synthetic air (50 mL min^{-1}), temperature up to 900 °C and at heating rate of 20 °C min^{-1} in α -alumina sample holders. The reference substance was pure α -alumina in DTA measurements. X-ray powder diffraction patterns were measured on a Siemens D-5000 X-ray diffractometer using CuK_{α} radiation ($\lambda = 1.541 \text{ \AA}$) and setting of 34 kV and 20 mA. The peaks were identified using ICDD bases [30–31].

Results and discussion

The results of the elemental analysis agree well with the formulation $[Pd_3(\mu-N_3)(\mu-Pz)_5]_n$ (**1**), $[Pd_3(\mu-N_3)(\mu-mPz)_5]_n$ (**2**), $[Pd_3(\mu-N_3)(\mu-IPz)_5]_n$ (**3**), $[Pd_6(\mu-N_3)_2(\mu-Pz)_5(\mu-mPz)_5]_n$ (**4**), $[Pd_6(\mu-N_3)_2(\mu-Pz)_5(\mu-dmPz)_5]_n$ (**5**) and $[Pd_6(\mu-N_3)_2(\mu-Pz)_5(\mu-IPz)_5]_n$ (**6**) [16]. IR evidences clearly evidenced the exobidentate nature of pyrazolate ligands by the absence of the ν_{NH} band at ca. 3400–3200 cm^{-1} as well as by the shift of the ν_{ring} absorption to lower frequency (1491–1530 cm^{-1}) when compared with that one of the free ligands (1533–1596 cm^{-1}). A strong ν_{sN_3} band appeared in the 2081–2087 cm^{-1} region in all IR spectra being therefore consistent of bridging azide [16].

Thermal behavior studies

The TG and DTA curves obtained for the compounds **1–6** are shown in Figure 3 and 4 and the results of the thermal investigations are listed in Table 1.

Figure 3. TG and DTA curves of the complexes $[Pd_3(\mu-N_3)(\mu-L)_5]_n$ {L = Pz (**1**), mPz (**2**), IPz (**3**)}.

Figure 4. TG and DTA curves of the complexes $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-L})_5]_n$ {L = mPz' (4), dmPz' (5), IPz (6)}

Table 1 Thermal analysis data for the compounds $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-Pz})_5]_n$ (1), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-mPz})_5]_n$ (2), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-IPz})_5]_n$ (3), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-mPz})_5]_n$ (4), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-dmPz})_5]_n$ (5) and $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-IPz})_5]_n$ (6)

Complex	Step	$\Delta T / ^\circ\text{C}$	$\Delta m / \%$	DTA peak/ $^\circ\text{C}$	
				endo	exo
1	1	70–248	– 5.15		161
	2	248–297	–44.68		293
	3	97–809	+ 2.52		
	4	809–854	– 6.49	824	
	residue		46.20		
2	1	143–276	– 5.95		173
	2	276–397	–49.72		295, 335
	3	397–800	+4.02		
	4	800–865	– 5.67	822	
	residue		42.69		
3	1	147–310	– 4.93		160
	2	310–395	–22.05		378
	3	395–566	–48.35		513
	4	566–808	+ 1.08		
	5	808–860	– 1.34	814	
4	1	148–245	– 4.29		174
	2	245–354	–49.02		331
	3	354–802	+3.42		
	4	802–866	– 6.02	831	
	residue		44.11		
5	1	105–216	– 7.71		181
	2	216–367	–48.18		315, 339
	3	367–805	+2.87		
	4	805–867	– 4.60	831	
	residue		42.38		
6	1	126–230	– 3.89		152
	2	230–384	–17.82		
	3	384–583	– 44.07		510
	4	583–805	+1.16		
	5	805–860	– 3.39	818	
	residue		31.99		

* m_{initial} : (1–6) $\cong$ 7.000 mg.

The thermal degradation pattern of **1** consists of a gradual mass loss of 5.15 % over the temperature range 70–248 $^\circ\text{C}$. This first decomposition stage is ascribed to the elimination of small molecules that are released from the decomposition of the chain termination, which is accompanied by an exothermic signal of low intensity at 161 $^\circ\text{C}$. Therefore, it seems reasonable to consider that the polynuclear backbone of **1** is thermally stable until 248 $^\circ\text{C}$. A further heating to 297 $^\circ\text{C}$ resulted in an abrupt weight loss of 44.68 % attributed to the oxidation of the main polynuclear chain, being accompanied by a very intense exothermic signal at 293 $^\circ\text{C}$. A progressive mass gain of 2.52 % up to 809 $^\circ\text{C}$ is ascribed to the formation of additional Pd which is further decomposed into Pd (Calcd. 45.83 %, Found 46.20 %) at 854 $^\circ\text{C}$. This event is associated with the endothermic peak at 824 $^\circ\text{C}$ which is characteristic of the decomposition of PdO to Pd [30–31].

A small mass loss of 5.95 % upon heating of the sample in the range of 143–276 $^\circ\text{C}$ is observed in the TG–DTA curves of compound **2**. Similarly to the thermal behavior of **1**, the main chain of **2** remains stable until 276 $^\circ\text{C}$. A further increase in the temperature to 397 $^\circ\text{C}$ resulted in two overlapped steps with a total mass loss of 49.72 % which are related to two intense exothermic events at 295 and 335 $^\circ\text{C}$.

Compound **3** decomposed more slowly than **1** and **2**. The first step (147–310 °C) is characterized by a mass loss of 4.93 % accompanied by an exothermic signal at 160 °C, probably associated with the partial release of iodine at the 4 position on the pyrazolyl ring [10]. Afterwards, two consecutive mass losses of 22.05 % and 48.35 % are related to the thermal breakdown of the main chain, leading to a mixture of Pd and PdO. Two exothermic signals at 378 °C and 513 °C are involved in this oxidation process.

The thermal decomposition pattern of compound **4** is similar to that observed for **1**. The first stage (148–245 °C) is characterized by a progressive and slow mass loss of 4.29 % associated with an exothermic event at 174 °C. The breakdown of the polynuclear backbone of **4** is detected with a further increase of temperature to 354 °C, resulting in a considerable mass loss of 49.02 % accompanied by a broad exothermic event centered at 331 °C, affording a mixture of Pd and PdO.

Compound **5** started to degrade at 105 °C, from which is noticed a mass loss of 7.71 % accompanied by a weak exothermic signal at 181 °C. A mass loss of 48.18 % is observed in the range of 216–367 °C step related to the breakdown of the main chain. This abrupt mass loss is accompanied by two exothermic signals at 315 °C and 339 °C, leading to a mixture of

PdO and Pd⁰. A slight and progressive mass gain of 2.87 % occurred up to 805 °C which is ascribed to the oxidation of Pd⁰ to PdO. The decomposition of PdO to Pd⁰ is observed in the last mass loss (4.60 %) between 805 and 867 °C, which is accompanied by endothermic peak at 831 °C.

The TG-DTA curves for compound **6** are similar to those obtained for **3**. The first step (126–230 °C) is characterized by a slow and progressive mass loss of 3.89 %, accompanied by an exothermic signal at 152 °C. A mass loss of 17.82 % is noticed as the temperature rises to 384 °C, followed by a substantial mass loss of 44.07 % at 583 °C attributed to the breakdown of the polynuclear structure, affording a mixture of Pd⁰ and PdO.

From the inspection of TG curves some interesting trends can be observed. The TG curves showed that the introduction of different ligands pyrazole in the backbone of the polynuclear compounds causes significant effects on their thermal stability. Compounds **1**, **2** and **4** gradually lose *ca.* 5 wt. % of their total mass as the temperature rises from 70, 143 and 148 °C to 248, 276 and 245 °C, respectively. It seems probable that this first decomposition step is attributed to the elimination of small molecules that are released from the degradation of the chain ends. The appearance of an exothermic event in the range of 161–174 °C in the DTA curves of **1**, **2** and **4** agrees well

with this proposition. A further increase of the above mentioned temperatures, the main chain of **1**, **2** and **4** decomposes quickly, losing about 45–49 wt. % at 297, 397 and 354 °C, respectively. Consequently, it can be concluded that the number of pyrazolato ligands containing methyl groups at the 4 position has a crucial effect on its thermal stability. Taking into account the initial temperature of decomposition, as the number of 4-methylpyrazolato groups increases in the polynuclear backbone, the thermal stability increases according to the sequence: $2 \approx 4 > 1$. The presence of 4-iodopyrazolate in the polynuclear chain (ex. **3** and **6**) also increases the thermal stability when compared to **1**, following the trend: $3 > 6 > 1$. Compound **5**, which contains pyrazolate and 3,5-dimethylpyrazolate groups in its composition, loses ~ 8 wt. % of their total mass as the temperature rises from 105 to 216 °C. From these results it is noticed that **5** presents higher thermal stability than the compound **1**, but is less thermally stable than the 4-methyl and 4-iodopyrazolate-based derivatives **2**, **3**, **4**, and **6**.

Conclusions

The synthesis and thermal behavior studies on the polynuclear compounds $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-Pz})_5]_n$ (**1**), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-mPz})_5]_n$ (**2**), $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-IPz})_5]_n$ (**3**), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-mPz})_5]_n$ (**4**), $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-dmPz})_5]_n$ (**5**) and $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-IPz})_5]_n$ (**6**)

{pyrazolate (Pz), 4-methylpyrazolate (mPz), 3,5-dimethylpyrazolate (dmPz), 4-iodopyrazolate (IPz)} have been described in this work. The results showed that all thermal decompositions initiate with the release of organic and inorganic ligands, together with uptake of O_2 , leading to the formation of a mixture of Pd^0 and PdO . TG studies showed that the introduction of substituted pyrazolato groups in the composition of the coordination polymers affect significantly their thermal stability. Taking into account the initial decomposition temperatures, the following thermal stability sequence could be established:

- i) Compounds $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-L})_5]_n$: $\text{L} = \text{IPz} \approx \text{mPz} > \text{Pz}$
- ii) Compounds $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-L})_5]_n$: $\text{L} = \text{mPz} > \text{IPz} > \text{dmPz}$

These finding may indicate that coordination of presence of substituents at the 4 position exerts an extra effect on the thermal stability of compounds **1–6** probably due to packing effects. The introduction of an iodo or methyl group in position 4 of the ring pyrazolate increases the thermal stability of the polynuclear of formula $[\text{Pd}_3(\mu\text{-N}_3)(\mu\text{-L})_5]_n$. In the case of mixed polynuclear complexes $[\text{Pd}_6(\mu\text{-N}_3)_2(\mu\text{-Pz})_5(\mu\text{-L})_5]_n$ is evident that the presence of pyrazolate substituted at the 3 and 5 (L= dmPz) positions significantly increases

the repulsive interactions along the polymer chain, resulting in a decrease in thermal stability. In this sense, compound **5** represents a good candidate to be further investigated as a precursor for the photolithography of Pd films due to its low thermal stability and good solubility in chloroform.

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