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# Thermal and spectroscopic investigation on *N*,*N*-dimethylbenzylamine based cyclopalladated compounds containing isonicotinamide

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**Abstract** Synthesis, spectroscopic characterization and thermal analysis of the [Pd(dmba)(Cl)(iso)] (**1**), [Pd(dmba)(NCO)(iso)] (**2**), [Pd(dmba)($N_3$)(iso)] (**3**) and [Pd(dmba)(Br)(iso)] (**4**) (dmba = *N*,*N*′-dimethylbenzylamine; iso = isonicotinamide) compounds are described in this work. The complexes were investigated by infrared spectroscopy (IR), differential thermal analysis (DTA) and thermogravimetry (TG) and the residues of the thermal decomposition were identified as $Pd^o$ by X-ray powder diffraction. The thermal stability order of the complexes varied as [Pd(dmba)(Cl)(iso)] (**1**) > [Pd(dmba)(Br)(iso)] (**4**) > [Pd(dmba)(NCO)(iso)] (**2**) > [Pd(dmba)($N_3$)(iso)] (**3**).

**Keywords** Palladium(II) · Isonicotinamide · Spectroscopy · Thermal behavior

## Introduction

Vigorous research efforts have been devoted to synthesize new cyclopalladated compounds mainly due to their potential uses as technologically relevant materials (e.g. liquid crystals) [1], catalysts [2], and antitumor drugs [3]. Despite the increased attention on the field of Pd(II) cyclometallated species less attention have been paid to their derivatives containing isonicotinamide, a pyridine derivative with an amide group (–$CONH_2$) in $\gamma$-position, which possesses strong anti-tubercular, anti-pyretic, fibrinolytic and anti-bacterial properties [4]. It was assumed that new interesting biologically active compounds could be obtained by the cleavage of orthopalladated dimers of general formulae [Pd(dmba)($\mu$-X)]$_2$ (X = bridging anionic group; dmba = *N*,*N*-dimethylbenzylamine) by isonicotinamide. Following up our interest on the thermal behavior of palladium(II) compounds [5–8] herein the synthesis, spectroscopic characterization and thermal investigation of the [Pd(dmba)(Cl)(iso)] (**1**), [Pd(dmba)(NCO)(iso)] (**2**), [Pd(dmba)($N_3$)(iso)] (**3**) and [Pd(dmba)(Br)(iso)] (**4**) compounds using TG and DTA techniques is reported.

## Experimental

### General comments

All the synthesis have been carried out at room temperature. All reagents were obtained from commercial suppliers. The starting complexes [Pd(dmba)($\mu$-X)]$_2$ (X = Cl, NCO, $N_3$, Br) were prepared as described in [9].

### Preparation of the complexes [Pd(dmba)X(iso)]; X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**)

Isonicotinamide (40 mg; 0.327 mmol) was dissolved in 5 mL of methanol and then was added to a solution containing 0.27 mmol of the appropriate [Pd(dmba)($\mu$-X)]$_2$ (X = Cl, NCO, $N_3$, Br) precursor dissolved in 15 mL of methanol/acetone (2:1 vol:vol). The mixtures were stirred magnetically for 1 h. The obtained white suspensions were filtered off and the solids were washed thoroughly with methanol. The synthesized compounds with general formulae [Pd(dmba)(X)(iso)] (X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**)) were recrystallized from dichloromethane/pentane (1:1) and then dried in vacuo. The yields varied from 80% to 90%.

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## Instrumentation

Melting points were determined using a Mettler model MQAPF-302 microscope. Elemental analyses of carbon, nitrogen and hydrogen were performed on a microanalyser elemental analyser CHN, model 2400 PerkinElmer. Infrared spectra were recorded in KBr pellets on a Nicolet model SX-FT-Impact 400 spectrophotometer in the 4000–400 $cm^{-1}$ spectral range. Thermal analyses (TG) and differential thermal analyses (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 $CuK_\alpha$ radiation ($\lambda = 1.541$ Å) and setting of 34 kV and 20 mA. The peaks were identified using ICDD bases [10].

## Results and discussion

The results of the elemental analyses and the thermogravimetric data together with IR spectroscopy data, confirmed the proposed formulae for the compounds **1–4**. The results of the analyses and melting points are shown in Table 1.

## Infrared spectra

The maintenance of the structural integrity of the orthometallatted ring after the interaction with isonicotinamide was clearly evidenced by comparison of the IR spectra of **1–4** with those ones of the precursors $[Pd(dmba)(\mu\text{-}X)]_2$ (X = Cl, NCO, $N_3$, Br) [9]. The characteristic bands of the cyclometallated ring at 3049–3197 $cm^{-1}$ ($\nu CH_{ring}$), 2923–2979 $cm^{-1}$ ($\nu_{as}CH_3$), 2885–2896 $cm^{-1}$ ($\nu_s CH_3$) in IR spectra of **1–4** were found unchanged when compared to those observed for the precursors. The coordination of isonicotinamide through pyridinic-type nitrogen atom was inferred by the shift of the absorption band attributed to the ring breathing vibrational mode to higher frequency (ca. 1053 $cm^{-1}$) in the IR spectra of **1–4** when compared to that one of the free ligand (993 $cm^{-1}$) [11]. It is worth mentioning that characteristic bands of amide group at 3417–3332 $cm^{-1}$ ($\nu$N–H) and 1666–1681 $cm^{-1}$ ($\nu$C=O) in the IR spectra of **1–4** did not essentially alter when compared to those observed for the free ligand, suggesting that the amide group does not take part in coordination [12]. Concerning to the pseudohalide ligands, the presence of terminal *N*-cyanate group in (**2**) was evidenced by the $\nu_{as}$NCO band at 2212 $cm^{-1}$ whereas the terminal azide ligand in (**3**) was inferred on basis of the $\nu_{as}$NNN absorption at 2036 $cm^{-1}$ [13]. The proposed molecular structures for cyclopalladated complexes **1–4** are shown in Fig. 1.

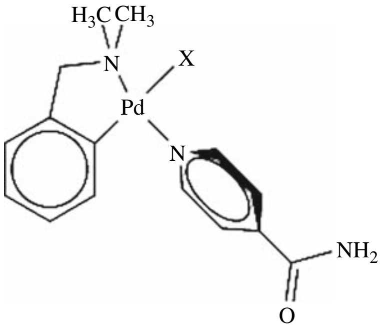
**Table 1** Elemental analyses and melting points for compounds **1–4**

| Complex | M.P. (°C) | Carbon (%) | | Nitrogen (%) | | Hydrogen (%) | |
|---|---|---|---|---|---|---|---|
| | | Calc. | Found | Calc. | Found | Calc. | Found |
| **1** | 208–209 | 49.52 | 49.24 | 10.27 | 10.55 | 4.28 | 4.56 |
| **2** | 190–191 | 46.77 | 47.48 | 12.01 | 13.84 | 4.30 | 4.48 |
| **3** | 183–185 | 45.02 | 44.51 | 20.49 | 20.76 | 4.65 | 4.48 |
| **4** | 213 *dec.* | 40.70 | 42.64 | 9.49 | 9.70 | 4.10 | 4.34 |

## Thermogravimetric analysis

The TG and DTA curves for the compounds [Pd(dmba)(Cl)(iso)] (**1**), [Pd(dmba)(NCO)(iso)] (**2**), [Pd(dmba)($N_3$)(iso)] (**3**) and [Pd(dmba)(Br)(iso)] (**4**) are shown in Fig. 2. Table 2 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.

Comparison of X-ray powder diffractograms of the final products obtained after the pyrolysis of the ligands in the thermal decomposition of **1** and **4** with ICDD data bases, showed the characteristic peaks of a mixture of Pd (card 05-0681) and PdO (card 06-0515) [10]. After this stage, the TG curves of **1** and **4** exhibited a slight mass increase up to ca. 800 °C due to the oxidation of the remaining $Pd^0$ to PdO, which was also identified by X-ray powder diffraction. Finally, the decomposition of PdO to $Pd^0$ is completed at ca. 860 °C. Complexes **2** and **3** degrade into PdO (card 06-0515) [10] which further decomposes into $Pd^0$ at ca. 860 °C. The TG-DTA curves of the compounds [Pd(dmba)(X)(iso)] showed that the anionic X group has a significant influence on thermal decomposition. Taking into account



X = Cl (1), NCO (2), $N_3$ (3), Br (4)

**Fig. 1** Proposed structure of the compounds [Pd(dmba)X(iso)]; X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**)

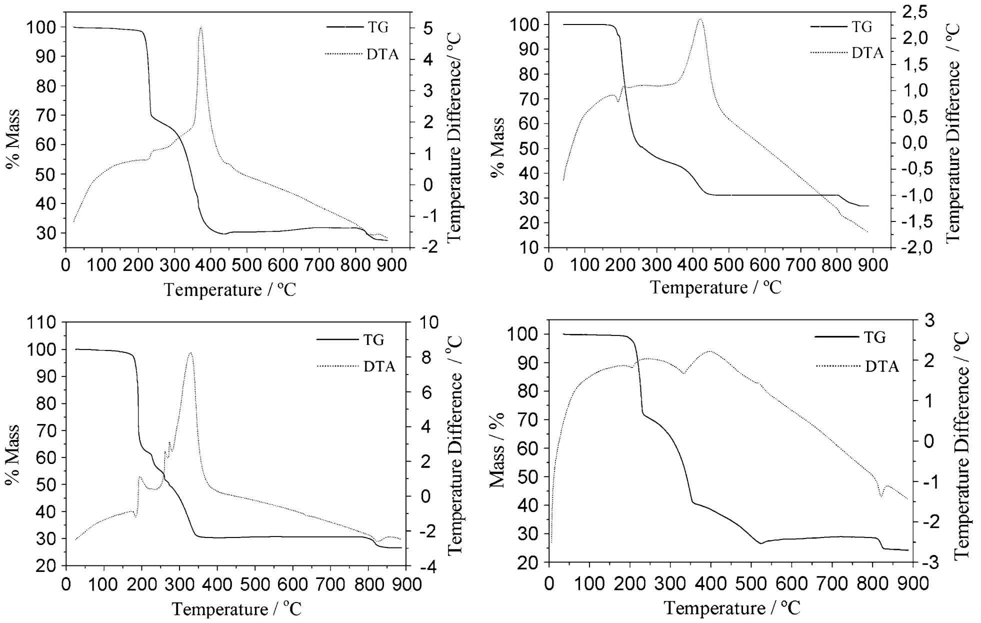


**Fig. 2** TG and DTA curves of the complexes [Pd(dmba)(X)(iso)] (X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**))

**Table 2** Thermal analysis data for compounds [Pd(dmba)(X)(iso)] (X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**))

| Complex | Step | ΔT (°C) | Δm (%) | | DTA Peaks (°C) | | Assignment |
|---|---|---|---|---|---|---|---|
| | | | Found | Calc. | Endo | Exo | |
| **1** | *1* | 224–240 | −30.63 | −30.84 | 224 | 240 | –iso |
| | *2* | 240–441 | −39.69 | −40.50 | – | 372 | –dmba, –Cl, +0.25 $O_2$ |
| | *3* | 441–798 | +2.05 | +2.01 | – | – | + 0.25 $O_2$ |
| | *4* | 798–864 | −4.02 | −4.01 | 834 | – | –0.5 $O_2$ |
| | *Residue* | – | 27.71 | 26.66 | | | $Pd^{o}$ |
| **2** | *1* | 194–329 | −55.35 | −57.23 | 192 | 207 | –0.5 dmba, –NCO, –iso |
| | *2* | 329–463 | −13.46 | −12.60 | – | 419 | –0.5 dmba, +0.5 $O_2$ |
| | *3* | 801–867 | −4.36 | −3.94 | 811 | – | –0.5 $O_2$ |
| | *Residue* | – | 26.83 | 26.23 | | | $Pd^{o}$ |
| **3** | *1* | 190–379 | −69.34 | −69.76 | 184 | 195, 262–329 | –dmba, –$N_3$, –iso, +0.5 $O_2$ |
| | *2* | 780–856 | −3.95 | −4.01 | 824 | – | –0.5 $O_2$ |
| | *Residue* | – | 26.71 | 26.23 | | | $Pd^{o}$ |
| **4** | *1* | 216–233 | −27.94 | −27.75 | 227 | – | –iso |
| | *2* | 233–357 | −31.15 | −33.14 | 351 | – | –0.5 dmba, –Br |
| | *3* | 357–525 | −14.29 | −13.32 | – | 529 | –0.5 dmba, +0.25 $O_2$ |
| | *4* | 525–805 | +1.93 | +1.80 | – | – | +0.25 $O_2$ |
| | *5* | 805–863 | −3.87 | −3.60 | 823 | – | –0.5 $O_2$ |
| | *Residue* | – | 24.68 | 23.99 | | | $Pd^{\circ}$ |

the initial temperature of the decomposition process, the thermal stability of the complexes [Pd(dmba)(X)(iso)] (X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**)) varies in the sequence of Cl > Br > NCO ≈ $N_3$. The lower thermal stability of **3** and **4** could be probably associated to the higher reactivity of the polyatomic and unsaturated pseudohalide groups than the monoatomic halide ions [13]. Such behaviour was similar to those observed in our previous studies on the thermal behaviour of other Pd(II) complexes containing halides and pseudohalides as ligands [5, 6].

The first decomposition step observed in TG curve of **1** is attributed, by mass calculation, to the pyrolysis of isonicotinamide, followed by the elimination of dmba and Cl ligands together with uptake of $O_2$. TG curves of the pseudohalide-based compounds **2** and **3** exhibit a different pattern of decomposition. The cyanato-compound **2** degrades in two steps whereas two consecutive and overlapped mass losses characterize a single stage of decomposition of the azido-derivative **3**. Complex **4** started to degrade at slightly lower temperature (216 °C) than **1**. The first stage is assigned, by mass calculation, to the pyrolysis of isonicotinamide whereas the elimination of Br group together with the partial degradation of dmba ligand are probably suggested to take place during the second decomposition stage. The last step of the degradation is attributed, by mass calculation, to the gradual elimination of the remaining dmba fragment as a carbonaceous residue of varied composition.

DTA curves of the synthesized compounds exhibited a weak endothermic signal over the range 184–227 °C which is in agreement with the melting temperature found for cyclometallated complexes **1–3**. Except for compound **4**, an intense exothermic peak in the temperature range 330–420 °C is probably attributed to the pyrolysis of the ligands. In addition, the DTA curves show an endothermic peak corresponding to thermal decomposition of PdO to Pd° in the range of 811–834 °C.

## Conclusions

The synthesis, IR spectroscopic characterization and investigation on the thermal behavior of the compounds of general formulae [Pd(dmba)(X)(iso)] {X = Cl (**1**), NCO (**2**), $N_3$ (**3**), Br (**4**)} have been described in this work. Taking into account the initial temperature of the decomposition process, it was possible to establish the following thermal stability trend: [Pd(dmba)(Cl)(iso)] (**1**) > [Pd(dmba)(Br)(iso)] (**4**) > [Pd(dmba)(NCO)(iso)] (**2**) > [Pd(dmba)($N_3$)(iso)] (**3**). Such order agrees well with those detected in our previous studies on the thermal stability of other Pd(II) complexes [5, 6] which also showed that the low thermal stability of the azido-complex is probably ascribed to the known explosive nature of inorganic azides.

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