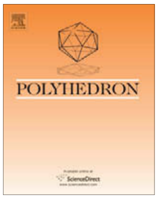
Polyhedron 28 (2009) 286–290

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis and characterization of mono and polymeric cyclopalladated compounds: Crystal and molecular structure of $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)] \cdot H_2O$ (pz = pyrazine)

Sandra R. Ananias [a,b,c], Janaina G. Ferreira [b,c], Antonio E. Mauro [c], Adelino V.G. Netto [c], Stanlei I. Klein [c], Regina H.A. Santos [b,*]

[a] Departamento de Química, Faculdade de Ciências – UNESP, C.P. 1.401, CEP 17033-360, Bauru, SP, Brazil
[b] Departamento de Química e Física Molecular, Instituto de Química de São Carlos – USP, C.P. 780, CEP 13560-970, SP, Brazil
[c] Departamento de Química Geral e Inorgânca, Instituto de Química – UNESP, C.P. 355, CEP 14801-970, Araraquara, SP, Brazil

ARTICLE INFO

Article history:
Received 4 July 2008
Accepted 22 October 2008
Available online 16 December 2008

Keywords:
Cyclometallated
Palladium
Nitro compounds

ABSTRACT

In the treatment of cyclometallated dimer $[Pd(dmba)(\mu\text{-}Cl)]_2$ (dmba = N,N-dimethylbenzylamine) with $AgNO_3$ and acetonitrile the result was the monomeric cationic precursor $[Pd(dmba)(NCMe)_2](NO_3)$ (NCMe = acetonitrile) (**1**). Compound **1** reacted with *m*-nitroaniline (*m*-NAN) and pirazine (pz), originating $[Pd(dmba)(ONO_2)(m\text{-}NAN)]$ (**2**) and $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)] \cdot H_2O$ (**3**), respectively. These compounds were characterized by elemental analysis, IR and NMR spectroscopy. The IR spectra of (**2–3**) display typical bands of monodentade O-bonded nitrate groups, whereas the NMR data of **3** are consistent with the presence of bridging pyrazine ligands. The structure of compound **3** was determined by X-ray diffraction analysis. This packing consists of a supramolecular chain formed by hydrogen bonding between the water molecule and nitrato ligands of two consecutive $[Pd_2(dmba)_2(ONO_2)_2(\mu\text{-}pz)]$ units.

1. Introduction

Over the past years the chemistry of cyclopalladated compounds, mainly of those derived from N-donor ligands, has been investigated by numerous research groups [1], due to important applications of these compounds in various fields, such as organic and organometallic synthesis [2], new materials (e.g. metallomesogens) [3], catalysis [4] and medical science (e.g. antitumor drugs) [5].

The relatively low cost and ready availability [6] of $[Pd(dmba)(NCMe)_2](NO_3)$ (**1**), with two of its *cis* coordination sites occupied by quite easily removable ligands, prompted us to try this compound in reactions of the self-assembly type. The general idea had been set forth by Fujita by using traditional transition metal complexes and bidentated nitrogen ligands [7]; moreover, Huck already succeeded in producing dendrimers from cyclopalladated compounds [8], and Spek, van Koten and their group advanced the features of 90° square planar platinum and palladium (II) metallated complexes as corner acceptors units [9]. Therefore, compound **1** seemed suitable for the preparation of tetramers and higher nuclearity compounds, if one could bridge two distinct terminal diamines to the $[Pd(dmba)]^{2+}$ fragments. However, only one terminal amine was allowed to be coordinated to the metal atom in **1**, originating monomers from monoamines and dimer compounds from the addition of diamines to its solutions. The behavior of **1** toward the used nitrogen ligands is discussed below, and the solid state structure of the pyrazine dimer **3** is presented.

2. Experimental

2.1. General comments

The syntheses were performed at room temperature. Commercial reagents and solvents were employed without further purification. The precursor $[Pd(dmba)(NCMe)_2](NO_3)$ (**1**) was prepared according to procedures described in the literature [6].

2.2. Synthesis of $[Pd(dmba)(ONO_2)(m\text{-}NAN)]$ (**2**)

0.0720 g (0.0520 mmol) of *m*-nitroaniline (*m*-NAN), dissolved in 10 cm^3 of dichloromethane was added to 15 cm^3 of solution **1** (0.100 g, 0.260 mmol), in the same solvent. The mixture was stirred for 30 min, and the resulting yellow precipitate was isolated by filtration. The product was thoroughly washed with ether and pentane and dried *in vacuo*. The yield was about 90% after recrystallization from dichloromethane and pentane. $PdN_4O_5C_{15}H_{18}$ (**2**) requires: C, 40.87; H, 4.08; N, 12.71. Found: C, 40.3; H, 3,93; N, 12.4%.

2.3. Synthesis of $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)]$ (**3**)

A solution of 0.389 mmol (0.031 g) of pirazine (pz) in 5 cm^3 of dichloromethane was added to a solution of 0.15 g (0.389 mmol)

---

[*] Corresponding author. Tel./fax: +55 16 3373 9975.
E-mail address: reginas@iqsc.usp.br (R.H.A. Santos).

0277-5387/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2008.10.048

of [Pd(dmba)(MeCN)2](NO_3) (**1**) in 10 cm^3 of dichloromethane. The mixture was stirred for 1 h. The yellow solid which precipitated was filtered, washed with acetone and pentane and dried *in vacuo*, and re-crystallized. The yield was about 80%. Calc. for $Pd_2N_6O_6C_{22}H_{28}$: C, 38.5; H, 4.08; N, 12.26. Found: C, 39.0; H, 2.95; N, 13.5%.

2.4. Physical measurements

Infrared spectra were recorded as KBr pellets on a Nicolet Impact 400 spectrophotometer (range 4000–400 cm^{-1}). ^1H and ^{13}C NMR spectra were obtained as DMSO-d_6 solutions and referred to the high field $SiMe_4$ signal, on a Varian INOVA 500 spectrometer. Molar conductivities were measured in nitromethane solutions ($c \approx 1 \times 10^{-3}$ mol L^{-1}) with a Digimed-DM-31 conductimeter. Elemental analyses were performed by the Central Analítica at IQSC/University of São Paulo.

2.5. X-ray structure determination for compound 3

A single crystal of the compound [{Pd(dmba)(ONO_2)}$_2$(μ-pz)] (**3**) was mounted on a Enraf-Nonius CAD4 diffractometer at room temperature using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection was taken in the ω–2θ scan mode. The unit cell parameters were determined using 25 automatically centered reflections. Table 1 shows the data collection and refinement conditions. The intensity data were reduced to F_0 and corrected by absorption factors using the PSISCAN method [10]. The structures were solved by the WINGX system [11], using SIR92 [12] and SHELX97 [13]. The hydrogen atoms belonging to compound **3** were located in their ideal positions. The water H atoms were placed at calculated positions using the HYDROGEN [14]. All non-hydrogen atoms were refined anisotropically. The geometric analysis was performed by the PLATON system [15].

3. Results and discussion

3.1. Characteristics of [Pd(dmba)(NCMe)$_2$](NO_3) (1) and [Pd(dmba)(ONO_2)}(m-NAN)] (2)

[Pd(dmba)(NCMe)$_2$](NO_3), (**1**), can be easily prepared from dichloromethane solutions of [Pd(dmba)Cl_2] upon the addition of silver nitrate dissolved in a mixture of dichloromethane and acetonitrile [6]. This precursor is very interesting on its own, due to its exquisite physical properties, which seems to be somewhat dictated by the physical conditions to which it is submitted. For instance, the ionic formulation for **1** seems to be evident from its formulae, and from its solid state IR spectrum, which shows low intensity bands at 2308 and 2249 cm^{-1}, attributed mainly to A_{1g} CN stretches and CCN combination bands of coordinated nitriles [16,17], and quite intense bands for the presence of ionic nitrates [18,19] at 1387 (ν ONO, vs) and 852 cm^{-1} (δ ONO, s). Nevertheless, ready solubility of this compound in solvents such as chloroform is not characteristic of a purely ionic compound. Indeed, molar conductance measurements of **1** made in nitromethane indicated a value of 27.55 μS cm^{-1}, which collocates that species among those considered non-electrolytes [20].

In this context, it is also interesting to research the ^1H and ^{13}C NMR spectra of **1**. In spite of the ubiquitous square planar coordination geometry of the [Pd(dmba)(NCMe)$_2$] core, the 125 MHz ^{13}C NMR of **1** in $CDCl_3$ at room temperature seemed to be exceedingly simple, for it did not show the magnetic inequivalence of the ^{13}C nuclei of the acetonitriles. This magnetic inequivalence was expected on the grounds that the acetonitriles must be accommodated, one in the *trans* position to the dmba's nitrogen, and the other, *trans* to the metallated carbon anchor of that ligand. However, in the NMR spectrum there is only one singlet NMR resonance for the two nitriles' CH_3CN at ca. 119, and another singlet resonance CH_3CN carbon at 3 ppm. The other ^{13}C resonances of that spectrum are indicated in Fig. 1.

Table 1
Crystal data and details of the structure determination for [{Pd(dmba)(ONO_2)}$_2$(μ-pz)] · H_2O (**3**).

Empirical formula	$C_{22}H_{28}N_6O_6Pd_2 \cdot H_2O$
Formula weight	703.36
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	13.402(2)
b (Å)	12.933(2)
c (Å)	14.864(3)
β (°)	95.56(1)
V (Å^3)	2564.2(8)
Z [dimer/cell]	4
D_{calc} (Mg/m^3)	1.822
$F(000)$	1408
μ(Mo Kα) (mm^{-1})	1.456
Crystal size (mm)	0.25 × 0.25 × 0.40
Temperature (K)	243
Radiation Mo Kα (Å)	0.71073
$\theta_{min.-max.}$ (°)	2.5, 30.0
Dataset	$-18 \leq h \leq 18$, $0 \leq k \leq 18$, $-20 \leq l \leq 0$
Total unique data, R_{int}	3860, 3727, 0.023
Observed data ($I > 2.0(I)$)	3204
N_{ref}, N_{par}	3727, 170
R, wR, S	0.0470, 0.1440, 1.07
$w = 1/[s^2(F_o^2) + (0.0867P)^2 + 9.5183P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Maximum and average shift/error	0.00, 0.00
Minimum and maximum residual density (e/Å^3)	−1.46, 2.10

Upon N-coordination with the palladium metal in cyclopalladated complexes such as **1**, is formed a puckered five-membered ring with a low barrier of inversion. Therefore, fast exchanges from axial to equatorial position are possible, and the benzylic (–N–CH_2–) protons, as well the protons of the [–NMe_2] group of dmba usually appear as singlets in the proton NMR spectrum, and this analysis is valid for complex **1**, where those groups resonate at 3.91 and 2.78 ppm. However, this fast inversion on the NMR time scale does not explain the equivalence of the ^{13}C NMR signals of the coordinated acetonitriles. The 500 MHz ^1H spectrum of **1** showed two separated signals for the two distinct acetonitrile groups at 2.78 and 2.36 ppm. The downfield shifted signal at 2.78 ppm was assigned to the methyl group of the acetonitrile in cis position to the metallated aromatic ring since, it is located in the deshielding area generated by the metallated aromatic ring. This signal appeared in the spectrum overlapped by the six-proton singlet of the [–NMe_2] fragment of dmba. A closer examination on other acetonitrile substituted cyclopalladates point to a similar difficulty in a proper assignment of their NMR spectra [21].

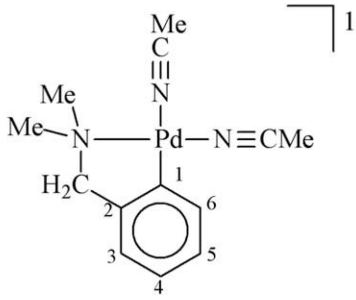


Fig. 1. Additional ^{13}C resonances for the metal containing core of **1**: Me_2N = 51; H_2C = 73; 1 = 147; 2 = 143; 3,6 = 123; 4 = 134; 5 = 123 ppm.

In the first attempt to test the capacity of the precursor compound **1** to react with heterocyclic nitrogen donors, it was chosen the *m*-nitroaniline ligand only as monosubstituted compound; despite the 1:2 stoichiometry of the addition. The IR spectrum of the product suggested the coordination of the *m*-nitroaniline ligand by the disappearance of the bands assigned to νCN of the precursor. However, new bands for a different type of nitrate ligand were also readily assigned in that spectrum, at 1417 and 1305 (νONO), and at 806 cm^{-1} (δNO), evidencing the presence of a monodentade O-bound nitrate group [18,19].

The ^1H NMR spectrum of **2** showed four multiplets, two at 7.37 and 7.23 ppm assigned to the *m*-nitroaniline, and two at 7.05 and 6.9 ppm, relative to the H-3 to H-5 dmba protons. The upfield shift of dmba's H-6 proton at 5.79 ppm should be the result of the shielding effect of the nearby aromatic ring of the *m*-NAM ligand, a conclusion which allows to allocate the nitrogen ends of *m*-NAM and dmba, *trans* to each other in the complex [22]. Thus, the nitrato ligand, which acts as pseudo-halogen in the structure of compound **2**, is in trans position to the metallated carbon, according to the antisymbiotic effect [x]. The ($-N-CH_2-$) protons of the dmba ligand resonate at 4.03 ppm, and the [$N-(CH_3)_2$] fragment was indicated by the proton resonance at 2.63 ppm. In the ^{13}C NMR spectrum of **2** there are three important signals: the metallated, the benzylic and the [$-NMe_2$] carbons, resonating at 148.7, 71.4 and 50.5 ppm, respectively, indicating the presence of dmba in the complex. These evidences and the microanalysis data pointed to the monomeric structure [Pd(dmba)(ONO_2)(*m*-NAN)] for compound **2**.

3.2. Characteristics of cyclopalladated complex [{Pd(dmba)(ONO_2)}$_2$(μ-pz)] (3)

The ability of precursor **1** to act as a corner acceptor unit for self-assembled species was tested with the potential bridging ligand pz.

The reactions of **1** with pyrazine were the simplest, in the way that only one type of compound could be detected by the occurrence of only one precipitate, after the mixture of reactants was stirred at room temperature. This compound was determined as μ-pz dinuclear, O-bound NO_3 palladium complex of the type [{Pd(dmba)(ONO_2)}$_2$(μ-pz)], (**3**). For instance, the IR spectrum showed the expected bands at 1621 and 1031 cm^{-1} attributed to the CN stretch and CH deformation of pz, respectively; and the characteristic trio of absorptions for the $-ONO_2$ coordinated nitrate at 1424, 1296 and 810 cm^{-1} [18,19]. The ^{13}C NMR spectrum of **3** showed the metallated carbon from dmba at 148.1 ppm. The proton NMR spectrum confirms the presence of the pyrazine by signals at 8.84 and 8.74 ppm. Although the signal for symmetrically coordinated pyrazine occurs above 8.6 ppm [23], the presence of two signals for **3** indicated some kind of molecular arrangement as they were the pz protons magnetically non-equivalent. The signals for the diastereotopic protons of the $-CH_2-$ and [$-NMe_2$] groups of metallated dmba appear in the ^1H NMR spectrum of **3** as slightly broadened resonances at the normal positions of 4.01 and 2.84 ppm, respectively.

3.3. X-ray structure of [{Pd(dmba)(ONO_2)}$_2$(μ-pz)] · H_2O (3)

Suitable crystals of [{Pd(dmba)(ONO_2)}$_2$(μ-pz)] · H_2O (**3**) were grown by slow evaporation of a water–acetone solution. The X-ray structure showed that the asymmetric unit consists of a Pd(dmba)(ONO_2) unit linked to half of the pyrazine ring, forming a dimer made by two fold crystallographic axis (Fig. 1). In the asymmetric unit it is also found half water molecule, with the oxygen atom lying in other twofold axis Fig. 2.

The X-ray diffraction study permitted the correct interpretation of the analytical and NMR data, by showing the molecule as a dinuclear compound, with one pz bridging the two metals. The square planar coordination of each palladium atom is composed by the metallated carbon and the nitrogen atom from the dmba, the nitrogen from pz, and the coordinated oxygen of the NO_3 group. This feature could be inferred, but it was not explicit from previous spectroscopic studies. This coordination may reflect the powerful trans-influence of the C–Pd bond, which would labilize a bond between the metal and any incoming σ-donor, neutral L ligand, inducing the coordination to conform to a C–Pd–L *cis* environment in the final compound. In the solid structure, the palladium atom occupies a position slightly below the mean squares plane defined by C_1, N_1, O_1 and N_2 (0.537(1) Å).

Selected interatomic bond lengths and angles are given in Tables 2 and 3. In molecule of **3**, the various bonds and angles involving the metals and directly coordinated atoms agree with previous reports found in the literature for this class of metallated compounds [24–29], but a few particular characteristics of **3** must be discussed. For instance, the short Pd–C_1 bond length of 1.971(4) Å is shorter than a Pd(II)–C sp^3 bond of 2.14 Å [21]. This value may reflect a typical Pd(II)–C sp^2 bond, but there seem to be a consensus that the Pd–C bonds in metallated benzenoid rings must involve some multiple bond character, which would cause a further shortening of this peculiar Pd–C bond [30a]. Also, the trans Pd–O bond

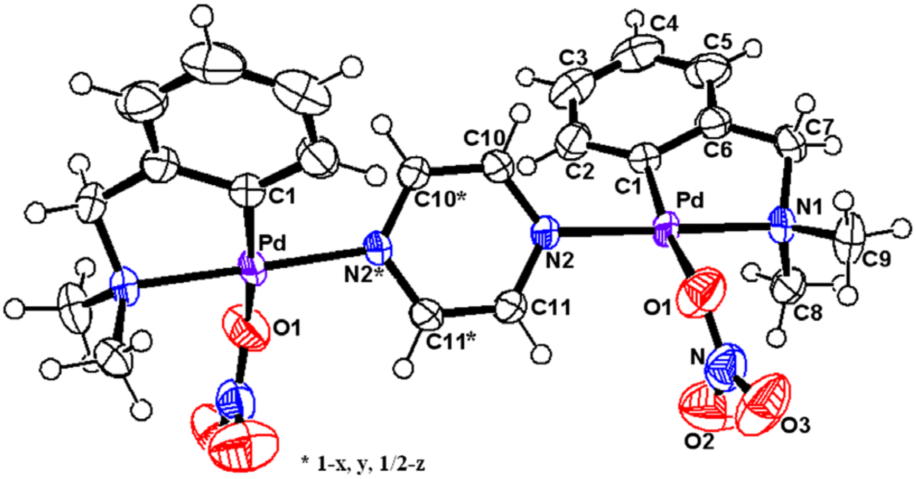


Fig. 2. ORTEP drawing with labeling scheme for [$Pd_2(dmba)_2$(μ-pz)$(NO_3)_2$]. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Bond distances (Å) for $[\{Pd(dmba)(ONO_2)\}_2((-pz)] \cdot H_2O$ (**3**).

Pd	O1	2.208(4)	Pd	C1	1.971(4)
Pd	N1	2.063(3)	Pd	N2	2.049(3)
O1	N	1.237(5)	O2	N	1.249(7)
O3	N	1.211(6)			
N1	C7	1.497(5)	N1	C8	1.494(5)
N1	C9	1.478(6)	C6	C7	1.493(6)
C1	C2	1.395(6)	C3	C4	1.381(9)
C1	C6	1.417(5)	C4	C5	1.385(8)
C2	C3	1.392(7)	C5	C6	1.380(6)
N2	C10	1.342(5)	C10	C10*	1.383(7)
N2	C11	1.334(5)	C11	C11*	1.383(8)
O1W	H1W	0.930			

* Symmetry code: 1 − *x*, *y*, 1/2 − z.

Table 3
Selected angles (°) for $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)] \cdot H_2O$ (**3**).

O1	Pd	N1	95.8(1)	O1	N	O3	122.3(5)
O1	Pd	N2	87.6(1)	O2	N	O3	119.3(5)
O1	Pd	C1	169.1(2)	O1	N	O2	118.4(5)
N1	Pd	N2	176.4(1)	H1OW	O1W	H1OW**	104.77
N1	Pd	C1	82.0(1)	C1	C2	C3	119.4(5)
N2	Pd	C1	94.9(1)	C2	C3	C4	121.7(5)
Pd	O1	N	119.2(4)	C3	C4	C5	119.3(5)
Pd	N1	C8	110.0(3)	C4	C5	C6	120.2(5)
Pd	N1	C9	113.8(3)	C1	C6	C5	120.9(4)
Pd	N1	C7	106.5(2)	C2	C1	C6	118.4(4)
Pd	N2	C10	125.1(2)	C1	C6	C7	115.3(3)
Pd	N2	C11	118.4(2)	C5	C6	C7	123.7(4)
Pd	C1	C2	128.3(3)	C7	N1	C9	109.0(4)
Pd	C1	C6	113.3(3)	C8	N1	C9	108.6(4)
N2	C10	C10*	121.6(2)	C7	N1	C8	108.8(4)
N2	C11	C11*	121.8(2)	N1	C7	C6	108.5(3)
C10	N2	C11	116.6(3)				

* Symmetry code: 1 − *x*, *y*, 1/2 − *z*.
** Symmetry code: −*x*, *y*, 1/2 − z.

Table 4
Hydrogen Bonds (Å, °) for $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)] \cdot H_2O$ (**3**).

D–H···*A*	D–H	H···A	D···A	*D*–H···*A*	Symetry code
O1W–H1W···O3	0.930	2.13	3.043(8)	167.0	*x*, −*y*, −1/2 + *z*
C3–H3···O2	0.940	2.50	3.195(9)	131.1	1 − *x*, −*y*, −*z*
C7–H72···O3	0.980	2.52	3.460(6)	161.8	*x*, −*y*, −1/2 + *z*
C11–H11···Cg3	0.941	2.85	3.804(5)	114	1 − *x*, −*y*, −*z*
C7–H71···Cg3	0.979	3.00	3.492(5)	164	1/2 − *x*, −1/2 − *y*, −*z*

Cg3: benzene ring.

(2.208(4) Å) is in good agreement with a square planar Pd(II) complex structure [29].

The most striking features of the crystal structure of **3** is the tilt (57.6(2)°) of the plane of pz relative to the square plane of the two palladium atoms (C_1, N_1, O_1 and N_2). The pyrazine ring is highly symmetric because it is formed by symmetry operation.

The solid state shows the presence of hydrogen bonds (Table 4). Molecules of **3** self-assemble into a supramolecular chain through intermolecular hydrogen bonds between crystallization water molecules and nitrato ligands of **3**, as can be observed in Fig. 3. As a result of the oxygen atom (from the water molecule) being positioned on the crystallographic twofold axis the polymeric chain is generate by symmetry.

In addition to this hydrogen bond, there are two C–H···O (3.195(9) and 3.460(6) Å) and two C–H···π (3.804(5) and 3.492(5) Å) interactions contributing to the stabilization of the crystal packing, which results in a complex three-dimensional framework.

As mentioned above, the other noteworthy feature of **3** which was disclosed by the X-ray analysis was the severe tilt of the pz plane of 57.6(2)° relative to the square planes defined by the metals and their four immediate bonded atoms. In this geometrical arrangement around a d^8 transition metal, the crystal field theory predicts that the metal's empty $d_{x^2-y^2}$ orbital shall be antibonding, with the other four d orbitals lying close in energy, with the d_{z^2} orbital assuming the role of the HOMO of the ML_4 molecule. In this way, following the σ coordination, there will be essentially two modes through which d–π interactions may develop. The two modes involve the metal and ligand B_{1g} and B_{2g} orbitals. The interaction of the empty B_{1g} $d_{x^2-y^2}$ with the pz HOMO B_{1g} should lower the energy of that otherwise essentially antibonding orbital, and this d←π interaction may thus help in further stabilization of the whole molecular assembly. On the other hand, the full d_{xy} orbital, of B_{2g} symmetry, may interact with the LUMO of pz, which is also B_{2g}, allowing for the development of an effective mechanism for $d \rightarrow \pi^*$ back donation. The interesting thing is that the d←π and $d \rightarrow \pi^*$ overlaps can only develop if the plane of pz is severely tilted in relation to the *xy* plane defined by the ML_4 core, a tilting that, in the present case, is 57.6(2)°. These d←π interactions may be found in the half-filled $d_{x^2-y^2}$ of Cu(II) atoms and the B_{1g} HOMO of pz which had been held responsible for magnetic processes in copper dimers and supramolecules [31]. A number of other metal pyrazine compounds which have been analyzed by X-ray crystallography also showed variations in the orientation of the plane of the complexes and the plane of coordinated pz, although the stabilizing effect of such canting has not always been emphasized [32].

4. Conclusions

The nitrate group from the ionic $[Pd(dmba)(MeCN)_2](NO_3)$, (**1**), seem to render this compound to be susceptible to a double substitution to yield $[Pd(dmba)L_2]^+$ complexes only with very strong σ donating L such as bipy, in which the interactions enables the detection of polycations from strongly conducting nitromethane solutions [33]. With poorer σ donors such as *m*-NAM or pz only complexes of the type $[Pd(dmba)(ONO_2)L]$ are formed. The biligand nature of pz ensures the formation of the dinuclear compound $[Pd(dmba)(ONO_2)]_2(\mu\text{-}pz)$. This complex showed the square planes defined by the metals ML_4 cores severely tilted in relation to the

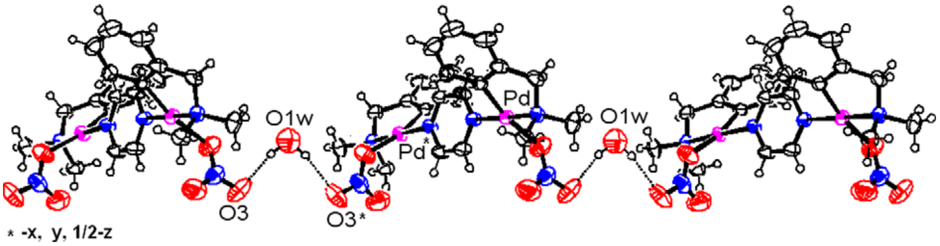


Fig. 3. Supramolecular chain formed by hydrogen bonding in the crystal structure of $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-}pz)] \cdot H_2O$.

plane of pz, suggesting the operation of strong $d \leftarrow \pi$ and $d \rightarrow \pi^*$ interactions between the metals and the pyrazine ring.

Acknowledgements

The authors wish to acknowledge CNPq, FAPESP and CAPES for the financial support.

Appendix A. Supplementary data

CCDC 692054 contains the supplementary crystallographic data for $[\{Pd(dmba)(ONO_2)\}_2(\mu\text{-pz})] \cdot H_2O$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.10.048.

References

[1] (a) S.R. Ananias, A.E. Mauro, K. Zutin, C.M.C. Picchi, R.H.A. Santos, Transition Met. Chem. 29 (2004) 284;
(b) B.J. O'Keefe, P.J. Steel, Acta Crystallogr., Sect. C 56 (2000) 440;
(c) R. Ares, M. Lópes-Torres, A. Fernández, M.T. Pereira, A. Suárez, R. Mosteiro, J.J. Fernández, J.M. Vila, J. Organomet. Chem. 665 (2003) 87;
(d) J. Vicente, A. Arcas, D. Bautista, M.C.R. de Arellano, J. Organomet. Chem. 663 (2002) 164;
(e) J.W. Slater, J.P. Rouke, J. Organomet. Chem. 688 (2003) 112.

[2] (a) D.L. Davies, O. Al-Duaij, J. Fawcett, K. Singh, J. Organomet. Chem. 693 (2008) 965;
(b) G. Zhao, Q.G. Wang, T.C.W. Mak, J. Organomet. Chem. 574 (1999) 311;
(c) M. Benito, C. López, X. Solans, M. Font-Bardía, Tetrahedron: Asymmetry 9 (1998) 4219;
(d) A.D. Ryabov, R. van Eldik, G. Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386;
(e) S. Tollari, S. Cenini, C. Tunice, G. Palmisano, Inorg. Chim. Acta 272 (1998) 18;
(f) J. Spencer, M. Pfeffer, Adv. Met.-Org. Chem. 6 (1998) 103.

[3] (a) P. Espinet, J. Perez, M. Marcos, M.B. Ros, J.L. Serrano, J. Barderã, A.M. Levelut, Organometallics 9 (1990) 2028;
(b) J. Buey, P. Espinet, J. Organomet. Chem. 507 (1996) 137;
(c) G.W.V. Cave, D.P. Lydon, J.P. Rourke, J. Organomet. Chem. 555 (1998) 81;
(d) A.M.G. Godquin, Coord. Chem. Rev. 178–180 (1998) 1485;
(e) D.J. Saccomando, C. Black, G.W.V. Cave, D.P. Lydon, J.R. Rourke, J. Organomet. Chem. 601 (2000) 305.

[4] (a) S.A. Kurzeev, G.M. Kazankov, A.D. Ryabov, Inorg. Chim. Acta 305 (2000) 1;
(b) S.M. Islam, A. Bose, B.K. Palit, C.R. Saha, J. Catal. 173 (1998) 268;
(c) A. Bose, C.R. Saha, J. Mol. Catal. 49 (1989) 271.

[5] (a) J.S. Casas, E.E. Castellano, J. Ellena, M.S. Garcıa-Tasende, M.L. Pérez-Parallé, A. Sánchez, A. Sánchez-González, J. Sordo, A. Touceda, J. Inorg. Biochem. 102 (2008) 33;
(b) C. Bincoletto, I.L.S. Tersariol, C.R. Oliveira, S. Dreher, A.C.F. Caíres, Bioinorg. Med. Chem. 13 (2005) 3047;
(c) J.D. Higgins, L. Neely, S. Fricker, J. Inorg. Biochem. 49 (1993) 149;
(d) A.G. Quiroga, C.N. Ranninger, Coord. Chem. Rev. 248 (2004) 119.

[6] S.R. Ananias, A.E. Mauro, V.M. Nogueira, P.S. Haddad, E.T. de Almeida, Eclét. Quím. 26 (2001) 87.

[7] (a) J.M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Verlagsgesellschaft, Weinhein, 1995;
(b) Z. Qin, M.C. Jennings, R.J. Puddephartt, Inorg. Chem. 42 (2003) 1956;
(c) M. Fujita, Chem. Soc. Rev. 27 (1998) 417;
(d) S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853;
(e) D.S. Cati, J. Ribas, J. Ribas-Ariño, H. Stoeckli-Evans, Inorg. Chem. 43 (2004) 1021.

[8] (a) R.F. Carina, A.F. Williams, G.G. Bernardinelli, J. Organomet. Chem. 548 (1997) 45;
(b) W.T.S. Huck, F.C.J.M. van Veggel, B.L. Kropman, D.H.A. Blank, E.G. Keim, M.M.A. Smithers, D.N. Reinhoudt, J. Am. Chem. Soc. 117 (1996) 8293;
(c) W.T.S. Huck, F.C.J.M. van Veggel, D.N. Reinhoudt, Angew. Chem., Int. Ed. Engl. 32 (1993) 392.

[9] C.H.M. Amijs, A. Berger, F. Soulimani, T. Visser, G.P.M. van Klink, M. Lutz, A.L. Spek, G. van Koten, Inorg. Chem. 44 (2005) 6567.

[10] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta. Crystallogr., Sect. A 24 (1968) 351.

[11] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343.

[13] G.M. Sheldrick, SHELX97 – Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[14] M. Nardelli, J. Appl. Crystallogr. 32 (1999) 563.

[15] A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) C34.

[16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd., Wiley Interscience Pub., New York, 1978.

[17] G. Socrates, Infrared Characteristic Group Frequencies, 2nd., Wiley, England, 1994.

[18] C.C. Addison, O. Sutton, Complexes containing the nitrate ion, in: F.A. Cotton (Ed.), Progress in Inorganic Chemistry, vol. 8, Wiley Interscience, New York, 1967, p. 195.

[19] N.F. Curtis, Y.M. Curtis, Inorg. Chem. 4 (1965) 804.

[20] W.J. Geary, J. Coord. Chem. Rev. 7 (1971) 81.

[21] J.M. Valke, F. Maassarani, P. van der Sluis, A.L. Spek, J. Boersma, G. van Koten, Organometallics 13 (1994) 2320.

[22] D.St.C. Black, G.B. Deacon, G.L. Edwards, Aust. J. Chem. 47 (1994) 217.

[23] H. Suzuki, N. Tajima, K. Tatsumi, Y. Yamamoto, Chem. Commun. (2000) 1801.

[24] J.M. Vila, M.T. Pereira, J.M. Ortigueira, A. Amoedo, M. Graña, G. Alberdi, M. Lópes-Torres, A. Fernández, J. Organomet. Chem. 663 (2002) 239.

[25] L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York, 1960. p. 224.

[26] A.E. Mauro, A.C.F. Caires, R.H.A. Santos, M.T.P. Gambardella, J. Coord. Chem. 48 (1999) 521.

[27] A.M. Santana, A.E. Mauro, E.T. De Almeida, R.H.A. Santos, J.R. Zóia, J. Coord. Chem. 53 (2001) 163.

[28] J.L. Serrano, L. García, J. Pérez, E. Pérez, J. Vives, G. Sánchez, G. López, E. Molins, A.G. Orpen, Polyhedron 21 (2002) 1589.

[29] T. Hudgens, D. Johnson, W. Cordes, T. Barclay, D. Jeter, J. Chem. Crystallogr. 24 (7) (1997) 247.

[30] G.R. Newcome, D.L. Kohl, F.R. Fronkzec, J. Am. Chem. Soc. 104 (1982) 994.

[31] (a) M. Hackmeyer, J.L. Whitten, J. Chem. Phys. 54 (1971) 3739;
(b) H.W. Richardson, W.E. Hatfield, J. Am. Chem. Soc. 98 (1976) 835;
(c) W. Kaim, Angew. Chem., Int. Ed. Engl. 22 (1983) 171;
(d) G. Beobide, O. Castillo, A. Luque, U. Garcia-Couceiro, J.P. Garcia-Terán, P. Román, Inorg. Chem. 45 (2006) 5369.

[32] See, for instance, the interesting iridium tetramer described by H. Suzuki et al., J. Chem. Soc., Chem. Commun. (2000) 1801.

[33] R.D. Sommer, A.L. Rheingold, A.J. Goshe, B. Bosnich, J. Am. Chem. Soc. 123 (2001) 3940.