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Crystal structures and DFT analysis of Palladium(II) complexes with Schiff bases derived from *N*,*N*-dialkyl-*p*-phenylenediamines

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Graphical Abstract



Highlights

- Two new Schiff base Pd(II) N,O-chelate complexes were synthetized.
- Used ligands were derived from *N*,*N*-dialkyl-*p*-phenylenediamines and salicylaldehyde.
- Spectroscopic, thermal and elemental analyzes agree with the proposed structures.
- The crystal structures and Hirshfeld surface analysis of the new complexes were determined by X-ray diffraction.
- Pd(II) complexes stereochemistry and UV-Vis spectra were elucidated by DFT.

ABSTRACT

Herein, new palladium(II) complexes with Schiff bases derived from salicylaldehyde *N*,*N*-dialkyl-*p*-phenylenediamines obtained. The ligands and were 2-((4-(N,N-dimethylamino)aniline)formimidoyl)phenol (N,N-metph-sOH - L₁) and 2-((4-(*N*,*N*-diethylamino)aniline)formimidoyl)phenol (*N*,*N*-etph-sOH - L₂) and complexes $[Pd(N,N-metph-sO)_2]$ (C₁) and $[Pd(N,N-etph-sO)_2]$ (C₂) were characterized by elemental analysis, infrared (IR) and UV-Vis spectroscopy, ¹H and ¹³C nuclear magnetic resonance (NMR), thermogravimetry (TG) and differential thermal analysis (DTA), and the results agree with the proposed structures. The crystal structures data showed the formation of N,O-chelate with the pairs of phenolate O and imine N occupying the trans positions. Hirshfield surface analysis was employed to elucidate the intermolecular contacts which drive the different supramolecular assemblies of C_1 and C2. In addition, Density Functional Theory (DFT) calculations were also performed to better understand the electronic properties. Additional DFT calculations were also devoted to elucidate the stereochemistry of these palladium complexes toward the cistrans isomerism among these square-planar Pd(II) NO-Schiff base complexes. Timedependent DFT (TD-DFT) analysis was applied to shed light on the nature of the electronic transitions determined in the UV-Vis spectra.

Keywords: Pd(II) complexes, Schiff bases, Single crystal XRD, Thermal studies, DFT.

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1. INTRODUCTION

The coordination chemistry of palladium complexes with Schiff base ligands has excited great interest among chemists in recent years, due to the applications of these compounds in catalysis and their relevance to bioinorganic systems in a wide variety of biological applications, such as antimicrobial [1,2], antifungal [3] and antitumoral activity [4,5,6] as well as other biochemical and pharmacological proprieties.

In bioinorganic systems, palladium complexes were introduced after the success of platinum(II) compounds [7], since the coordinating geometry and ionic radius of palladium(II) are similar to platinum(II) ions [8]. However, palladium(II) compounds demonstrate ligand-exchange kinetics that are 10⁵ times faster than the analogous platinum(II), which can facilitate the hydrolysis of the leaving groups that dissociate readily in solution before the complex reaches the pharmacological target [8].

Chelating ligands have been used to overcome this high lability, forming thermodynamically stable and kinetically inert palladium(II) complexes [9,10]. In this context, Schiff bases are an important class of ligands in Coordination Chemistry, because these compounds are versatile ligands in the formation of transition metal complexes [11,12].

Schiff bases are obtained by the condensation reaction of aldehydes and amines under specific conditions [13,14]. The presence of the iminic group (-C = N-) allows these molecules to easily bind to metal ions by the nitrogen atom, once this group has electron donor properties. The existence of other regions that are suitable for coordination (SH or OH) enables the formation of the chelate compound with increased kinetic and thermodynamic stability [15,16].

As a part of our on-going research work with interest in the structural chemistry of palladium compounds, we herein report the synthesis, spectral characterization, single cristal X-ray diffraction and theoretical studies of new Pd(II) complexes with Schiff bases (L1 and L2) (Scheme 1) obtained by reaction of salicylaldehyde with *N*,*N*-dialkyl-*p*-phenylenediamines. These ligands were chosen based on their similarity to other ligands that showed biological activity when free [17] or coordinated to palladium [4,18] or other metals [19]. Our research group is dedicated to synthesis, characterization and investigation of biological activity of new transition metal complexes candidates to metallodrugs, like antitumoral [5,20,21], antileishmanial

[22,23,24], antifungal [24] and tuberculostatic [20,24,25]. Ligands and complexes were characterized by IR, UV-Vis, ¹H and ¹³C{¹H} NMR spectroscopies as well as elemental and thermal analysis. In addition, the crystal structures of the complexes (C_1 and C_2) were determined, allowing us to unambiguously confirm the geometry of the complexes. Hirshfeld surface analysis (HS) was carried out to a better understanding of crystallographic interactions and packing nature within their crystal structures. Moreover, density functional theory (DFT) calculations were also performed to better understand the electronic properties, and time-dependent DFT (TD-DFT) analysis was applied to shed light on the nature of the electronic transitions determined in the UV-Vis spectra. A detailed characterization of obtained compounds in this work was necessary in order to allow the reproducibility and reliability in the bioassays that will be performed *a posteriori*.



Scheme 1. Synthetic route for Schiff bases (L_1 and L_2) and corresponding palladium(II) complexes (C_1 and C_2).

2. MATERIAL AND METHODS

2.1. Preparations

All reagents and solvents were obtained from commercial suppliers and used without further purification. The lithium tetrachloropalladate(II), palladium chloride, salicylaldehyde and *N*,*N*-dialkyl-*p*-phenylenediamines were used as received from Aldrich.

2.2. Instrumentation

Infrared spectra (IR) were recorded using KBr disk on a Shimadzu-IR-Prestige-21 spectrophotometer in the spectral range 400-4,000 cm⁻¹. The percentages of C, H and N were determined by elemental analysis using a Leco Instruments Ltda, model TruSpec CHNS-O instrument. The %Pd was obtained by thermogravimetric analysis (TG). NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz (¹H) and 75 MHz (¹³C), using CDCl₃ as solvent. Thermogravimetry (TG) and differential thermal analysis (DTA) data were obtained from a TA Instruments equipment - Q 600, under dry synthetic air flow (100 mL min⁻¹), mass sample of approximately 10 mg, alumina crucible and heating rate of 20 °C min⁻¹ from room temperature to 900 °C. The reference substance used in DTA measurements was pure α alumina. The electronic absorption was recorded by a THERMO Scientific-Evolution 60, using MeCN as solvent. X-ray powder diffraction (XRD) patterns were obtained by Rigaku Ultima IX equipment using K α Cu wavelength (λ =1.5418 Å) setting of 34 kV and 20 mA.

2.3. X-ray crystallography

Yellow (C₁) and orange (C₂) single-crystals were grown from evaporation of a solution of the complex in CDCl₃. Well-shaped single crystals were chosen for the X-ray diffraction experiment that was performed at 293 K on an automatic diffractometer Rigaku XtaLAB mini II diffractometer (graphite monochromator) with Mo K α radiation ($\lambda = 0.71073$ Å). CrysAlisPro [26] were used for data collection, cell refinement, data

reduction, and multi-scan method absorption correction. The structures of C_1 and C_2 were solved and refined using the software SHELXT2014 [27] from the OLEX2 suite [28]. All atoms, except hydrogen, were clearly identified and refined by least squares full matrix F^2 with anisotropic thermal parameters. The crystallographic tables were generated by OLEX2 [28] and the structure representations by Mercury software [29]. The main crystal data collections and structure refinement parameters for C_1 and C_2 are summarized in Table 1, as well as the CCDC deposit numbers for supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, from the Cambridge or Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 01223-336-033). Relevant interatomic bond lengths and angles are listed in Table 2. The Hirshfeld surfaces (HS) and the 2D-fingerprint plots were carried out with CrystalExplorer package [50]. The 2D-fingerprint plots were performed from a fraction of points in the Hirshfeld surface based on the normalized contact distances defined as d_i (distance from the surface to the nearest atom in another molecule) and d_e (distance from the surface to the nearest atom in the molecule itself) across the metal complexes.

2.4. Synthesis of N,N-metph-sOH - (L_1)

The used Schiff bases have been reported in the literature [31,32], however, a new methodology was applied to obtain them, as described in Scheme 1 (the indicative numbers on the atoms were used for the NMR assignments). To a solution of 1.0710 g (19.09 mmol) of KOH in heated methanol (70 mL) were added 1.9865 g (9.50 mmol) of *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride and 1.00 mL (9.51 mmol) of salicylaldehyde. The mixture was stirred at room temperature (approximately 25 °C) for 3 h. Then, the obtained precipitate was filtered off, washed with water and dried in vacuum. Finally, it was recrystallized with methanol. Yield: 78%. Anal. Calc. for $C_{15}H_{16}N_2O$ (%): C 75.0, H 6.7, N 11.7; Found: C 74.9, H 6.7, N 11.8. IR (KBr, cm⁻¹): 2889 w (vC-H), s 1614 s (vC=N), 1591 s (v_{ring}), 1518(v_{ring}), 1456 m (v_{ring}), 1366 s (γOH), 1280 s (vC-N), 1196 s (vC-O), 810 s (γ_{p-ring}), 756 s (γ_{o-ring}). ¹H NMR δ_{ppm} (multiplicity; integration; J; assignment): 13.78 (s; 1H; 1), 8.61 (s; 1H; 8), 7.38-7.32 (m; 2H; 4, 6), 7.29 (d; 2H; 9.1 Hz; 10), 7.01 (d; 1H; 8.1 Hz; 3), 6.92 (t; 1H; 8.0 Hz; 5), 6.75 (d; 2H; 9.0 Hz; 11), 3.00 (s; 6H; 13). ¹³C NMR δ_{ppm} (assignment): 160.95 (2), 157.63 (8), 149.94 (12), 137.10 (9), 132.04 (4), 131.56 (6), 122.23 (10), 119.81 (7), 118.85 (5),

117.05 (3), 112.78 (11), 40.63 (13). ¹³C NMR DEPT 135 δ_{ppm} (assignment): 157.56 (8), 132.06 (4), 131.63 (6), 122.27 (10), 118.90 (5), 117.06 (3), 112.76 (11), 40.64 (13).

2.5. Synthesis of N,N-etph-sOH - (L₂)

The Schiff base L_2 was obtained as described in section 2.4, however the *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride was replaced by 2.4920 g (9.50 mmol) of *N*,*N*-diethyl-*p*-phenylenediamine sulfate (Scheme 1). Yield: 85%. Anal. Calc. for C₁₇H₂₀N₂O (%): C 76.1, H 7.5, N 10.4; Found: C 75.9, H 7.5, N 10.2. IR (KBr, cm⁻¹): 2964 w (vC-H), 1614 s (vC=N), 1591 s (v_{ring}), 1517 s (v_{ring}), 1458 m (v_{ring})1404 s (δ CH₂), 1360 s (γ OH) 1269 s(vC-N), 1196 s (vC-O), 818 s (γ_{p-ring}), 756 s (γ_{o-ring}). ¹H NMR δ_{ppm} (multiplicity; integration; J; assignment): 13.86 (s; 1H; 1), 8.62 (s; 1H; 8), 7.40-7.31 (m; 2H; 4, 6), 7.28 (d; 2H; 9.0 Hz; 10), 7.02 (d; 1H; 8.1 Hz; 3), 6.92 (t; 1H; 7.4 Hz; 5), 6.71 (d; 2H; 9.0 Hz; 11), 3.40 (q; 8H; 7.0; 13), 1.20 (t; 6H; 7.0 Hz; 5). ¹³C NMR δ_{ppm} (assignment): 160.92 (2), 156.84(8), 147.30 (12), 136.05 (9), 131.84 (4), 131.44 (6), 122.50 (10), 119.91 (7), 118.82 (5), 117.02 (3), 112.05 (11), 44.61 (13), 12.68 (14). ¹³C NMR DEPT 135 δ_{ppm} (assignment): 156.77 (8), 131.90 (4), 131.55 (6), 122.60 (10), 118.90 (5), 117.05 (3), 112.01 (11), 44.63 (13), 12.73 (14).

2.6. Synthesis of $[Pd(N,N-metph-sO)_2] - (C_1)$

To a solution of lithium tetrachloropalladate(II), Li₂[PdCl₄], prepared as described in the literature [33] with 200.2 mg (1.13 mmol) of PdCl₂ and 106.9 mg (2.52 mmol) of LiCl in methanol (40 mL), was added a L₁ solution (543.1 mg, 2.26 mmol) in methanol (40 mL). Then, a solution of triethylamine (315 μ L, 2.26 mmol) in methanol (5 mL) was added slowly and the reaction mixture was stirred for 24 h at room temperature. The precipitate was filtered off, washed (with methanol, water and ethyl ether), dried in vacuum and recrystallized from chloroform (Scheme 1). Yield: 62%. Anal. Calc. for C₃₀H₃₀N₄O₂Pd (%): C 61.6, H 5.2, N 9.6, Pd 18.19; Found: C 61.4, H 5.2, N 9.3, Pd 18.53. IR (KBr, cm⁻¹): 2794 w (vC-H), 1610 s(vC=N), 1514 s (v_{ring}), 1440 s (v_{ring}), 1319 s(vC-N), 1190 s (vC-O), 824 m (γ_{p-ring}), 756 s (γ_{o-ring}). ¹H NMR δ_{ppm} (multiplicity; integration; J; assignment): 7.71 (s; 2H; 8), 7.22 (d; 4H; 8.9 Hz; 10), 7.16-7.07 (m; 4H; 4, 6), 6.75 (d; 4H; 8.8 Hz; 11), 6.48 (t; 2H; 7.3 Hz; 5), 6.27 (d; 2H; 8.4 Hz; 3), 3.00 (s; 12H; 13). ¹³C NMR δ_{ppm} (assignment): 165.16 (2), 162.16 (8), 149.36 (12), 139.52 (9),

134.65 (4), 134.24 (6), 125.22 (10), 120.70 (7), 120.52 (5), 114.86 (3), 111.92 (11), 41.02 (13). ¹³C NMR DEPT 135 δ_{ppm} (assignment): 162.16 (8), 134.67 (4), 134.29 (6), 125.22 (10), 120.53 (5), 114.90 (3), 111.92 (11), 41.05 (13).

2.7. Synthesis of complex $[Pd(N, N-etph-sO)_2] - (C_2)$

The C₂ complex was prepared as described in section 2.6, using 606.5 mg (2.26 mmol) of L₂ instead of L₁ (Scheme 1). Yield: 65%. Anal. Calc. for C₃₄H₃₈N₄O₂Pd (%): C 63.7, H 6.0, N 8.7, Pd 16.60; Found: C 63.4, H 6.3, N 8.5, Pd 16.91. IR (KBr, cm⁻¹): 2976 w (vC-H), 1607(vC=N), 1514 s (v_{ring}), 1440 s (v_{ring}), 1321 s(vC-N), 1186 s (vC-O), 818 m (γ_{p-ring}), 756 s (γ_{o-ring}). ¹H NMR δ_{ppm} (multiplicity; integration; J; assignment): 7.72 (s; 2H; 8), 7.19 (d; 4H; 8.9 Hz; 10), 7.16-7.06 (m; 4H; 4, 6), 6.69 (d; 4H; 8.8 Hz; 11), 6.48 (t; 2H; 7.3 Hz; 5), 6.29 (d; 2H; 8.4 Hz; 3), 3.41 (q; 8H; 7.0 Hz; 13), 1.21 (t; 12H; 7.0 Hz; 14). ¹³C NMR δ_{ppm} (assignment): 165.15 (2), 161.84 (8), 146.39 (12), 138.37 (9), 134.49 (4), 134.20 (6), 125.43 (10), 120.87 (7), 120.52 (5), 114.82 (3), 111.32 (11), 44.84 (13), 12.59 (14). ¹³C NMR DEPT 135 δ_{ppm} (assignment): 161.83 (8), 134.45 (4), 134.19 (6), 125.40 (10), 120.49 (5), 114.80 (3), 111.18 (11), 44.75 (13), 12.58 (14).

2.8. Computational details

The calculations were performed leveraging density functional theory (DFT) and the PBE0 (also known as PBE1PBE) functional [34,35] used in the Gaussian 09 program package [36]. The stationary point on the potential energy surface was fully optimized, while the harmonic vibration frequencies were used to characterize the optimized structures as true energy minima based on the absence of imaginary frequencies. The LANL2TZ basis set [37,38] was carried out for the palladium atom, and 6-31G(d,p) [39,40] was used for the other atoms. Nevertheless, def2-QVZPPD basis sets [41] were applied for all elements in single-point calculations with the purpose to refine the electronic energy evaluating the dimeric assembly and the energy difference between *cis/trans* configurations [in these cases, the zero-point vibrational energy was obtained with LANL2TZ/6-31G(d,p)]. In addition, the acetonitrile solvation effect was accounted for with the integral equation formalism variant of the polarizable continuum model (IEF-PCM) [42]. Natural population analysis (NPA) [43] was employed to evaluate the atomic charge distribution, and the Mayer bond index [44] was used to predict the bond order on the coordination sphere. The NBO6 program package [45] was used to carry out the natural bond orbital (NBO) analysis. The results were analyzed using Avogadro [46] and VMD [47] softwares.

3. RESULTS AND DISCUSSION

Synthesis of Schiff bases L_1 and L_2 was carried out by heating a solution of *N*,*N*-dialkyl-*p*-phenylenediamine salt (*N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride or *N*,*N*-diethyl-*p*-phenylenediamine sulfate) and salicylaldehyde in methanol with KOH for 3 h (Scheme 1). The choice of *N*,*N*-dialkyl-*p*phenylenediamines allows for fine tuning of electronic and steric properties of ligands, therefore influencing the resulting metal complexes properties.

As depicted in the experimental section, the lithium tetrachloropalladate(II), $Li_2[PdCl_4]$ precursor was employed for the synthesis of the complexes C_1 : $[Pd(N,N-metph-sO)_2]$ and C_2 : $[Pd(N,N-etph-sO)_2]$ (Scheme 1). These complexes were isolated in good yield and purity, and the structures were characterized by elemental analysis (experimental section), ${}^{13}C{}^{1}H$ and ${}^{1}H$ NMR spectroscopy, UV-Vis and IR spectra and TG-DTA. In addition, the structures of C_1 and C_2 were determined by X-ray crystallography.

3.1. Single Crystal X-ray Analysis

The crystallographic structures (Figure 1) confirm the proposed C_1 and C_2 structures and coordination mode for L_1 and L_2 , where the coordination sphere is square-planar with the pairs of phenolate O and imine N occupying the *trans* positions. The X-ray experimental data and structure refinement for the reported structures are summarized in Table 1, and the selected bond lengths and angles are presented in Table 2. For both complexes the Pd–O and Pd–N bond distances are 1.92 and 2.02 Å respectively, similar to those seen in related complexes [48-50]. The O-Pd-N and O-Pd-O bond angles are close to 90° and 180°, respectively, as expected due to the low tensioned chelate formed. The crystal structure of compound C_2 presents two symmetry-independent molecules (C_2A and C_2B), although the two molecules are

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structurally very similar, as can be seen from the overlap shown in Figure 2, and do not display significative differences for bond angles and lengths.

Complex	C ₁	C ₂	
CCDC code	1916130	1916131	
Empirical formula	$C_{30}H_{30}N_4O_2Pd$	$C_{34}H_{38}N_4O_2Pd$	
Formula weight	585.00	641.08	
Temperature/K	293(2)	293(2)	
Crystal system	orthorhombic	📞 triclinic	
Space group	Pbca	P-1	
a/Å	9.1540(6)	10.2574(4)	
b/Å	12.0400(8)	10.6494(4)	
c/Å	23.9393(12)	14.9306(6)	
α/°	90	70.211(3)	
β/°	90	83.816(3)	
$\gamma/^{\circ}$	90	76.144(3)	
Volume/Å ³	2638.4(3)	1489.34(11)	
Z	4	2	
$\rho_{calc}g/cm^3$	1.473	1.43	
μ/mm^{-1}	0.738	0.66	
F(000)	1200	664	
Crystal size/mm ³	$0.463 \times 0.311 \times 0.054$	$0.623 \times 0.512 \times 0.340$	
Radiation	MoKα ($\lambda = 0.71073$)	MoKa ($\lambda = 0.71073$)	
2Θ range for data collection/°	5.602 to 54.206	5.156 to 54.204	
Index ranges	$\begin{array}{c} \text{-11} \leq h \leq 11, \text{-14} \leq k \leq 15, \text{-30} \\ \leq l \leq 30 \end{array}$	$\begin{array}{c} \text{-13} \leq h \leq 13, \text{-13} \leq k \leq 13, \text{-19} \\ \leq l \leq 19 \end{array}$	
Reflections collected	17376	32749	
Independent reflections	2916 [$R_{int} = 0.0358$, $R_{sigma} = 0.0247$]	6569 [$R_{int} = 0.0270, R_{sigma} = 0.0162$]	
Data/restraints/paramet ers	2916/0/159	6569/0/377	
Goodness-of-fit on F ²	1.119	1.18	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0381, wR_2 = 0.0891$	$R_1 = 0.0281, wR_2 = 0.0669$	
Final R indexes [all data]	$R_1 = 0.0743, wR_2 = 0.1124$	$R_1 = 0.0392, wR_2 = 0.0782$	
Largest diff. peak/hole / e Å ⁻³	0.40/-0.36	0.46/-0.61	

Table 1. Crystal data and structure refinement for $(C_1 \text{ and } C_2)$

Table 2. A comparative analysis between experimental and the calculated values with

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Dond		C ₁	C ₂	
Bona -	Exp	PBE0	Exp	PBE0
Pd_1-O_1	1.972(2)	1.992	1.9768(16)	1.996
$Pd_1 - O_1^{1}$	1.972(2)	1.992	1.9768(16)	1.996
$Pd_1-N_1^1$	2.013(3)	2.045	2.0275(18)	2.047
Pd_1-N_1	2.013(3)	2.045	2.0275(18)	2.047
Pd_2-O_2	-		1.9666(17)	1.992
$Pd_2-O_2^2$	-		1.9666(17)	1.992
Pd_2-N_3	-		2.0253(19)	2.047
$Pd_2-N_3^2$	-		2.0253(19)	2.047
Angle				
$O_1Pd_1O_1^{-1}$	180.0	180.00	180.00(3)	180.00
$O_1Pd_1N_1$	87.65(10)	88.06	90.98(7)	91.78
$O_1Pd_1N_1^{-1}$	92.35(10)	91.94	89.02(7)	92.20
$O_1^1 P d_1 N_1^1$	92.35(10)	91.94	90.98(7)	91.78
$O_1^1 P d_1 N_1$	87.65(10)	88.06	89.02(7)	92.20
$N_1^1 P d_1 N_1$	180.0	180.00	180.00(11)	180.00
$O_2Pd_2O_2^2$	-		180.00(6)	180.00
$O_2Pd_2N_3$	-		92.48(8)	92.07
$O_2Pd_2N_3^2$	-		87.52(8)	91.96
$O_2^2 P d_2 N_3^2$	-		92.48(8)	92.07
$O_2^2 P d_2 N_3$	-		87.52(8)	91.96
$N_1^1 P d_1 N_1$	-		180.0	180.00

PBE0 functional involving selected bond lengths (in Å) and angles (in $^\circ)$ for C_1 and C_2 complexes.

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Figure 1. ORTEP view of C_1 and C_2 (ellipsoids at 30% of probability).



Figure 2. Structural overlap of two symmetry-independent molecules in compound C_2

The fingerprint plots of C_1 and the independent conformers in C_2 (A and B) are shown in Figure 3-1 (see also Figures S1-S3 in the supplementary material). It can be noted that the fingerprints do not show prominent spikes which are mainly due the absence of strong donor/acceptor electrons among intermolecular interactions. The H···H intermolecular contacts (see Figure 4) are the major contributions to the Hirshfeld surface areas exhibiting values around 60% indicating that the crystal packing of these metal complexes is governed by van der Waals contacts. The C···H interactions are represented by internal spikes in the bottom area corresponding to 28% of HS, including a C-H···Cg one (π -Ring) founded in C₂ (see Figure S4 in the supplementary material). In contrast, the N···H and O···H interactions are not extensive with small contributions around 3% and 5%, respectively (Figure 4-1). A Pd···H contact was also identified displaying 2.9%, 1.6% and 1.0% of C₁, C₂A and C₂B HS, respectively. These contacts (i.e. Pd···H, O···H and N···H) appeared as sharp spikes in the fingerprint plots indicating that these interactions are significantly short.



Figure 3. 1- 2D-plot (fingerprints) derived from the Hirshfeld surface summarizing the contribution of intermolecular interactions in the nearest environment of C_1 , C_2A and C_2B . 2- Comparative quantitative analysis (%) of the intermolecular contacts derived from the Hirshfeld Surfaces (HS) of the complexes



Figure 4. 2D-fingerprint plots derived from the Hirshfeld surface of C_1 for the H...H, C...H, O...H and Pd...H contacts.

Examining the molecular electrostatic potential maps, $Pd\cdots H$ contacts were considerably visible showing red spots over the Hirshfeld surfaces. These $Pd\cdots H$ red spots are visible only in C_1 , while the main spots in C_2A and C_2B are assigned by the $C\ldots H$ contacts (see Figures S5 and S6). This occurs due to the small torsion angles between the ligand rings in C_1 of 88.55° against 125.49° and 131.08° in C_2A and C_2B , respectively. Thereby, these metal $\cdots H$ interactions modulate the molecular packing and conferring supramolecular differences between C_1 and C_2 .



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Figure 5. Hirshfeld Surface displaying the electrostatic potential map of C_1 . The Pd...H and C...H interactions are evidenced.

3.2. Infrared spectra

The IR spectra of free Schiff bases L_1 and L_2 show bands related to aromatic and aliphatic C–H stretching vibrations in the range 2830–3100 cm⁻¹, while C=N, C=C and C–O stretching vibrations were detected between 1150 and 1620 cm⁻¹ [51,52]. As expected, the latter bands shift to lower wavenumbers after coordination of these ligands to palladium. For example, the band at ~1614 cm⁻¹ associated with the stretching frequency of the imine C=N bond in L_1 shifted to ~1604 cm⁻¹ in C_1 , which is indicative of imine nitrogen coordination to the metal center, as reported for other palladium Schiff bases in the literature [48,51-53]. The v(C-O) bands in the ligands L_1 and L_2 were observed at approximately 1196 cm⁻¹ [54], and after coordination, they shifted to 1190 and 1186 cm⁻¹, respectively, due to the coordination of an oxygen atom to palladium. The changes observed for v(C=N) and v(C-O) suggests the formation of *N*,*O*-chelate complexes, as previously described for other Schiff base palladium complexes [55]. Figure 6 shows the vibrational spectrum in the fingerprint infrared region of the L_1 and L_2 ligands and C_1 and C_2 complexes. The complete infrared spectra are available in the supplementary material (figure S8).



Figure 6. Fingerprint region IR spectra of ligands L_1 and L_2 , and complexes C_1 and C_2 , in KBr.

3.3. ¹H and ¹³C NMR spectra

Figures 7 and 8 show, respectively, ¹H and ¹³C{¹H} NMR spectra (complete ¹H NMR spectra are available in the supplementary material). In the ¹H NMR spectrum of

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free ligands (L_1 and L_2), signals δ (ppm) at approximately 13.8 and 8.6 were observed, which were assigned to hydroxyl group [56] and –CH=N– (imine proton), respectively [53-56]. Aromatic hydrogen atom resonances were observed in the range of 6.00–7.40 and were attributed to the protons present in the aromatic region. *N*-alkyl hydrogens signals were observed in the range of 2.80–3.60. After coordination to Pd(II), an upfield chemical shift was observed (to approximately 7.71) for the imine signal in the C_1 and C_2 complexes. Palladium-N coordination reduces the double-bond current effects in the –HC=N functional group (anisotropic effect), decreasing the deshielding [4]. This shift is also observed in all phenyl ring hydrogens, with the biggest displacements of H3 and H5. This is because these regions present more electronic density by the presence of electron donating group OH [57]. Hence, these hydrogens are more likely to changes caused by coordination. Others palladium complexes also presented the same behavior [4,48,58]. Furthermore, the OH signal was not observed in the spectra of the complexes, as expected, suggesting the chelating *O-N* formation [56].



Figure 7. Detailed ¹H NMR spectra of all synthesized compounds



In the L_1 and L_2 ¹³C NMR spectrum, signals δ (ppm) at approximately 161 and 157 were observed, attributed to oxygen-bonded aromatic carbon and iminic carbon, respectively [55]. After coordination to Pd(II), C2 and C8 for C₁ and C₂ presented deshielded signals as expected at approximately 165 and 162, respectively. ¹³C DEPT 135 experiments agree with the proposed assignments (see Figure S10 in the supplementary material).

3.4. Thermal Analysis

In order to investigate the thermal behavior of the ligands and complexes, TG-DTA curves were obtained. Figure 9 presents the TG-DTA curves of all synthesized compounds. The thermal decomposition steps, mass loss (calculated and experimental) and final residue percentages are summarized in the supplementary material (Table S1). The final residues were analyzed by X-ray powder diffraction (XRD) (see Figure S11 in the supplementary material), and peaks were identified on the basis of ICSD to Pd⁰ (648680) [59].



Figure 9. TG-DTA curves of all synthesized compounds

The TG curve of compound L_1 shows two decomposition steps, resulting in a residual mass of 0.14%, which indicates complete compound decomposition. Furthermore, the DTA curve also shows an endothermic peak at 142 °C before decomposition, corresponding to the melting of L_1 . The thermal behavior of ligand L_2 is very similar to that of L_1 , and the residual mass at the end of the decomposition was 0.27%. An endothermic peak (105 °C) before the decomposition start, which corresponds to the L_2 melting, is also observed in DTA curve.

The TG-DTA curves of complexes C_1 and C_2 show a very similar decomposition pattern. Unlike ligands, which have well-defined melting points, the complexes begin to decompose without melting point. Both TG curves present three main decomposition stages. The resulting mass after the first two decomposition steps (20.88% for C_1 and 19.81% for C_2) is compatible with the formation of PdO (calc. 20.93% for C_1 and 19.10% for C_2). The mass loss between 760 and 850 °C, associated with the observation of an endothermic peak, in the DTA curve, at 816 °C, indicates the reduction of PdO to Pd⁰. This behavior, presented in the last step, is characteristic of most palladium complexes and has already been widely discussed in the literature [52,53,60,61]. The residual mass of Pd⁰ obtained was 18.53% (calc. 18.19%) for C_1 and 16.91% (calc. 16.60%) for C_2 .

Thermal study was also essential to determine the thermal stability of synthesized compounds, because this is an important property for possible pharmacological application. It is observed that coordination did not cause a significant difference in thermal stability with respect to free ligands. All compounds are stable up to 150 ° C. Thermal stability of the compounds can be ordered in the following sequence: $L_1 < C_1 < L_2 < C_2$.

3.5. Computational analysis

A good accordance in the prediction of the $Pd-N_2O_2$ coordination spheres and among the chelate rings was observed when comparing the experimental and calculated geometries of the palladium complexes. In **C**₁, slight changes can be seen in the orientation of aniline rings and *N*-methyl groups, while in **C**₂, only the *N*-ethyl groups are out of the plane (see Figure S12 in the supplementary material). Other DFT methods including B3LYP [62,63], M06 [64], M06-2X [64], wB97XD [65] and B97D [66] were also employed in order to compare their accuracy to predict the experimental geometry

of the structures investigated here (see Figure S13, S14 and Table S2). The differences among the DFT methods were lower than 10% in the mean absolute error (MAE) among bonds, angles and the dihedral angles, which points out the small influence from the functional employed. An additional analysis on PBE0 was devoted to evaluate the influence of more polarized basis sets functions toward the ligand [LANL2TZ/6-31G(2df,2pd)], the metal [def2-TZVP/6-31G(d,p)] and also for the whole system [def2-TZVP/def2-TZVP]. However, the small MAE values only mirrors that the PBE0 functional is less sensitive to the basis set changes (see Figure S15).

The frontier molecular orbitals shapes can be seen in Figure 10. The highest occupied molecular orbitals (HOMO) of the Pd-complexes have an electron density distribution that is exclusively toward the π -orbitals localized on the phenyl rings, whereas the lowest unoccupied molecular orbitals (LUMO) are predominantly π^* in nature and are localized in the chelate ring with a minor participation from the Pd 4dorbitals. In the ligands, their HOMOs are mainly composed by π -orbitals distributed in the aniline rings and iminic moieties and with a contribution from the lone pair electrons of the nitrogen atom in the amine group, while their LUMOs are π^* in nature and more delocalized. Hence, no significant difference can be noted on the HOMO-LUMO (HL) energy gap values between ligands and the metal-complexes, which occurs due to the similar nature among the frontier molecular orbitals. The HL energy difference of the palladium complexes was around 3.7 eV, which is in good agreement with other Pd complexes [67-69]. Moreover, molecular electrostatic potential (MEP) maps were also applied to gain a deeper insight into the charge distribution in the ligand and metal-complex structures (see Figure 11). The negative charges in the ligands are localized along the phenyl rings and the iminic groups with the positive regions mostly on alkyl groups. In contrast, these Pd-complexes showed positive regions mainly distributed in the coordination sphere, while negative regions are observed toward the *N*,*N*-dialkyl-*p*-phenylenediamine groups and the phenyl rings of salicylaldehyde.



Figure 10. Electronic density (with an isovalue of 0.05 a.u.) of the frontier orbitals (HOMO and LUMO) with the energy difference (in eV) for the structures L_1 and C_1 calculated in the gas phase with the PBEO functional.



Figure 11. The molecular electrostatic potential (with an isovalue of 0.001 a.u.) of the structures C_1 and L_1 mapped where the regions in blue and red indicated positive and negative potentials, respectively. The top side view shows the front of the solid surface, and the bottom side view shows the back of the surface, where the molecular disposition is also displayed

Two asymmetric independent molecules were observed in the unit cell of complex C_2 . In this regard, a DFT simulation was performed using the crystallographic coordinates as the starting point to the optimization procedure to evaluate the electronic properties of this dimeric assemble (see Figure 12). The interaction energy was computed considering the energy difference between the dimer motif energy and two times the energy obtained for the C_2 structure showing a value of -4.5 kcal mol⁻¹. This small interaction energy only enhances that van der Waals forces govern the formation of this self-assembled dimer similarly as can been seen elsewhere [70-73]. By viewing the MEP surface, any change can be seen in the charge distribution with the interaction of another C_2 complex that mirrors the small interaction between both molecules. This is in good accordance with NPA charges, which assigned the same charge distribution in each molecule of the self-assembled dimer (as shown in Table S3 in the

supplementary material). Indeed, a very slight change is also observed when examining the HL gap energy. In this assembly, HOMO is still characterized by π -orbitals on aniline aromatic rings, although it is distributed along one of the phenylamine rings of each molecule, while LUMO shows the same composition and is localized in one of the palladium complexes. Moreover, it was possible to characterize the main interactions involving the N-alkyl groups of the two molecules applying the second-order perturbation theory analysis of the Fock matrix (E₂) implemented in the NBO program. The main interactions involve the charge transfer process from the Pd d-orbital in to the $\sigma(C-H)$ anti-bonding of the alkyl group [Pd-d $\rightarrow\sigma^*(C-H)_{alkyl}$], which is followed by the donor-acceptor interaction between the $\pi(C=C)$ bonds of the phenolate group and $\sigma^*(C-H)_{alkyl}$ [$\pi(C=C)\rightarrow\sigma^*(C-H)_{alkyl}$] as well as between the $\pi(C=C)$ bonds of aniline rings and $\sigma^*(C-H)_{alkyl}$. These three donor-acceptor interactions represent the total interaction energy of 1.5 kcal mol⁻¹, while the other interactions represent very small contributions of 0.1 kcal mol⁻¹.



Figure 12. The optimized structure of the two asymmetric independent molecules observed in the unit cell of complex C_2 with the interaction energy (in kcal mol⁻¹) calculated in the gas phase with the PBEO functional (in the left side). In the middle is showed the molecular electrostatic potential (with an isovalue of 0.0001 a.u.). In the right side can be seen the electronic density (with an isovalue of 0.05 a.u.) of the frontier orbitals (HOMO and LUMO) with the energy difference (in eV).

Additional DFT calculations were also devoted to elucidate the stereochemistry of these palladium complexes toward the *cis-trans* isomerism among these square-

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planar Pd(II) N_2O_2 -Schiff base complexes (see Figure 13). Despite that, the transconfiguration is the usual structural arrangement in the crystal molecular packings of palladium complexes [74-79], there are some cases where the structures can assume two crystallographic independent cis- and trans-configurations in the crystal packing [67-69] or even both forms in solution [80]. In this way, DFT simulations were also performed to understand the main differences between these palladium complexes with trans and cis-forms. Considering the electric dipole moments, cis-arrangements presented values close to 11 Debye, while the trans ones have zero dipole moments due to their symmetric structures. The energy difference between the *cis-trans* stereoisomers are around 5 kcal mol^{-1} , which only reinforces the *trans*-configurations as the most stable isomer. These energy gaps between both forms are associated with a small increase in the electrostatic and steric repulsions. Further calculations on the solvent effect with the polarized continuum solvent model showed any influence in the energy gap among *cis-trans* orientations. In addition, a comparative analysis of the MEP surfaces assigned any change among the stereoisomers along the localization of positive and negative regions as well as in the NPA charge distribution. Similar molecular orbital shapes were also predicted between both configurations, which explained the same HL gap energies. On the other hand, slight increases in the Pd-O bond order indices were predicted and followed by a slight decrease in the Pd-N ones.



Figure 13. The relative stability (in kcal mol⁻¹) between *cis-trans* configurations of complexes C_1 and C_2 calculated in the gas phase and on the solvent effect with the IEF-PCM solvent model for acetonitrile (in brackets) with the PBE0 functional.

3.6. UV-Vis and TD-DFT analysis

Time-dependent DFT (TD-DFT) calculations were carried out in order to elucidate the UV-Vis spectra (as shown in Table S5 in the supplementary material). In the ligands, it can be noted that the UV-Vis spectra present a large intense band varying from 295 to 488 nm. This former band involves the transition from HOMO to LUMO, thereby indicating mixed transitions involving $\pi \rightarrow \pi^*$ and $\eta \rightarrow \pi^*$ charge transfer processes. These bands showed a shoulder around 330 nm, which is also centered on mixed transitions. This mixed composition is also predicted for the bands observed around 248 nm. In contrast, the Pd-complexes showed absorption bands at 414 nm that are mainly assigned by a H \rightarrow L transition corresponding to a ligand-to-(metal-ligand) charge transfer (LMLCT) process with a minor contribution of a ligand-to-ligand charge transfer (LLCT) based in the H–1 \rightarrow L+1 transition with a weak oscillator strength.

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Another broad absorption band is detected at 315 nm in the complex C_1 with assignments based on a LMLCT and a LLCT in character, followed by transitions with a weak oscillator strength attributed to (metal-ligand)-to-(metal-ligand) (MLMLCT) and ligand-to-metal (LMCT) charge transfer processes. In C_2 , this band is observed at 327 nm with a shoulder at 366 nm. The different shape of this band in C_2 can be explained by a major contribution involving a LMLCT character with different picture among the minor contributions that also stem from a (metal-ligand)-to-ligand charge transfer (MLLCT). In addition, the third and most intense band is around 248 nm and can be described with a mixed LLCT/LMCT contribution. Furthermore, the results presented here are different when compared with other Pd-complexes [67-69,81,82].

4. CONCLUSIONS

In this work, we have successfully synthesized and characterized two new palladium complexes, C1 and C2, with Schiff bases derived from salicylaldehyde and N,N-dialkyl-p-phenylenediamines. FT-IR and NMR experiments showed N,O-chelate coordination compounds, as expected. Elemental analysis data (C,H,N) and %Pd obtained by TG agree with the proposed structures, thus indicating the formation of two new Schiff base palladium chelate complexes. Crystal structures of $C_1 \mbox{ and } C_2$ were obtained and determined by X ray diffraction confirming that coordination sphere is square-planar with the pairs of phenolate O and imine N occupying the *trans* positions. Furthermore, HS analysis showed that H...H, H...C and Pd...H are present in the interactions in the packages. These results showed that the different torsion angles present in the ligands may contribute to different percentages of each contacts, such as the observed for Pd...H interactions. DFT analysis was performed to understand the electron density distribution of the frontier molecular orbitals shapes and the molecular electrostatic potential maps were applied the charge distribution in the ligand and metalcomplex structures. Moreover, DFT calculations toward the two asymmetric independent molecules observed in the unit cell of complex C_2 showed an interaction energy of -4.5 kcal mol⁻¹, reinforcing that van der Waals forces govern the formation of this self-assembled dimer. DFT simulations involving the cis-trans isomerism showed an energy difference around 5 kcal mol^{-1} which are associated with a small increase in the electrostatic and steric repulsions, enhancing the trans-configurations as the most stable isomer.

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Highlights

- Two new Schiff base Pd(II) N,O-chelate complexes were synthetized.
- Used ligands were derived from N,N-dialkyl-p-phenylenediamines and ٠ salicylaldehyde.
- Spectroscopic, thermal and elemental analyzes agree with the proposed • structures.
- The crystal structures and Hirshfeld surface analysis of the new complexes were ٠ determined by X-ray diffraction.
- Pd(II) complexes stereochemistry and UV-Vis spectra were elucidated by DFT. •

Author Contributions Statements

The author contributions statements were based on CRediT (Contributor Roles Taxonomy)

Luís Eduardo Sarto: Conceptualization, Methodology, Investigation, Formal analysis, Writing – Original Draft. Wladimir Pereira Duarte Badaró: Conceptualization, Methodology. Elba Pereira de Gois: Methodology. Marília Imaculada Frazão Barbosa: Investigation, Formal analysis. Claudia Torres: Formal analysis, Writing – Review & Editing. Rommel Bezerra Viana: Investigation, Formal analysis, Writing – Original Draft. João Honorato: Investigation, Formal analysis, Writing – Original Draft. Eduardo Ernesto Castellano: Supervision. Eduardo Tonon de Almeida: Conceptualization, Methodology, Writing – Review & Editing, Supervision, Project administration.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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