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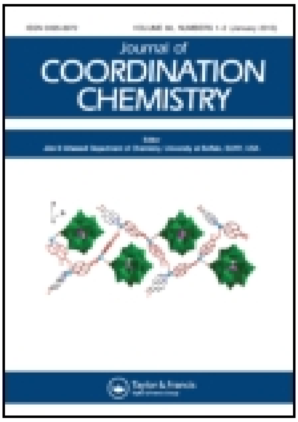

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Anion effect on the coordination behavior of *N,O*-hybrid pyrazole ligand towards Pd(II): synthesis, characterization, and supramolecular properties

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Four new Pd(II) coordination complexes using 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)ethanol (**L**) with different counter-anions have been prepared to examine their effect on the coordination mode of the ligand as well as on the self-assembly of the supramolecular structure. Reaction of *trans*-$[PdCl_2(L)_2]$ (**R**) with $AgCF_3SO_3$ gives the ionic complex $[Pd(L)_2](CF_3SO_3)_2$ (**1**). When $AgNO_3$ is used, $[Pd(NO_3)(L)_2](NO_3)$ (**2**) and $[Pd(L)_2](NO_3)_2$ (**3**) are obtained in the ratio 70 : 30, respectively, where the nitrate ion is present in- and/or outside the coordination sphere. Reaction of **R** with Ag_2SO_4 in the presence of $(NH_4)_2C_2O_4$ yields $[Pd(C_2O_4)(L)_2]$ (**4**). These new complexes have been characterized by elemental analyzes, conductivity measurements, mass spectrometry, IR, ^{1}H and ^{13}C {^{1}H} NMR spectroscopies, and X-ray diffraction, whenever possible. The denticity varies from N-monodentate to NO-bidentate, depending on the conditions, showing the versatility of **L**. Finally, the results of X-ray diffraction analyzes of **1** reveal that $CF_3SO_3^-$ plays a fundamental role in self-assembly, generating a 2-D supramolecular layer with different inter- and intra-molecular interactions. The easy preparation and the high efficiency of this ligand make it a promising alternative to improve established systems.

Keywords: *N*-Hydroxyalkylpyrazole ligand; Palladium(II) complexes; Supramolecular chemistry

1. Introduction

Investigation of self-assembly processes in supramolecular chemistry and design of solid-state compounds known as metal-organic frameworks (MOFs) are at the forefront of modern materials chemistry [1]. These materials have potential applications in molecular recognition and porous materials [2]. The dimensionality of these systems can be increased by non-covalent interactions like hydrogen bonds, $\pi\cdots\pi$, C–H$\cdots\pi$, and/or other van der Waals interactions, and such changes affect the final properties of the supramolecular organization [3]. Hydrogen bonding is a particularly powerful building motif for use in crystal engineering and a great variety of hydrogen bonding donor–acceptor-pairs exists,

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*Corresponding author. Email: Josefina.Pons@uab.cat making them a particularly smart choice for construction of self-assembling structures [4]. Hydrogen bonds provide unique directionality and are usually easily introduced into structures and their numbers can be varied through the appropriate ligand.

The search for ligands for effectively controlling the stability of these architectures also is a recurrent topic in catalysis [5]. As a result, a very large range of ligand platforms is available [6]. A number of studies of metallic complexes derived from pyrazole rings have been described with regard to the synthesis and characterization of novel materials with applications in molecular recognition and magnetism [7]. In our group, compounds containing (*NN*) [8], (*NP*) [9], (*NNN*) [10], (*NON*) [11], (*NSN*) [12], (*NNNN*) [13], (*NOON*) [14], and (*NSSN*) [15] ligands have been reported as smart classes of ligands prompting formation of mono- and dinuclear complexes with different coordination modes. Some have proved to play an important role in the formation of different kinds of self-assembly dispositions [16].

Pd(II) coordination architectures are influenced by several factors, ranging from the functionality of the ligands, to the metal-to-ligand ratio, the nature of the counter-anions, and the reaction conditions. Recently, we synthesized and characterized two regioisomers, 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)ethanol (**L**) and 2-(5-methyl-3-phenyl-1*H*-pyrazol-1-yl)ethanol (**L′**), and studied their reaction with $[MCl_2(CH_3CN)_2]$ (M = Pd(II), Pt(II)) obtaining *trans*-$[MCl_2(L)_2]$ (M = Pd(II), Pt(II); L =L, L′) where the ligands are monodentate (N_{pz}) [17]. This family of ligands, designed into various combinations of the donor-atom set termed as “mixed ligands” or “hybrid ligands,” are intriguing due to their different coordination modes.

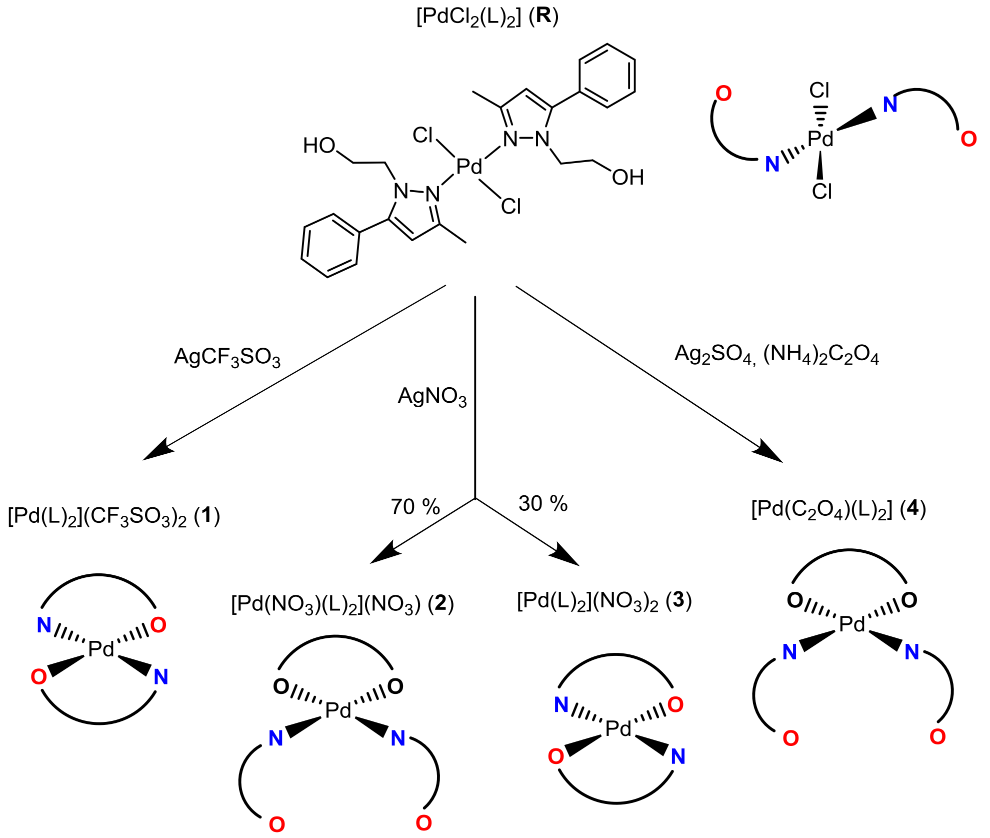
Thus, herein, we have investigated the synthesis and characterization of a new family of complexes with different anions, $[Pd(L)_2](CF_3SO_3)_2$ (**1**), $[Pd(NO_3)(L)_2](NO_3)$ (**2**), $[Pd(L)_2](NO_3)_2$ (**3**), and $[Pd(C_2O_4)(L)_2]$ (**4**), to analyze the different coordination modes of **L** (N_{pz} or N_{pz}, −OH), depending on the anion present in each complex as well as their contribution to the final supramolecular structure.

2. Results and discussion

2.1. *Synthesis and general characterization of complexes*

The reaction of *trans*-$[PdCl_2(L)_2]$ (**R**) (L = 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)ethanol) [17] with different Ag^+ salts ($AgCF_3SO_3$, $AgNO_3$, and Ag_2SO_4) was studied (scheme 1). When $AgCF_3SO_3$ is used, the complex $[Pd(L)_2](CF_3SO_3)_2$ (**1**) is obtained where $CF_3SO_3^-$ are non-coordinated (scheme 1). However, a mixture of $[Pd(NO_3)(L)_2](NO_3)$ (**2**) and $[Pd(L)_2](NO_3)_2$ (**3**) in 70 : 30 ratio is obtained when $AgNO_3$ is present in the reaction. This ratio of **2** and **3** was calculated through integration of the pyrazolic proton signals in the ^1H NMR spectrum. The solvent used in the two reactions is methanol and the proportion of *trans*-$[PdCl_2(L)_2]/Ag^+$ is 1 : 2. Finally, **R** reacts with Ag_2SO_4 and $(NH_4)_2C_2O_4$, in a proportion 1 : 1 : 1.5, to give $[Pd(C_2O_4)(L)_2]$ (**4**) (scheme 1).

Complexes **1–4** were characterized by elemental analyzes, mass spectrometry, conductivity measurements, IR, and 1-D and 2-D NMR spectroscopies. The NMR signals were assigned by reference to the literature [18] and from DEPT, COSY, HSQC, and NOESY spectra. Single crystal X-ray diffraction was also obtained for **1**. Elemental analyzes of **1**–**4** are consistent with the proposed formulas. The positive ionization spectra (MS(ESI+)) showed a peak with



Scheme 1. Synthetic strategies for the preparation of the complexes **1**–**4**.

an *m/z* value of 255 (100%) for **1** and **3**, attributable to $[Pd(L)_2]^{2+}$; **2** has a peak with an *m/z* value of 573 (48%) attributable to $[Pd(NO_3)(L)_2]^+$, and finally for **4** two peaks with *m/z* values of 622 (100%) and 600 (32%) are attributable to $[Pd(C_2O_4)(L)_2 + Na]^+$ and $[Pd(C_2O_4)(L)_2 + H]^+$, respectively. The observed molecular peaks of the cations exhibit the same isotope distribution as theoretical ones.

Conductivity for **1** ($185\,\Omega^{-1}\,cm^2\,M^{-1}$) is in agreement with 1 : 2 electrolytes in methanol. Conductivity for **4** ($21\,\Omega^{-1}\,cm^2\,M^{-1}$) shows that the complex is a non-electrolyte, thus indicating that the oxalate is coordinated to palladium in methanol. A different behavior is observed for the mixture of **2** and **3** in methanol ($140\,\Omega^{-1}\,cm^2\,M^{-1}$); this value is between 1 : 1 and 1 : 2 electrolytes, confirming the proposed chemical formulas. The reported values for 10^{-3} M solutions of 1 : 1 electrolyte complexes in methanol are between 80 and $115\,\Omega^{-1}\,cm^2\,M^{-1}$, while they are between 160 and $220\,\Omega^{-1}\,cm^2\,M^{-1}$ for 1 : 2 electrolyte complexes [19].

IR spectra of **1**–**4**, in KBr, are similar to those of *trans*-$[PdCl_2(L)_2]$, the most characteristic bands being those attributable to the phenyl, methyl, pyrazolyl, and alcohol groups. For all complexes, the band attributable to *ν*(O–H) appears between 3478 and 3374 cm^{-1}. For **1** (3456 cm^{-1}) and **3** (3478 cm^{-1}), *ν*(O–H) appears as a well-defined band, probably due to the coordination of the –OH group to the Pd atom, whereas for **2** (3374 cm^{-1}) and **4** (3385 cm^{-1})

it appears as a broad band, similar to the observed band for **R** (3398 cm^{-1}) [18] and another *trans*-$[PdCl_2(L'')_2]$ complex (L″ = 2-(5-phenyl-3-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol) (3278 cm^{-1}), where the OH group remains non-coordinated [20].

A detailed analysis of the IR spectra of **1**–**4** also gives hints about interactions involving the anions. The IR spectrum of **1** shows a number of strong absorptions at 1260–1000 cm^{-1} due to the asymmetric and symmetric vibrations of the SO_3^- and vibration of S–O. In this complex, the bands appear at 1259 and 1163 cm^{-1} [21].

In the IR spectrum of the mixture of **2** and **3**, the band at 1384 cm^{-1} and the very weak one in the overtone region (1800–1700 cm^{-1}) can be ascribed to nitrate (asymmetric and symmetric) stretching modes and combination of symmetric stretching and in-plane bending, respectively. These two complexes show a complicated spectrum in this region, which is consistent with the presence of both ionic and coordinated NO_3^-. Three bands appear at 1765, 1739, and 1712 cm^{-1}. The band that appears at 1765 cm^{-1} can be attributed to bidentate NO_3^- (coordinated), while bands at 1739 and 1712 cm^{-1} ($\Delta = 27$ cm^{-1}) are attributed to bidentate NO_3^- (coordinated) [22]. In the IR spectrum of **4**, characteristic bands of carboxyl groups are at 1654 cm^{-1} for asymmetric stretching and at 1557 cm^{-1} for symmetric stretching [23]. The value ($\nu_{as}(CO_2)$–$\nu_s(CO_2)$) (97 cm^{-1}) suggests a chelating carboxylate. The absence of the expected absorption at 1700 cm^{-1} for the protonated carboxylic groups indicates that all carboxyl groups of the ligand have been deprotonated [24].

^1H and $^{13}C\{^1H\}$ NMR spectra of **1–4**, in $CDCl_3$ showed the expected resonances. The observed bands are those attributable to H_{pz}, which appear between 6.33 and 6.20 ppm. The values are comparable to those observed for *trans*-$[PdCl_2(L)_2]$ (L = L (6.19 ppm) and L′ (6.31 ppm)) [17], but display higher field shift than other Pd(II) complexes (7.25–7.42 ppm) [20]. These values of chemical displacement (δ) for the four complexes show a large displacement compared to the same signal for the free ligand (H_{pz} appears at 5.96 ppm). These data indicate that **L** is coordinated to Pd(II) through the pyrazolyl, as shown in scheme 1. The ethylene protons of the N_{pz}–CH_2–CH_2–OH chain appear as two triplets between 4.94 and 4.40 ppm and 4.00 and 3.84 ppm, with ^1H–^1H coupling constants between 4.1 and 5.3 Hz.

In **2** and **4**, the signal attributable to the proton of the alcohol group (−O*H*) is not observed. However, in **1** and **3** it appears as a broad band at 5.55 and 4.85 ppm, respectively, probably due to coordination of –OH to Pd(II). Finally, the signals attributable to CH_{pz} in the NMR spectra of **1** and **3** appear at lower fields [C_{pz}: 109.0 (**1**), 107.4 (**3**)] and for **2** and **4** at higher fields [C_{pz}: 103.8 (**2**) and 101.2 (**4**)] than for the free ligand (105.6 ppm). It is important to highlight that the NMR spectra of **1**–**3** and **2**–**4**, respectively, are very similar, probably indicating a similar distribution around palladium of **L**.

2.2. *Crystal structure for $[Pd(L)_2](CF_3SO_3)_2$ (1)*

Through crystallization from $CHCl_3$/diethyl ether (1 : 1) solution, orange single crystals for **1** (suitable for X-ray diffraction) were obtained, with triclinic space group P(−1). The crystal structure consists of discrete $[Pd(L)_2]^{2+}$ and $CF_3SO_3^-$ anions (figure 1). Table 1 lists some selected bond distances and angles for **1**. The central Pd lies on an inversion center. $[Pd(L)_2]^{2+}$ is typical square planar geometry, coordinated to two pairs of nitrogens and two pairs of oxygens belonging to two **L**. Each ligand is bidentate and uses the pyrazolic nitrogen and oxygen of the alcohol to form two six-membered metalocycle rings with a twist boat conformation. Phenyl rings are on opposite sites of the coordination plane.

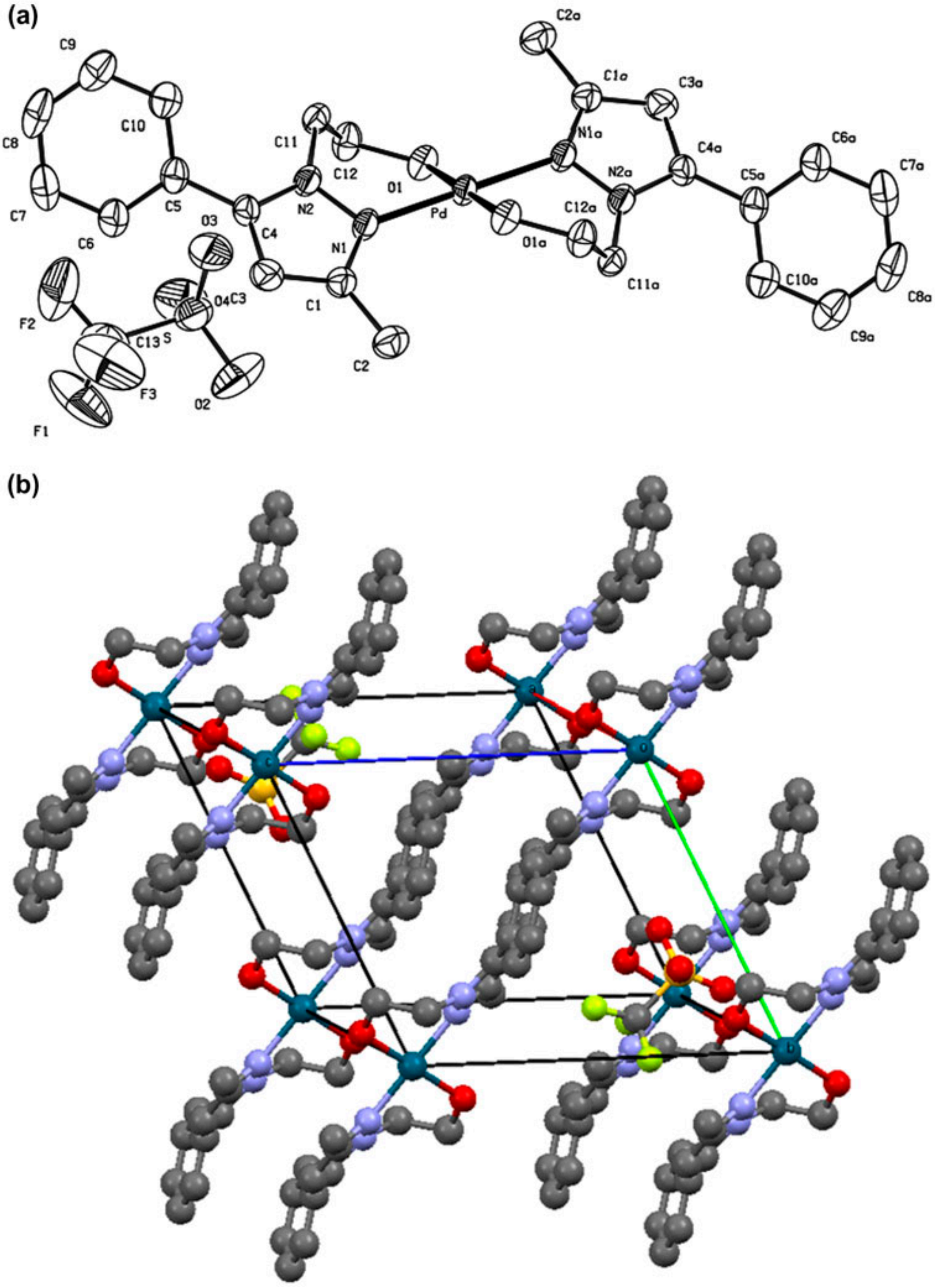


Figure 1. (a) ORTEP diagram of **1** and (b) the cell packing showing an atom labeling scheme. Amplitude displacement ellipsoids (50%) are shown. Hydrogens are omitted for clarity. “a” letters in the atom labels indicate that these atoms are at equivalent position (2 − *x*, −*y*, −*z*).

Table 1. Selected bond lengths (Å) and angles (°) for $[Pd(L)_2](CF_3SO_3)_2$ (**1**). #1 symbol equivalent position (2 − *x*, −*y*, −*z*).

Bond lengths (Å)		Bond angles (°)	
Pd–N(1)	2.003(4)	N(1)–Pd–O(1)	89.23(14)
Pd–O(1)	2.021(3)	N(1)#1–Pd–(1)	90.77(14)
		N(1)#1–Pd–N(1)	180.0(3)
		O(1)–Pd–O(1)#1	180.00(13)

Complexes with a $[Pd(N_{pz})(OH)X_2]$ *core* are not found in literature, but complexes with a $[Pd(N)(OH)X_2]$ *core* are present in 16 complexes [25]. The values of bond distances Pd–N_{pz} [2.003(4) Å] and Pd–OH [2.021(3) Å] are in agreement with the values described in literature: Pd–N_{pz} [1.989–2.042 Å] and Pd–OH [2.019–2.648 Å] [26]. The N(1)–Pd–O(1) bite angle is 89.23(14)°. **L** is not completely planar. The phenyl group is slightly twisted with respect to the pyrazole ring, with an angle of 39.6(3)°. This value is lower than that obtained for *trans*-$[PdCl_2(L)_2]$ [17]. The hydroxyethyl, which is bonded to N1, moves away from the chelating plane giving a torsion angle N1–N2–C11–C12 of 53.5°. This value is lower than that obtained for **R**, probably due to coordination of the −OH group to the metal [17].

2.3. *Extended supramolecular structure for $[Pd(L)_2](CF_3SO_3)_2$ (1)*

The molecules' structural units utilize single/cooperative non-covalent interactions as the driving forces to construct supramolecular architectures with reversible functional properties when they are used in the process of self-assembly [26]. Among all these non-covalent interactions, different kinds of hydrogen bonds and $\pi\cdots\pi$ stacking interactions are the driving forces used for creation of supramolecular frameworks [27].

In **1** ($[Pd(L)_2](CF_3SO_3)_2$) through classical coordinated interactions, one Pd(II) and two chelated **L** generate a complex unit (figure 1). This unit is further linked to two $CF_3SO_3^-$, initially not directly coordinated to Pd, through hydrogen bond bridges ($R_{O1–H10\cdots O2}$ = 1.769(2) Å; $°_{O1–H10\cdots O2}$ = 169.60(3)°) (figure 2). This intermolecular contact is categorized as short/strong (<2.52 Å) [28]. Surprisingly, **1** does not show intermolecular π–π stacking interaction although the angle between the two planes formed by C5–C10 of two asymmetric 1 − *x*, −*y*, −*z* molecules is 0°, confirming a perfect face-to-face interaction between two anti-parallel phenyl rings. The distance between their centroids [7.530(4) Å] is quite large compared to values found in the literature [3.0–4.6 Å] [29].

$CF_3SO_3^-$ in **1**, through cooperative intermolecular interactions between SO_3 ($R_{S–O4\cdots H11}$ = 2.633(2) Å, $°_{S–O4\cdots H11}$ = 140.63(2); $R_{S–O3\cdots H11A}$ = 2.503(3) Å, $°_{S–O3\cdots H11A}$ = 132.65(2); $R_{S–O3\cdots H12}$ = 2.392(3) Å, $°_{S–O3\cdots H12}$ = 133.09(4)), and CF_3 groups ($R_{C13–F3\cdots H6}$ = 2.643 (2) Å, $°_{C13–F3\cdots H6}$ = 137.17(2)) with the alkyl chain of **L** is able to generate a 1-D supramolecular chain along the *a* axis (figure 3). The intermolecular Pd···Pd distance in this undulating 1-D chain is 10.352(2) Å, similar to values described in literature for Pd···Pd intermetallic distances [15].

$CF_3SO_3^-$ anions located in neighboring positions generate a 2-D supramolecular layer [figure 4(a)]. All phenyl groups are located on the external parts of the layer generating important hydrophobic interactions [figure 4(b)]. Among the non-covalent interactions, hydrophobic interactions, usually existing among alkyl chains of biological macromolecules, are difficult to observe from a crystallographic perspective [30].

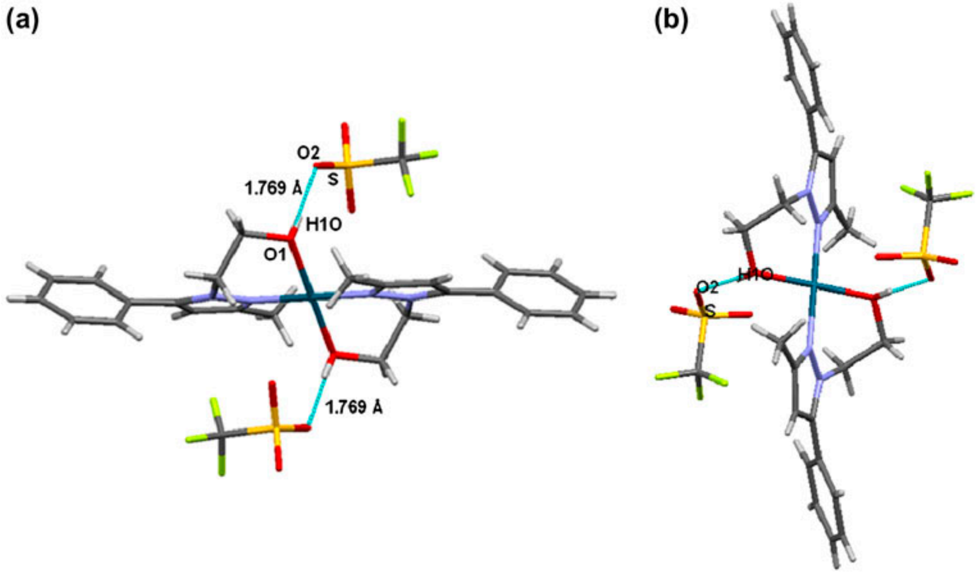


Figure 2. (a) Supramolecular view of **1** and (b) lateral view with intermolecular interactions of $CF_3SO_3^-$ anions.

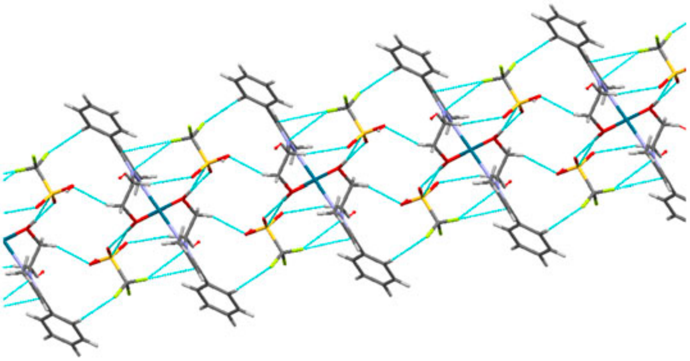


Figure 3. 1-D supramolecular chain stabilized by hydrogen bond interactions between adjacent units of **1**.

3. Conclusion

We have presented the synthesis and characterization of four new complexes $[Pd(L)_2](CF_3SO_3)_2$ (**1**), $[Pd(NO_3)(L)_2](NO_3)$ (**2**), $[Pd(L)_2](NO_3)_2$ (**3**), and $[Pd(C_2O_4)(L)_2]$ (**4**). **1**–**3** are ionic where two of them (**1** and **3**) have $[Pd(L)_2]^{2+}$ as cation with a bidentate **L** (N_{pz}, OH) in *anti* disposition. However, $[Pd(C_2O_4)(L)_2]$ (**4**) is molecular, with a bidentate $C_2O_4^{2-}$ and two *cis* monodentate (N_{pz}) **L**. We have proven the different tendency in the coordinative ability of ($CF_3SO_3^- < NO_3^- < C_2O_4^{2-}$). The denticity of **L** varies from N-monodentate to NO-bidentate, depending on the conditions, thus demonstrating the versatility of **L**.

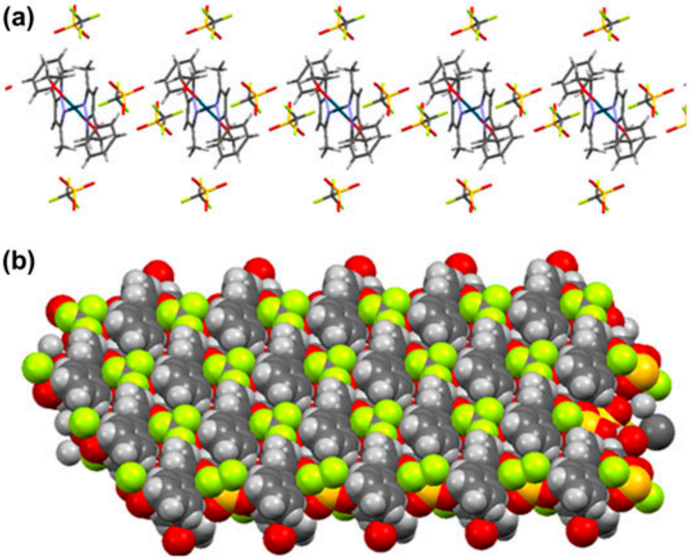


Figure 4. (a) 1-D supramolecular chain stabilized by hydrogen bond interactions between adjacent units and CF_3SO_3 anions. (b) 2-D supramolecular layer view of the self-assembled network of **1**.

Finally, the results of X-ray diffraction analyzes of **1** reveal that the $CF_3SO_3^-$ anion plays a fundamental role in the self-assembly process, generating a 2-D supramolecular layer with different inter- and intramolecular interactions. These new Pd(II) complexes represent a powerful tool for construction of new MOFs.

4. Experimental

4.1. *General details*

All reactions were carried out using a vacuum line and Schlenk techniques. All reagents were commercial grade materials used without further purification. Solvents were dried and distilled by standard methods.

C, H, and N analyzes were carried out by the staff of the Chemical Analyzes Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) with 10^{-3} M of methanol employing a Crison and micro CM 2200 conductimeter. Infrared spectra were acquired on a Perkin–Elmer FT spectrophotometer series 2000 as KBr pellets or polyethylene films from 4000 to 100 cm^{-1} under nitrogen. ^1H and $^{13}C\{^1H\}$ NMR, HSQC, and NOESY spectra were acquired on an NMR-FT Bruker AC-250 MHz spectrometer in $CDCl_3$ solutions at room temperature. Chemical shifts (δ) are given in ppm. Mass spectra [MS(ESI+)] were obtained in methanol with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

The syntheses of 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)ethanol (**L**) and $[PdCl_2(L)_2]$ were carried out according to our previously published methods [17].

4.2. *Synthesis of [Pd(L)$_2$](CF$_3$SO$_3$)$_2$ (1)*

A mixture of *trans*-[PdCl$_2$(L)$_2$] (0.40 g, 0.69 mM) and AgCF$_3$SO$_3$ (0.35 g, 1.38 mM) in dry CH$_3$OH (100 mL) was stirred for 4 h in the dark. The solution was centrifuged and filtered through Celite. The solvent was removed under reduced pressure and the remaining orange solid that appeared was filtered off, washed with diethyl ether (5 mL), and dried in vacuum. Suitable crystals for X-ray study were grown from a CHCl$_3$/diethyl ether (1 : 1) mixture.

Compound **1**: (Yield: 48%). Anal. Calcd for $C_{26}H_{28}S_2N_4O_8F_6Pd$: C, 38.61; H, 3.47; N, 6.93. Found: C, 38.82; H, 3.58; N, 7.05%. MS(ESI+): *m*/*z* (%) = 255 (100, [Pd(L)$_2$]$^{2+}$). Conductivity (Ω^{-1} cm^2 M^{-1}, 1.1 × 10^{-3} M in methanol): 185. IR (KBr, cm^{-1}): 3456 ν(O–H), 3038 ν(C–H)$_{ar}$, 2924, 2853 ν(C–H)$_{al}$, 1558 (ν(C=C), ν(C=N))$_{ar}$, 1499, 1457 (δ(C=C), δ(C=N))$_{ar}$, 1259, 1163 ν(CF$_3$SO$_3$), 1030 δ(C–H)$_{ar,\ ip}$, 769, 700 δ(C–H)$_{ar,\ oop}$; (polyethylene, cm^{-1}): 513, 475 ν(Pd–N), ν(Pd–O). ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.49 [10H, s, H_{ph}], 6.25 [2H, s, CH_{pz}], 5.15 [br, N_{pz}CH$_2$CH$_2$OH], 4.94 [4H, t, ^3J = 5.1 Hz, N_{pz}CH_2CH$_2$OH], 3.95 [4H, t, ^3J = 5.1 Hz, N_{pz}CH$_2$CH_2OH], 2.83 [6H, s, CH_3]. ^{13}C{^{1}H} NMR (CDCl$_3$, 250 MHz) δ: 130.7–128.7 (C_{ph}), 109.0 (CH$_{pz}$), 62.1 (N_{pz}CH$_2$$CH_2$OH), 51.8 ($N_{pz}$$CH_2CH_2$OH), 14.7 ($CH_3$).

4.3. *Synthesis of [Pd(NO$_3$)(L)$_2$](NO$_3$) (2) and [Pd(L)$_2$](NO$_3$)$_2$ (3)*

A mixture of *trans*-[PdCl$_2$(L)$_2$] (0.40 g, 0.69 mM) and AgNO$_3$ (0.23 g, 1.38 mM) in dry CH$_3$OH (100 mL) was stirred for 5 h in the dark. The solution was centrifuged and filtered through Celite. The solvent was removed under reduced pressure and the remaining yellow solid that appeared was filtered off, washed with diethyl ether (5 mL), and dried in vacuum.

Compound **2** + **3**: (Yield: 62%). Anal. Calcd for $C_{24}H_{28}N_6O_8Pd$: C, 45.43; H, 4.42; N, 13.25. Found: C, 45.26; H, 4.58; N, 13.45%. MS(ESI+): *m*/*z* (%) = 573 (48, [Pd(NO$_3$)(L)$_2$]$^+$), 255 (100, [Pd(L)$_2$]$^{2+}$). Conductivity (Ω^{-1} cm^2 M^{-1}, 9.3 × 10^{-4} M in methanol): 140. IR (KBr, cm^{-1}): 3478, 3374 ν(O–H), 3095 ν(C–H)$_{ar}$, 2926 ν(C–H)$_{al}$, 1765 $\nu_1 + \nu_3$(NO$_3$)$_{ionic}$, 1739, 1712 $\nu_1 + \nu_3$(NO$_3$)$_{bidentate}$, 1552 (ν(C=C), ν(C=N))$_{ar}$, 1498, 1456 (δ(C=C), δ(C=N))$_{ar}$, 1384 ν_{as}(NO$_3$), 1074 δ(C–H)$_{ar,\ ip}$, 770, 701 δ(C–H)$_{ar,\ oop}$; (polyethylene, cm^{-1}): 502, 468 ν(Pd–N), ν(Pd–O).

Compound **2**: ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.49–7.40 [10H, m, H_{ph}], 6.33 [2H, s, CH_{pz}], 4.40 [4H, t, ^3J = 4.5 Hz, N_{pz}–CH_2–CH$_2$–OH], 3.99 [4H, t, ^3J = 4.5 Hz, N_{pz}–CH$_2$–CH_2–OH], 2.49 [6H, s, CH_3]. ^{13}C{^{1}H} NMR (CDCl$_3$, 250 MHz) δ: 140.1–121.0 (C_{ph}), 103.8 (CH$_{pz}$), 65.6 (N_{pz}-CH$_2$–CH$_2$–OH), 50.6 (N_{pz}–CH$_2$–CH$_2$–OH), 19.5 (CH$_3$).

Compound **3**: ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.53 [10H, s, H_{ph}], 6.20 [2H, s, CH_{pz}], 4.90 [4H, t, ^3J = 5.3 Hz, N_{pz}CH_2CH$_2$OH], 4.75 [br, N_{pz}CH$_2$CH$_2$OH], 4.00 [4H, t, ^3J = 5.3 Hz, N_{pz}CH$_2$CH_2OH], 2.84 [6H, s, CH_3]. ^{13}C{^{1}H} NMR (CDCl$_3$, 250 MHz) δ: 140.1–121.0 (C_{ph}), 107.4 (CH$_{pz}$), 62.4 (N_{pz}CH$_2$$CH_2$OH), 51.4 ($N_{pz}$$CH_2CH_2$OH), 12.7 ($CH_3$).

4.4. *Synthesis of [Pd(C$_2$O$_4$)(L)$_2$] (4)*

A mixture of *trans*-[PdCl$_2$(L)$_2$] (0.10 g, 0.17 mM), Ag$_2$SO$_4$ (0.054 g, 0.17 mM), and (NH$_4$)$_2$C$_2$O$_4$ (0.030 g, 0.24 mM) in dry CH$_3$CN (50 mL) was stirred for 14 h in the dark. The solution was centrifuged and filtered through Celite. The solvent was evaporated and the resulting residue was extracted with 5 mL of CH$_2$Cl$_2$. The yellow solid was precipitated with hexane, filtered, washed with diethyl ether (5 mL), and dried in vacuum.

Compound **4**: (Yield: 45%). Anal. Calcd for $C_{26}H_{28}N_4O_6Pd$: C, 52.77; H, 4.01; N, 9.36. Found: C, 51.92; H, 4.22; N, 9.39%. MS(ESI+): *m*/*z* (%) = 622 (100, $[Pd(C_2O_4)(L)_2 + Na]^+$), 600 (32, $[Pd(C_2O_4)(L)_2 + H]^+$). Conductivity (Ω^{-1} cm^2 M^{-1}, 1.0×10^{-3} M in methanol): 21. IR (KBr, cm^{-1}): 3385 ν(O–H), 3027 ν(C–H)$_{ar}$, 2921, 2875 ν(C–H)$_{al}$, 1654 ν(C=O)$_{as}$, 1589 (ν(C=C), ν(C=N))$_{ar}$, 1557 ν(C=O)$_s$, 1468, 1452 (δ(C=C), δ(C=N))$_{ar}$, 1069 δ(C–H)$_{ar,\ ip}$, 761, 699 δ(C–H)$_{ar,\ oop}$; (polyethylene, cm^{-1}): 518, 472 ν(Pd–N), ν(Pd–O). ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.52–7.30 [10H, s, H_{ph}], 6.32 [2H, s, CH_{pz}], 4.57 [4H, t, ^3J = 4.1 Hz, $N_{pz}CH_2CH_2OH$], 3.84 [4H, t, ^3J = 4.1 Hz, $N_{pz}CH_2CH_2OH$], 2.65 [6H, s, CH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$, 250 MHz) δ: 166.4 (C_2O_4), 145.2–127.8 (C_{ph}), 101.2 (CH_{pz}), 64.2 ($N_{pz}CH_2CH_2OH$), 53.7 ($N_{pz}CH_2CH_2OH$), 18.6 (CH_3).

4.5. *X-ray crystal structure analyzes of $[Pd(L)_2](CF_3SO_3)_2$ (1)*

Suitable crystals for X-ray diffraction of $[Pd(L)_2](CF_3SO_3)_2$ (**1**) were obtained through crystallization from a $CHCl_3$/diethyl ether (1 : 1) mixture. Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer using the $\omega/2\theta$ scan technique. Intensities were recorded with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Unit cell parameters were determined from automatic centering of 25 reflections (12° < θ < 21°); 4702 reflections were measured in the range 2.50° ≤ θ ≤ 29.97° with 4645 non-equivalent by symmetry (*R* int (on *I*) = 0.023). 2998 reflections were assumed as observed applying

Table 2. Crystallographic data for $[Pd(L)_2](CF_3SO_3)_2$ (**1**).

Molecular formula	$C_{26}H_{28}F_6S_2N_4O_8Pd$
Formula weight	809.04
Temperature (K)	293(2)
Wavelength (Å)	0.71069
System, space group	Triclinic, *P*(−1)
Unit cell dimensions	
a (Å)	8.896(5)
b (Å)	9.367(8)
c (Å)	11.266(7)
α (°)	110.61(6)
β (°)	92.12(5)
γ (°)	111.00(6)
U (Å^3)	805.9(10)
Z	1
D_{Calcd} (g cm^{-3})	1.667
μ (mm^{-1})	0.793
F (0 0 0)	408
Crystal size (mm^3)	0.2 × 0.1 × 0.1
hkl ranges	$-12 \le h \le 12$, $-13 \le k \le 7$, $-8 \le l \le 15$
2θ Range (°)	2.50–29.97
Reflections collected/unique [R_{int}]	4702/4645 [*R*(int) = 0.0236]
Completeness to θ (%)	98.9
Absorption correction	None
Data/restraints/parameters	4645/0/214
Goodness-of-fit on F^2	1.012
Final *R* indices [I > 2 $\sigma(I)$]	$R1 = 0.0601$, $wR_2 = 0.1147$
R indices (all data)	$R1 = 0.1443$, $wR_2 = 0.1369$
Largest diff. peak and hole (e Å^{-3})	0.739 and −0.810

the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made. The structure was solved by direct methods, using the SHELXS computer program (SHELXS-97) [31] and refined by full-matrix least-squares, with the SHELXL-97 computer program [32], using 4645 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w \| Fo |^2 - | Fc |^2 |^2$, where $w = [\sigma^2(I) + (0.0558P)^2 + 0.0338P]^{-1}$ and $P = (| Fo |^2 + 2 | Fc |^2/3$. All hydrogens were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which it is linked. The final $R(F)$ factor and $R(F^2)$ values as well as the number of parameters and other details concerning the refinement of the crystal structure are given in table 2.

Supplementary material

Crystallographic data for the structure in this article have been deposited with the Cambridge Crystallographic Data Center; CCDC-923550 for $[Pd(L)_2](CF_3SO_3)_2$ (**1**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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