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Synthesis and characterization of Pd(II), Pt(II), Cu(I), Ag(I) and Cu(II) complexes with N,O-hybrid pyrazole ligand

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ABSTRACT

The coordination behavior of *N,O*-hybrid pyrazole-based metal-organic frameworks are described. 2-(3,5-pyridyl-1*H*-pyrazol-1-yl)ethanol (**L**) and its Pd(II), Pt(II), Cu(I), Ag(I) and Cu(II) complexes with different anions have been synthesized and characterized by elemental analysis, conductivity, mass spectrometry, IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectroscopies. Complex **1** was also characterized by single crystal X-ray diffraction. For complex **7** has also been possible to perform the UV-Vis and magnetic susceptibility measurements. All complexes are monomers, except the complexes obtained by reaction of the ligand (**L**) with $\text{M}(\text{MeCO}_2)_2$ ($\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{II})$) or CuBr_2 , which are dimers.

1. Introduction

In recent decades, the design of hybrid functional materials has been receiving special attention because of their potential applications in different areas [1]. A well-known approach for the preparations of such systems is the synthesis of metal-organic frameworks where transition metal ions and nitrogen containing heterocyclic ligands have proven to be useful for the construction of solid-state architectures [2]. One of the most studied ligands in coordination chemistry with nitrogen heterocyclic structure is the pyrazole ring [3]. Pyrazole-based ligands have been successfully used for constructing a wide array of architectures with different properties, such as magnetism, conductivity, catalytic activity, luminescence and porosity. Those frameworks could find uses in different applications, such as gas storage, separation, drug delivery, chemical sensing and optoelectronics [4]. The increasing need for evolved systems and demanding assemblies has led to the emergence of hetero-donating functions [5], among which *N,O*-hybrid ligands such as *N*-hydroxyalkylpyrazole ligands are smart candidates [6]. In addition, complexes having *N,O*-donor atoms are very important because of their significant biomedical properties such as antibacterial [7], antifungal [8], anticancer [9] and herbicidal activity [10].

In this context, we have extensively studied the synthesis and coordination of the *N*-hydroxyalkylpyrazole derived ligands, in particular *N*-hydroxyalkylpyrazole [11], *N*-hydroxyalkyl-3,5-dimethylpyrazole [12], *N*-hydroxyalkyl-3,5-diphenylpyrazole [13], *N*-hydroxyalkyl-3-methyl-5-phenylpyrazole [14], *N*-hydroxyalkyl-5-methyl-3-phenylpyrazole [14], *N*-hydroxyalkyl-3-phenyl-5-pyridylpyrazole [15], *N*-hydroxyalkyl-5-phenyl-3-pyridylpyrazole [15] and *N*-hydroxyalkyl-3-pyridyn-5-trifluoromethylpyrazole [16], as well as studied their reactivity towards different

transition metal ions like Pd(II) [12a,13,17], Pt(II) [14,18], Zn(II) [5,12a], Cd(II) [6], Hg(II) [6] and Cu(II) [12a].

As a continuation of these studies, in this paper we present the synthesis and characterization of a *N*-hydroxyalkylpyrazole derived ligand and assayed its reactions with different transition metals. In particular, we present the reaction of the 2-(3,5-pyridyl-1*H*-pyrazol-1-yl)ethanol (**L**) with [MCl₂(CH₃CN)₂] (M = Pd(II) (**1**), Pt(II) (**2**)), M(MeCO₂)₂ (M = Pd(II) (**3**), Pt(II) (**4**)), CuBr (**5**), Ag(CF₃SO₃) (**6**) and CuBr₂ (**7**). Complexes **1-7** were characterized by elemental analyses, mass spectrometry, conductivity measurements and IR spectroscopy, and for compound **1** X-ray crystal structure is presented. Moreover, complexes **1-6** were also characterized by 1D and 2D NMR spectroscopies. For compound **7**, the UV-Vis and magnetic properties were also studied.

2. Results and discussion

2.1. Synthesis and characterization of the ligand

The 2-(3,5-pyridyl-1*H*-pyrazol-1-yl)ethanol (**L**) ligand, was obtained from the precursor bis(2-pyridin-2-yl)propane-1,3-dione [19]. The β-diketone was synthesized following a Claisen condensation of the methyl-2-pyridinecarboxylate and 2-acetylpyridine, using NaOH as base and dry toluene as solvent. Treatment of β-diketone with 2-hydroxyethylhydrazine in ethanol at room temperature gave the **L** ligand in 83% yield.

The synthesized **L** ligand was characterized by elemental analyses, infrared spectrum, ¹H and ¹³C{¹H} NMR and electrospray mass spectrometry (ESI(+)-MS). For the assignment of the ¹³C{¹H} NMR spectrum, we have employed HSQC technique.

The ^1H NMR spectrum display the *ortho*-pyridinic hydrogen (Scheme 1) at $\delta = 8.46$ and 8.41 ppm ($^3J = 5.8$ Hz, $^3J = 4.3$ Hz) as doublets. The pyrazolic hydrogen was observed at $\delta = 7.05$ ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presents the signal at $\delta = 104.9$ ppm attributable to the CH of the pyrazole [20]. In the mass spectrum (ESI(+)-MS), one signal appears at 267 (100%), attributable to $[\text{L}+\text{H}]^+$.

2.2. Synthesis and characterization of the $[\text{MCl}_2(\text{L})]$ (M = Pd(II) (**1**) and Pt(II) (**2**))

The reaction of the ligand **L** with $[\text{MCl}_2(\text{CH}_3\text{CN})_2]$ (M = Pd(II) (**1**), Pt(II) (**2**)), in an acetonitrile solution and in the 1M:1L ratio is presented in Scheme 1. The elemental analyses are consistent with the formula $[\text{MCl}_2(\text{L})]$ for the two compounds. The positive ionization spectra (ESI(+)-MS) of complexes **1** and **2**, give a peaks with m/z values of 408 (100%) (**1**) and 497 (100%) (**2**), attributable to $[\text{MCl}(\text{L})]^+$. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones. The molar conductivity values of 10^{-3} M samples, in DMSO are in agreement with the presence of non-electrolyte complexes [21].

The IR spectra in the range of $4000\text{-}400\text{ cm}^{-1}$, show that the ligand is coordinated to Pd(II) or Pt(II) (Figure S1). The most important bands of the pyridine and pyrazole groups $[\nu(\text{C}=\text{C}), (\text{C}=\text{N})]_{\text{ar}}$ and $[\delta(\text{C}=\text{C}), (\text{C}=\text{N})]_{\text{ar}}$ increase their frequency, whereas $\delta(\text{C}-\text{H})_{\text{oop}}$ band decrease its frequency when it is part of the complexes. The IR spectra of the complexes **1** and **2** show an important shift of the $\nu(\text{O}-\text{H})$ band at 3431 (**1**) and 3395 (**2**) cm^{-1} [20]. The IR spectra of both compounds, between 600 and 100 cm^{-1} have been also recorded (Figure S2). The complexes **1** and **2** show the $\nu(\text{M}-\text{N})$ band (440 (**1**) and 425 (**2**) cm^{-1}). Moreover, the spectra of the complexes display two bands (348, 326 (**1**) and 335, 318 (**2**) cm^{-1}), corresponding to $\nu(\text{M}-\text{Cl})$, which are typical of compounds with a *cis* disposition of the chlorine ligands around Pd(II) or Pt(II) [22].

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{195}Pt NMR spectra of the compounds **1** and **2** were recorded in $\text{DMSO-}d_6$, due to the low solubility of these complexes in other deuterated solvents. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the proposed structure and proved the coordination of the ligand (**L**) to the metal atoms.

In the ^1H NMR spectra, characteristic signals for *ortho*-pyridinic hydrogens are observed between 9.40 and 8.77 ppm as doublets, with ^1H - ^1H coupling constants between 5.7 and 5.3 Hz. The values of the field shift and coupling constants are of the same order of those obtained for other complexes with *N*-alkylpyridylpyrazole [23] and *N*-hydroxyalkylpyridylpyrazole [15] ligands, but display higher field shift than $[\text{PdCl}_2(\text{L}')]$, $[\text{Pd}(\text{L}')_2](\text{BF}_4)_2$ and $[\text{PdCl}(\text{L}')](\text{BF}_4)$ ($\text{L}' = 2$ -(3-pyridin-2-yl)-5-trifluoromethyl-1*H*-pyrazol-1-yl)ethanol. This fact is probably due to the presence of the trifluoromethyl group [24].

Other observed signals, are those attributable to H_{pz} , which appear at 7.80 (**1**) and 7.82 (**2**) ppm. These values show a large displacement compared to the same signal for the free ligand (7.05 ppm). The values are comparable to those observed for other complexes that contain *N*-hydroxyalkylpyridylpyrazole ligands [15].

The ethylene protons of the $\text{N-CH}_2\text{-CH}_2\text{-OH}$ chains appear as two triplets at 5.30, 3.75 (**1**) ppm and 5.41, 3.71 (**2**) ppm, with ^1H - ^1H coupling constants between 5.5 and 4.8 Hz. In these complexes, the signal attributable to a proton of the alcohol group (*O-H*) appears as triplet at 4.73 (**1**) ppm ($^3J = 5.6$ Hz) and 4.72 (**2**) ppm ($^3J = 4.8$ Hz).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, characteristic signals for the *ortho*-pyridinic carbons are observed between 149.3 and 148.7 ppm. Other observed signals are those attributable to C_{pz} , which appear to 105.9 (**1**) and 104.9 (**2**) ppm. The carbons of the $\text{N-CH}_2\text{-CH}_2\text{-OH}$ chain appear between 60.6 and 53.0 ppm.

The ^{195}Pt -NMR signal of **2** is observed at -2184 ppm as a broad one. This value indicates the existence of the complex *cis*- PtN_2Cl_2 chromophores [25]. The value is in accordance with data published in the literature for $[\text{PtCl}_2(\text{L})]$ ($\text{L} = 2$ -[5-phenyl-1-(3,6,9-trioxodecane)-1*H*-pyrazol-3-yl]pyridine, 1-[2-diethylamino)ethyl -3,5-dimethylpyrazole, 1-[2-dioctylamino)ethyl-3,5-dimethylpyrazole and 1,8-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-3,6-dioxaoctane [26].

2.2.1 Crystal and Molecular Structure of complex *cis*- $[\text{PdCl}_2(\text{L})]$ (**1**)

The crystal quality was poor but an X-ray diffraction analysis was carried out and clearly revealed the structure of the complex. The crystal structure of compound **1** consist of monomeric *cis*- $[\text{PdCl}_2(\text{L})]$ molecules (Fig. 1). Selected parameters and details concerning the refinement of the crystal structure are gathered in Table 1 and bond distances and angles are given in Table 2. The metal atom is surrounded by a *core* composed of one **L** coordinated *via* one pyrazole nitrogen and one pyridine nitrogen, finishing the coordination of the metal with two chlorine ligands in a *cis* disposition (Fig. 1). **L** behaves as a chelated bidentate ligand (bite angle of $79.5(2)^\circ$) forming a five-membered metallocycle, which has a planar configuration.

The $[\text{PdCl}_2(\text{N}_{\text{pz}})(\text{N}_{\text{py}})]$ *core* (containing terminal chlorine atoms in a *cis* disposition) is found in ten complexes described in the literature.²⁷ The bond distances Pd- N_{py} (2.043(6) Å, where py =pyridine) are in the same order as Pd- N_{pz} (2.061(5) Å, where pz = pyrazole). Both distances are consistent with other palladium complexes containing analogous ligands (2.020-2.125 Å) and (1.968-2.070 Å), respectively.²⁷ The Pd-Cl bond lengths (2.270(2) and 2.281(2) Å) can be regarded as normal compared with the distances found in the literature (2.269-2.307 Å).²⁷

It is important to mention that **L** has non-planar disposition. The coordinated pyridyl group is slightly twisted with respect to the pyrazole ring, the *py-pz* dihedral angle 2.4(3)°, whereas in the more twisted non-coordinated pyridyl group, the *py-pz* angle is 37.2(3)°. The angles dihedrals are comparable to the compound [PtCl₂(L)] (6.5°, 35.1°). The hydroxyethyl group, which is bonded to N(3), moves away from the chelating plane giving a torsion angle N2-N3-C14-C15 of 86.15°.

We have investigated the extended structure and the self-assembly pattern of [PdCl₂(L)] (**1**) units in the crystal through intermolecular C–H···Cl bonding interactions (2.699 Å and 162.5°). This results in the generation of one-dimensional chains in the crystal structure along the crystallographic [110] direction (Figure 2). The intermolecular contacts can be considered as “weak” on the basis of the contact distances and angles.²⁸ In addition, the distance between adjacent Pd atoms is 9.048(3) Å. The potentially active *H* atom of the alcohol group of the **L** ligand is engaged in intramolecular bond with the *N* atom of the pyridine group, which acts as the receptor for this kind of interaction. Each [PdCl₂(L)] unit present one O–H10···N4 intramolecular bonding (2.220(4) Å and 126.6°). In this structure, it is important to take into account that these one-dimensional chains are arranged in such a way that chains in close-contact are anti parallel (Figure 3).

2.3. Synthesis and characterization of the [M(MeCO₂)(L)]₂(MeCO₂)₂ (M = Pd(II) (3) and Pt(II) (4))

The reaction of the ligand **L** with [M(MeCO₂)₂] (M = Pd(II), Pt(II)) in a CH₂Cl₂ solvent and in the 1M:1L ratio, gave rise to dimeric complexes [M(MeCO₂)(L)]₂(MeCO₂)₂ (M = Pd(II) (**3**), Pt(II) (**4**)) (Scheme 1). The elemental analysis are consistent with the formula [M(MeCO₂)₂(L)] for the two compounds. The

positive ionization spectra (ESI(+)-MS) of complexes **3** and **4**, give peaks with m/z values at 431 (100%) (**3**), and 520 (100%) (**4**), attributable to $[M(\text{MeCO}_2)(\text{L})]^+$. The molecular peaks of the cations are observed with the same isotope distribution of the theoretical ones. The molar conductivity values of 10^{-3} M samples in methanol are in agreement with the presence of 1:2 electrolyte compounds [21]. The IR spectra of complexes **3** and **4** in the range 4000-400 cm^{-1} , display absorptions of *N*-hydroxyalkylpyridylpyrazole derived ligands [15]. For the two compounds, the most characteristic bands are those attributable to the alcohol, pyridyl and pyrazole groups: $\nu(\text{O-H})$ 3382, 3295 (**3**) and 3342, 3281 (**4**) cm^{-1} , $[\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})]_{\text{ar}}$ 1573 (**3**) and 1562 (**4**) cm^{-1} , $[\delta(\text{C}=\text{C}), \delta(\text{C}=\text{N})]_{\text{ar}}$ 1452 (**3**) and 1426 (**4**) cm^{-1} , $\delta(\text{C-H})_{\text{oop}}$ 773, 704 (**3**) and 762, 694 (**4**) cm^{-1} .²⁰ Moreover, for these two compounds bands appear at 1636, 1612, 1590 (**3**) and 1624, 1594, 1572 (**4**) cm^{-1} , that correspond to $\nu_{\text{as}}(\text{COO})$ and also at 1465, 1447, 1437 (**3**) cm^{-1} , and 1453, 1432, 1405 (**4**) cm^{-1} , corresponding to $\nu_{\text{s}}(\text{COO})$. These complexes show a complicated spectra in this region, separate by $\Delta = 195\text{-}125$ (**3**) and $171\text{-}119$ (**4**) cm^{-1} . These Δ values are consistent with the presence of both ionic and coordinated acetate groups, pointing out the presence of dimeric species [22,29]. IR spectra of complexes **3** and **4** in the 600-100 cm^{-1} region were also studied. The presence of bands at 418 (**3**) and 404 (**4**) cm^{-1} , assigned to $\nu(\text{M-N})$, confirm the coordination of the *N* atoms of the organic ligand to the metallic atom.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for complexes **3** and **4** recorded in CDCl_3 solution, show the signal of coordinated ligand (**L**) and acetate groups.

In the ^1H NMR spectra, the signals of *ortho*-pyridinic hydrogens are observed between 8.62 and 8.03 ppm as doublets, with $^1\text{H}\text{-}^1\text{H}$ coupling constants between 5.5 and 4.1 Hz (Figure S3). Other observed signals are attributable to H_{pz} at 7.21 (**3**) and 6.42 (**4**) ppm. The ethylene protons of the $\text{N-CH}_2\text{-CH}_2\text{-OH}$ chains appear as two triplets at

4.86, 3.77 (**3**), and 4.52, 3.54 (**4**) ppm, with ^1H - ^1H coupling constants between 5.4 and 4.9 Hz. In these complexes the signal attributable to proton of the alcohol group (*O-H*) appears as a broad signal at 4.22 (**3**) and 4.02 (**4**) ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra display the signals C_{pz} at 105.5, 104.3 (**3**), and 104.7, 102.1 (**4**) ppm. Furthermore, the signals of the $\text{N-CH}_2\text{-CH}_2\text{-OH}$ chains between 66.8 and 51.8 ppm.

The methyl of the acetate groups display two signals in the ^1H NMR spectra and in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. These signals appear at 2.93, 1.91 and 24.1, 23.5 (**3**) ppm, and 1.89, 1.71 and 21.9, 20.3 (**4**) ppm. The presence of two signals for each type of proton or carbon, could indicate the presence of two types of acetates: bridged (2.93, 1.89 ppm and 24.1, 21.9 ppm) and ionic (1.91, 1.71 ppm and 23.5, 20.3 ppm). The same signals are observed for complexes of Pd(II) and Pt(II) with *N*-polyetherpyridylpyrazole derived ligands [24].

The ^{195}Pt -NMR signal of **4** displays one signal at -3385 ppm. The presence of only one resonance is consistent with the equivalence of both platinum atoms in their composition [30]. Unfortunately, no suitable crystals were obtained for complexes **3** and **4**.

2.4. Synthesis and characterization of the Cu(I), Ag(I) and Cu(II) complexes

The reaction of the ligand **L** with CuBr or AgCF₃SO₃ in ethanol with 1M:2L ratio, yielded the compounds [Cu(L)₂]Br (**5**) and [Ag(L)₂](CF₃SO₃) (**6**) (Scheme 1). The synthesis of **6** was done protected from light radiation, and this compound decomposes slowly in solid or solution. The elemental analysis for the two compounds is in agreement with the proposed formulas. The positive ionization spectra (ESI(+)-MS) of complexes **5** and **6**, give peaks with *m/z* values of 596 (100%) and 640 (100%), respectively attributable to [M(L)₂]⁺ (Figure S4). The molar conductivity of 10⁻³ M

solutions of compounds **5** and **6** in CH₃OH and DMSO, respectively show values of 90 and 62 Ω⁻¹cm²mol⁻¹, respectively. Those values are attributable to a 1:1 electrolyte [21]. The IR spectra of the two compounds in the range of 4000-400 cm⁻¹, support that the ligand **L** is coordinated to the metallic center (Figure S5). The complex **6** shows signals at 1259 and 1166 cm⁻¹, attributable to ν(C-F) and ν(S-O), respectively (Figure S6) [31]. The ¹H NMR signals of *ortho*-pyridinic hydrogens appear at higher fields respect to the free ligand 8.67, 8.62 (**5**) and 8.57, 8.46 (**6**) ppm, and the signals of N-CH₂-CH₂-OH chain also appear at higher fields respect to the free ligand 4.54, 4.02 (**5**) and 4.42, 3.84 (**6**) ppm. The signals in the ¹³C{¹H} NMR spectra, appear at lower fields than for the free ligand: [C_{ortho/ortho'}: 158.5, 153.2 (**5**) and 151.5, 151.1 (**6**) ppm; C_{pz}: 108.2 (**5**) and 106.4 (**6**) ppm (Figure S7). It is important to highlight that the NMR spectra of complexes **5** and **6** are very similar, so probably the two ligands in these complexes are disposed in a similar distribution around the metallic center.

Finally, the reaction of the ligand **L** with CuBr₂·H₂O in ethanol using 1:1 M/L ratio led to the compound [CuBr(L)]₂Br₂ (**7**) (Scheme 1). The elemental analysis is consistent with the proposed formula. The ESI(+)-MS of **7**, display a peak with *m/z* value of 410 (100%), attributable to [CuBr(L)]⁺. Moreover, the molar conductivity value in CH₃OH (198 Ω⁻¹cm²mol⁻¹) for **7** is in agreement with the presence of 1:1 electrolyte compound [21]. The IR spectrum of **7** displays absorptions of 2-(3,5-pyridyl-1*H*-pyrazol-1-yl)ethanol (**L**) ligand. The most characteristic bands are ν(O-H) at 3299 cm⁻¹, [ν(C=C), ν(C=N)]_{ar} between 1611-1568 cm⁻¹ and δ(C-H)_{oop} at 785 cm⁻¹ [20]. The IR spectrum in the region 600-100 cm⁻¹ was also recorded. The bromide complex show one band at 304 cm⁻¹ attributable to ν(Cu-Br) absorption. The ν(Pd-N) absorption band appears at 420 cm⁻¹, in agreement with available data [32]. The electronic spectrum of this compound, exhibit one broad band at 582 nm (ε = 35 mol⁻¹cm⁻¹) in 10⁻² M

methanolic solution. This result did not allow us to infer the geometry of the metal center [33] and another band is observed at 320 nm, which correspond to L → M charge transfer transition between stacked aromatic rings in the complex [34]. The magnetic moment (BM) value was obtained at room temperature and showed a magnetic moment of 1.80 BM, which is in the range of 1.75-2.20 BM, consistent with that present in Cu(II) compounds without interaction Cu...Cu [35].

3. Conclusion

We have presented the reaction of the ligand 2-(3,5-pyridyl-1*H*-pyrazol-1-yl)ethanol (**L**), towards [MCl₂(CH₃CN)₂] (M = Pd(II) (**1**), Pt(II) (**2**)), [M(MeCO₂)₂] (M = Pd(II) (**3**), Pt(II) (**4**)), CuBr (**5**), Ag(CF₃SO₃) (**6**) and CuBr₂ (**7**). The study of the coordination chemistry behavior of this **L** ligand with different transition metals, revealed the formation of monomers [MCl₂(L)] (M = Pd(II) (**1**), Pt(II) (**2**)), [Cu(L)₂]Br (**5**) and [Ag(L₂)](CF₃SO₃) (**6**) and dimers [M(MeCO₂)(L)]₂(MeCO₂)₂ (M = Pd(II) (**3**), Pt(II) (**4**)), and [CuBr(L)]₂Br₂ (**7**) complexes. All new complexes were characterized by analytical and spectroscopic techniques.

This kind of hybrid *N*-ethanol-3,5-dipyridylpyrazole ligand is a potential agent in supramolecular crystal engineering due to the different bonding properties of the heteroatoms (*N* vs. *O*) present in the structure of the ligand.

4. Experimental

4.1. General methods

All reactions were performed under a nitrogen atmosphere with the use of vacuum line and standard Schlenk techniques. All reagents were **commercially available** and were used without further purification. All solvents were dried and distilled under N₂ by standard methods prior to use.

Elemental analyses (C, H, N) were carried out by the staff of the Chemical Analysis Services of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at 25.0 ± 0.1 °C in 10^{-3} M in DMSO or methanol solvents, employing CyberScan CON 500 (Euthech Instruments) conductimeter. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. Infrared spectra were recorded from KBr disks or polyethylene films on a Perkin-Elmer 2000 spectrometer in the region 4000 - 400 cm^{-1} under a nitrogen atmosphere. The ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR and HMQC spectra were run on a NMR-FT Bruker 250 MHz spectrometer in $\text{DMSO-}d^6$ or CDCl_3 solutions at room temperature. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR were recorded at 298 K in $\text{DMSO-}d^6$ solutions and at 77.42 MHz on a DPX-360 MHz Bruker spectrometer using aqueous solutions of $[\text{PtCl}_6]^{2-}$ (0 ppm) as an external reference, with delay times of 0.01 s. Chemical shifts (δ) are given in ppm. Electronic spectra in solution were run on a Kontron-Uvikon 860 in methanol, between 800 and 350 nm. Magnetic susceptibility measurements were performed on polycrystalline samples with a Quantum Design susceptometer in the range 2-300 K under magnetic fields of 0.3 T. Diamagnetic corrections were estimated from Pascal tables.

Synthesis of bis(2-pyridin-2-yl)propane-1,3-dione has been previously reported in the literature [19]. Samples of $[\text{MCl}_2(\text{CH}_3\text{CN})_2]$ ($\text{M} = \text{Pd(II)}, \text{Pt(II)}$) were prepared as described in the literature [36,37].

4.2. Synthesis of the ligand 2-(3,5-pyridyl-1H-pyrazol-1-yl)ethanol (L)

Bis(2-pyridin-2-yl)propane-1,3-dione (1.10 mmol, 0.25 g) was dissolved in ethanol (25 mL). To this solution, 2-hydroxyethylhydrazine (1.30 mmol, 0.10 g) was added, and the mixture was stirred for 6 h at room temperature. After removing the solvent under

vacuum, the product was extracted from the oily residue with $\text{H}_2\text{O}/\text{CHCl}_3$ (1/1). The collected organic layers have been dried with anhydrous Na_2SO_4 and have been removed under vacuum. Purification was done by silica column chromatography using ethyl acetate. The ligand was obtained as a white solid.

L: (Yield: 83%), mp. 30-35 °C. Anal. Calc. for: $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}$ (266.30 amu): C, 67.65; H, 5.30; N, 21.04. Found: C, 67.56; H, 5.37; N, 21.34%. IR (NaCl, cm^{-1}): 3282 $\nu(\text{O-H})$, 3050 $\nu(\text{C-H})_{\text{ar}}$, 2928-2859 $\nu(\text{C-H})_{\text{al}}$, 1591-1569 ($\nu(\text{C=C})$, $\nu(\text{C=N})_{\text{ar}}$), 1484 ($\delta(\text{C=C})$, $\delta(\text{C=N})_{\text{ar}}$), 1098-1086 $\delta(\text{C-H})_{\text{ar, ip}}$, 764, 678 $\delta(\text{C-H})_{\text{ar, oop}}$. ^1H NMR (CDCl_3 solution, 250 MHz, 298 K): 8.46/8.41 [1H/1H, d, $^3J = 5.8$ Hz, $^3J = 4.3$ Hz, $H_{\text{ortho}}/H_{\text{ortho}'}$], 8.16/7.99 [1H/1H, t, $^3J = 7.8$ Hz, $^3J = 6.9$ Hz, $H_{\text{para}}/H_{\text{para}'}$], 7.92/7.88 [1H/1H, d, $^3J = 7.5$ Hz, $^3J = 8.1$ Hz, H_4/H_4'], 7.05 [1H, s, H_{pz}], 7.52/7.43 [1H/1H, m, $H_{\text{meta}}/H_{\text{meta}'}$], 5.86 [1H, br, $\text{NCH}_2\text{-CH}_2\text{OH}$], 4.60 [2H, t, $^3J = 5.2$ Hz, $\text{NCH}_2\text{-CH}_2\text{OH}$], 4.04 [2H, t, $^3J = 5.4$ Hz, $\text{NCH}_2\text{-CH}_2\text{OH}$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: (CDCl_3 solution, 63 MHz, 298 K) δ : 148.9/147.9 ($C_{\text{ortho}}/C_{\text{ortho}'}$), 140.5/139.6 ($C_{\text{para}}/C_{\text{para}'}$), 126.4/125.8 ($C_{\text{meta}}/C_{\text{meta}'}$), 124.7/122.6 (C_4/C_4'), 104.9 (C_{pz}), 62.2 ($\text{NCH}_2\text{-CH}_2\text{OH}$), 52.7 ($\text{NCH}_2\text{-CH}_2\text{OH}$) ppm. ESI(+)(m/z) (%) = 267 (100%) $[\text{L}+\text{H}]^+$.

4.3. Synthesis of the complexes $[\text{MCl}_2(\text{L})]$ (M = Pd(II) (1); Pt(II) (2))

The ligand (**L**) (0.40 mmol (0.11 g) dissolved in dry acetonitrile (20 mL) was added to a solution of $[\text{MCl}_2(\text{CH}_3\text{CN})_2]$ (0.40 mmol: 0.10 g Pd(II); 0.14 g Pt(II)) in dry acetonitrile (50 mL). For Pd(II) the solution resulting was stirred at room temperature for 12 h, and for Pt(II) the mixture was heated to reflux for 24 h. The solutions were concentrated until a crystalline precipitated appeared.

The complexes precipitated as orange (Pd(II)) or yellow (Pt(II)) needles and were recrystallized in acetone. The orange and yellow solids were filtered off, washed with diethyl ether (5 mL) and dried under vacuum.

1: (Yield. 68 %). Anal. Calc. for: C₁₅H₁₄N₄OCl₂Pd (443.62 amu): C, 40.62; H, 3.18; N, 12.63. Found: C, 40.51; H, 2.86; N, 12.58%. Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 9.3×10^{-4} M in DMSO): 31. IR: (KBr, cm^{-1}): 3431 $\nu(\text{O-H})$, 3103 $\nu(\text{C-H})_{\text{ar}}$, 2979-2860 $\nu(\text{C-H})_{\text{al}}$, 1585-1572 ($\nu(\text{C=C})$, $\nu(\text{C=N})_{\text{ar}}$), 1467, 1442 ($\delta(\text{C=C})$, $\delta(\text{C=N})_{\text{ar}}$), 1090 $\delta(\text{C-H})_{\text{ar,ip}}$, 761 $\delta(\text{C-H})_{\text{ar,oop}}$; (polyethylene, cm^{-1}): 440 $\nu(\text{Pd-N})$, 348, 326 $\nu(\text{Pd-Cl})$. ¹H NMR: (DMSO-*d*₆ solution, 250 MHz, 298 K) δ : 9.03/8.77 [1H/1H, d, ³*J* = 5.5 Hz, ³*J* = 5.3 Hz, *H*_{ortho}/*H*_{ortho'}], 8.32/8.05 [1H/1H, t, ³*J* = 7.3 Hz, ³*J* = 6.5 Hz, *H*_{para}/*H*_{para'}], 8.21/7.88 [1H/1H, d, ³*J* = 7.0 Hz, ³*J* = 7.9 Hz, *H*₄/*H*_{4'}], 7.80 [1H, s, *H*_{pz}], 7.66/7.56 [1H/1H, m, *H*_{meta}/*H*_{meta'}], 5.30 [2H, t, ³*J* = 5.5 Hz, NCH₂-CH₂OH], 4.73 [1H, t, ³*J* = 5.6 Hz, NCH₂-CH₂OH], 3.75 [2H, t, ³*J* = 5.8 Hz, NCH₂-CH₂OH] ppm. ¹³C{¹H} NMR: (DMSO-*d*₆ solution, 63 MHz, 298 K) δ : 149.3/149.1 (*C*_{ortho}/*C*_{ortho'}), 141.2/137.7 (*C*_{para}/*C*_{para'}), 125.1/124.3 (*C*_{meta}/*C*_{meta'}), 124.3/122.2 (*C*₄/*C*_{4'}), 105.9 (*C*_{pz}), 60.6 (NCH₂-CH₂OH), 51.8 (NCH₂-CH₂OH) ppm. ESI(+)(*m/z*) (%) = 408 (100%) [PdCl(L)]⁺.

2: (Yield. 54 %). Anal. Calc. for: C₁₅H₁₄N₄OCl₂Pt (532.28 amu): C, 33.85; H, 2.65; N, 10.53. Found: C, 33.53; H, 2.82; N, 10.41%. Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 1.0×10^{-3} M in DMSO): 30. IR: (KBr, cm^{-1}): 3395 $\nu(\text{O-H})$, 3057 $\nu(\text{C-H})_{\text{ar}}$, 2970-2922 $\nu(\text{C-H})_{\text{al}}$, 1574-1558 ($\nu(\text{C=C})$, $\nu(\text{C=N})_{\text{ar}}$), 1456, 1410 ($\delta(\text{C=C})$, $\delta(\text{C=N})_{\text{ar}}$), 1055 $\delta(\text{C-H})_{\text{ar,ip}}$, 754 $\delta(\text{C-H})_{\text{ar,oop}}$; (polyethylene, cm^{-1}): 425 $\nu(\text{Pt-N})$, 335, 318 $\nu(\text{Pt-Cl})$. ¹H NMR: (DMSO-*d*₆ solution, 250 MHz, 298 K) δ : 9.40/8.77 [1H/1H, d, ³*J* = 5.7 Hz, ³*J* = 5.4 Hz, *H*_{ortho}/*H*_{ortho'}], 8.36/8.04 [1H/1H, t, ³*J* = 7.2 Hz, ³*J* = 7.8 Hz, *H*_{para}/*H*_{para'}], 8.15/7.88 [1H/1H, d, ³*J* = 8.4 Hz, ³*J* = 8.3 Hz, *H*₄/*H*_{4'}], 7.82 [1H, s, *H*_{pz}], 7.72/7.57 [1H/1H, m, *H*_{meta}/*H*_{meta'}], 5.41 [2H, t, ³*J* = 5.0 Hz, NCH₂-CH₂OH], 4.72 [1H, t, ³*J* = 4.8 Hz, NCH₂-

CH₂OH], 3.76 [2H, t, ³J = 4.8 Hz, NCH₂-CH₂OH] ppm. ¹³C{¹H} NMR: (DMSO-*d*₆ solution, 63 MHz, 298 K) δ: 149.1/148.7 (*C*_{ortho}/*C*_{ortho'}), 137.4/136.7 (*C*_{para}/*C*_{para'}), 136.6/123.1 (*C*_{meta}/*C*_{meta'}), 122.6/119.1 (*C*₄/*C*_{4'}), 104.9 (*C*_{pz}), 60.3 (NCH₂-CH₂OH), 53.0 (NCH₂-CH₂OH) ppm. ¹⁹⁵Pt{¹H} (DMSO-*d*₆, 77.0 MHz) -2184 (s) ppm. ESI(+)(*m/z*) (%) = 497 (100%) [PtCl(L)]⁺.

4.4 Synthesis of the complex [Pd(MeCO₂)(L)]₂(MeCO₂)₂ (3)

To a Schlenk flask containing deoxygenated CH₂Cl₂ (20 mL) was added in the following order, the ligand (L) (0.19 mmol, 0.050 g) and the [Pd(MeCO₂)₂] (0.19 mmol, 0.041 g). The resulting solution was stirred at room temperature for 16 h and concentrated on a vacuum line to one fifth of the initial volume. After stirring at 25 °C for 6 h, the crystalline precipitate appeared. The orange solid was filtered off, washed with diethyl ether (5 mL) and then dried under vacuum.

3: (Yield. 87 %). Anal. Calc. for C₃₈H₄₀N₈O₁₀Pd₂ (981.61 amu): C, 46.50; H, 4.11; N, 11.41. Found: C, 46.47; H, 4.04; N, 11.17%. Conductivity (Ω⁻¹cm²mol⁻¹, 1.1x10⁻³ M in CH₃OH): 185. IR: (KBr, cm⁻¹): 3386, 3295 ν(O-H), 3068-3016 ν(C-H)_{ar}, 2910 ν(C-H)_{al}, 1636, 1612, 1590 ν_{as}(COO), 1573 (ν(C=C), ν(C=N))_{ar}, 1465, 1447, 1437 ν_s(COO), 1452 (δ(C=C), δ(C=N))_{ar}, 1079, 1057 δ(C-H)_{ar,ip}, 773, 704 δ(C-H)_{ar,oop}; Δ(ν_{as}(COO)-ν_s(COO)) = 199-125 cm⁻¹; (polyethylene, cm⁻¹): 418 ν(Pd-N). ¹H NMR: (CDCl₃ solution, 250 MHz, 298 K) δ: 8.62/8.17 [1H/1H, d, ³J = 5.5 Hz, ³J = 4.3 Hz, *H*_{ortho}/*H*_{ortho'}], 7.94/7.81 [1H/1H, t, ³J = 7.3 Hz, *H*_{para}/*H*_{para'}], 7.80/7.60 [1H/1H, d, ³J = 7.1 Hz, *H*₄/*H*_{4'}], 7.21 [1H, s, *H*_{pz}], 7.31/7.21 [1H/1H, m, *H*_{meta}/*H*_{meta'}], 4.86 [2H, t, ³J = 5.1 Hz, NCH₂-CH₂OH], 4.22 [1H, br, NCH₂-CH₂OH], 3.77 [2H, q, ³J = 5.4 Hz, NCH₂-CH₂OH], 2.03 [3H, s, CH₃-COO_{bridged}], 1.91 [3H, s, CH₃-COO_{ionic}] ppm. In this complex, the signal attributable

to proton hydroxyl (OH) is not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR: (CDCl_3 solution, 63 MHz, 298 K) δ : 151.0, 149.9, 149.4, 141.2 ($C_{\text{ortho}}/C_{\text{ortho}}'$), 140.0, 138.4, 137.8, 124.9 ($C_{\text{para}}/C_{\text{para}}'$), 124.6-122.0 ($C_{\text{meta}}/C_{\text{meta}}'$ and C_4/C_4'), 106.3, 105.5 (C_{pz}), 66.8, 61.8 ($\text{NCH}_2\text{-CH}_2\text{OH}$), 59.2, 53.0 ($\text{NCH}_2\text{-CH}_2\text{OH}$), 24.1, 23.5 ($\text{CH}_3\text{COO}_{\text{bridged}}$ and $\text{CH}_3\text{COO}_{\text{ionic}}$)ppm. ESI(+)(m/z) (%) = 431 (31%) $[\text{PdAc}(\text{L})]^+$.

4.5. Synthesis of complex $[\text{Pt}(\text{Ac})(\text{L})]_2(\text{Ac})_2$ (4)

The ligand (L) (0.20 mmol, 0.053 g) dissolved in deoxygenated CH_2Cl_2 (30 mL) was added to a solution of $[\text{Pt}(\text{CH}_3\text{COO})_2]$ (0.20 mmol, 0.058 g) in deoxygenated CH_2Cl_2 (50 mL). The resulting solution was stirred at room temperature for 48 h and concentrated on a vacuum line to one-fifth of the initial volume, a yellow solid was obtained, which was filtered off, washed with diethyl ether (20 mL) and dried under vacuum.

4: (Yield. 45 %). Anal. Calc. for $\text{C}_{38}\text{H}_{40}\text{N}_8\text{O}_{10}\text{Pt}_2$ (1158.93 amu): C, 39.38; H, 3.48; N, 9.67. Found: C, 39.06; H, 3.25; N, 9.48%. Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 1.3×10^{-3} M in CH_3OH): 178. IR: (KBr, cm^{-1}): 3342, 3281 $\nu(\text{O-H})$, 3042-3007 $\nu(\text{C-H})_{\text{ar}}$, 2872 $\nu(\text{C-H})_{\text{al}}$, 1624, 1594, 1572 $\nu_{\text{as}}(\text{COO})$, 1562 ($\nu(\text{C=C})$, $\nu(\text{C=N})$) $_{\text{ar}}$, 1453, 1432, 1405 $\nu_{\text{s}}(\text{COO})$, 1426 ($\delta(\text{C=C})$, $\delta(\text{C=N})$) $_{\text{ar}}$, 1048, 1031 $\delta(\text{C-H})_{\text{ar,ip}}$, 762, 694 $\delta(\text{C-H})_{\text{ar,oop}}$; $\Delta(\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO})) = 219\text{-}119 \text{ cm}^{-1}$; (polyethylene, cm^{-1}): 404 $\nu(\text{Pt-N})$. ^1H NMR: (CDCl_3 solution, 250 MHz, 298 K) δ : 8.48/8.03 [1H/1H, d, $^3J = 5.2 \text{ Hz}$, $^3J = 4.1 \text{ Hz}$, $H_{\text{ortho}}/H_{\text{ortho}}'$], 7.83/7.72 [1H/1H, t, $^3J = 6.5 \text{ Hz}$, $H_{\text{para}}/H_{\text{para}}'$], 7.63/7.43 [1H/1H, d, $^3J = 6.9 \text{ Hz}$, H_4/H_4'], 7.15/7.02 [1H/1H, m, $H_{\text{meta}}/H_{\text{meta}}'$], 6.42 [1H, s, H_{pz}], 4.52 [2H, t, $^3J = 4.9 \text{ Hz}$, $\text{NCH}_2\text{-CH}_2\text{OH}$], 4.22 [1H, br, $\text{NCH}_2\text{-CH}_2\text{OH}$], 3.54 [2H, q, $^3J = 5.1 \text{ Hz}$, $\text{NCH}_2\text{-CH}_2\text{OH}$], 1.89 [3H, s, $\text{CH}_3\text{-COO}_{\text{bridged}}$], 1.74 [3H, s, $\text{CH}_3\text{-COO}_{\text{ionic}}$] ppm. In this complex, the signal attributable

to proton hydroxyl (OH) is not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR: (CDCl_3 solution, 63 MHz, 298 K) δ : 149.5, 148.6, 147.9, 139.4 ($C_{\text{ortho}}/C_{\text{ortho}}'$), 139.4, 136.7, 135.2, 121.4 ($C_{\text{para}}/C_{\text{para}}'$), 123.4-121.6 ($C_{\text{meta}}/C_{\text{meta}}'$), 120.7-118.5 (C_4/C_4'), 104.7, 102.1 (C_{pz}), 64.5, 59.2 ($\text{NCH}_2\text{-CH}_2\text{OH}$), 57.5, 51.8 ($\text{NCH}_2\text{-CH}_2\text{OH}$), 21.9, 20.3 ($\text{CH}_3\text{COO}_{\text{bridged}}$ and $\text{CH}_3\text{COO}_{\text{ionic}}$) ppm. $^{195}\text{Pt}\{^1\text{H}\}$ (DMSO- d_6 , 77.0 MHz) -3385 (s) ppm. ESI(+)(m/z) (%) = 520 (100%) $[\text{Pt}(\text{MeCO}_2)(\text{L})]^+$.

4.6. Synthesis of the complex $[\text{Cu}(\text{L})_2]\text{Br}$ (5)

To a Schlenk flask containing deoxygenated absolute ethanol (50 mL) was added in the following order, the CuBr (0.19 mmol, 0.027 g) and the ligand (L) (0.38 mmol, 0.10 g). The resulting solution was stirred at room temperature for 14 h. The solution was concentrated and a white precipitate appeared. The solid obtained was filtered off, and washed with diethyl ether (5 mL) under anaerobic conditions and dried under vacuum.

5: (Yield. 82 %). Anal. Calc. for $\text{C}_{30}\text{H}_{28}\text{CuN}_8\text{O}_2$ (596.14 amu): C, 53.30; H, 4.17; N, 16.57. Found: C, 53.56; H, 4.27; N, 16.46%. Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 1.2×10^{-3} M in CH_3OH): 90. IR: (KBr, cm^{-1}): 3325 $\nu(\text{O-H})$, 3075 $\nu(\text{C-H})_{\text{ar}}$, 2941 $\nu(\text{C-H})_{\text{al}}$, 1604-1566 ($\nu(\text{C=C})$, $\nu(\text{C=N})_{\text{ar}}$), 1464 ($\delta(\text{C=C})$, $\delta(\text{C=N})_{\text{ar}}$), 1098, 1086 $\delta(\text{C-H})_{\text{ar,ip}}$, 765, 696 $\delta(\text{C-H})_{\text{ar,oop}}$. ^1H NMR: (DMSO- d_6 solution, 250 MHz, 298 K) δ : 8.67/8.62 [1H/1H, d, $^3J = 4.7$ Hz, $^3J = 4.8$ Hz, $H_{\text{ortho}}/H_{\text{ortho}}'$], 8.52/8.08 [1H/1H, t, $^3J = 7.3$ Hz, $^3J = 7.0$ Hz, $H_{\text{para}}/H_{\text{para}}'$], 8.05/7.94 [1H/1H, d, $^3J = 7.3$ Hz, H_4/H_4'], 7.62 [1H, s, H_{pz}], 7.83/7.55 [1H/1H, m, $H_{\text{meta}}/H_{\text{meta}}'$], 4.54 [2H, t, $^3J = 5.1$ Hz, $\text{NCH}_2\text{-CH}_2\text{OH}$], 4.02 [2H, t, $^3J = 5.1$ Hz, $\text{NCH}_2\text{-CH}_2\text{OH}$]. In this complex, the signal attributable to proton hydroxyl (OH) is not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR: (DMSO- d_6 solution, 63 MHz, 298 K) δ : 158.5/153.2 ($C_{\text{ortho}}/C_{\text{ortho}}'$), 143.4/140.2 ($C_{\text{para}}/C_{\text{para}}'$), 129.3/127.2 (C_4/C_4'), 126.1/123.4 ($C_{\text{meta}}/C_{\text{meta}}'$), 108.2 (C_{pz}), 64.5, ($\text{NCH}_2\text{-CH}_2\text{OH}$), 58.6 ($\text{NCH}_2\text{-CH}_2\text{OH}$) ppm. ESI(+)(m/z) (%) = 596 (100%) $[\text{Cu}(\text{L})_2]^+$.

4.7. Synthesis of the complex [Ag(L)₂](CF₃SO₃) (6)

The ligand (L) (0.19 mmol, 0.050 g) dissolved in absolute ethanol (20 mL) was added to a solution of AgCF₃SO₃ (0.094 mmol, 0.024 g) in absolute ethanol (30 mL). The solution was stirred at room temperature for 10 h. The resulting solution was concentrated to one fifth of the initial volume. The complex precipitates as a white solid, which is filtered off, washed with diethyl ether (5 mL) and dried under vacuum.

6: (Yield. 78 %). Anal. Calc. for C₃₁H₂₈AgF₃N₈O₅S (789.53 amu): C, 47.16; H, 3.57; N, 14.19. Found: C, 47.32; H, 3.25; N, 14.03%. Conductivity (Ω⁻¹cm²mol⁻¹, 1.0x10⁻³ M in DMSO): 62. IR: (KBr, cm⁻¹): 3432 ν(O-H), 3087 ν(C-H)_{ar}, 2989-2856 ν(C-H)_{al}, 1598 (ν(C=C), ν(C=N))_{ar}, 1462, 1438 (δ(C=C), δ(C=N))_{ar}, 1259 ν(C-F), 1166 ν(S-O), 1045 δ(C-H)_{ar,ip}, 765, 696 δ(C-H)_{ar,oop}. ¹H NMR: (DMSO-*d*₆ solution, 250 MHz, 298 K) δ: 8.57/8.46 [1H/1H, d, ³J = 4.7 Hz, ³J = 4.8 Hz, H_{ortho}/H_{ortho}'], 8.05/7.93 [1H/1H, t, ³J = 7.8 Hz, ³J = 7.5 Hz, H_{para}/H_{para}'], 7.97/7.81 [1H/1H, d, ³J = 8.0 Hz, H₄/H₄'], 7.35 [1H, s, H_{pz}], 7.56/7.47 [1H/1H, m, H_{meta}/H_{meta}'], 4.42 [2H, t, ³J = 4.8 Hz, NCH₂-CH₂OH], 3.84 [2H, t, ³J = 4.6 Hz, NCH₂-CH₂OH]. In this complex, the signal attributable to proton hydroxyl (OH) is not observed. ¹³C{¹H} NMR: (DMSO-*d*₆ solution, 63 MHz, 298 K) δ: 151.5/151.1 (C_{ortho}/C_{ortho}'), 139.9/139.4 (C_{para}/C_{para}'), 126.0/125.5 (C₄/C₄'), 125.5/122.6 (C_{meta}/C_{meta}'), 106.4 (C_{pz}), 61.7, (NCH₂-CH₂OH), 54.7 (NCH₂-CH₂OH) ppm. ESI(+)(m/z) (%) = 640 (100%) [Ag(L)₂]⁺.

4.8. Synthesis of the complex [CuBr(L)]₂Br₂ (7)

To a solution of the ligand (L) (0.45 mmol, 0.12 g) dissolved in 50 mL of deoxygenated ethanol was added CuBr₂·H₂O (0.45 mmol, 0.10 g). A green solid immediately appeared and it was kept in the mother liquor for 15 h with constant stirring, then was filtered under nitrogen atmosphere, washed with deoxygenated ethanol (5 mL) and

diethyl ether (10 mL), and dried under vacuum. The same product was obtained when 1:2 Cu:L molar ratio was used.

7: (Yield. 44 %). Anal. Calc. for $C_{30}H_{28}Br_4Cu_2N_8O_2$ (979.30 amu): C, 36.79; H, 2.88; N, 11.44. Found: C, 36.53; H, 2.92; N, 11.43%. Conductivity ($\Omega^{-1}cm^2mol^{-1}$, 9.2×10^{-4} M in CH_3OH): 198. IR: (KBr, cm^{-1}): 3299 $\nu(O-H)$, 3079 $\nu(C-H)_{ar}$, 2977-2791 $\nu(C-H)_{al}$, 1611-1568 ($\nu(C=C)$, $\nu(C=N)_{ar}$), 1465, 1437 ($\delta(C=C)$, $\delta(C=N)_{ar}$), 1054, 1035 $\delta(C-H)_{ar,ip}$, 785 $\delta(C-H)_{ar,oop}$; (polyethylene, cm^{-1}): 421 $\nu(Cu-N)$, 283 $\nu(Cu-Br)$. UV-Vis (CH_3OH , 1.04×10^{-2} M), $\lambda(\epsilon) = 582(35)$, $320(11234)$ nm. $\mu_{eff} = 1.80$ BM. ESI(+)(m/z) (%) = 410 (100%) $[CuBr(L)]^+$.

4.9. X-Ray crystal structure Analysis of complex *cis*-[PdCl₂(L)] (1)

Suitable crystals for X-ray diffraction of compound *cis*-[PdCl₂(L)] (1) were obtained through crystallization from acetonitrile. Data were collected on a MAR345 diffractometer with an image plate detector. Unit-cell parameters were determined from automatic centering of 5082 reflections ($3^\circ < \theta < 31^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K α radiation. ($\lambda = 0.71069$ Å). All the reflections were measured in the range $2.74^\circ \leq \theta \leq 28.83^\circ$ and 2415 of which were non-equivalent by symmetry ($R_{int}(on I) = 0.037$). Lorentz-polarization and absorption corrections were made.

The structure was solved by Direct methods and refined by full-matrix least-squares method, using 2415 reflections, (very negative intensities were not assumed)^[38]. The function minimized was $\sum w \left| |F_o|^2 - |F_c|^2 \right|^2$, where $w = [\sigma^2(I) + (0.1144P)^2 + 1.6586P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. 3H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 11H atoms 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 which is linked. The final R(F) factor and R(F²) values as well as the number of parameters and other details concerning the refinement of the crystal structure are gathered in Table 1.

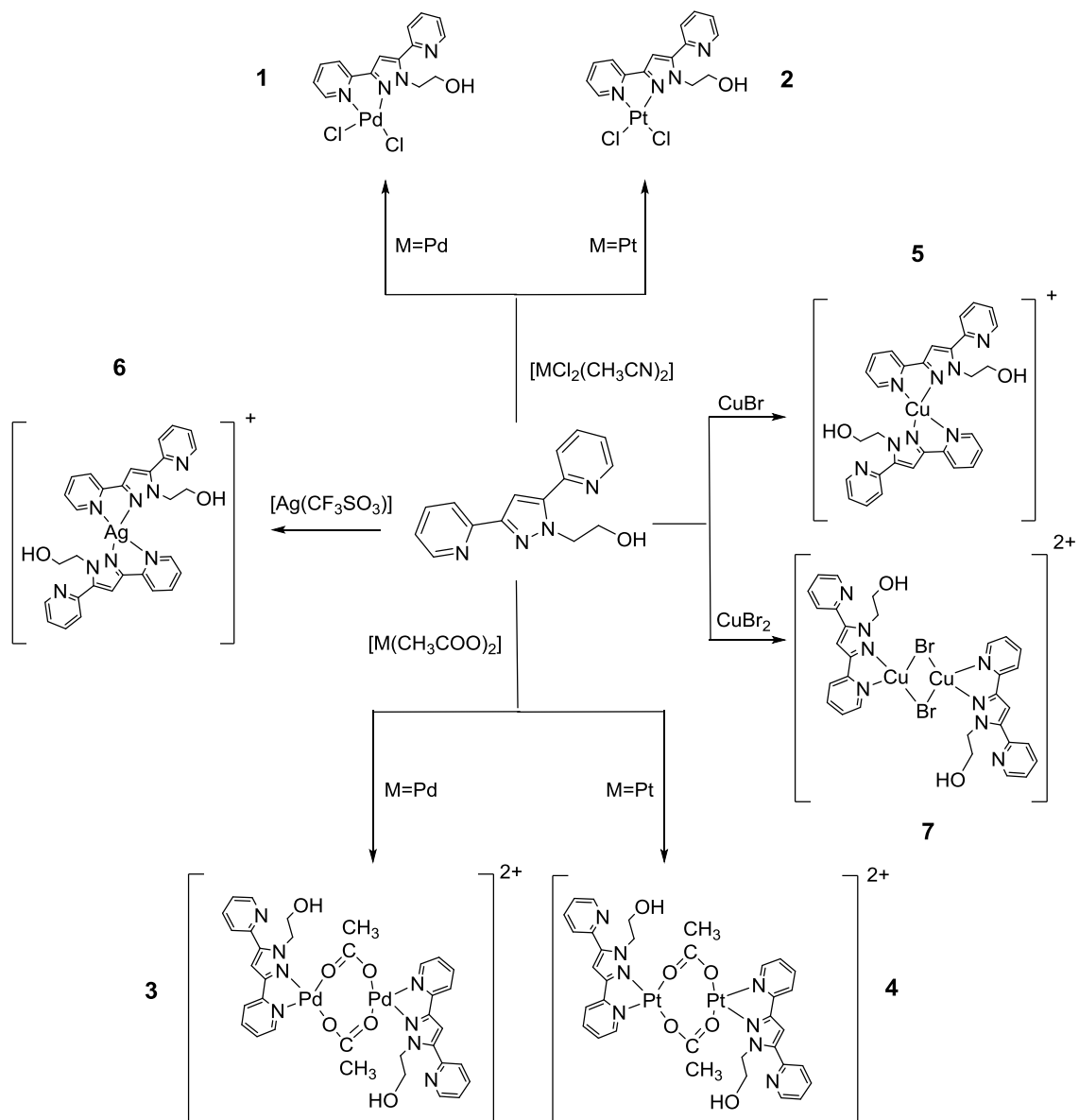
Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number CCDC 1483635 for compound [PdCl₂(L)] (**1**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ. (Fax: +44 1223 33603); e-mail: deposit@ccdc.com.ac.uk [www.http://ccdc.cam.ac](http://ccdc.cam.ac)

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Scheme 1



Figures Captions

Figure 1 ORTEP diagram of complex **1** showing atom-labeling scheme. 50% probability amplitude displacement ellipsoids are shown. Hydrogen atoms are omitted for clarity. See Table 2 for selected values of bond lengths and bond angles.

Figure 2 a) Schematic drawing of the one-dimensional supramolecular architecture of complex **1** and **b)** a close-up observation. The hydrogen atoms have been omitted for clarity.

Figure 3 Schematic drawing of the anti-parallel disposition of the one-dimensional chains in **1**. The hydrogen atoms have been omitted for clarity.

Figure 1.

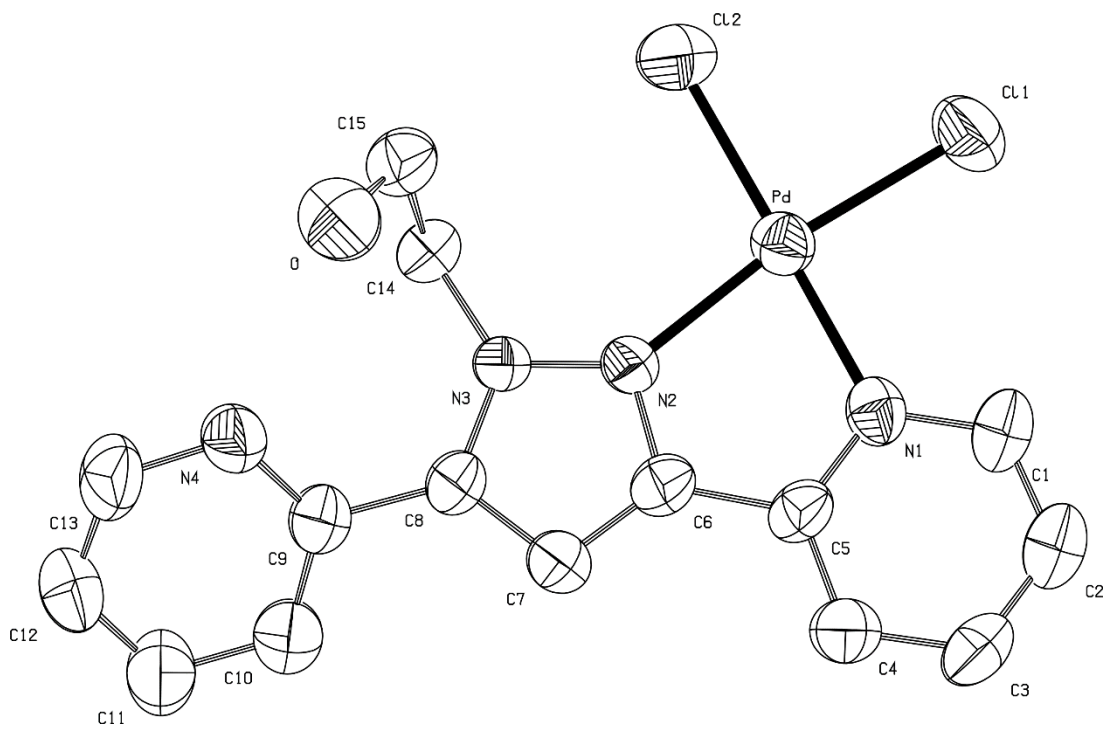


Figure 2.

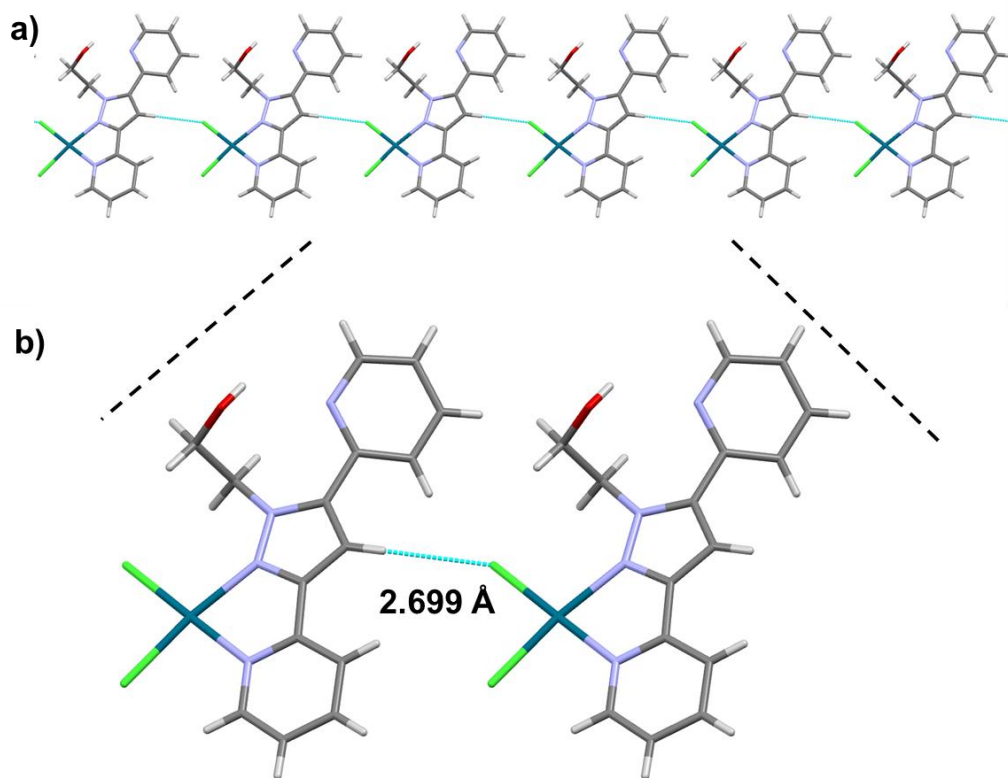


Figure 3.

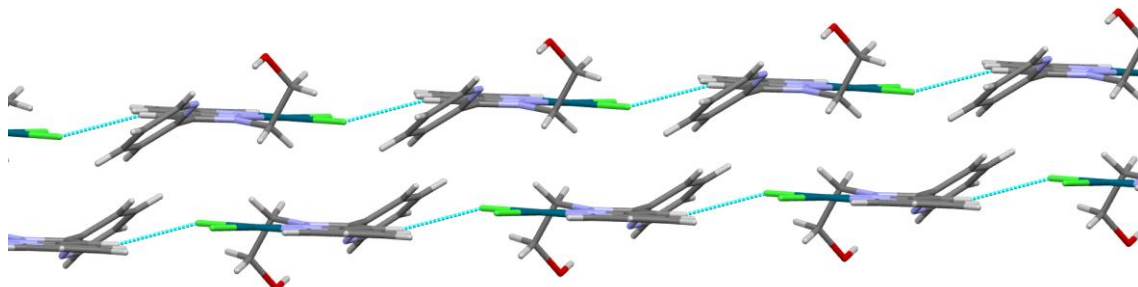


Table 1 Crystallographic data for *cis*-[PdCl₂(L)] (**1**)

	<i>cis</i> -[PdCl ₂ (L)] (1)
Empirical Formula	C ₁₅ H ₁₄ Cl ₂ N ₄ OPd
Formula weigh	443.60
Temperature (K)	293(2)
Wavelength (Å)	0.71069
System, space group	Monoclinic P2 ₁ /c
Unit cell dimensions	
a (Å)	9.0480(10)
b (Å)	22.1780(10)
c (Å)	8.1020(10)
β (°)	103.2300(10)
V (Å ³)	1582.7(3)
Z	4
D _{calc} (g cm ⁻³)	1.862
μ (mm ⁻¹)	1.519
F(000)	880
Crystal size (mm ³)	0.2x0.1x0.1
hkl ranges	0 ≤ h ≤ 10 0 ≤ k ≤ 29, -7 ≤ l ≤ 7
2θ Range (°)	1.836 to 28.835
Reflections	7317/2465
Collected/unique/[R _{int}]	[R(int) = 0.0373]
Completeness to θ = 25.240	68.8%
Absorption correction	None
Data/restrains/parameters	2465/1/209
Goodness-of-fit on F ²	1.146
Final R indices [I > 2 σ (I)]	R ₁ = 0.0578, wR ₂ = 0.1532
R indices (all data)	R ₁ = 0.0814, wR ₂ = 0.1786
Extinction coefficient	0.027(3)
Largest diff. peak and hole (e Å ⁻³)	1.255 and -1.023

Table 2 Selected bond lengths (Å) and bond angles (°) for *cis*-[PdCl₂(L)] (**1**)

<i>Bond length (Å)</i>			
Pd-N(1)	2.043(6)	Pd-Cl(1)	2.270(2)
Pd-N(2)	2.061(5)	Pd-Cl(2)	2.281(2)
<i>Bond angles (°)</i>			
N(1)-Pd-N(2)	79.5(2)	N(2)-Pd-Cl(1)	172.05(16)
Cl(1)-Pd-Cl(2)	88.09(9)	N(1)-Pd-Cl(2)	179.30(16)
N(1)-Pd-Cl(1)	92.55(17)	N(2)-Pd-Cl(2)	99.83(16)

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