Pd(II) and Pt(II) Coordination Chemistry with Hybrid Pyridine-Pyrazole Ligands: from 3D-Frameworks Structures in Molecular Complexes

Miguel Guerrero,[A] José A. Pérez,[A] Teresa Calvet,[B] Mercè Font-Bardía,[C] and Josefina Pons[A,D]

[A]Departament de Química, Unitat de Química Inorgànica, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain.

[B]Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028-Barcelona, Spain.

[C]Unitat de Difracció de RX. Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Solé i Sabarís 1-3, 08028-Barcelona, Spain.

[D]Corresponding author. Email: Josefina.Pons@uab.es

Abstract

In this paper we studied the reaction of ligands 2-[5-phenyl-1-(3,6,9-trioxodecane)-1H-pyrazol-3-yl]pyridine (L1) and 3,5-bis(2-pyridyl)-1-(3,6,9-trioxodecane)-1H-pyrazole (L2) with $[MCl_2(CH_3CN)_2]$ (M=Pd(II), Pt(II)), to obtain monomeric complexes $[MCl_2(L)]$ (M=Pd(II): L=L1 (1), L=L2 (2); M=Pt(II): L=L1 (3), L=L2 (4)). Additionally, the reaction of $[Pd(CH_3COO)_2]$ with L1 (5) and L2 (6) was also studied pointing out dimeric structures with bridged acetates between the Pd(II) atoms. All complexes were characterised by elemental analyses, conductivity measurements, infrared spectroscopy (IR), ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopies, and electrospray ionisation mass spectrometry (MS-ESI(+)). The crystal structure of complex $[PtCl_2(L1)]$ (3) was determined by X-ray diffraction methods; it consists of a mononuclear complex where L1 acts as a bidentate chelate ligand. Moreover, we also studied the extended structure observing that the ether, present in the alkyl chain of the ligand, chlorine, and platinum moieties play a fundamental role in the final disposition of the supramolecular structure. All these results show how the design of an appropriate hybrid ligand can strongly influence the structural control of the molecular packing.

1. INTRODUCTION

During the past 20 years the smart design of new multi-functional composites[1] with appealing properties have been of great interest and have been actively pursued in fields like materials chemistry, crystal engineering, or biomedicine.[2–5] One of the most important issues in this field is to achieve the correct molecular packing through the smart design of all the elements involved, which, in turn, will affect the macroscopic properties of the material. Moreover, non-covalent interactions like hydrogen bonding are a particularly powerful building motif for the construction of self-assembling supramolecular structures.[6–8]

In the process of self-assembly of metallic complexes there are two main issues to take into account: a) the number and type of coordinating moieties which contains the used ligand in the reaction, and b) the coordination number and the preferred geometry of the chosen metallic centre. Regarding the ligand, heterocycles represent an intelligent option because of their ring structure containing heteroatoms with different coordination behaviour; this fact has been clearly proved in the past century with wide application in all areas of coordination chemistry, for example, of azole-derived ligands.[9] Moreover, pyrazole ligands, which are able to be engaged in hydrogen bonding and have been used in liquid crystals, self-assembled species, and catalysis,[10,11] are considered excellent candidates to build 1D, 2D, and 3D frameworks due to their steric profile being highly dependent on the presence o substituents, their size, and their position on the aromatic ring.[12]

We have previously described the synthesis, characterisation, and reactivity towards Pd(II) of several families of hybrid 3,5-dimethylpyrazole ligands containing N-polyetheralkyl chains'[13,14] with phenyl groups in different relative positions'[15,16] as well as using the mixed-donor ligand 1,8-bis(3,5-dimethyl-1H-pyrazol-1yl)-3,6-dioxaoctane.[17] A high versatility of these ligands has been observed and their denticity varies from N,N-bidentate (chelate or bridge) to N,O,O,Ntetradentate (equatorial or axial).[17] Furthermore, these hybrid pyrazole ligands have also been found to accommodate a range of metal coordination geometries (tetrahedral, cis/trans-square planar, or octahedral) and nuclearity

78 (monomer, dimer, or polymer), as a consequence of the coordination requirement of the

79 metals, the reaction conditions, and the variety of the donor atoms.[18,19]

80   As an extension of the above results, we have recently described the synthesis and

81 characterisation of a new family of N-polyetherpyrazole ligands introducing pyridine

82 substituents: 2-[5-phenyl-1-(3,6,9-trioxodecane)-1H-pyrazol-3-yl] pyridine (L1) and 3,5-

83 bis(2-pyridyl)-1-(3,6,9-trioxodecane)-1H-pyrazole (L2) (M. Guerrero, J. A. Pérez, V.

84 Branchadell, et al., unpubl. data). Due to their potential application in supramolecular

85 chemistry, here we present a study of the synthesis and characterisation of new Pd($_{II}$) and

86 Pt($_{II}$) complexes with these hybrid pyridine-pyrazole ligands, and compare with closely

87 related complexes.

88

89

90

91

92

93

2. RESULTS AND DISCUSSION

Synthesis and Spectroscopic Properties of Complexes 1–4

Complexes cis-[MCl$_2$(L)] (M=Pd$_{(II)}$: L=L1 (1), L2 (2); M=Pt$_{(II)}$: L=L1 (3), L2 (4)) were obtained when [MCl$_2$(CH$_3$CN)$_2$] (M=Pd$_{(II)}$, Pt$_{(II)}$) was reacted with the corresponding pyrazole ligand (L1, L2) using 1M: 1 L ratio in an acetonitrile solution (Scheme 1). The ability of L1 and L2 to coordinate Pd$_{(II)}$ and Pt$_{(II)}$ metallic centres is comparable to other complexes with N-alkylpyrazole,[20–22] and N-hydroxyalkylpyrazole[23–25] ligands.

The elemental analyses are consistent with the formula [MCl$_2$(L)] (M=Pd$_{(II)}$, Pt$_{(II)}$) for compounds 1–4. The positive ionisation mass spectra (ESI(+)-MS) of compounds 1–4 give peaks with m/z values of 509 (100 %) (1), 510 (100 %) (2), 598 (100 %) (3), and 599 (100 %) (4); all of them are attributable to [M-Cl]$^+$ (M=Pd$_{(II)}$, Pt$_{(II)}$). Molecular peaks are observed with the same isotope distribution as the theoretical ones. Complexes 1–4 are slightly soluble in common organic solvents, such as acetone, dichloromethane, or ethanol. Thus, dimethyl sulfoxide was used for the conductivity measurements. The obtained values (22–36O^{-1} cm^2 mol^{-1}) show the non-ionic behavior of 1–4 (conductivity values for a non-electrolyte are below 50O^{-1} cm^2 mol^{-1} in DMSO solution).[26,27] The IR spectra studied in the range of 4000–400 cm^{-1} show the coordination of the ligands to the Pd$_{(II)}$ or Pt$_{(II)}$ atom (Fig. S1, Crystallographic data). The (n(C=C), n(C=N))ar (ar=aromatic) bands of the pyrazole ligand increase in frequency when part of the complex, whereas no significant change is observed in the n(C-O-C)as (as¼asymmetric) band.[28,29]

The IR spectra of complexes 1–4 in the 600–100 cm^{-1} region were also studied. The presence of bands between 492–462 cm^{-1} for Pd$_{(II)}$ and 483–450 cm^{-1} for Pt$_{(II)}$ complexes, assigned to n(M-N), confirm the coordination of the Npz (pz=pyrazole) of the ligand to the metallic atom. It is remarkable to point out that both palladium and platinum complexes display two n(M-Cl) bands between 356 and 331 cm^{-1}, indicating that the chlorine atoms

120 are coordinated to the M(II) atom in cis disposition,[30] due to the chelating structure of the
121 ligand.

122 ^{1}H, ^{13}C{^{1}H}, and HSQC NMR spectra for complexes 1–4 in CDCl$_3$ show the signals
123 of the coordinated ligands.[28,29] All NMR signals are reported in detail in the Experimental
124 section. In the ^{1}H NMR spectra, characteristic signals for the CH(pz) are observed between
125 7.00 and 6.73 ppm. The protons of the 3,6,9-trioxodecane chain appear between 5.59 and
126 3.31 ppm, and the protons of the methyl group of the chain between 3.41 and 3.32 ppm.

127 In the ^{13}C{^{1}H} NMR spectra the signals attributable to CH(pz) appear between 108.4
128 and 104.6 ppm, the carbons of the 3,6,9-trioxodecane chain between 71.8 and 49.3 ppm, and
129 the carbon of the methyl group of the chain between 59.9 and 58.8 ppm. Interestingly, when
130 the ligand is part of the complex the signals of CH(pz) in the ^{1}H NMR decrease in chemical
131 shift, while the signals increase in chemical shift in the ^{13}C{^{1}H} NMR.

132 Additionally, ^{195}Pt{^{1}H} NMR experiments for complexes 3 and 4, at 298 K, have
133 been also recorded in CDCl$_3$ and display only one signal for each complex at d=-2187 ppm
134 (3) and -2173 ppm (4). These values appear in the range described in the literature for
135 complexes with [PtCl$_2$N$_2$] core (between -2447 and -1198 ppm).[30–32] These data illustrate
136 how sensitive the platinum chemical shift is to the average ligand environment.

137 *Crystal and Molecular Structure of Complex cis-[PtCl$_2$(L1)] (3)*

138 The crystal structure of 3 consists of discrete cis-[PtCl$_2$(L1)] molecules linked by
139 intermolecular forces (Fig. 1). Selected bond distances and angles are given in Table 1 and
140 other parameters and details concerning the refinement of the crystal structures are gathered
141 in Table 2.

142 The platinum centre has typical square-planar geometry (with a slight tetrahedral
143 distortion) showing the largest deviation from the mean coordination plane (0.014 Å). The
144 metal atom is coordinated to one L1 ligand via one pyrazole nitrogen, one pyridine nitrogen,
145 and two chlorine atoms in a cis-disposition. The L1 ligand behaves as a chelated bidentate
146 ligand (bite angle of 78.6(4)°) forming a five-membered metallocycle.

The bond distances Pt-N$_{py}$ (2.040(9) Å , where py¼pyridine) are in the same order as Pt-N$_{pz}$ (2.050(9)Å). The Pt-N$_{py}$, Pt-N$_{pz}$, and Pt-Cl distances are in the usual range found for other platinum complexes containing analogous ligands.[33] The [PtCl$_2$(N$_{py}$)(N$_{pz}$)] core (containing pyrazole, pyridine nitrogen atoms, and terminal chlorine atoms) is found in seven complexes describes in the literature.[22,34–36] It is important to mention that L1 is not positioned in a planar way; pyridyl and phenyl groups of the ligands are clearly twisted with respect to the pyrazole ring. Whereas the pyridyl group is slightly twisted (py-pz dihedral angle 4.18), the phenyl group (ph) shows a significant torsion with respect to pyrazole (ph-pz dihedral angle 55.68). The 3,6,9-trioxodecane group, which is bonded to N(3), moves away from the chelating plane giving a torsion angle (N(2)-N(3)-C(15)-C(16)) of -74.08; this value is lower than others previously reported ([PdCl$_2$(LA)] (LA=1-octyl-3,5-bis (2-pyridyl)pyrazole).[22]

Extended Structure of cis-[PtCl$_2$(L1)] (3)

In order to shed light on the final disposition of the selfassembled structure it is necessary to study the interactions between the metal centres and the organic ligands. In this case, the extended structure analyses revealed a novel threedimensional network (Fig. 2). What is more important, the presence of intermolecular hydrogen bonds (C-H···Cl) have been studied in recent times. These kind of interactions have proved to be key for the final configuration of the supramolecular structure of solids.[37–39] So, we have investigated the self-assembly pattern of complex [PtCl$_2$(L1)] (3) in the crystal structure mainly through different intermolecular hydrogen bonding interactions (C-H···Cl and C-H···O) and also intermetallic interactions (Pt···Pt). All the bonding parameters are gathered in Table 3.

Three different H atoms (H7, H19, and H21) (Fig. 2) are engaged in hydrogen bonds with the Cl atom, which acts as the sole receptor for the interactions. Each [PtCl$_2$(L1)] unit is linked to seven neighbouring molecules, via C-H···Cl hydrogen bonding (bond distances and angles ranging between 2.72–2.94 Å and 140–1708, respectively), accompanied by cooperative C-H···O interactions (bond distances and angles ranging between 2.54–2.704 Å and 143–1568, respectively), forming layers of molecules with opposite distributions showing clear interdigitation. This fact confirms that the oxygen atoms, present in the alkyl

176 chain of L1, play an important role in the generation of these directional hydrogen bonding

177 interactions. All the C-H···X (X=Cl or O) intermolecular contacts can be considered as

178 'weak' on the basis of the contact distances and angles.[40] Moreover, important

179 intermetallic interactions (3.403(1)A°) have also been observed between adjacent Pt atoms

180 (Fig. 2).

181 *Synthesis and Spectroscopic Properties of Complexes 5 and 6*

182   To study the effect of the anion, we have also studied the reaction of L1 and L2 with

183 $[Pd(Ac)_2]$ (Ac=CH_3COO^-), giving rise to dimeric complexes $[Pd(Ac)(L)]_2(Ac)_2$ (L=L1 (5)

184 and L2 (6)). In contrast to complexes 1–4, complexes 5 and 6 are soluble in acetone,

185 dichloromethane, and ethanol. The proposed formula was confirmed by elemental analyses.

186 The positive ionisation mass spectra (MS-ESI(+)), of complexes 5 and 6, give peaks with

187 m/z values of 529 (100 %) (5) and 530 (100 %) (6), attributable to $[Pd(Ac)(L)]^+$. Molecular

188 peaks of the cations and the theoretical ones are observed with the same isotope distribution.

189   Conductivity values of 10^{-3}Msamples in methanol solution ($197\Omega^{-1}$ cm^2 mol^{-1} (5),

190 $200\Omega^{-1}$ cm^2 mol^{-1} (6)) are in agreement with the presence of 1 : 2 electrolyte compounds

191 by comparison with reported compounds (between 160 and $220\Omega^{-1}$ cm^2 mol^{-1}).[26,27]

192   The IR spectra of complexes 5 and 6 show absorption bands assigned to the

193 asymmetric and symmetric n(OCO) stretching modes and the typical bands of

194 polyetherpyrazole-derived ligands.[28,29] The IR spectra of these complexes containing the

195 acetate anion were recorded between 1650 and 1400 cm^{-1}, allowing us to determine the

196 coordination mode of the acetate group. These complexes show a complicated spectrum in

197 this region and display bands between 1642–1591 and 1473–1432 cm^{-1}, separated by

198 Δ=205–126 cm^{-1} (Fig. S1, Crystallographic data). These D values are consistent with the

199 presence of both ionic and coordinated acetate groups, pointing out the presence of dimeric

200 species.[30,41]

201   ^1H and $^{13}C\{^1H\}$ NMR spectra for complexes 5 and 6 recorded in $CDCl_3$ solution

202 show signals for coordinated ligands (L1, L2) and acetate groups. In the ^1H NMR spectra

203 the bands attributable to CH(pz) appears at 6.71 (5) and 7.08 (6) ppm; moreover the signals

204 that correspond to the protons of the chain $N_{pz}(CH_2CH_2O)_3CH_3$ appear between 4.74 and

205 3.19 ppm and the protons of the methyl groups at 3.30 and 3.29 ppm. The $^{13}C\{^1H\}$ NMR

206 spectra display the signals of CH(pz) at 104.5 (5) and 105.9 (6) ppm, the signals of the chain

207 $N_{pz}(CH_2CH_2O)_3CH_3$ between 71.8 and 49.3 ppm, and the carbons of the methyl groups at

208 59.0 and 58.9 ppm.

209 The methyl of the acetate groups display two signals in each of the ^1H NMR spectra

210 and the $^{13}C\{^1H\}$ NMR spectra. These signals appear at 2.10 and 1.98 ppm (for ^1H), and

211 23.0 and 22.9 ppm (for ^{13}C) (5) and 2.13 and 2.05 (for ^1H), and 23.4 and 22.8 ppm (for ^{13}C)

212 (6). The presence of two signals for each type of proton could indicate the presence of two

213 types of acetates: bridged (2.10, 2.13 ppm; 23.0, 23.4 ppm) and ionic (1.98, 2.05 ppm; 22.9,

214 22.8 ppm). Unfortunately, no suitable single crystals could be obtained for complexes 5 and

215 6.

216

217

218

219

220

3. CONCLUSIONS

We have studied new Pd(II) and Pt(II) monomeric complexes with 2-[5-phenyl-1-(3,6,9-trioxodecane)-1H-pyrazol-3-yl] pyridine (L1) and 3,5-bis(2-pyridyl)-1-(3,6,9-trioxodecane)- 1H-pyrazole (L2) ligands (1–4). Additionally, the reaction of [Pd(CH$_3$COO)$_2$] with L1 (5) and L2 (6) was also studied, showing formation of dimeric structures with bridged acetates between the Pd(II) atoms. All new complexes have been characterized by elemental analyses, conductivity measurements, infrared and ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt{^{1}H} NMR spectroscopies, and MS-ESI(+) spectrometry.

The crystal structure of complex [PtCl$_2$(L1)] (3) was determined by X-ray diffraction methods showing a square planar geometry unit where the platinum centre is coordinated to one bidentate L1 ligand and two chlorine atoms in cis disposition. The extended structure shows that the ether moieties, present in the alkyl chain of the ligand, as well as Cl and Pt atoms, play a fundamental role in the final disposition in the supramolecular structure. All these results show how the design of an appropriate hybrid ligand can strongly influence structural control of molecular packing.

4. EXPERIMENTAL

General Details

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

Conductivity measurements were performed at room temperature in dimethyl sulfoxide (DMSO) or methanol solutions (10^{-3} M) employing a Crison i-micro CM 2200 conductimeter. Elemental analyses (C, H, N) were carried out by the Chemical Analyses Service of the Universitat Autònoma de Bacelona on a Carlo Erba CHNS EA-1108 instrument. Infrared spectra were run on a Perkin–Elmer FT spectrophotometer series 2000 cm^{-1} as KBr pellets or polyethylene films in the range 4000–100 cm^{-1} under a nitrogen atmosphere. ^{1}H and ^{13}C{^{1}H} NMR, HSQC, and NOESY spectra were run on a NMR-FT Bruker AC-250MHz spectrometer in CDCl3 solutions, at room temperature. ^{195}Pt{^{1}H}NMR were recorded at 298K in CDCl3 solutions, and at 77.42MHz on a DPX-360MHz Bruker spectrometer using aqueous solutions of $[PtCl_6]^{2-}$ (0 ppm) as an external reference, with delay times of 0.01 s. Chemical shifts (δ) are given in ppm. Mass spectra [MS-ESI(þ)] were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

Samples of $[PdCl_2(CH_3CN)_2]$[42] and $[PtCl_2(CH_3CN)_2]$[43] were prepared as described in the literature. 2-[5-Phenyl-1-(3,6,9-trioxodecane)-1H-pyrazol-3-yl]pyridine (L1) and 3,5-bis(2-pyridyl)-1-(3,6,9-trioxodecane)-1H-pyrazole (L2) ligands were prepared according to the methods by us (Scheme 1) (M. Guerrero, J. A. Pérez, V. Branchadell, et al., unpubl. data).

Synthesis of the Complexes [PdCl₂(L)] (L5L1 (1); L2 (2))

A solution of $[PdCl_2(CH_3CN)_2]$ (0.088 g, 0.34 mmol) in 75mL of dry acetonitrile was treated with a solution of L1 or L2 (0.125 g, 0.34 mmol) dissolved in 5mL of dry acetonitrile. After 12 h of stirring at room temperature, the solution was concentrated until a crystalline precipitate appeared. The complex was obtained as orange needles. The solid was

recrystallised from dichloromethane. The solid was filtered off, washed with diethyl ether (5 mL), and dried under vacuum.

1. (75% yield). (Found: C 46.5, H 4.7, N 7.6. $C_{21}H_{25}N_3Cl_2O_3Pd$ requires C46.3, H4.6, N7.7 %). Conductivity (1.0×10^{-3} M in DMSO): $25\,\Omega^{-1}\,cm^2\,mol^{-1}$. ν_{max}(KBr)/cm^{-1} 3114 ν(C-H)aromatic (ar), 2899 n(C-H)aliphatic (al), 1625 (ν(C=C), ν(C=N))ar, 1458 (δ(C=C), δ(C=N))ar, 1133 ν(C-OC) as, 1045 δ(C-H)ar, vibration in the plain (ip), 784 δ(C-H)ar, vibration out of the plane (oop); (polyethylene, cm^{-1}): 492, 481 ν (Pd-N), 349, 340 ν(Pd-Cl). δH (CDCl$_3$, 250MHz) 9.01 (1H, d, ^3J=5.6, H$_{ortho}$, py), 7.80–7.60 (3H, m, H$_{py}$), 7.51–7.41 (5H, m, H$_{ph}$), 6.73 (1H, s, H$_{pz}$), 4.92 (2H, t, ^3J=4.8, NCH$_2$CH$_2$O), 3.99 (2H, t, ^3J=4.8, NCH$_2$CH$_2$O), 3.47 (8H, m, (CH$_2$CH$_2$O)$_2$), 3.32 (3H, s, OCH$_3$). dC (CDCl$_3$, 62.9MHz) 148.9 (C$_{ortho}$, py), 136.7, 130.3, 129.1, 128.5, 122.2 (C$_{py}$, C$_{ph}$), 130.3–128.5 (C$_{ph}$), 105.6 (C$_{pz}$), 71.7 (NCH$_2$CH$_2$O), 70.6–69.8 (CH$_2$CH$_2$O)$_2$, 58.8 (OCH$_3$), 49.3 (NCH$_2$CH$_2$O). *m/z* (ESI+) 509 (100, [PdCl(L1)]$^+$)

2. (72% yield). (Found: C 44.0, H 4.3, N 10.2. $C_{20}H_{24}N_4Cl_2O_3Pd$ requires C 44.0, H 4.4, N 10.3 %). Conductivity (9.8×10^{-4} M in DMSO): $22\,\Omega^{-1}\,cm^2\,mol^{-1}$. ν_{max}(KBr)/cm^{-1} 3090 ν(C-H)ar, 2875 ν(C-H)al, 1611, 1571 (ν(C=C), ν(C=N))ar, 1459, 1438 (δ(C=C), δ(C=N))ar, 1104 ν(C-O-C)as, 1030 δ(C-H)ar, ip, 783, 768 δ(C-H)ar, oop; (polyethylene, cm^{-1}): 479, 464 ν(Pd-N), 356, 342 ν(Pd-Cl). δ_H (CDCl$_3$, 250 MHz) 9.32 (1H, d, 3J=5.4, H$_{ortho}$, py), 8.68 (1H, d, 3J¼4.7, H$_{ortho}$, py), 7.98–7.27 (6H, m, H$_{py}$), 6.97 (1H, s, H$_{pz}$), 5.52 (2H, t, 3J=4.7, NCH$_2$CH$_2$O), 3.89 (2H, t, 3J=4.7, NCH$_2$CH$_2$O), 3.41 (3H, s, OCH$_3$), 3.31 (8H, m, (CH$_2$CH$_2$O)$_2$). δC (CDCl$_3$, 62.9 MHz) 154.0 (C$_{ortho}$, py), 150.9 (C$_{ortho}$, py), 140.1, 139.3, 130.6, 126.7, 124.8, 121.4 (C$_{py}$), 108.4 (C$_{pz}$), 71.8 (NCH$_2$CH$_2$O), 70.6–70.1 (CH$_2$CH$_2$O)$_2$, 59.9 (OCH$_3$), 52.8 (NCH$_2$CH$_2$O). *m/z* (ESI+) 510 (100, [PdCl(L2)]$^+$)

Synthesis of the Complexes [PtCl$_2$(L)] (L5L1 (3); L2 (4))

295 A solution of [PtCl$_2$(CH$_3$CN)$_2$] (0.118 g, 0.34 mmol) in 75mL of dry acetonitrile

296 was treated with a solution of L1 or L2 (0.125 g, 0.34 mmol) dissolved in 10mL of dry

297 acetonitrile. The resulting solution was stirred and heated at reflux for 24 h, before

298 concentrating on a vacuum line to one fifth of the initial volume. The yellow solution was

299 filtered off, washed with diethyl ether (5 mL), and dried under vacuum.

300 **3**. (68% yield). (Found: C 39.6, H 3.7, N 6.7. C$_{21}$H$_{25}$N$_3$Cl$_2$O$_3$Pt requires C 39.8, H

301 4.0, N 6.6 %). Conductivity (1.2x10^{-3}M in DMSO): 36 O^{-1} cm^2 mol^{-1}. ν_{max}(KBr)/cm^{-1}

302 3104 ν(C-H)ar, 2868 ν(C-H)al, 1619 (ν(C=C), n(C=N))ar, 1466 (δ(C=C), δ(C=N))ar, 1122

303 ν(C-O-C)as, 1032 δ(C-H)ar, ip, 782, 765 δ(C-H)ar, oop; (polyethylene, cm^{-1}): 483, 471

304 ν(Pt-N), 348, 334 ν(Pt-Cl). δ_H (CDCl$_3$, 250 MHz) 9.69 (1H, d, 3J¼5.9, H$_{ortho}$, py), 8.02–

305 7.62 (3H, m, H$_{py}$), 7.53–7.50 (5H, m, H$_{ph}$), 6.75 (1H, s, H$_{pz}$), 5.05 (2H, t, 3J=5.7,

306 NCH$_2$CH$_2$O), 4.06 (2H, t, 3J=5.7, NCH$_2$CH$_2$O), 3.46 (8H, m, (CH$_2$CH$_2$O)$_2$), 3.32 (3H, s,

307 OCH$_3$). δ_C (CDCl$_3$, 62.9 MHz) 149.4 (C$_{ortho}$, py), 139.0, 130.1, 129.7, 128.7, 124.5, 120.8

308 (C$_{py}$, C$_{ph}$), 106.8 (C$_{pz}$), 71.7 (NCH$_2$CH$_2$O), 71.6–70.0 (CH$_2$CH$_2$O)$_2$, 58.8 (OCH$_3$), 49.8

309 (NCH$_2$CH$_2$O). 195Pt{1H} (CDCl$_3$, 77.0 MHz) -2187 (s). *m/z* (ESI+) 598 (100, [PtCl(L1)]$^+$)

310 **4**. (65% yield). (Found: C 37.6, H 3.7, N 8.7. C$_{20}$H$_{24}$N$_4$Cl$_2$O$_3$Pt requires C 37.9, H

311 3.8, N 8.8 %). Conductivity (9.6x10^{-4}M in DMSO): 32O^{-1} cm^2 mol^{-1}. ν_{max}(KBr)/cm^{-1}

312 3099 ν(C-H)ar, 2881 ν(C-H)al, 1621, 1591 (ν(C¼C), ν(C=N))ar, 1447 (δ(C=C),

313 δ(C=N))ar, 1108 ν(C-O-C)as, 1033 δ(C-H)ar, ip, 790 δ(C-H)ar, oop; (polyethylene, cm^{-1}):

314 465, 450 ν(Pt-N), 342, 331 ν(Pt-Cl). δ_H (CDCl$_3$, 250 MHz) 9.64 (1H, d, ^{3}J=5.7, H$_{ortho}$,

315 py), 8.72 (1H, d, 3J=4.8, H$_{ortho}$, py), 8.04–7.37 (6H, m, H$_{py}$], 7.00 (1H, s, H$_{pz}$], 5.59 (2H,

316 t, 3J¼4.8, NCH$_2$CH$_2$O), 3.94 (2H, t, 3J=4.8, NCH$_2$CH$_2$O), 3.41 (3H, s, OCH$_3$) 3.32 (8H,

317 m, (CH$_2$CH$_2$O)$_2$). δ_C (CDCl$_3$, 62.9 MHz) 149.8 (C$_{ortho}$, py), 149.5 (C$_{ortho}$, py), 139.3,

318 137.2, 124.7, 124.2, 121.2 (C$_{py}$), 105.0 (C$_{pz}$), 71.8 (NCH$_2$CH$_2$O), 70.4, 70.1 (CH$_2$CH$_2$O)$_2$,

59.0 (OCH$_3$), 50.2 (NCH$_2$CH$_2$O). ^{195}Pt{1H} (CDCl$_3$, 77.0 MHz) -2173 (s). m/z (ESI+) 599

(100, [PtCl(L2)]$^+$)

Synthesis of the Complexes [Pd(Ac)(L)]$_2$(Ac)$_2$ (L5L1 (5); L2 (6))

The reactions were carried out under nitrogen atmosphere. To a Schlenk flask containing deoxygenated warm CH$_2$Cl$_2$ (50 mL), was added Pd(CH$_3$COO)$_2$ (0.045 g, 0.20 mmol) and L1 or L2 (0.074 g, 0.20 mmol). The resulting solution was stirred at room temperature for 16 h and then concentrated on a vacuum line to one-fifth of the initial volume; crystalline solids were obtained, which were filtered off, washed with ethanol, and dried under vacuum.

5. (80% yield). (Found: C 50.7, H 5.1, N 7.3. C$_{50}$H$_{62}$N$_6$O$_{14}$Pd$_2$ requires C 50.7, H 5.3, N 7.1 %). Conductivity (1.1x10^{-3}M in CH$_3$OH): 197 O^{-1} cm^2 mol^{-1}. nmax(KBr)/cm^{-1} 3068 ν(C-H)ar, 2877 ν(C-H)al, 1647 (ν(C=C), ν (C=N))ar, 1635, 1591 ν(COO)as, 1472 ν(COO)s, 1465, 1432 (δ(C=C), δ(C=N))ar, 1102 ν(C-O-C)as, 1079, 1031 δ(C-H)ar, ip, 787, 770 δ(C-H)ar, oop; (polyethylene, cm^{-1}): 512 ν(Pd-O), 485 ν(Pd-N). δH (CDCl$_3$, 250 MHz) 8.15 (2H, d, ^{3}J=5.0, H$_{ortho}$, py), 7.97–7.32 (6H, m, H$_{py}$), 7.49–7.47 (8H, m, H$_{ph}$), 6.71 (2H, s,H$_{pz}$), 4.31 (4H, t, ^{3}J=4.7, NCH$_2$CH$_2$O), 3.85 (4H, t, ^{3}J=4.7, NCH$_2$CH$_2$O), 3.51 (16H, m, (CH$_2$CH$_2$O)$_2$), 3.30 (6H, s, OCH$_3$), 2.10 (6H, s, (CH$_3$COO)$_{bridged}$), 1.98 (6H, s, (CH$_3$COO)$_{ionic}$). dC (CDCl$_3$, 62.9 MHz) 178.7 (CH$_3$COO)$_{bridged+ionic}$, 178.5 (CH$_3$COO)$_{bridged+ionic}$, 149.6 (C$_{ortho}$, py), 140.0, 130.3, 129.8, 128.9, 124.3, 121.0 (C$_{py}$), 130.3–128.9 (C$_{ph}$), 104.5 (C$_{pz}$), 71.8 (NCH$_2$CH$_2$O), 70.3, 69.7 (CH$_2$CH$_2$O)$_2$, 59.0 (OCH$_3$), 49.5 (NCH$_2$CH$_2$O), 23.0 (CH$_3$COO)$_{bridged+ionic}$, 22.9 (CH$_3$COO)$_{bridgedþionic}$. *m/z* (ESI+) 529 (100, [Pd(Ac)(L1)]$^+$)

6. (82% yield). (Found: C 48.5, H 4.9, N 9.4. C$_{48}$H$_{60}$N$_8$O$_{14}$Pd$_2$ requires C 48.6, H 5.1, N 9.5 %). Conductivity (1.0x10^{-3}M in CH$_3$OH): 200Ω^{-1} cm^2 mol^{-1}. nmax(KBr)/cm^{-1} 3075 n(C-H)ar, 2867 n(C-H)al, 1651 (n(C=C), n(C=N))ar, 1642, 1602 n(COO)as, 1477 n(COO)s, 1473, 1437 (d(C=C), d(C=N))ar, 1107 n(C-O-C)as, 1062, 1035 d(C-H)ar, ip, 789, 773 d(C-H)ar, oop; (polyethylene, cm^{-1}): 508 n(Pd-O), 483 n(Pd-N). dH (CDCl$_3$, 250 MHz) 8.56 (2H, d, ^{3}J=4.8, H$_{ortho}$, py), 8.19 (2H, d, ^{3}J=4.7, H$_{ortho}$, py), 7.83–7.05 (12H, m, H$_{py}$], 7.08 (2H, s, H$_{pz}$], 4.74 (4H, t, 3J=4.8, NCH$_2$CH$_2$O), 3.80 (4H, t, ^{3}J=4.8, NCH$_2$CH$_2$O), 3.29 (6H, s, OCH$_3$), 3.19 (16H, m, (CH$_2$CH$_2$O)2), 2.13 (6H, s, (CH$_3$COO)$_{bridged}$), 2.05 (6H, s, (CH$_3$COO)$_{ionic}$). dC (CDCl$_3$, 62.9 MHz) 179.3 (CH$_3$COO)$_{bridged+ionic}$, 179.1(CH$_3$COO)$_{bridged+ionic}$, 149.8 (C$_{ortho}$, py), 149.4 (C$_{ortho}$, py), 138.3,

348   137.8, 124.3, 124.1, 123.4, 122.8 (Cpy), 105.9 (Cpz), 71.8 (NCH$_2$CH$_2$O), 70.6, 70.1 (CH$_2$CH$_2$O)$_2$,

349   58.9 (OCH$_3$), 49.3 (NCH$_2$CH$_2$O), 23.4 (CH$_3$COO)$_{bridged+ionic}$, 22.8 (CH$_3$COO)$_{bridged+ionic.}$ m/z

350   (ESI+) 530 (100, [Pd(Ac)(L2)]$^+$)

X-Ray Crystal Structure Analyses of Complex [PtCl$_2$(L1)] (3)

352   Suitable crystals for X-ray diffraction of compound cis-[PtCl$_2$(L1)] (3) were obtained

353   through crystallisation from acetonitrile. Data were collected on an Enraf-Nonius CAD4 four-circle

354   diffractometer using the ϖ/2θ scan technique. Intensities were collected with graphite

355   monochromatised Mo Kα radiation (λ = 0.71069Å). Unit cell parameters were determined from

356   automatic centring of 25 reflections (12° < θ > 21°). 7037 reflections were measured in the range

357   2.31° ≤ θ ≥ 29.98°, 6763 of which were non-equivalent by symmetry (R int (on I) = 0.055). 3008

358   reflections were assumed as observed applying the condition I .2σ(I). Three reflections were

359   measured every 2 h as orientation and intensity control, significant intensity decay was not observed.

360   Lorentz-polarisation and absorption corrections were made.

361   The structure was solved by direct methods and refined by the full-matrix least-squares

362   method, using 6763 reflections (very negative intensities were not assumed).[44] The function

363   minimised was $\Sigma w \parallel Fo|^2 - |Fc|^2|^2$, were w = $[\sigma^2(I) + (0.0386P)^2]^{-1}$ and P = $(|Fo|^2 + 2|Fc|^2)/3$. All H

364   atoms were computed and refined, using a riding model with an isotropic temperature factor equal

365   to 1.2 times the equivalent temperature factor of the atom which are linked. The final R(F) factor and

366   R (F^2) values as well as the number of parameters and other details concerning the refinement of the

367   crystal structure are gathered in Table 2.

368

369

370

371

5. CRYSTALLOGRAPHIC DATA

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number CCDC 916483 for compound [PtCl$_2$(L1)] (3). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ. (Fax: +44 1223 33603); email: deposit@ ccdc.com.ac.uk www.htpp://ccdc.cam.ac.

6. ACKNOWLEDGEMENTS

7. REFERENCES

[1]   R. Bishop, Chem. Soc. Rev. 1996, 25, 311. doi:10.1039/CS9962500311

[2]   C. B. Aakerôy, K. R. Seddon, Chem. Soc. Rev. 1993, 22, 397. doi:10.1039/CS9932200397

[3]   W. Jones,OrganicMolecular Solids 1997 (CRCPress: BocaRaton, FL).

[4]   G. R. Desiraju, The Crystal as a Supramolecular Entity 1996 (John Wiley & Sons: Chichester).

[5]   N. A. J. M. Sommerdijk, Angew. Chem. Int. Ed. 2003, 42, 3572. doi:10.1002/ANIE.200390544

[6]   J. M. Lehn, Supramolecular Chemistry: Concepts and Perspectives 1995 (VCH: Weinheim).

[7]   M. D. Hollingsworth, Science 2002, 295, 2410.

[8]   M. Guerrero, J. Pons, M. Font-Bardia, T. Calvet, J. Ros, Polyhedron 2010, 29, 1083. doi:10.1016/J.POLY.2009.11.018

[9]   F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed. Engl. 2008, 47, 3122. doi:10.1002/ANIE.200703883

[10]   J. Pérez, L. Riera, Eur. J. Inorg. Chem. 2009, 4913. doi:10.1002/EJIC. 200900694

[11]   M. Guerrero, J. Pons, J. Ros, J. Organomet. Chem. 2010, 695, 1957. doi:10.1016/J.JORGANCHEM.2010.05.012

[12]   J. J. Neumann, M. Suri, G. Frank, Angew. Chem. Int. Ed. Engl. 2010, 49, 7790. doi:10.1002/ANIE.201002389

[13]   A. Boixassa, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 2003, 346, 151. doi:10.1016/S0020-1693(02)01384-1

[14]   C. Luque, J. Pons, T. Calvet, M. Font-Bardía, J. García-Antón, J. Ros, Inorg. Chim. Acta 2011, 367, 35. doi:10.1016/J.ICA.2010.11.041

[15]   M. Guerrero, J. Pons, V. Branchadell, T. Parella, X. Solans, M. Font-Bardia, J. Ros, Inorg. Chem. 2008, 47, 11084. doi:10.1021/IC8013915

429 [16] M. Guerrero, J. García-Antón,M. Tristany, J. Pons, J. Ros, K. Philippot, B. Chaudret,
430   P. Lecante, Langmuir 2010, 26, 15532. doi:10.1021/LA1016802

431 [17] M. Guerrero, J. Pons, T. Parella, M. Font-Bardía, T. Calvet, J. Ros, Inorg. Chem. 2009,
432   48, 8736. doi:10.1021/IC900908N

433 [18] (a) M. Guerrero, J. Pons, J. Ros, M. Font-Bardía, V. Branchadell, Cryst. Growth Des.
434   2012, 12, 3700. doi:10.1021/CG300506C (b) A. de Leon, M. Guerrero, J. García-
435   Antón, J. Ros, M. Font-Bardia, J. Pons, CrystEngComm 2013, 15, 1762.

436 [19] (a) M. Guerrero, J. Pons, J. Ros, M. Font-Bardía, O. Vallcorba, J. Rius, V. Branchadell,
437   A. Merkoc¸i, CrystEngComm 2011, 13, 6457. doi:10.1039/C1CE05626C (b) S.
438   Muñoz, M. Guerrero, J. Ros, T. Parella, M. Font-Bardia, J. Pons, Cryst. Growth Des.
439   2012, 12, 6234. doi:10.1021/CG3014333

440 [20] V. Montoya, J. Pons, V. Branchadell, J. García-Antón, X. Solans, M. Font-Bardía, J.
441   Ros, Organometallics 2008, 27, 1084. doi:10.1021/OM7009182

442 [21] V. Montoya, J. Pons, V. Branchadell, J. García-Antón, X. Solans, M. Font-Bardía, J.
443   Ros, Organometallics 2007, 26, 3183. doi:10.1021/OM070093U

444 [22] V. Montoya, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 2006, 359,
445   25. doi:10.1016/J.ICA.2005.07.047

446 [23] V. Montoya, J. Pons, V. Branchadell, J. García-Antón, X. Solans, M. Font-Bardía, J.
447   Ros, Inorg. Chim. Acta 2007, 360, 625. doi:10.1016/J.ICA.2006.08.058

448 [24] S. Muñoz, J. Pons, J. Ros, M. Font-Bardía, C. A. Kilner, M. A. Halcrow, Inorg. Chim.
449   Acta 2011, 373, 211. doi:10.1016/J.ICA. 2011.04.027

450 [25] M. Guerrero, J. Pons, M. Font-Bardía, T. Calvet, J. Ros, Aust. J. Chem. 2010, 63, 958.
451   doi:10.1071/CH10040

452 [26] L. K. Thompson, F. L. Lee, E. J. Gabe, Inorg. Chem. 1988, 27, 39.
453   doi:10.1021/IC00274A010

454 [27] W. J. Geary, Coord. Chem. Rev. 1971, 7, 81. doi:10.1016/S0010-8545 (00)80009-0

455 [28] D. H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry 1995
456   (McGraw Hill: London).

457 [29] E. Pretch, T. Clerc, J. Seibl, W. Simon, Tables of Determination of Organic

Compounds. 13C NMR, 1H NMR, IR, MS, UV/Vis, Chemical Laboratory Practice 1989 (Springer: Berlin).

[30] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th edn 1986 (Wiley & Sons: New York, NY).

[31] C. Luque, J. Pons, T. Calvet, M. Font-Bardía, J. García-Antón, J. Ros, Inorg. Chim. Acta 2011, 367, 35. doi:10.1016/J.ICA.2010.11.041

[32] L. Scuzová, Z. Trávnicek, M. Zatloukal, I. Popa, Bioorg. Med. Chem. 2006, 14, 479. doi:10.1016/J.BMC.2005.08.033

[33] V. Montoya, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 2005, 358, 2763. doi:10.1016/J.ICA.2005.01.028

[34] L. Holland, W.-Z. Shen, P. von Grabe, P. J. S. Miguel, F. Pichierri, A. Springer, C. A. Schalley, B. Lippert, Dalton Trans. 2011, 40, 5159. doi:10.1039/C0DT01408G

[35] T. V. Segapelo, I. A. Guzei, L. C. Spencer, W. E. Van Zyl, J. Darkwa, Inorg. Chim. Acta 2009, 362, 3314. doi:10.1016/J.ICA.2009.02.046

[36] E. Budzisz, M. Miernicka, I.-P. Lorenz, P. Mayer, U. Krajewska, M. Rozalski, Polyhedron 2009, 28, 637. doi:10.1016/J.POLY.2008. 12.013

[37] G. Aullón,D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, Chem. Commun. 1998, 67, 653. doi:10.1039/A709014E

[38] M. J. Calhorda, Chem. Commun. 2000, 10, 801. doi:10.1039/A900221I

[39] V. Balamurugan, J. Mukherjee, M. S. Hundal, R. Mukherjee, Struct. Chem. 2007, 18, 133. doi:10.1007/S11224-006-9113-2

[40] J. W. Steed, J. L. Atwood, Supramolecular Chemistry, 2nd edn 2009 (John Wiley & Sons: New York, NY).

[41] J. Pons Picart, F. J. Sánchez, J. Casabó , J. Rius, A. Alvarez-Larena, J. Ros, Inorg. Chem. Commun. 2002, 5, 130. doi:10.1016/S1387-7003 (01)00358-6

[42] S. Komiya, Synthesis of Organometallic Compounds: A Practice Guide 1997 (Ed. Board: New York, NY).

[43] F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, J. Chem. Soc., Dalton Trans. 1990,

486   199. doi:10.1039/DT9900000199

487   [44] G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112.

488

489

490

491

492

493

494

495

496

497

498

499

500

501   **Table 1** Selected bond lengths [Å] and bond angles [8] for cis-[PtCl$_2$(L1)] (3)

502

Bond length [Å]			
Pt-N(1)	2.040(9)	Pt-Cl(1)	2.298(3)
Pt-N(2)	2.050(9)	Pt-Cl(2)	2.307(3)
Bond angles [°]			
N(1)-Pt-N(2)	78.6(4)	N(1)-Pt-Cl(2)	179.1(3)
Cl(1)-Pt-Cl(2)	87.08(14)	N(2)-Pt-Cl(1)	172.2(2)
N(1)-Pt-Cl(1)	93.7(3)	N(2)-Pt-Cl(2)	100.6(3)

503

504

505

506   **Table 2.** Crystallographic data for cis-[PtCl$_2$(L1)] (3)

507

	cis-[PtCl$_2$(L1)] (3)
Molecular formula	C$_{21}$H$_{25}$Cl$_2$N$_3$O$_3$Pt
Formula weigh	633.43
Temperature (K)	293(2)
Wavelength (Å)	0.71069
System, space group	Monoclinicic, P2$_1$/c
Unit cell dimensions	
a (Å)	9.093(11)
b (Å)	17.669(6)
c (Å)	16.537(4)
β (°)	117.65(4)
V (Å^3)	2353(3)
Z	4
D$_{calc}$ (g cm^{-3})	1.788
μ (mm^{-1})	6.215
F(000)	1232
Crystal size (mm^3)	$0.2 \times 0.1 \times 0.1$
hkl ranges	$-12 \le h \le 12 - 24 \le k \le 6, -12 \le l \le 23$
2 θ Range (°)	2.31 to 29.98
Reflections collected/ unique/[R$_{int}$]	7089/6813[R(int) = 0.0560]
Completeness to θ	99.4
Absorption correction	None
Data/restrains/parameters	6813/5/242
Goodness-of-fit on F^2	0.986
Final R indices [I >2 σ (I)]	R1 = 0.0722, wR$_2$ = 0.1168
R indices (all data)	R1 = 0.2289, wR$_2$ = 0.1496
Largest diff. peak and hole (e Å^{-3})	1.323 and −1.244

508

509

510

511

512 **Table 3**. Distances [Å] and angles [deg] related to hydrogen bonding in complex 3

513

Symmetry codes: (i) $-1+x, y, z$; (ii) $-1+x, 1/2-y, -1/2+z$; (iii) $-1+x$, $y, -1+z$; (iv) $1+x, y, 1+z$; (v) $1-x, -y, -z$; (vi) $1-x, -y, -z$

	D-H	D⋯A	A⋯H	D-H⋯A
C(7)–H(7)⋯Cl(2)^i	0.93	3.64(1)	2.72	170
C(19)–H(19)⋯Cl(1)^{ii}	0.97	3.76(2)	2.94	142
C(21)–H(21)⋯Cl(1)^{iii}	0.96	3.73(2)	2.94	140
C(1)–H(1)⋯O(3)^{iv}	0.93	3.33(1)	2.54	143
C(14)–H(14)⋯O(3)^v	0.93	3.43(2)	2.62	146
C(15)–H(15A)⋯O(2)^{vi}	0.97	3.60(2)	2.70	156

514

515

516

517

518 **Figures Captions**

519 **Figure 1**. ORTEP diagram of complex cis-[PtCl$_2$(L1)] (3) showing all non-hydrogen atoms
520 and the atom-numbering scheme; 50% probability displacement ellipsoids are shown.

521 **Figure 2**. Aview of the three-dimensional layered supramolecular architecture of cis-
522 [PtCl$_2$(L1)] (3) along the [100] direction, generated by C-H···Cl (blue) and C-H···O (red)
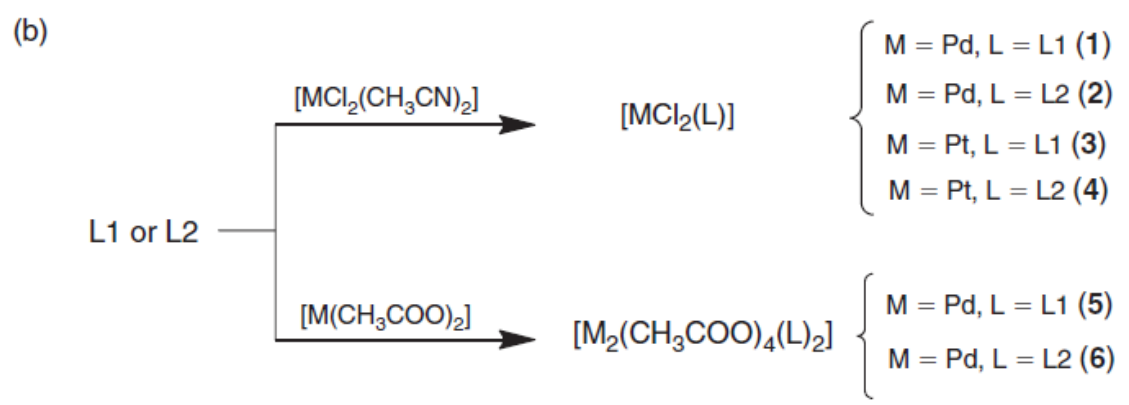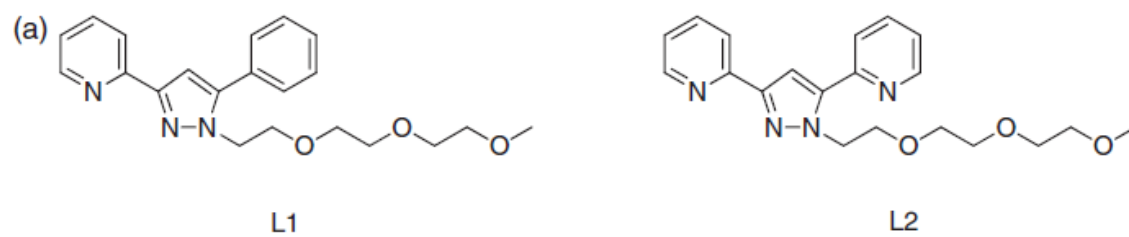523 intermolecular interactions.

524

525

526

527

528

529

530 **Scheme 1.**
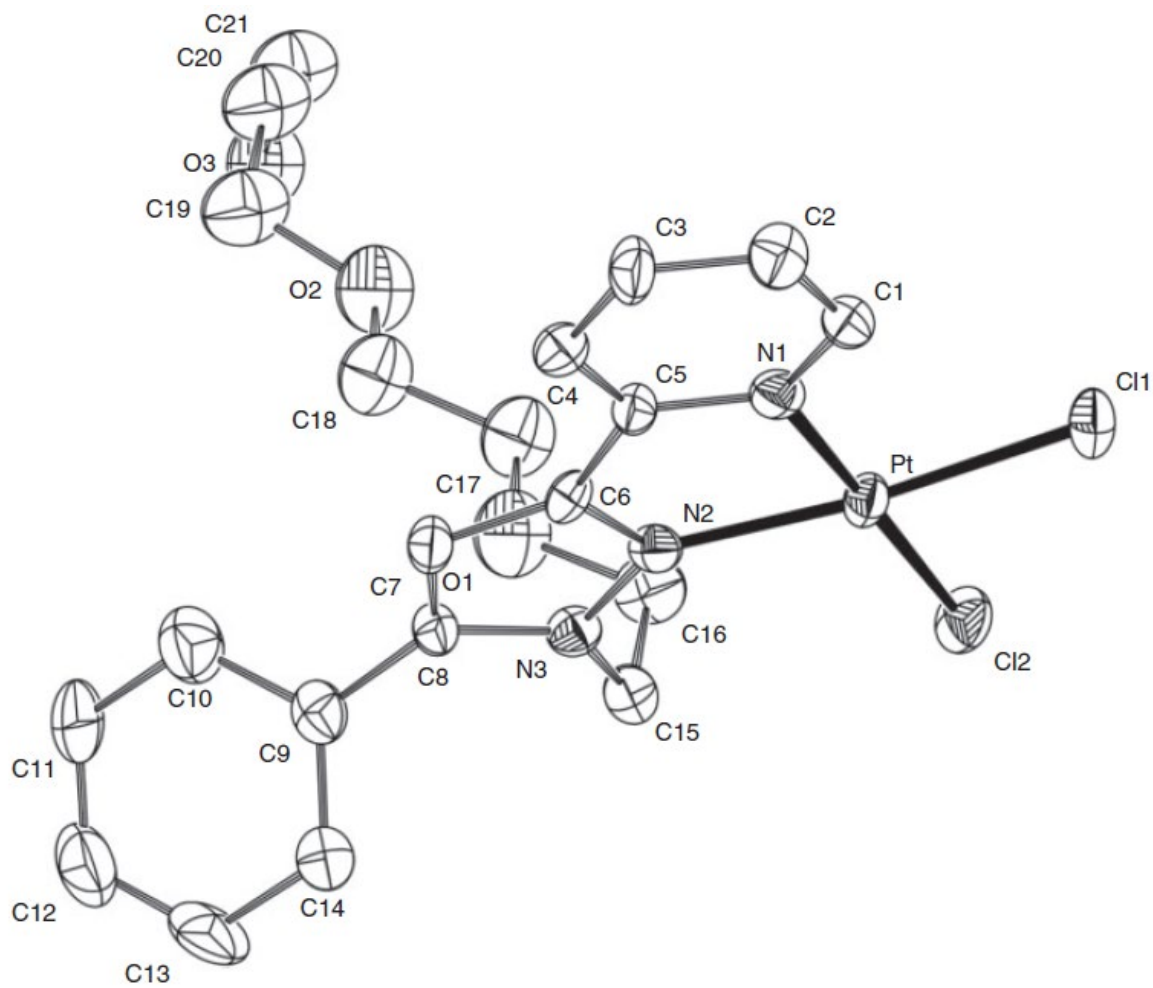
531

(a)

L1

L2

(b)

$$\text{L1 or L2} \xrightarrow{[MCl_2(CH_3CN)_2]} [MCl_2(L)]$$

$$\begin{cases} M = Pd, L = L1 \ (\textbf{1}) \\ M = Pd, L = L2 \ (\textbf{2}) \\ M = Pt, L = L1 \ (\textbf{3}) \\ M = Pt, L = L2 \ (\textbf{4}) \end{cases}$$

$$\text{L1 or L2} \xrightarrow{[M(CH_3COO)_2]} [M_2(CH_3COO)_4(L)_2]$$

$$\begin{cases} M = Pd, L = L1 \ (\textbf{5}) \\ M = Pd, L = L2 \ (\textbf{6}) \end{cases}$$

532

533

534

535

536 **Figure 1**

537

538
539
540
541

Figure 2