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# Study of the coordination behaviour of (3,5-diphenyl-1*H*-pyrazol-1-yl)ethanol against Pd(II), Zn(II) and Cu(II)

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## ABSTRACT

A new easily synthetic route with a 96% yield of ligand 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethanol (**L**) is obtained. The reactivity of **L** against Pd(II), Zn(II) and Cu(II) leads to  $[PdCl_2(L)_2]$  (1),  $[ZnCl_2(L)]$  (2) and  $[CuCl(L')]_2$  (3) (**L**' is the ligand **L** without alcoholic proton), respectively. According to the different geometries imposed by the metallic centre and the capability of **L** to present various coordination links, it has been obtained complexes with square planar (1 and 3) or tetrahedral (2) geometry and different nuclearity: monomeric (1 and 2) or dimeric (3). Complete characterisation by analytical and spectroscopic methods, resolution of **L** and 1–3 by single-crystal X-ray diffraction and magnetic studies for complex 3 are presented.

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Inorganica Chimica Acta

# 1. Introduction

The research in coordination chemistry has grown progressively during the last decades. The potential application of hybrid ligands which permits to connect organic molecules to metals by two different heteroatoms (N, S, O, P, etc.) to form metallocycles has focused much interest. It is well known that the relationship between the steric and electronic preferences to metal ion and the coordination properties of the ligand plays an important role in the structure of the compounds. In this context, many ligands that contain a flexible bridge between the active centres can adapt better to the specific preferences of different metal ion in different ways. In particular, the coordination behaviour of *N*-pyrazole ligands has been intensively studied for its potential applicability to different fields, pharmaceutical, catalyst and magnetic properties and others. These studies are extensively reported in the literature [1].

In the last 10 years, our group has focused our aims in the synthesis and characterisation of new *N*-pyrazole 1,3,5-trisubstitued ligands and we have studied their coordination behaviour with transition metals [2]. One of our research lines is the synthesis and characterisation of new *N*-pyrazole ligands substituted in the positions 3 and 5 by -H,  $-CH_3$ ,  $-CF_3$ , -pyridine or -phenyl groups

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and in the position 1 by hydroxyalkyl chain N-(CH<sub>2</sub>)<sub>x</sub>-OH (x = 1, 2 or 3) and N-(CH<sub>2</sub>)<sub>y</sub>-S-(CH<sub>2</sub>)<sub>z</sub>-OH (y = 2, z = 2 and y = 2, z = 3) (Fig. 1) [3].

In order to continue with this investigation, our goal is synthesise and characterise the ligand 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethanol (**L**) and study their coordination behaviour against Pd(II), Zn(II) and Cu(II). Ligand **L** has been reported previously by Bondavalli et al. [4]. In their work, these authors presented the synthesis of the ligand **L** and other related ligands and the study of its depressive, anthiarritmic and analgesic properties. Also, in 2008, Jiang et al. publish a work where described the synthesis of the ligand **L**, in one step, for reaction between benzoylchloride, the al-kyne appropriate and 2-hydroxyethyl hydrazine in presence of CuI/[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] as catalyst with 68% yield [5].

In this paper, the complete characterisation of **L** and its complexes are reported and the discussion is focused on the NMR, magnetic, crystallographic and magnetic properties.

# 2. Results and discussion

2.1. Synthesis and characterisation of 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanol (L)

Ligand **L** is described in the literature by Bondavalli et al. [4] and Jiang co-workers [5]. However, in this paper, we reported a new



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Fig. 1. N-pyrazole, O-alcohol ligands developed previously in our group.

easily one-step synthetic route with a 96% yield. A solution of 1,3diphenylpropan-1,3-dione and 2-hydroxiethylhydrazine (1:1.3) in dry toluene is refluxed in a Dean-Stark apparatus during 12 h. The resulting solution is evaporated to dryness obtaining a white crystalline solid that corresponds to **L** ligand (Scheme 1). The compound has been characterised by elemental analysis, mass spectrometry, IR, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, COSY, HSQC and NOESY NMR experiments. All of them are in agreement with expected proposed ligand [4–6].

The structure of **L** is confirmed by single crystal X-ray diffraction from prismatic crystals obtained by the slow evaporation of a nitromethane solution of **L**. ORTEP picture and selected bonds distances and angles are shown in Fig. 2 and Table 1. The asymmetric unit of the structure of **L** contains four unique molecules connected by hydrogen bonds between the proton of the alcohol (CH<sub>2</sub>–OH) and the free pair electrons of the pyrazole (O1–H…N5). These interactions permit to create a supramolecular structure in a zig-zag disposition. The distances and the angles O–H…N [1.899–1.953 Å; 173–178°] are in agreement with other values described in the literature [7].



Fig. 2. ORTEP drawing of L showing all non-hydrogen atoms and numbering scheme; 50% probability amplitude displacement ellipsoid shown. Lines  $(\cdots)$  show hydrogen bonds.

# 2.2. Synthesis and general characterisation of complexes 1-3

Treatment of  $[PdCl_2(CH_3CN)_2]$ ,  $ZnCl_2$  and  $CuCl_2$  with **L** lead to compounds  $[PdCl_2(\mathbf{L})_2]$  (**1**),  $[ZnCl_2(\mathbf{L})]$  (**2**) and  $[CuCl(\mathbf{L}')]_2$  (**3**) ( $\mathbf{L}'$ , the ligand **L** without alcoholic proton group), respectively (Scheme 1). Compounds **1** and **3** have been obtained using a 1:1 metal:li-



 Table 1

 Distances (Å) and angles (°) of hydrogen bonds of L.

O–H…N O–H (Å) O–H…N (Å) O…N	(Å) O–H…N (°)
O1(A)-H1(A)···N(5B)         0.906         1.906         2.812           O1(B)-H1(B)···N(5C)         0.933         1.899         2.828           O1(C)-H1(C)···N(5D)         0.895         1.953         2.846           O1(D)-H1(D)···N(5D)         0.895         1.918         2.836	178.35 173.84 175.24 173.71

gand ratio and compound **2** with a 1:2 metal:ligand ratio. The solubility of starting compounds has imposed the solvents used for synthesis (dichloromethane for **1**, ethanol for **2** and nitromethane for **3**). The deprotonation of the **L** ligand in the synthesis of compound **3** has occurred spontaneously.

Compounds **1–3** were characterised by elemental analysis, mass spectrometry, conductivity measurements, IR spectroscopy and single crystal X-ray diffraction. Also, compounds **1** and **2** have been characterised by NMR spectroscopy employing  $CDCl_3$  and  $CD_3OD$ , respectively, while compound **3** has been characterised by magnetic measurements and EPR in solid and in a frozen solution of nitromethane.

Elemental analyses of **1–3** are consistent with the formula predicted. MS-ESI(+) of **1** gives peaks with m/z values of 671 (100%) and 633 (85%), attributable to  $[PdCl(L_2)_2]^+$  and  $[Pd(L_2)-H]^+$ , respectively. Compound **2** presents one peak at 363 (100%) corresponding to  $[ZnCl(L)]^+$ , while **3** shows peak values at 691 (4%) and 591 (100%), corresponding to  $[Cu_2Cl(L)_2]^+$  and  $[Cu(L)_2]^+$ , respectively.

The molar conductivity of 10<sup>-3</sup> M solutions of compounds 1 and 2 in acetone and acetonitrile, respectively, shows values between 4 and 12  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, attributable to non-electrolyte compounds [8]. The molar conductivity of compound **3** was not measured the conductivity because of the low solubility of the compound in the typical solvents. The IR spectra of the complexes 1-3 in the range 4000–400 cm<sup>-1</sup>, show that **L** ligand is coordinated to metallic centre. The most characteristic bands are those attributable to pyrazolyl group, [v(C=C), v(C=N)], [ $\delta(C=C)$ ,  $\delta(C=N)$ ], and  $\delta(C-H)_{oop}$  [9]. It is word noting that, in the IR spectra of compounds 1 and 2, a broad band appears between 3500 and 3400 cm<sup>-1</sup>, showing the presence of the alcohol group v(O-H). Interestingly, the shape and position of this band could indicate if hydrogen bond interactions are present [10]. In **3**, the band attributable to v(O-H) is not observed, due to that in this complex the group O-H is deprotonated.

The <sup>1</sup>H, <sup>13</sup>C(<sup>1</sup>H) and bidimensional NMR studies (COSY, NOESY and HSQC) of **1** and **2** give information about the disposition of the ligand connected to the metal in solution. The <sup>1</sup>H and <sup>13</sup>C(<sup>1</sup>H) NMR of **1** and **2** do not show important differences against the



**Fig. 3.** Plot of  $\chi_M T$  vs. *T* (circles) for compound **3**. The solid lines represent best fits of the data to the Bleaney–Bowers equation; see text for details and fitting parameters.

spectrum of free ligand in the aromatic and methyl regions. Nevertheless, the two compounds show a significant change of the multiplicity of the signal of the protons  $CH_2$ -OH. The free ligand presents the signal as a triplet at  $\delta$  = 3.96 ppm but when the ligand is coordinated to the metallic centre the signals appear as multiplets [3.93 (1), 3.87 (2) ppm]. The change in the multiplicity could be caused by the increase of the rigidity of the chain N-CH<sub>2</sub>CH<sub>2</sub>-OH when the ligand coordinates to the metal centre. In 2, the formation of a chelate ring between L and Zn(II) ion could explain the difficult of the chain to rotate. On the other hand, 1 does not form a chelate between L and the Pd(II), but the rigidity could be imposed by the formation of hydrogen bonds between the proton CH<sub>2</sub>-OH and the chlorine atoms. The signal of the proton O-H of compound **1** appears as a multiplet at  $\delta$  = 2.07 ppm and the distance and angle values between 01-H10...Cl2 [2.491 Å, 163.25°] are in agreement with this hypothesis.

# 2.3. Magnetic susceptibility and EPR measurements of 3

The variable temperature magnetic susceptibility behaviour of a powder sample of **3** is consistent with a strongly antiferromagnetically coupled dinuclear compound (Fig. 3). At 300 K the compound shows  $\chi_M T = 0.19 \text{ cm}^3 \text{ mol}^{-1}$  K, substantially less that the spin-only value for two weakly interacting Cu(II) ions (0.75 cm<sup>3</sup> mol<sup>-1</sup> K) [8].  $\chi_M T$  decreases further upon cooling, reaching a value of 0.02 cm<sup>3</sup> mol<sup>-1</sup> K at 5 K. These data were modelled by the Bleaney–Bowers equation for a dimer of two *S* = ½ ions (Eq. (1), which uses the  $H = -2I(S_1 \cdot S_2)$  Hamiltonian convention) [11].

$$\chi_{\rm M} = \frac{2Ng^2\beta^2}{kT} \left[ 3 + \exp\left(\frac{-2J}{kT}\right) \right]^{-1} (1-\rho) + \frac{Ng^2\beta^2}{2kT}\rho \tag{1}$$

where *J* is the superexchange coupling constant, *N* is Avogadro's number,  $\beta$  is the Bohr magneton, *k* is Boltzmann's constant and  $\rho$  is the mole fraction of a mononuclear paramagnetic impurity. A good fit to the data was obtained, yielding  $J = -286(3) \text{ cm}^{-1}$  and  $\rho = 0.08(1)$  (Fig. 3). A fixed *g* value of 2.10 was employed in this calculation, based on the EPR spectrum of the compound (see below). This *J* value is in good agreement with Haase's magnetostructural correlation for  $[Cu_2(OR)_2]^{2+}$  complexes (R = alkyl), which predicts  $J \approx -310 \text{ cm}^{-1}$  for the observed average Cu–O–Cu bridge angle in **3** of 100.6° (see below) [12].

The X-band EPR spectrum of a powder sample of 3 at 120 K shows a weak unsymmetric peak at g = 2.10, a typical value for a Cu(II) compound (Fig. 4, top) [13]. There is some structure on the low-field side of this peak, which may correspond to a poorly resolved  $g_{\parallel}$  component of the resonance, split by hyperfine coupling to one or both of the copper nuclei (<sup>63</sup>Cu and <sup>65</sup>Cu both have nuclear spin I = 3/2). However, this could not be unambiguously interpreted. Dicopper(II) compounds often show a characteristic "halffield" resonance near 1500 G, corresponding to a spin-forbidden  $\Delta m_{\rm S}$  = ±2 transition between the  $m_{\rm S}$  = -1 and +1 Zeeman levels [13]. Such a peak was not detected for 3. This behaviour is consistent with a strong antiferromagnetism. The S = 0 magnetic ground state of the compound is essentially fully populated at the temperature of the EPR measurement (120 K), so the spin-forbidden transition between the Zeeman levels of the *S* = 1 excited spin state was not observed.

In frozen nitromethane solution, the EPR spectrum of **3** now has resolved axial symmetry, with  $g_{\parallel} = 2.24$ ,  $g_{\perp} = 2.07$  and  $A_{\parallel}$ {<sup>63,65</sup>Cu} = 170 G (Fig. 4, bottom). This spectrum is typical of a mononuclear Cu(II) centre, with a square planar, square pyramidal or octahedral coordination geometry (and a  $\{d_{x^2-y^2}\}^1$  electron configuration) [13]. This spectrum strongly implies that **3** does not retain its dinuclear structure in this solvent, because decomposes to one or more mononuclear species.



**Fig. 4.** *X*-band EPR spectra of **3** at 120 K. Top, a powder sample; bottom, a nitromethane solution of the compound.

# 2.4. Crystal and molecular structure of 1-3

The structures of **1–3** were confirmed by single crystal X-ray diffraction.

ORTEP pictures and selected bond lengths (Å) and angles values (°) are shown in Figs. 5–7 and Table 2.

Prismatic orange crystals of **1** have been obtained by the slow evaporation of a chloroform solution of this compound. The structure of **1** (Fig. 5, table 2) consists of discrete Pd(II) molecules connected by hydrogen bonds. The Pd(II) is linked to two molecules of



**Fig. 5.** ORTEP drawing of **1** showing all non-hydrogen atoms and numbering scheme; 50% probability amplitude displacement ellipsoid shown.



Fig. 6. ORTEP drawing of 2 showing all non-hydrogen atoms and numbering scheme; 50% probability amplitude displacement ellipsoid shown.



**Fig. 7.** ORTEP drawing of **3** showing all non-hydrogen atoms and numbering scheme; 50% probability amplitude displacement ellipsoid shown. Solvent molecules are omitted for clarity.

**L** via  $\kappa^1$ -N<sub>pyrazole</sub> and finishes its coordination with two chlorine atoms in a *trans* disposition. The Pd(II) atom has a square-planar geometry. The values of distances Pd–N [2.033(2), 2.009(3)Å] and Pd–Cl [2.2972(13), 2.3118(13)Å] are in agreement with the values described in the literature: Pd–N [1.989–2.042Å] and Pd–Cl [2.280–2.349Å] [6]. Moreover, **1** presents intermolecular hydrogen bonds interactions between O(1)–H(10)…Cl(2) creating a 1-D chain (Fig. 8). The distances H(10)…Cl(2) [2.491Å] and O(1)…Cl(2) [3.245Å] and the value of the angle O(1)–H(10)…Cl(2) [163.25°] are in agreement with the values described in the literature [7].

As our knowledge, 56 crystalline structures of Pd(II) compounds with the [2N<sub>pz</sub>, 2CI] *core* are described in the literature [7]. Twentysix of them show an empirical formula [PdCl<sub>2</sub>B<sub>2</sub>] (B = derived pyrazole ligand), where the metallic centre is connected to ligands B via  $\kappa^{1}$ -N<sub>pz</sub> and finishes its coordination with two chlorine atoms in a *-trans* disposition [7].

Prismatic colourless crystals of **2** where obtained from a methanol:diethyl ether solution. The structure consists of discrete Zn(II)

Table 2								
Selected	bond	lengths	(Å)	and	angles	(°)	of	1-3.

	1		2		3
Pd(1)-N(2) Pd(2)-N(22) Pd(1)-Cl(1) Pd(2)-Cl(2) O(1)-H(10) H(10)Cl(2) O(1)Cl(2) N(2)-Pd(1)-N(2) N(22)-Pd(2)-N(22) Cl(1)-Pd(1)-Cl(1)	1 2.033(2) 2.009(3) 2.2972(13) 2.3118(13) 0.78(5) 2.491(5) 3.245(3) 180.00(12) 180.00(14) 180.0	$\begin{array}{c} Zn(1)-N(2)\\ Zn(1)-O(1)\\ Zn(1)-Cl(1)\\ Zn(1)-Cl(2)\\ N(2)-Zn(1)-O(1)\\ N(2)-Zn(1)-Cl(1)\\ O(1)-Zn(1)-Cl(1)\\ N(2)-Zn(1)-Cl(2)\\ \end{array}$	2 2.025(3) 2.105(3) 2.1981(13) 2.2007(13) 92.15(12) 114.59(11) 100.78(11) 115.66(11)	$\begin{array}{c} Cu(1)-O(5)\\ Cu(1)-O(25)\\ Cu(1)-Cl(4)\\ Cu(1)-Cl(3)\\ Cu(2)-O(5)\\ Cu(2)-O(25)\\ Cu(2)-N(29)\\ Cu(2)-N(9)\\ O(5)-Cu(1)-O(25)\\ Cl(3)-Cu(1)-Cl(4)\\ \end{array}$	3 1.9631(17) 1.9815(17) 2.2473(7) 2.2565(7) 1.8982(17) 1.9115(17) 1.957(2) 1.982(2) 75.59(7) 98.31(3)
Cl(2)-Pd(2)-Cl(2) $O(1)-H(10)\cdots Cl(2)$	180.0 163.25(5)			O(5)-Cu(2)-O(25) N(9)-Cu(2)-N(29)	78.77(7) 99.43(9)



Fig. 8. 1-D chain of 1 created by hydrogen bonds.

molecules linked by van der Waals forces (Fig. 6, Table 2). The environment around Zn(II) centre consists of two chlorine atoms and one **L** ligand coordinated via  $\kappa^2$ -N,O building a six-membered metallocycle with a distorted boat conformation. The Zn(II) centre has a distorted tetrahedral geometry. The distances Zn–N

[2.025(3) Å] and Zn–Cl [2.1981(13), 2.2007(13) Å] and the angles N–Zn–O  $[92.15(12)^{\circ}]$  and N–Zn–Cl  $[114.59(11)^{\circ}, 115.66(11)^{\circ}]$  are in agreement with the values described for similar compounds in the literature: Zn–N [1.997-2.144 Å], Zn–Cl [2.144-2.269 Å], N–Zn–O  $[83.379^{\circ}-99.439^{\circ}]$  and N–Zn–Cl  $[101.299^{\circ}-122.894^{\circ}]$  [7].



Fig. 9. View of Cu1...Cl4 interaction of 3.

However, the distance Zn1–O1 [2.105(3) Å] presents a higher value than the values described in the literature: Zn–O and Zn–OH [1.915–2.060 Å] [7].

In the literature, there are described 96 compounds of Zn(II) with the [N<sub>pz</sub>, O<sub>alcohol</sub>, 2CI] *core* [7], 34 of them are monomeric compounds and the metallic centre is linked by ligand via  $\kappa^2$ -N,O forming metallocycles of five, six and seven members. In all cases, the geometry around Zn(II) is distorted tetrahedral.

Finally, green prismatic crystals of 3 were obtained by slow evaporation of a solution of nitromethane: diethyl ether of **3**. The structure consists of a bimetallic Cu(II) complex linked by van der Waals forces and the crystalline structure contains nitromethane molecules (Fig. 7, Table 2). The Cu2 is connected via  $\kappa^2$ -N,O to two ligands in a head-to-head arrangement generating two six-membered metallocycles with a distorted boat conformation. Each ligand has lost its hydroxyl group proton and the oxygen connects the Cu2 with Cu1 building a new four-membered metallocycle. Finally, Cu1 finishes its coordination with two chlorines in a cis disposition. The Cu(II) centres have a distorted square-planar geometry observed by the values of the angles Cl(3)-Cu(1)-Cl(4) [98.31(3)°], O(5)-Cu(1)-O(25) [75.59(7)°], O(5)-Cu(2)-O(25) [78.77(7)°] and N(9)-Cu(2)-N29 [99.43(9)°] and by the values of the distances between Cu1 and the plane O(5)–O(25)–Cl(3)–Cl(4) [0.109 Å] and Cu2 and the plane N(9)-N(29)-O(5)-O(25) [0.044 Å]. The values of the distances Cu(2)–N(9) [1.982(2) Å], Cu(2)–N(29) [1.957(2) Å], Cu(1)–Cl(3) [2.2565(7) Å], Cu(1)–Cl(4) [2.2473(7) Å], Cu(1)--Cu(2) [2.9831(4) Å], the dihedral angle between the planes O(5)-O(25)-Cl(3)-Cl(4) and N(9)-N(29)-O(5)-O(25) [27.93°]. All the data described below are in agreement with the values of similar structures described in the literature [14].

The oxo bridges Cu(2)–O(25)–Cu(1) and Cu(2)–O(5)–Cu(1) are asymmetric and the values of the distances Cu(1)–O(5) [1.9631(17) Å] and Cu(1)–O(25) [1.9815(17) Å] are slightly higher than the values of the distances Cu(2)–O(5) [1.8982(17) Å] and Cu(2)–O(25) [1.9115(17) Å]. Finally, compound **3** shows a weak axial intermolecular interaction Cu(1)···Cl(4<sup>*i*</sup>) [3.068 Å; symmetry code (*i*) –*x*, 1 – *y*, –*z*] that associates the molecules into dimers in the crystal lattice (Fig. 9).

# 3. Conclusion

A new easily one-step synthetic route with 96% yield of hybrid ligand 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethanol (L) is presented. Also, three new complexes with transition metals containing L are reported. The noticeable different coordination capability of L and the geometry imposed by the metallic centre lead to a diversity of structures and characteristics for each compound. In  $[PdCl_2(L)_2]$  (1), the metallic centre has the preference to be coordinated to two ligands **L** via  $\kappa^1$ -N generating an ideal square planar geometry. Also, the ligand disposition permits to build hydrogen bonds creating a 1-D chain. The interaction is observed in solid and solution. Complex [ZnCl<sub>2</sub>(L)] (2) presents ligand L connected to Zn(II) via  $\kappa^2$ -N,O building a six-membered metallocycle ring with a distorted boat conformation and distorted tetrahedral geometry. Although a large quantity of structures are collected in the literature, the distance Zn–OH presents higher values than the values described in the literature. Finally,  $[CuCl(\mathbf{L}')]_2$  (3) presents a dinuclear compound where one of the Cu(II) atom is connected via  $\kappa^2$ -N,O to two ligands in a head-to-head arrangement generating two metallocycles of six members with a distorted boat conformation. Each ligand has lost its alcohol group proton and the oxygen connects stronger to metallic centres. Also, magnetic studies reveal **3** is an antiferromagnetic compound and EPR implies **3** does not retain its dinuclear structure in the solvent, but decomposes to one or more mononuclear species, in contrast with complexes **1** and **2** that maintain the same structure in solid and solution.

# 4. Experimental

## 4.1. General details

All reagents were commercial grade and were used without further purification. The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona, or the University of Leeds microanalytical service, using a Carlo Erba CHNS EA-1108 instrument separated by chromatographic column and thermoconductivity detector. Conductivity measurements were performed at room temperature in 10<sup>-3</sup> M acetonitrile or acetone solutions employing a CyberScan CON 500 (Eutech Instrument) conductimeter. Infrared spectra were run on a Perkin Elmer FT-2000 spectrophotometer as KBr pellets. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra and bidimensional NMR spectra were run on a NMR-FT Bruker AC-250 spectrometer. All NMR experiments were recorded on CDCl<sub>3</sub> or CD<sub>3</sub>OD solvents under nitrogen. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts ( $\delta$ ) were determined relative to internal TMS and are given in ppm. Electrospray Mass spectra (ESI<sup>+</sup>) were carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. Mass experiments were done on CH<sub>3</sub>CN, CH<sub>3</sub>CN/H<sub>2</sub>O or CH<sub>3</sub>NO<sub>2</sub> solvents. Variable temperature magnetic susceptibility measurements were performed by Dr. Harry Blythe (University of Sheffield, UK). A Quantum Design SQUID magnetometer was employed, using an applied field of 1000 G. A diamagnetic correction for the sample was estimated from Pascal's constants [11]. A diamagnetic correction for the sample holder was also applied. Observed and calculated data were refined using the program SIGMAPLOT [15]. X-band EPR spectra were run using a Bruker EMX spectrometer, at a microwave frequency of 9.54 GHz. The precursor compounds ZnCl<sub>2</sub> and CuCl<sub>2</sub> are commercially available and the compound [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] is prepared as described in the literature [16]. The ligand L is reported in the literature [4,5], but it has been obtained by a new synthetic route.

#### 4.2. Synthesis of 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanol (L)

A solution of 1,3-diphenylpropan-1,3-dione (8.92 mmol, 2.00 g) and 2-hydroxiethylhydrazine (11.56 mmol, 0.88 g) in dry toluene (50 mL) in a Dean-Stark apparatus during 12 h. The resulting solution is evaporated to dryness obtaining a white crystalline solid that corresponds to L (2.26 g, 8.56 mmol, 96%). Calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.20; H, 6.09; N, 10.94%. *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3241 *v*(OH), 3015 *v*(C–H)<sub>ar</sub>, 2950–2846  $v(C-H)_{al}$ , 1548  $v(C=C/C=N)_{ar}$ , 1483–1438  $\delta(C=C/C=N)_{ar}$ , 1076  $\delta$ (C–H)<sub>ip</sub>, 810, 765  $\delta$ (C–H)<sub>oop</sub>;  $\delta$ <sub>H</sub> (250 MHz; CDCl<sub>3</sub> at 298 K; Me<sub>4</sub>Si) 7.80-7.70 (m, 2H, orto-C<sub>6</sub>H<sub>5</sub>), 7.54-7.20 (m, 8H, C<sub>6</sub>H<sub>5</sub>), 6.56 (s, 1H, pz-CH), 4.20 (t,  ${}^{3}J_{HH}$  = 5.0 Hz, 2H, pz-CH<sub>2</sub>CH<sub>2</sub>-OH), 3.96 (t,  ${}^{3}J_{HH}$  = 5.0 Hz, 2H, pz-CH<sub>2</sub>CH<sub>2</sub>-OH);  $\delta_{C}$  (63 MHz; CDCl<sub>3</sub> at 298 K; Me<sub>4</sub>Si) 151.4, 146.1 (pzC-Ph), 133.3, 130.6 (pz-CPh), 129.9-125.9 (C<sub>6</sub>H<sub>5</sub>), 103.7 (pz-CH), 62.5 (pz-CH<sub>2</sub>CH<sub>2</sub>-OH), 51.3 (pz-CH<sub>2</sub>CH<sub>2</sub>-OH); *m*/*z* (ESI<sup>+</sup>) 265 (37%, [LH]<sup>+</sup>), 233 (100, [L-CH<sub>2</sub>OH]<sup>+</sup>), 219 (79,  $[L-CH_2CH_2OH]^+).$ 

# 4.3. Synthesis of the complexes

# 4.3.1. Synthesis of [PdCl<sub>2</sub>(**L**)<sub>2</sub>] (**1**)

A solution of L (2.00 mmol, 0.529 g) dissolved in dichloromethane (10 mL) was added to a solution of  $[PdCl_2(CH_3CN)_2]$ 

Table 3							
Crystallographic	data	for	L.	1.	2	and	3.

	L	1	2	3
Formula	$C_{17}H_{16}N_2O$	$C_{34}H_{32}Cl_2N_4O_2Pd$	$C_{17}H_{16}Cl_2N_2OZn$	C <sub>34</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> Cu <sub>2</sub> .1.15 CH <sub>3</sub> NO <sub>2</sub>
Formula weight	264.32	705.96	400.61	794.82
Temperature (K)	150(2)	293(2)	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
System, space group	triclinic, <i>P</i> 1	triclinic, PĪ	orthorhombic, P <sub>212121</sub>	monoclinic, $P_{21/c}$
Unit cell dimensions				
a (Å)	10.5557(1)	11.603(5)	7.748(3)	14.0637(11)
b (Å)	12.2791(2)	11.679(4)	13.492(5)	12.2620(10)
c (Å)	22.0690(3)	13.443(5)	16.156(4)	21.8142(16)
α (°)	85.0305(6)	87.09(2)	90.00	90.00
β (°)	76.3817(6)	88.52(3)	90.00	98.824(3)
γ (°)	89.6723(8)	61.24(2)	90.00	90.00
V (Å <sup>3</sup> )	2769.28(6)	1594.9(11)	1688.9(10)	3717.3(5)
Ζ	8	2	4	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.268	1.470	1.575	1.420
$\mu$ (mm <sup>-1</sup> )	0.080	0.786	1.775	1.332
F(000)	1120	720	816	1627
Crystal size (mm <sup>3</sup> )	$0.36 \times 0.30 \times 0.22$	$0.2\times0.1\times0.1$	$0.2\times0.1\times0.1$	$0.16 \times 0.15 \times 0.03$
Crystal colour	colourless	orange	colourless	green
hkl ranges	$-13\leqslant h\leqslant 13$ , $-15\leqslant k\leqslant 15$ ,	$-16\leqslant h\leqslant 16$ , $-16\leqslant k\leqslant 16$ ,	$-10\leqslant h\leqslant 10$ , $-18\leqslant k\leqslant 16$ ,	$-18\leqslant h\leqslant 18$ , $-16\leqslant k\leqslant 16$ ,
	$-28 \leqslant l \leqslant 28$	$-18 \leqslant l \leqslant 18$	$-22 \leqslant l \leqslant 22$	$-29 \leqslant l \leqslant 29$
$2\theta$ range (°)	1.84-27.48	1.52-30.00	2.92-29.99	2.21-28.52
Reflections collected/unique/	59 193/12 649	16405/8410[R(int)=0.0347]	16 505/4799 [ <i>R</i> (int) = 0.0455]	85 535/9190 [ <i>R</i> (int) = 0.0495]
[R <sub>int</sub> ]	[R(int) = 0.0996]			
Completeness to $\theta$ (%)	99.8	90.3	98.0	97.3
Absorption correction	multi-scan	none	none	multi-scan
Data/restrains/Parameters	12 649/0/734	8410/0/470	4799/0/212	9190/30/474
Goodness-of-fit (GOF) on $F^2$	1.004	1.188	1.246	1.078
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0480, wR_2 = 0.1129$	$R_1 = 0.0503, wR_2 = 0.0966$	$R_1 = 0.0515, wR_2 = 0.1344$	$R_1 = 0.0380, wR_2 = 0.1054$
R indices (all data)	$R_1 = 0.0868, wR_2 = 0.1305$	$R_1 = 0.0636, wR_2 = 0.1031$	$R_1 = 0.0574, wR_2 = 0.1454$	$R_1 = 0.0497, wR_2 = 0.1114$
Largest difference in peak and hole (e $Å^{-3}$ )	0.235 and -0.242	0.909 and -0.947	0.841 and -1.107	1.062 and -0.352

(1.00 mmol, 0.259 g) in dichloromethane (15 mL). The mixture was stirred during 12 h and the solution was concentrated to 5 mL and precipitated with 10 mL of cold diethyl ether obtaining an orange crystalline powder that corresponds to 1 (0.80 mmol, 0.565 g, 80%). Calc. for C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Pd: C, 57.84; H, 4.57; N, 7.94. Found: C, 58.09; H, 4.41; N, 7.81%. Conductivity  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ ;  $1.00 \times 10^{-3}$  M in acetone) 4;  $v_{max}$ (KBr)/cm<sup>-1</sup> 3497 v(OH), 3060  $v(C-H)_{ar}$ , 2944, 2884  $v(C-H)_{al}$ , 1554  $v(C=C/C=N)_{ar}$ , 1482–1447  $\delta$ (C=C/C=N)<sub>ar</sub>, 1074  $\delta$ (C-H)<sub>ip</sub>, 761, 698  $\delta$ (C-H)<sub>oop</sub>;  $\delta$ <sub>H</sub> (250 MHz; CDCl<sub>3</sub> at 298 K; Me<sub>4</sub>Si) 8.12-8.04 (m, 4H, orto-C<sub>6</sub>H<sub>5</sub>), 7.59-7.34 (m, 16H,  $C_6H_5$ ), 6.34 (s, 2H, pz-CH), 4.73 (t,  ${}^{3}J_{HH}$  = 11.9 Hz, 4H, pz-CH<sub>2</sub>CH<sub>2</sub>-OH), 3.93 (m, 4H, pz-CH<sub>2</sub>CH<sub>2</sub>-OH), 2.07 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>-OH); δ<sub>C</sub> (63 MHz; CDCl<sub>3</sub> at 298 K; Me<sub>4</sub>Si) 155.1, 150.4 (pzC-Ph), 133.1 (pz-CPh), 130.8-128.8 (C<sub>6</sub>H<sub>5</sub>), 109.3 (pz-CH), 59.7 (pz-CH<sub>2</sub>CH<sub>2</sub>-OH), 52.1 (pz-CH<sub>2</sub>CH<sub>2</sub>-OH); *m*/*z* (ESI<sup>+</sup>) 671 (100%;  $[PdCl(L)_2]^+$ ), 633 (85%,  $[Pd(L)_2-H]^+$ ).

#### 4.3.2. Synthesis of [ZnCl<sub>2</sub>(**L**)] (2)

A solution of L (1.00 mmol, 0.264 g) dissolved in absolute ethanol (10 mL) was added to a solution of ZnCl<sub>2</sub> (1.00 mmol, 0.146 g) dissolved in absolute ethanol (15 mL). Also, 3 mL of triethylorthoformiate were added to the previous solution and the mixture was stirred during 12 h. The solution was evaporated to dryness and the white powder obtained was washed with cold diethyl ether leading to **2** (0.30 mmol, 0.120 g, 94%). Calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>OCl<sub>2</sub>Zn: C, 50.97; H, 4.03; N, 6.99. Found: C, 50.79; H, 4.05; N, 7.25%. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; 1.03 × 10<sup>-3</sup> M in acetonitrile) 12;  $v_{max}$ (KBr)/cm<sup>-1</sup> 3446 v(O–H), 3060 v(C–H)<sub>ar</sub>, 2931, 2861 v(C–H)<sub>al</sub>, 1551 v(C=C/C=N)<sub>ar</sub>, 1481–1453  $\delta$ (C=C/C=N)<sub>ar</sub>, 1077  $\delta$ (C–H)<sub>ip</sub>, 763, 698  $\delta$ (C–H)<sub>oop</sub>;  $\delta_{H}$  (250 MHz; CD<sub>3</sub>OD at 298 K; Me<sub>4</sub>Si) 7.76–7.67 (m, 2H, *orto*-C<sub>6</sub>H<sub>5</sub>), 7.52–7.17 (m, 8H, C<sub>6</sub>H<sub>5</sub>), 6.58 (s, 1H, pz-CH), 4.15 (t, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz, 2H, pz-CH<sub>2</sub>CH<sub>2</sub>–OH);  $\delta_{C}$  (63 MHz; CD<sub>3</sub>OD at 298 K; Me<sub>4</sub>Si) 151.5, 146.8

(pzC-Ph), 133.5, 130.8 (pz-CPh), 129.6–125.5 ( $C_{6}H_{5}$ ), 103.6 (pz-CH), 61.1 (pz-CH<sub>2</sub>-OH), 51.5 (pz-CH<sub>2</sub>CH<sub>2</sub>-OH); m/z (ESI<sup>+</sup>) 363 (100%, [ZnClL]<sup>+</sup>).

# 4.3.3. Synthesis of [CuCl(L')]<sub>2</sub> (3)

A solution of **L** (1.00 mmol, 0.264 g) dissolved in nitromethane (10 mL) was added to a solution of CuCl<sub>2</sub> (1.00 mmol, 0.134 g) dissolved in nitromethane (15 mL). The mixture was stirred during 12 h and the solution was concentrated to dryness and a green solid was obtained. The solid is redissolved in 5 mL of nitromethane and 50 mL of diethyl ether were added slowly. After 24 h green prismatic crystals were obtained corresponding to **3** (0.80 mmol, 0.298 g, 11%); Calc. for C<sub>34</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Cu<sub>2</sub>·1.15CH<sub>3</sub>NO<sub>2</sub>: C, 53.12; H, 4.24; N, 9.08. Found: C, 53.35; H, 4.15; N, 8.75 %.  $v_{max}$ (KBr)/cm<sup>-1</sup> 3059 v(C–H)<sub>ar</sub>, 2924, 2846 v(C–H)<sub>al</sub>, 1550 v(C=C/C=N)<sub>ar</sub>, 1481–1451  $\delta$ (C=C/C=N)<sub>ar</sub>, 1075  $\delta$ (C–H)<sub>ip</sub>, 763, 698  $\delta$ (C–H)<sub>oop</sub>; *m*/*z* (ESI<sup>+</sup>) 691 (4%, [Cu<sub>2</sub>ClL<sub>2</sub>]<sup>+</sup>), 591 (100, [CuL<sub>2</sub>]<sup>+</sup>).

# 4.4. X-ray crystal structures of L and 1-3

Suitable prismatic crystals for X-ray diffraction of L (colourless) and 1 (orange), 2 (colourless) and 3 (green) were obtained by slow evaporation of the following solutions: nitromethane (L), chloroform (1), methanol:diethyl ether (2) and nitromethane:diethyl ether (3).

Diffraction data for **L** and **3** were measured using Bruker X8 Apex diffractometer, with graphite-monochromated Mo K $\alpha$  radiation generated by a rotating anode and was fitted with an Oxford Cryostream low temperature device. Diffraction data for **1** and **2** were measured on a MAR 345 diffractometer with an image plate detector and intensities were collected with graphite monochromatized Mo K $\alpha$  radiation.

Unit-cell parameters were determined from 59 193 (L), 217 (1), 4197 (2) and 85 535 (3) reflections  $[2 < \theta < 28 (L), 3 < \theta < 31 (1),$  $3 < \theta < 30$  (**2**) and  $2 < \theta < 29$  (**3**)] and refined by least-squares method.

For L, 59193 reflections were measured in the range  $1.84 < \theta < 27.48$  and 12 649 of them were non-equivalent by symmetry  $[R_{int} (on I) = 0.0996]$ . Eight thousand one hundred and five reflections were assumed as observed applying the condition  $I > 2\sigma$  (I). Lorentz-polarisation and multi-scan absorption corrections were made.

For 1, 16 405 reflections were measured in the range  $1.52 < \theta < 30.00$  and 8410 of them were non-equivalent by symmetry [ $R_{int}$  (on I) = 0.0347]. Eight thousand four hundred and ten reflections were assumed as observed applying the condition  $I > 2\sigma(I)$ . Lorentz-polarisation but no absorption corrections were made.

For **2**, 16 505 reflections were measured in the range  $2.92 < \theta < 29.99$  and 4799 of them were non-equivalent by symmetry [ $R_{int}$  (on I) = 0.0455]. Four thousand five hundred and forty five reflections were assumed as observed applying the condition  $I > 2\sigma$ (I). Lorentz-polarisation but no absorption corrections were made.

For 3, 85 535 reflections were measured in the range 2.21 <  $\theta$  < 28.52 and 9190 of them were non-equivalent by symmetry  $[R_{int} (on I) = 0.0495]$ . Seven thousand five hundred and seventy seven reflections were assumed as observed applying the condition  $I > 2\sigma$  (I). Lorentz-polarisation and multi-scan absorption corrections were made.

The structures of L, 1–3 were solved by direct methods, using SHELXS-97 computer program [17] and refined by full-matrix leastsquares method with shelxL-97 computer program [18], using 59 193 (L), 16 405 (1), 16 505 (2) and 85 535 (3) reflections. The function minimised was  $\Sigma w ||F_0|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2(I) + \sigma^2(I)]^2$  $(0.0691P)^2]^{-1}$  (L),  $w = [\sigma^2(I) + (0.0200P)^2 + 2.0772P]^{-1}$  (L),  $w = [\sigma^2(I) + (0.0200P)^2 + 2.0772P]^{-1}$  $[\sigma^2(I) + (0.0709)^2 + 1.3269P]^{-1}$  (2) and  $w = [\sigma^2(I) + (0.0515P)^2 + 1.3269P]^{-1}$ 4.9940P]<sup>-1</sup> (**3**). For the four crystalline structures  $P = (|F_0|^2 + 2$  $|F_{c}|^{2}$ )/3.

All hydrogen atoms were computed using a riding model, except the O-bound H atoms in **L**, which were located in the Fourier map and allowed to refine freely with a refined common  $U_{iso}$  thermal parameter of 0.069(3) Å<sup>2</sup>. The refined O–H distances in that structure range from 0.90(2)–0.93(2) Å. The rest of the parameters refined and other details concerning the refinement of the crystal structures are gathered in Table 3.

#### Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 794898 for compound L, 794899 for compound 1, 794900 for compound **2** and 794901 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ. UK: fax: + 44 1223336033; e-mail: diposit@ccdc.cam.acuk or www.htpp:// ccdc.cam.ac.uk.

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