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## Preparation, separation and characterisation of two regioisomers of a *N*-hydroxyalkylpyridylpyrazole ligand: A structural investigation of their coordination to Pd(II), Pt(II) and Zn(II) centres

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#### ABSTRACT

The reaction of the  $\beta$ -diketone 1-phenyl-3-(pyridyn-2-yl)propane-1,3-dione, and the monosubstituted hydrazine 2-hydroxyethylhydrazine has been investigated. Two regioisomers were identified, 2-(3-phenyl-5-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.2) in 57:43 ratio. The separation of the regioisomers was done by silica column chromatography using ethyl acetate as eluent.

Palladium(II) and platinum(II),  $[MCl_2(pzol.1)_2]$ ,  $[MCl_2(pzol.2)]$ , and zinc(II),  $[ZnCl_2(pzol.1)]$ ,  $[ZnCl_2(pzol.2)]$  complexes were synthesised and characterised. The crystals and molecular structures of  $[PdCl_2(pzol.2)] \cdot H_2O$  and  $[ZnCl_2(pzol.2)]$  were solved by X-ray diffraction, and consist of mononuclear complexes. In complex  $[PdCl_2(pzol.2)] \cdot H_2O$ , the Pd(II) centre has a typical square planar geometry, with a slight tetrahedral distortion. The tetra-coordinated atom is bonded to one pyridinic nitrogen, one pyrazolic nitrogen and two chlorine atoms in *cis* disposition. The pzol.2 ligand acts as a bidentate chelate forming a five-membered metallocycle ring. In complex  $[ZnCl_2(pzol.2)]$ , the Zn(II) is five-coordinated with two Zn–N bonds  $(Zn–N_{pz} \text{ and } Zn–N_{py})$ , one Zn–OH bond and two Zn–Cl bonds. The coordination geometry is intermediate between a trigonal bipyramid and a square pyramid. In this complex, the ligand pzol.2 is tridentated and forms two metallocycle rings.

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### 1. Introduction

The coordination chemistry of the pyrazole-derived ligands has been extensively studied in recent years [1]. In particular, the chemistry of *N*-hydroxyalkylpyrazole and *N*-hydroxyalkyl-3,5dimethylpyrazole compounds has been studied by Driessen et al. They have described the synthesis and characterisation of some of these ligands with Ni(II), Cu(II), and Co(II) [2]. Moreover, the [SnMe<sub>2</sub>Cl<sub>2</sub>(HL)] (HL = 1-hydroxymethylpyrazole) has also been studied [3].

In our group, we have continued the study of the *N*-hydroxyalkylpyrazole and *N*-hydroxyalkyl-3,5-dimethylpyrazole ligands. In particular, we have described the reaction of the ligands that contain hydroxymethyl, hydroxyethyl or hydroxypropyl moieties with Pd(II) and Pt(II), obtaining complexes with stoichiometry [MCl<sub>2</sub>(L')<sub>2</sub>]. In all these complexes, the ligand L' acts as monodentate *via N*-pyrazole [4].

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The pyrazole ring is present in many pharmacologically important compounds. Although many methods are known for the construction of this ring system, the search for novel synthetic methodology addressing the necessity for a particular regioisomer is always desirable [5].

In recent years, we have developed general synthesis of 1,3,5substituted pyrazole derived ligands, and focussed the research on the development of methods for regioselective synthesis [6].

In a recent paper, we presented the synthesis and characterisation of a new 1,3,5-substituted pyrazole derived ligand, containing an alcohol functionality: namely, 2-(3-(pyridyn-2-yl)-5-trifluoromethyl-1*H*-pyrazol-1-yl)ethanol (L") and its reactivity toward Pd(II). These reactions yield *cis*-[PdCl<sub>2</sub>(L")],  $[Pd(L'')_2](BF_4)_2$  and [PdCl(L")](BF<sub>4</sub>). In complexes *cis*-[PdCl<sub>2</sub>(L")] and  $[Pd(L'')_2](BF_4)_2$ , the ligand L" acts as bidentate *via* N-pyrazole and N-pyridine. However, for complex [PdCl(L")](BF<sub>4</sub>), the ligand L" acts as tridentate *via N*-pyrazole, *N*-pyridine and the oxygen atom of the alcohol group [7].

As an extension to these results, in the present paper we describe the preparation, separation and characterisation of two regioisomers of a 1,3,5-substituted pyrazole derived ligand,

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Scheme 1.

2-(3-phenyl-5-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol. 2) (Scheme 1). It is important to note that ligand pzol.2 has been previously reported by some of the authors of the present manuscript. The reactivity of pzol.2 towards Pd(II) has also been previously assayed, yielding [PdCl<sub>2</sub>(pzol.2)]. This complex was used in Heck reaction catalysis [8]. In the present manuscript, the reactivity of both pzol.1 and pzol.2 with  $[MCl_2(CH_3CN)_2]$  (M = Pd(II), Pt(II)) and ZnCl<sub>2</sub> was studied.

#### 2. Results and discussion

#### 2.1. Synthesis of the ligands

The 1-phenyl-3-(pyridyn-2-yl)propane-1,3-dione was prepared by Claysen condensation of methyl-2-pyridinecarboxylate and acetophenone, using NaOEt as base and dry toluene as solvent [9]. Treatment of 1-phenyl-3-(pyridyn-2-yl)propane-1,3-dione with 2-hydroxyethylhydrazine in ethanol at room temperature produced two regioisomers, 2-(3-phenyl-5-(pyridyn-2-yl)-1*H*pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridyn-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.2) in 93% yield. The separation of the regioisomers was carried out by silica column chromatography using ethyl acetate as eluent. The ratio of the regioisomers has been calculated through <sup>1</sup>H NMR experiments, especially from the integration of the pyrazolic proton (43 pzol.1: 57 pzol.2) (Scheme 1). Fig. 1 shows the <sup>1</sup>H NMR spectra of the ethylenic and pyrazolic hydrogens for the mixture of regioisomers (pzol.1 + p-zol.2) and for each regioisomers after separation.

The assignment of each one of the regioisomers was confirmed by NOESY experiments. The regioisomer pzol.1 presents NOEinteractions between the protons of the hydroxyalkyl chain and the pyridyl group. For pzol.2, no NOE-interactions between these groups were observed.

Both regioisomers were characterised by elemental analysis, infrared, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, and electrospray mass spectrometry (ESI(+)–MS). For the assignment of the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, we have employed HSQC techniques. The <sup>1</sup>H NMR spectra display the *ortho*-pyridinic hydrogen (Scheme 1) at  $\delta$  = 8.72 ppm (<sup>2</sup>J = 4.8 Hz) (pzol.1), and  $\delta$  = 8.64 ppm (<sup>2</sup>J = 4.5 Hz) (pzol.2) as doublets. The pyrazolic hydrogen was observed at  $\delta$  = 6.87 ppm (pzol.1), and 6.99 ppm (pzol.2). The <sup>13</sup>C{<sup>1</sup>H} NMR spectra contained the signals at  $\delta$  = 104.3 ppm (pzol.1), and 105.2 ppm (pzol.2), attributable to the CH of the pyrazole [10]. In the mass spectra (ESI(+)–MS) of pzol.1 and pzol.2 ligands, one signal is observed at 266 (100%), attributable to [L + Na]<sup>+</sup> (L = pzol.1, pzol.2).

#### 2.2. Synthesis and general characterisation of complexes

The reaction of the ligands (pzol.1, pzol.2) with  $[MCl_2(CH_3CN)_2]$ (M = Pd(II) [11] or Pt(II) [12]), in CH<sub>2</sub>Cl<sub>2</sub> for Pd(II) complexes and in



Fig. 1. <sup>1</sup>H NMR spectra of the methylenic and pyrazolic hydrogens for the mixture of regioisomers (pzol.1 + pzol.2) and for each regioisomers after separation.

acetonitrile for Pt(II) complexes, yields  $[MCl_2(pzol.1)_2]$  (M = Pd(II) (1), Pt(II) (3)) and  $[MCl_2(pzol.2)]$  (M = Pd(II) (2), Pt(II) (4)) complexes. The isolated products do not depend on the stoichiometries used in the synthesis of the complexes. In this way, reactions were performed with 1M:1L or 1M:2L molar ratios and the same results were obtained. The reaction of pzol.1 or pzol.2 ligands with ZnCl<sub>2</sub>, in 1ZnCl<sub>2</sub>/1L ratio, in absolute ethanol and in the presence of triethyl orthoformate, (CH(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>), for dehydration purposes, yields [ZnCl<sub>2</sub>(L)] (L = pzol.1 (5), pzol.2 (6)) (Scheme 1).

Compounds **1–6** were characterised by elemental analyses, mass spectrometry, conductivity measurements, IR, and 1D and 2D NMR spectroscopies. The NMR signals were assigned by reference to the literature [10] and from DEPT, COSY, HSQC, and NOESY spectra.

For complexes **1** and **3**, the elemental analyses agree with the formula  $[MCl_2(pzol.1)_2]$  (M = Pd(II), Pt(II)), and for complexes **2**, **4**, **5** and **6**, they agree with the formula  $[MCl_2(L)]$  (M = Pd(II), Pt(II), Zn(II), and L = pzol.1, pzol.2).

The positive ionisation spectra (ESI(+)–MS), of complexes **1** and **3**, give peaks with m/z values of 635 (100%) (**1**) and 724 (100%) (**3**), attributable to  $[M-2CI-H]^*$ . For complexes **2**, **4**, **5**, and **6**, peaks with m/z values of 408 (100%) (**2**), 496 (100%) (**4**), and 364 (100%) (**5** and **6**) are obtained, attributable to  $[M-CI]^*$ . Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones.

Conductivity values of  $10^{-3}$  M samples, in acetonitrile, for compounds **1**, **2**, **5**, and **6**, and in DMSO for compounds **3** and **4**, are in agreement with the presence of non-electrolyte compounds. The reported values for  $10^{-3}$  M solutions of non-electrolyte complexes are lower than  $120 \ \Omega^{-1} \ cm^2 \ mol^{-1}$  or  $50 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ , in acetonitrile or DMSO, respectively [13]. We have carried out the conductivity measurements in acetonitrile or DMSO, because in the

concentrations used for these experiments all the compounds are soluble in these solvents and we have not observed the substitution of any of the ligands by acetonitrile or DMSO.

The IR spectra of the complexes **1–6** in KBr pellets, display absorptions of the *N*-hydroxyalkylpyridylpyrazole derived ligands. For all complexes, the most characteristic bands are those attributable to the alcohol, pyridyl, pyrazole and phenyl groups: v(O-H) (3482–3283 cm<sup>-1</sup>), [v(C=C), v(C=N)]<sub>py</sub> (1619–1597 cm<sup>-1</sup>), [v(C=C), v(C=N)]<sub>py</sub> (1569–1510 cm<sup>-1</sup>), [ $\delta(C=C)$ ,  $\delta(C=N)$ ]<sub>py,pz</sub> (1468–1444 cm<sup>-1</sup>), [ $\delta(C-H)_{oop}$ ]<sub>py</sub> (783–763 cm<sup>-1</sup>) and [ $\delta(C-H)_{oop}$ ]<sub>pz</sub> (712–694 cm<sup>-1</sup>).

In the IR spectra for complexes **1**, **2**, **5** and **6**, the band attributable to v(O-H) appears between 3278 and 3238 cm<sup>-1</sup>, and for complexes **3** and **4**, appears at 3482 and 3461 cm<sup>-1</sup>, respectively. For complexes **1–4**, the band attributable to v(O-H) appears as a broad band. However, for complexes **5** and **6**, it appears as a well-defined band, probably due to the coordination of the –OH group to the Zn atom.

The IR spectra of all compounds, between 600 and 100 cm<sup>-1</sup>, were also recorded. The complexes **1** and **2** show the v(Pd-N) bands at 440 and 397 cm<sup>-1</sup>, respectively, and complexes **3** and **4** show the v(Pt-N) at 421 and 463 cm<sup>-1</sup>, respectively [14]. Finally, complexes **5** and **6** show defined bands corresponding to v(Zn-O) and v(Zn-N) at 422, 418 and 420, 413 cm<sup>-1</sup>, respectively [15]. Moreover, complexes **1** and **3** display one band at 334 and 357 cm<sup>-1</sup>, respectively, attributable to v(M-Cl) (M = Pd(II), Pt(II)), which are typical of compounds with a *trans* disposition of the chlorine atoms around the metal. In contrast, the spectra of complexes **2** and **4** display two bands at 327 and 302 cm<sup>-1</sup>, and 348 and 339 cm<sup>-1</sup>, respectively, corresponding to v(M-Cl) (M = Pd(II), Pt(II)), which are typical of compounds with a *cis* disposition of the chlorine atoms around the metal [14]. Finally, the complexes

**5** and **6** show two well-defined bands corresponding to v(Zn-Cl) at 302 and 281 cm<sup>-1</sup>, and 323 and 302 cm<sup>-1</sup>, respectively [16].

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the compounds **1–6** were recorded in DMSO-*d*<sub>6</sub>, due to the low solubility of these complexes in other deutered solvents. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were consistent with the proposed formulation and showed the coordination of the ligands (pzol.1 and pzol.2) to the metal atoms. In the <sup>1</sup>H NMR spectra, characteristic bands for the *orto*-pyridinic hydrogens are observed between 9.03 and 8.62 ppm as doublets, with <sup>1</sup>H–1H coupling constants values, between 5.6 and 5.8 Hz. The values of the field shift and coupling constants are of the same order as those obtained for other complexes with *N*-alkylpyridylpyrazole derived ligands [17], but display higher field shift than [PdCl<sub>2</sub>(L")], [Pd(L")<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and [PdCl(L")](BF<sub>4</sub>). (L" = 2-(3-(pyridyn-2-yl)-5-trifluoromethyl-1*H*-pyrazol-1-yl)ethanol, possibly due to the presence of the trifluoromethyl group, in these complexes [6].

Other observed bands are those attributable to  $H_{pz}$ , which appear between 7.42 and 7.25 ppm. The values are comparable to those observed for other complexes that contain *N*-hydroxyalkylpyrazole and *N*-hydroxyalkylpyridylpyrazole ligands [4,6, 17]. It is important to remark that for complexes **1** and **3**, in the <sup>1</sup>H NMR spectra, the  $H_{pz}$  appears at 7.25 and 7.45 ppm, respectively. These values show a large displacement compared to the same signal for the free ligand ( $H_{pz}$  appears at 6.87 ppm). These data seem to indicate that pzol.1 is coordinated to Pd(II) (complex **1**) or Pt(II) (complex **3**) through the pyrazolyl group, as shown in Scheme 1.

The ethylene protons of the N<sub>pz</sub>- $CH_2$ - $CH_2$ -OH chains appear as two triplets between 4.70 and 4.22 ppm and 3.85 and 3.78 ppm, with <sup>1</sup>H, <sup>1</sup>H coupling constants between 6.7 and 6.5 Hz.

In complexes **1–4**, the signal attributable to the proton of the alcohol group (O–*H*) is not observed. However, in complexes **5** and **6**, this signal appears as a triplet at 4.90 ppm ( ${}^{3}J$  = 6.6 Hz) and as a broad band at 5.14 ppm, respectively.

Additional <sup>195</sup>Pt{<sup>1</sup>H} NMR experiments for complexes **3** and **4**, at 298 K, revealed only one band for each complex. For these complexes, the signals appear at -2193 and -2185 ppm, respectively. These values appear in the range described in the literature for complexes with [PtCl<sub>2</sub>N<sub>2</sub>] *core* (-2279, -1198 ppm) [18]. These data illustrate how sensitive the platinum chemical shift is to the average ligand environment.

#### 2.3. Crystal and molecular structure of cis-[PdCl<sub>2</sub>(pzol.2)] $\cdot$ H<sub>2</sub>O (2)

The crystal and molecular structure of complex **2** consists of discrete *cis*-[PdCl<sub>2</sub>(pzol.2)] molecules and solvent molecules

(H<sub>2</sub>O), linked by hydrogen bonding (Fig. 2). The H<sub>2</sub>O molecules are disordered.

The palladium centre presents a typical square planar geometry (with a slight tetrahedral distortion) in which the largest deviation from the mean coordination plane is 0.058(3)Å. This distortion is higher than that found in [PdCl<sub>2</sub>(L'')] (L'' = 2-(3-(pyridyn-2-yl)-5-trifluoromethyl-1H-pyrazol-1-yl)ethanol (0.006(3)Å) [7]. The metal atom is coordinated to one pzol.2 ligand, *via* one pyrazole and one pyridine nitrogens, and two chlorine atoms in *cis* disposition. The pzol.2 behaves as a bidentate ligand forming a five membered metallocycle.

The  $[PdCl_2(N_{pz})(N_{py})]$  core (containing terminal chlorine atoms in a *cis* disposition) is found in eight complexes described in the literature [7,17a,19]. The Pd-N<sub>py</sub>, Pd-N<sub>pz</sub> and Pd-Cl bond lengths are in the range of bond distances found in the literature for similar complexes [7,17a,19a]. Selected bond distances and angles for this complex are gathered in Table 1.

The N1–Pd–N3 bite angle is 79.76(10)°. This angle is comparable to those found in the structures for analogous complexes described in the literature [7,17a,19a].

The ligand pzol.2 is not planar. The pyridyl and phenyl groups are twisted with respect to the pyrazole ring. The py-pz dihedral angle is  $9.28(4)^\circ$ , the ph-pz angle is  $57.05(4)^\circ$  and the py-ph angle is  $61.15(3)^\circ$ . The py-pz dihedral angle is higher and the pz-ph and py-ph dihedral angles are of the same order as those found for other complexes described in the literature [7,17a,19a].

The hydroxyethyl group, which is bonded to the N2 atom, moves away from the chelating plane giving a torsion angle N1–N2–C15–C16 of  $-67.5(4)^{\circ}$ . This value is lower than that found for the [PdCl<sub>2</sub>(L'')] complex (88.8(4)°) [7].

The *cis*-[PdCl<sub>2</sub>(pzol.2)] molecules are stacked in antiparallel manner and they form layers parallel to the crystallographic plane *ac*. Each molecule is connected to other two adjacent molecules through hydrogen bonding between a Cl1 atom and the hydroxy-ethyl oxygen O1 with a distance of 3.208(4) Å. The hydrogen bondings form a 1D network parallel to the [0 1 0] direction (Fig. 3a). The O1–H1 bond lengths have been geometrically fixed in refinement (0.82 Å) and the contact parameters between O1–H1 and Cl1 are H1…Cl1, 2.56 Å; O1…Cl1, 3.208 Å; O1–H1…Cl1, 138°, symmetry code: 1 - x,  $\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ .

The lattice structure is also stabilised by  $\pi \cdots \pi$  stacking interactions between the pyrazole ring and the pyridine ring of inversion related molecules. The angle between the planes formed by the pyrazole and pyridine rings in two different molecules is 9.28° and the distance between centroids is 3.758(3) Å. These values are in agreement with the interval found in the literature for this kind of interaction [3.3–3.8 Å] [20] (Fig. 3b).

#### 2.4. Crystal and molecular structure of [ZnCl<sub>2</sub>(pzol.2)](6)

Table 1

The crystal structure consists of discrete [ZnCl<sub>2</sub>(pzol.2)] molecules and solvent molecules (CH<sub>2</sub>Cl<sub>2</sub>), linked by hydrogen bondings (Fig. 4).

The central Zn(II) atom is penta-coordinated and surrounded by a N<sub>2</sub>Cl<sub>2</sub>O environment, adopting a distorted trigonal bipyramidal geometry. The value of the trigonality index ( $\tau$ ) is 0.56 [21], and

Selected bond lengths (Å) and bond angles (°) for  $\it cis-[PdCl_2(pzol.2)]\cdot H_2O$  (2) with estimated standard deviations (e.s.d.s) in parentheses.

	()	F	
Pd-N(1)	2.070(3)	Pd-Cl(1)	2.2892(17)
Pd-N(3)	2.042(3)	Pd-Cl(2)	2.2921(12)
N(3)-Pd-N(1)	79.76(10)	N(3)-Pd-Cl(2)	172.96(8)
N(1)-Pd-Cl(1)	172.86(7)	N(1)-Pd-Cl(2)	98.85(8)
N(3)-Pd-Cl(1)	93.20(8)	Cl(1)-Pd-Cl(2)	88.28(4)



**Fig. 2.** ORTEP diagram of complex [PdCl<sub>2</sub>(pzol.2)]·H<sub>2</sub>O (**2**) showing an atom labelling scheme. 50% probability amplitude displacement ellipsoids are shown. Hydrogen atoms are omitted for clarity.



**Fig. 3.** (a) View of hydrogen bonding in the crystal structure of [PdCl<sub>2</sub>(pzol.2)]·H<sub>2</sub>O (**2**) forming an infinite chain. (b) View in projection along the stacking axis for complex (**2**). Hydrogen atoms are omitted for clarity.



**Fig. 4.** ORTEP diagram of complex [ZnCl<sub>2</sub>(pzol.2)] (**6**) showing an atom labelling scheme. 50% probability amplitude displacement ellipsoids are shown. Hydrogen atoms are omitted for clarity.

the angle N1–Zn–O1 is  $157.11(7)^{\circ}$ . The equatorial plane is defined by two chlorine atoms and N2<sub>pz</sub> and in the axial positions N1<sub>py</sub> and O1(*OH*) atoms are present. The mean deviation of the zinc atom from the equatorial plane is 0.023(3) Å. The pzol.2 ligand acts as a tridentate chelate and forms two membered rings, a six-membered ring, with twisted-boat conformation, and a five-membered ring with planar conformation, which share and edge (Zn–N<sub>pz</sub>).

In the molecules, the angles in the equatorial plane range are between 116.05° and 123.42° and the axial O1–Zn–N1<sub>py</sub> subtends an angle of 157.11(7)°. The Zn–N1<sub>py</sub> [2.186(2) Å] is longer than the Zn–N2<sub>pz</sub> bonds [2.0809(18) Å]. Selected bond lengths and angles are listed in Table 2. The [ZnCl<sub>2</sub>(N)<sub>2</sub>(O)] *core*, containing two terminal chlorine atoms is present in 21 complexes described in the literature [22], but when the oxygen atom is one alcohol group, this *core* is only present in four complexes [23]. For compound **6**, the Zn–N<sub>pz</sub> [2.0809(18) Å], Zn–N<sub>py</sub> [2.186(2) Å], Zn–Cl [2.2081(11) Å,

#### Table 2

Selected bond lengths (Å) and bond angles (°) for [ZnCl<sub>2</sub>(pzol.2)] (**6**) with estimated standard deviations (e.s.d.s) in parentheses.

Zn-N(2)	2.0807(18)	Zn-Cl(1)	2.2081(11)
Zn-N(1)	2.186(2)	Zn-O(1)	2.2110(19)
Zn-Cl(2)	2.2631(12)		
N(2)-Zn-N(1)	75.95(8)	N(2)-Zn-O(1)	81.22(7)
N(2)-Zn-Cl(1)	120.49(5)	N(1)-Zn-O(1)	157.10(7)
N(1)-Zn-Cl(1)	97.58(6)	Cl(1)-Zn-O(1)	92.35(6)
N(2)-Zn-Cl(2)	116.05(5)		

2.268(12) Å] and Zn–O [2.2113(19) Å] bond lengths can be regarded as normal compared with the distances found in the literature. For Zn–N<sub>pz</sub>, the literature describes values between 1.945 and 2.172 Å [24], for Zn–N<sub>py</sub> between 2.030 and 2.227 Å [23a–c,25], for Zn–Cl between 2.188 and 2.373 Å [23,24a–g,25b] and for Zn–O between 1.923 and 2.281 Å [23,26].

The ligand pzol.2 is not planar. The pyridyl and phenyl groups are twisted with respect to the pyrazole ring. The py-pz dihedral angle is  $5.55(12)^\circ$ , the ph-pz angle is  $33.61(12)^\circ$  and the py-ph angle is  $32.88(9)^\circ$ .

The hydroxyethyl group, which is bonded to the N3 atom, moves away from the chelating plane giving a torsion angle N2–N3–C15–C16 of  $-20.8(3)^{\circ}$ . This value is lower than that obtained for [PdCl<sub>2</sub>(pzol.2)], probably due to the coordination of the OH group to the metal.

The molecules  $[ZnCl_2(pzol.2)]$  are stacked along the  $[1 \ 0 \ 0]$  direction. In contrast to complex **2**, in this case the inversion related molecules form dimers trough hydrogen bonding between Cl2 atom and the hydroxyethyl oxygen O1 with a distance of 3.087(2) Å (Fig. 5a). The O–H bond lengths have been geometrically fixed in refinement (0.82 Å) and the contact parameters between O–H and Cl are H···Cl, 2.65 Å; O···Cl, 3.087(2) Å; O–H···Cl, 115°; symmetry code: -x, 1 - y, 1 - z.

Moreover,  $\pi \cdots \pi$  interactions are observed between pyridinepyridine and pyrazole–pyrazole (Fig. 5b) rings. The angles between the planes formed by the pyridine and pyridine rings in two different molecules is 1.80° and the distance between centroids is 3.832(2) Å. The angle between the planes formed by the pyrazole and pyrazole rings in two different molecules is 10.79°, and the distance between centroids is 3.846(2) Å. The angles and distances are in agreement with the interval found in the literature for this kind of interactions [3.3–3.8 Å] [20].

#### 3. Conclusion

In summary, we present the preparation, separation and characterisation of two regioisomers of a *N*-hydroxyethylpyridylpyrazole derived ligand (pzol.1, pzol.2).

The study of the coordination of the pzol.1 ligand with Pd(II) and Pt(II) has revealed the formation of complexes  $[MCl_2(pzol.1)_2]$  (M = Pd(II); Pt(II)), and the reaction of the pzol.2 ligand with Pd(II) and Pt(II) yields *cis*- $[MCl_2(pzol.2)]$  complexes. In complexes  $[MCl_2(pzol.1)_2]$ , the ligand shows monodentate coordination (**N**<sub>pz</sub>), and for *cis*- $[MCl_2(pzol.2)]$  complexes the ligand shows bidentate coordination (**N**<sub>pz</sub>, **N**<sub>py</sub>). On the other hand, the reaction of the pzol.1 and pzol.2 ligands with ZnCl<sub>2</sub>, yields complexes  $[ZnCl_2(L)]$ . For L = pzol.1, the ligand acts as bidentate (**N**<sub>pz</sub>, **OH**) but for L = pzol.2, the ligand acts as tridentate (**N**<sub>pz</sub>, **N**<sub>py</sub>, **OH**).

Ligands pzol.1 and pzol.2 are potentially tridentate ( $N_{py}$ , $N_{pz}$ ,OH), but pzol.1 ligand can act as monodentate ( $N_{pz}$ ) or bidentate ( $N_{pz}$ , $N_{py}$ ) and pzol.2 ligand can act as bidentate ( $N_{pz}$ ,OH) or tridentate ( $N_{pz}$ , $N_{py}$ ,OH). These differences depend of the metal: for Pd(II) and Pt(II), the –OH group does not coordinate to the metal centre,



Fig. 5. (a) View of hydrogen bonding in the crystal structure of [ZnCl<sub>2</sub>(pzol.2)] (6) forming dimmers. (b) View in projection along the stacking axis for complex (6). Hydrogen atoms are omitted for clarity.

whereas for Zn(II) atom, the -OH group can coordinate to the metal centre.

### 4. Experimental section

### 4.1. General details

Standard Schlenk techniques were employed throughout the synthesis using a double manifold vacuum line with high purity dry nitrogen. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods.

The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) in  $10^{-3}$  M in acetonitrile and DMSO solutions employing a Cyber-Scan CON 500 (Euthech Instruments) conductimeter. Infrared spectra were run on a Perkin–Elmer FT spectrophotometer series 2000 cm<sup>-1</sup> as NaCl disks, KBr pellets or polyethylene films in the range 4000–100 cm<sup>-1</sup> under a nitrogen atmosphere.

The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} NMR, DEPT, COSY, HSQC and NOESY spectra were recorded on an NMR-FT Brucker AC-250 MHz spectrometer in CDCl<sub>3</sub> and DMSO- $d_6$  solutions, at room temperature. <sup>1</sup>H{<sup>195</sup>Pt} and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra were recorded at 298 K in DMSO- $d_6$  solutions, and 77.42 MHz on a DPX-360 MHz Bruker spectrometer using aqueous solutions of [PtCl<sub>6</sub>]<sup>2-</sup> (0 ppm) as an external reference and delay times, 0.01 s.

All chemical shifts values ( $\delta$ ) are given in ppm. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

Synthesis of 1-phenyl-3-pyridin-2-yl-propane-1,3-dione has previously been reported in the literature [9]. Samples of  $[MCl_2(CH_3CN)_2]$  (M = Pd(II) [10], Pt(II) [12], were prepared and described in the literature.

### 4.2. Synthesis of the ligands 2-(3-phenyl-5-(pyridyn-2-yl)-1H-pyrazol -1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridyn-2-yl)-1H-pyrazol-1-yl)ethanol (pzol.2)

The 1-phenyl-3-(pyridyn-2-yl)propane-1,3-dione (6.60 mmol, 1.49 g) was dissolved in ethanol (25 ml). To this solution 2-hydroxyethylhidrazine (6.60 mmol, 0.50 g) was added and the mixture was stirred at 0 °C for 2 h. The resulting solution was

stirred at room temperature for 3 h. After removing the solvent under vacuum, the product was extracted from the oily residuum with  $H_2O/CHCl_3$ . The collected organic layers were dried with anhydrous sulfate and remover under vacuum. Ligands were obtained in 93% yield as oils with sufficient purity (<sup>1</sup>H NMR). The separation of regioisomers was done by silica column chromatography using ethyl acetate as eluent.

*pzol.1:* Yield: 43%. *Anal.* Calc. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O (265.3): C, 72.43; H, 5.70; N, 15.84. Found: C, 72.33; H, 5.64; N, 15.88%. MS(ESI+): *m/z* (%) = 288 (100) [pzol.1 + Na]<sup>+</sup>; 266 (63) [pzol.1 + H]<sup>+</sup>. IR (NaCl/ cm<sup>-1</sup>): *v*(O–H) 3245, *v*(C–H)<sub>ar</sub> 3067, *v*(C–H)<sub>al</sub> 2954, 2857, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1590, 1567, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1551, [*δ*(C=C), *δ* (C=N)]<sub>ar</sub> 1451, *δ*(C–H)<sub>ip</sub>1088, 1057 *δ*(C–H)<sub>oop</sub> ar 783, *δ*(C–H)<sub>oop</sub> pz 694. <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz, 298 K) *δ* = 8.72 [d, 1H, <sup>3</sup>J 4.8 Hz, *H*<sub>orto</sub> py], 8.19–7.30 [m, 8H, H<sub>py</sub>, ph], 6.87 [s, 1H, *CH*(pz)], 4.71 [t, 2H, <sup>3</sup>J 5.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 4.19 [t, 2H, <sup>3</sup>J 5.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub> solution, 63 MHz, 298 K) *δ* = 151.2 [*C*<sub>orto</sub> py], 149.2 [*C*-py], 148.7 [*C*-ph], 137.9, 133.4 [*C*-Cpy, *C*-Cph], 129.4–123.4 [Cpy, Cph], 104.3 [CH(pz)], 63.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 53.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

*pzol.2*: Yield: 52%. *Anal.* Calc. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O (265.3): C, 72.43; H, 5.70; N, 15.84. Found: C, 72.22; H, 5.58; N, 15.78%. MS(ESI+): *m/z* (%) = 288 (100) [pzol.2 + Na]<sup>+</sup>, 266 (7) [pzol.2 + H]<sup>+</sup>. IR (NaCl/ cm<sup>-1</sup>): *v*(O–H) 3283, *v*(C–H)<sub>ar</sub> 3063, *v*(C–H)<sub>al</sub> 2935, 2873, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1595, 1567, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1550, [*δ*(C=C), *v*(C=N)]<sub>ar</sub> 1476, 1465, *δ*(C–H)<sub>ip</sub> 1072, 1049, *δ*(C–H)<sub>oop ar</sub> 787 *δ*(C–H)<sub>oop pz</sub> 700. <sup>1</sup>H NMR (CDCl<sub>3</sub> solution, 250 MHz, 298 K) *δ* = 8.64 [d, 1H, <sup>3</sup>*J* = 4.5 Hz, *H*<sub>orto py</sub>], 8.00–7.21 [m, 8H, H<sub>py, ph</sub>], 6.99 [s, 1H, CH(pz)], 4.31 [t, 2H, <sup>3</sup>*J* 5.0 Hz, N–C*H*<sub>2</sub>CH<sub>2</sub>–OH], 4.07 [t, 2H, <sup>3</sup>*J* 5.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub> solution, 63 MHz, 298 K) *δ* = 152.1 [*C*<sub>orto py</sub>], 149.6 [*C*-py], 146.3 [*C*-ph], 136.7, 131.9 [CCpy, CCph], 129.1–120.4 [Cpy, Cph], 105.2 [CH(pz)], 62.1 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 51.6 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

# 4.3. Synthesis of the complexes [PdCl<sub>2</sub>(pzol.1)<sub>2</sub>] (1) and [PdCl<sub>2</sub>(pzol.2)] (2)

The appropriate ligand (0.27 mmol: pzol.1, 0.072 g; pzol.2, 0.072 g) dissolved in dry dichloromethane (10 ml) was added to a solution of  $[PdCl_2(CH_3CN)_2]$  (0.13 mmol, 0.035 g for **1** and 0.27 mmol, 0.070 g for **2**) in dry dichloromethane (20 ml). The solution resulting was stirred at room temperature for 48 h. The solution was cooled down to 0 °C and diethyl ether (5 ml) was then

added to induce precipitation. The yellow solution was filtered off, washed twice 5 ml of diethyl ether and dried under vacuum.

**1**: Yield: 60%. *Anal.* Calc. for C<sub>32</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>PdCl<sub>2</sub> (707.9): C, 54.29; H, 4.27; N, 11.87. Found: C, 53.95; H, 4.54; N, 11.62%. MS(ESI+): *m*/ *z* (%) = 635 (100) [PdCl<sub>2</sub>(pzol.1)<sub>2</sub>-2Cl-H]<sup>+</sup>. Conductivity (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, 1.03 × 10<sup>-3</sup> M in acetonitrile): 12.3. IR (KBr/cm<sup>-1</sup>): *v*(O-H) 3261, *v*(C-H)<sub>ar</sub> 3061, *v*(C-H)<sub>al</sub> 2945, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1606, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1510, [ $\delta$ (C=C), *v*(C=N)]<sub>ar</sub> 1459,  $\delta$ (C-H)<sub>ip</sub> 1065,  $\delta$ (C-H)<sub>oop ar</sub> 766,  $\delta$ (C-H)<sub>oop pz</sub> 696. (Polyethylene/cm<sup>-1</sup>): (Pd-N) 440, *v*(Pd-Cl) 334. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub> solution, 250 MHz, 298 K)  $\delta$  = 8.69 [d, 1H, <sup>3</sup>*J* 5.6 Hz, *H*<sub>orto py</sub>], 8.20–7.30 [m, 8H, H<sub>py, ph</sub>], 7.25 [s, 1H, *CH*(pz)], 4.69 [t, 2H, <sup>3</sup>*J* 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 3.78 [t, 2H, <sup>3</sup>*J* 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub> solution, 63 MHz, 298 K)  $\delta$  = 151.4 [*C*<sub>orto py</sub>], 149.0 [*C*-py], 148.1 [*C*-ph], 137.6, 133.4 [CCpy, CCph], 130.4–122.6 [Cpy, Cph], 104.5 [CH(pz)], 63.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 53.1 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

**2**: Yield: 44%. Anal. Calc. for  $C_{16}H_{15}N_3OPdCl_2$  (442.6): C, 43.42; H, 3.42; N, 9.49. Found: C, 43.66; H, 3.52; N, 9.73%. MS(ESI+): *m/z* (%) = 408 (100) [PdCl\_2(pzol.2)–Cl]<sup>+</sup>. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.12 × 10<sup>-3</sup> M in acetonitrile): 7.1. IR (KBr/cm<sup>-1</sup>): *v*(O–H) 3278, *v*(C–H)<sub>ar</sub> 3060, *v*(C–H)<sub>al</sub> 2866, 1608 [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1608, 1551 [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1551, [ $\delta$ (C=C), *v*(C=N)]<sub>ar</sub> 1458,  $\delta$ (C–H)<sub>ip</sub> 1068,  $\delta$ (C–H)<sub>oop ar</sub> 764,  $\delta$ (C–H)<sub>oop pz</sub> 702. (Polyethylene/cm<sup>-1</sup>): *v*(Pd–N) 397, *v*(Pd–Cl) 327, 302. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub> solution, 250 MHz, 298 K)  $\delta$  = 9.03 [d, 1H, <sup>3</sup>J 5.6 Hz, *H*<sub>orto py</sub>], 8.30–7.50 [m, 8H, H<sub>py, ph</sub>], 7.42 [s, 1H, CH(pz)], 4.27 [t, 2H, <sup>3</sup>J 6.6 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 3.78 [t, 2H, <sup>3</sup>J 6.6 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub> solution, 63 MHz, 298 K)  $\delta$  = 152.1 [*C*<sub>orto py</sub>], 149.4 [*C*-py], 146.5 [*C*-ph], 136.9, 132.3 [CCpy, CCph], 129.0–120.4 [*C*py, Cph], 105.2 [CH(pz)], 62.4 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 52.0 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

# 4.4. Synthesis of the complexes [PtCl<sub>2</sub>(pzol.1)<sub>2</sub>] (**3**) and [PtCl<sub>2</sub>(pzol.2)] (**4**)

The appropriate ligand (0.27 mmol: pzol.1, 0.072 g; pzol.2, 0.072 g) dissolved in dry acetonitrile (25 ml) was added to a solution of  $[PtCl_2(CH_3CN)_2]$  (0.14 mmol, 0.047 g for **3** and 0.27 mmol, 0.094 g for **4**) in dry acetonitrile (50 ml). The resulting solution was stirred and refluxed for 24 h and concentrated on a vacuum line to one fifth of the initial volume. The yellow solution was filtered off, washed twice with 5 ml of diethyl ether and dried under vacuum.

3: Yield: 58%. Anal. Calc. for C<sub>32</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>PtCl<sub>2</sub> (796.6): C, 48.25; H, 3.80; N, 10.55. Found: C, 48.03; H, 3.58; N, 10.34%. MS(ESI+): m/z (%) = 724 (100) [PtCl<sub>2</sub>(pzol.1)<sub>2</sub>-2Cl-H]<sup>+</sup>. Conductivity  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, 1.18 \times 10^{-3} \text{ M} \text{ in DMSO})$ : 19.4. IR (KBr/cm<sup>-1</sup>): *v*(O-H) 3482, *v*(C-H)<sub>ar</sub> 3087, *v*(C-H)<sub>al</sub> 2907, 2861, [*v*(C=C),  $v(C=N)]_{ar}$  1615,  $[v(C=C), v(C=N)]_{pz}$  1520,  $[\delta(C=C), v(C=N)]_{ar}$ 1468, 1452, δ(C-H)<sub>ip</sub> 1078, δ(C-H)<sub>oop ar</sub> 783, δ(C-H)<sub>oop pz</sub> 712. (Polyethylene/cm<sup>-1</sup>): v(Pt–N) 421, v(Pt–Cl) 357. <sup>1</sup>H NMR (DMSO $d_6$  solution, 250 MHz, 298 K)  $\delta = 9.52$  [d, 1H, <sup>3</sup>J = 5.8 Hz,  $H_{\text{orto py}}$ ], 8.38–7.62 [m, 8H, H<sub>py, ph</sub>], 7.45 [s, 1H, CH(pz)], 4.98 [t, 2H, <sup>3</sup>] 4.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 4.05 [t, 2H, <sup>3</sup>J 4.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO- $d_6$  solution, 63 MHz, 298 K)  $\delta = 149.1 [C_{\text{orto py}}]$ , 147.4 [C-py], 138.3 [C-ph], 135.2, 131.7 [CCpy, CCph], 129.4-125.2 [Cpy, Cph], 107.2 [CH(pz)], 62.4 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 54.2  $[N_{pz}CH_2CH_2OH]$ . <sup>195</sup>Pt{<sup>1</sup>H} (DMSO-d<sub>6</sub> solution, 77 MHz, 298 K)  $\delta = -2193$  (s).

**4**: Yield: 56%. *Anal.* Calc. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OPtCl<sub>2</sub> (531.3): C, 36.17; H, 2.85; N, 7.91. Found: C, 36.09; H, 2.74; N, 7.81%. MS(ESI+): *m/z* (%) = 496 (100) [PtCl<sub>2</sub>(pzol.2)–Cl]<sup>+</sup>. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 0.95 × 10<sup>-4</sup> M in DMSO): 27.2. IR (KBr/cm<sup>-1</sup>): *v*(O–H) 3461, *v*(C–H)<sub>ar</sub> 3092, *v*(C–H)<sub>al</sub> 2914, 2854, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1619, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1522, [ $\delta$ (C=C), *v*(C=N)]<sub>ar</sub> 1464, 1444,  $\delta$ (C–H)<sub>ip</sub> 1083,  $\delta$ (C–H)<sub>oop ar</sub> 766,  $\delta$ (C–H)<sub>oop pz</sub> 700. *v*<sub>max</sub> (Polyethylene/cm<sup>-1</sup>): *v*(Pt–N) 463, *v*(Pt–Cl) 348, 339. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub> solution,

250 MHz, 298 K)  $\delta$  = 9.39 [d, 1H, <sup>3</sup>*J* = 5.6 Hz, *H*<sub>orto py</sub>], 8.31–7.59 [m, 8H, H<sub>py, ph</sub>], 7.50 [s, 1H, C*H*(pz)], 4.82 [t, 2H, <sup>3</sup>*J* 4.5 Hz, NC*H*<sub>2</sub>CH<sub>2</sub>OH], 3.83 [t, 2H, <sup>3</sup>*J* 4.5 Hz, NCH<sub>2</sub>C*H*<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub> solution, 63 MHz, 298 K)  $\delta$  = 149.1 [*C*<sub>orto py</sub>], 141.1 [*C*-py], 129.7 [*C*-ph], 129.4, 128.7 [CCpy, CCph], 124.9–122.2 [Cpy, Cph], 105.5 [CH(pz)], 60.3 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 51.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH]. <sup>195</sup>Pt{<sup>1</sup>H} (DMSO-*d*<sub>6</sub> solution, 77 MHz, 298 K)  $\delta$  = –2185 (s).

# 4.5. Synthesis of the complexes [*ZnCl*<sub>2</sub>(*pzol*.1)] (**5**) and [*ZnCl*<sub>2</sub>(*pzol*.2)] (**6**)

Zn(II) chloride (0.46 mmol, 0.062 g) was solved in 20 ml of absolute ethanol and 4 ml of triethyl orthoformate (for dehidratation purposes). Then, 0.46 mmol of the corresponding ligand (pzol.1, 0.122 g; pzol.2, 0.122 g) solved in absolute ethanol (10 ml) and a white solution was obtained. Upon standing, in same cases almost instantaneously crystalline materials started to precipitate. The solid product were isolated by filtration and dried under vacuum.

**5**: Yield: 45%. *Anal.* Calc. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OZnCl<sub>2</sub> (401.6): C 47.85, H 3.76, N 10.46. Found: C, 48.00; H, 3.83; N, 10.27%. MS(ESI+): *m/z* (%) = 364 (100) [ZnCl<sub>2</sub>(pzol.1)–Cl]<sup>+</sup>. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.23 × 10<sup>-3</sup> M in acetonitrile): 9.7. IR (KBr/cm<sup>-1</sup>): *v*(O–H) 3238, *v*(C–H)<sub>ar</sub> 3061, *v*(C–H)<sub>al</sub> 2940, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1597, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1569, [ $\delta$ (C=C), *v*(C=N)]<sub>ar</sub> 1464,  $\delta$ (C–H)<sub>ip</sub> 1032,  $\delta$ (C–H)<sub>oop ar</sub> 766,  $\delta$ (C–H)<sub>oop pz</sub> 694. (Polyethylene/cm<sup>-1</sup>): *v*(Zn–O), *v*(Zn–N), 422, 418, *v*(Zn–Cl) 302, 281. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub> solution, 250 MHz, 298 K)  $\delta$  = 8.70 [d, 1H, <sup>3</sup>*J* = 5.8 Hz, *H*<sub>orto py</sub>], 8.00–7.30 [m, 8H, H<sub>py, ph</sub>], 7.25 [s, 1H, *CH*(pz)], 4.90 [t, 1H, <sup>3</sup>*J* 6.6 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 4.70 [t, 2H, <sup>3</sup>*J* 6.5 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub> solution, 63 MHz, 298 K)  $\delta$  = 151.2 [*C*<sub>orto py</sub>], 149.1 [*C*-py], 148.3 [*C*-ph], 137.8, 132.0 [*C*-Cpy, C-Cph], 130.1–121.8 [Cpy, Cph], 104.7 [CH(pz)], 63.3 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 53.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

**6**: Yield: 46%. Anal. Calc. for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OZnCl<sub>2</sub> (401.6): C, 47.85; H, 3.76; N, 10.46. Found: C, 47.91; H, 3.82; N, 10.21%. MS(ESI+): *m/z* (%) = 364 (100) [ZnCl<sub>2</sub>(pzol.2)–Cl]<sup>+</sup>. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.27 × 10<sup>-3</sup> M in acetonitrile): 10.4. IR (KBr/cm<sup>-1</sup>): *v*(O–H) 3258, *v*(C–H)<sub>ar</sub> 3054, *v*(C–H)<sub>al</sub> 2942, [*v*(C=C), *v*(C=N)]<sub>ar</sub> 1608, [*v*(C=C), *v*(C=N)]<sub>pz</sub> 1549, [ $\delta$ (C=C), *v*(C=N)]<sub>ar</sub> 1461,  $\delta$ (C–H)<sub>ip</sub> 1049,  $\delta$ (C–H)<sub>oop ar</sub> 763,  $\delta$ (C–H)<sub>oop pz</sub> 698. *v*<sub>max</sub> (Polyethylene/cm<sup>-1</sup>): *v*(Zn–O), *v*(Zn–N) 420, 413, *v*(Zn–Cl) 323, 302. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub> solution, 250 MHz, 298 K)  $\delta$  = 8.62 [d, 1H, <sup>3</sup>*J* 5.7 Hz, *H*<sub>orto py</sub>], 8.10–7.43 [m, 8H, H<sub>py, ph</sub>], 7.36 [s, 1H, CH(pz)], 5.14 [br, 1H, NCH<sub>2</sub>CH<sub>2</sub>OH], 4.22 [t, 2H, <sup>3</sup>*J* 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>OH], 3.85 [m, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH]. <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub> solution, 63 MHz, 298 K)  $\delta$  = 152.3 [*C*<sub>orto py</sub>], 149.6 [*C*-py], 147.0 [*C*-ph], 137.1, 133.4 [CCpy, CCph], 129.3–120.2 [Cpy, Cph], 105.4 [CH(pz)], 62.2 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH], 51.9 [N<sub>pz</sub>CH<sub>2</sub>CH<sub>2</sub>OH].

#### 4.6. X-ray crystal structures for compounds 2 and 6

Suitable crystals for X-ray diffraction of compounds  $[PdCl_2(pzol. 2)]$  H<sub>2</sub>O (**2**) and  $[ZnCl_2(pzol.2)]$  (**6**) were obtained through crystallisation from a dichloromethane/diethyl ether (4:1) mixture.

For compounds **2** and **6** a prismatic crystal was selected and mounted on a MAR 345 diffractometer with an image plate detector. Unit-cell parameters were determined from 236 reflections for **2** and 319 reflections for **6** ( $3 < \theta < 31^\circ$ ) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo K $\alpha$  radiation. For **2**, 14 552 reflections were measured in the range  $2.60 \le \theta \le 32.43$ . 5696 of which were nonequivalent by symmetry ( $R_{int}$  (on I) = 0.044). 4631 reflections were assumed as observed applying the condition  $I \ge 2\sigma$  (I). For **6**, 16 763 reflections were measured in the range  $2.55 \le \theta \le 32.36$ , 5546 of which were non-equivalent by symmetry ( $R_{int}$  (on

#### Table 3

Crystallographic data for cis-[PdCl<sub>2</sub>(pzol.2)]H<sub>2</sub>O (2) and [ZnCl<sub>2</sub>(pzol.2)] (6).

	2	6
Formula	$C_{16}H_{17}Cl_2N_3O_2Pd$	C <sub>17</sub> H <sub>17</sub> Cl <sub>4</sub> N <sub>3</sub> OZn
Μ	460.63	486.51
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	14.192(9)	13.283(5)
b (Å)	8.083(3)	19.979(8)
c (Å)	16.980(9)	7.508(4)
α(°)	90	90
β (°)	112.60(3)	91.27(3)
γ (°)	90	90
$U(Å^3)$	1798.3(16)	1992.0(15)
Ζ	4	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.701	1.622
$\mu$ (mm $^{-1}$ )	1.342	1.781
F(000)	920	984
Crystal size	$0.2\times0.1\times0.1$	$0.1\times0.09\times0.08$
$\theta$ range (°)	2.60-32.43	2.55-32.36
Index range	-19 < h < 21,	-10 < h < 9,
	−11 < <i>k</i> < 12,	−28 < <i>k</i> < 24,
	-24 < <i>l</i> < 23	−17 < <i>l</i> < 17
Reflexions collected/	14 552/5696	16 763/5546
unique	$[R_{(int)} = 0.0442]$	$[R_{(int)} = 0.0651]$
Completeness to	99.3	98.8
$\theta = 25.00$ (%)		
Absorption correction	empirical	empirical
Maximum and	0.87 and 0.85	0.85 and 0.84
minimum		
transmission		
Data/restraints/	5696/0/242	5546/14/244
parameters		
Goodness-of-fit (GOF)	1.131	0.971
Final $R_1$ , $\omega R_2$	0.0460, 0.1287	0.0376, 0.0965
$R_1$ (all data), $\omega R_2$	0.0568, 0.1343	0.0576, 0.1026
Residual electron	1.214 and -0.501	0.460 and -0.463
density (e Å <sup>-3</sup> )		
2		

I) = 0.065). 3814 reflections were assumed as observed applying the condition  $I \ge 2\sigma$  (*I*).

Lorentz-polarisation and absorption corrections were made.

Both structures were solved by Direct methods, using SHELXS computer program (shelxs-97) [27] and refined by full matrix least-squares method with SHELXL-97 [28] computer program using 14 552 reflections for **2** and 16 763 for **6** (very negative intensities were not assumed).

For **2**, the function minimised was  $\sum w ||F_0|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2 (I) + 0.0743P^2 + 0.3221P]^{-1}$ , and  $P = (|F_0|^2 + 2 |F_c|^2)/3$ . For **6**, the function minimised was  $\sum w ||F_0|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2]$  $(I) + (0.0502P)^2$ ]<sup>-1</sup>. All H 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  $R_w(F^2)$  values as well as the number of parameters refined and other details concerning the refinement of the crystal structures are gathered in Table 3.

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#### **Appendix A. Supplementary material**

CCDC 778525 and 778524 contain the supplementary crystallographic data for  $[PdCl_2(pzol.2)] \cdot H_2O(2)$  and  $[ZnCl_2(pzol.2)](6)$ , respectively. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2010.11.041.

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