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Inorganica Chimica Acta 358 (2005) 617-622

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and characterisation of palladium(II) and platinum(II) compounds containing pyrazole-derived ligands: crystal structure of $[PdCl_2(HL^1)]$ (HL¹ = 3-phenyl-5-(2-pyridyl)pyrazole)

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> Received 30 June 2004; accepted 28 July 2004 Available online 13 November 2004

Abstract

Reaction of the ligands 3-phenyl-5-(2-pyridyl)pyrazole (HL^1), 3,5-bis(2-pyridyl)pyrazole (HL^2), 3-methyl-5-(2-pyridyl)pyrazole (HL^3) and 3-methyl-5-phenylpyrazole (HL^4) with [$MCl_2(CH_3CN)_2$] (M = Pd(II), Pt(II)) or [$PdCl_2(cod)$] gives complexes with stoichiometry [$PdCl_2(HL)_2$] ($HL = HL^1$, HL^2 , HL^3), [$Pt(L)_2$] ($L = L^1$, L^2 , L^3) and [$MCl_2(HL^4)_2$] (M = Pd(II), Pt(II)). The new complexes were characterised by elemental analyses, conductivity measurements, infrared and ¹H NMR spectroscopies. The crystal and molecular structure of [$PdCl_2(HL^1)$] was resolved by X-ray diffraction, and consists of monomeric *cis*-[$PdCl_2(HL^1)$] molecules. The palladium centre has a typical square planar geometry, with a slight tetrahedral distortion. The tetra-coordinated metal atom is bonded to one pyridine nitrogen, one pyrazolic nitrogen and two chloro ligands in a *cis* disposition. The ligand HL^1 is not completely planar. © 2004 Elsevier B.V. All rights reserved.

Keywords: Palladium complexes; Platinum complexes; Pyrazole complexes; Crystal structures

1. Introduction

The chemistry of pyrazole and pyrazolate metal complexes is described quite extensively in the literature [1– 5]. Previous studies showed the high catalytic activity, under mild conditions, of some polynuclear heterobridged pyrazolate complexes, thus encouraging the exploration of the unusual and specific features of the pyrazolate ligands [4,5]. Some authors have suggested that introducing appropriate substituents at positions 3, 4 or 5 of the heterocyclic ring may modify the nucleophilicity of N2 (sp²) and the acid character of pyrazole [6,7]. Over the last few years, we have developed the coordination chemistry of pyrazole-derived ligands as it has become apparent that this chemistry is rich in structural types, reactivity characteristics and ligands modes. Recently, our investigations have been directed towards the preparation of 3,5-substituted pyrazole ligands. These ligands have one or two chelating arms attached to the 3- and 5-positions of the pyrazole.

We have reported the synthesis and characterisation of polydentate ligands with nitrogen donors 3-phenyl-5-(2-pyridyl)pyrazole (\mathbf{HL}^{1}) [8], 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole ($\mathbf{HL}^{1'}$) [8], 3,5-bis(2-pyridyl)pyrazole (\mathbf{HL}^{2}) [9,10], 3-(6-methyl-2-pyridyl)-5-(2-pyridyl)pyrazole ($\mathbf{HL}^{2'}$) [11] and 3,5-bis(6-methyl-2-pyridyl)pyrazole ($\mathbf{HL}^{2''}$) [11]. We have also studied their reactivity with the divalent metal ions Co [8,11–13], Ni [10–12,14], Pd [15], Cu [11,16–19], Zn [12] and Cd [12]. Some of these ligands were previously studied by other authors, thus,

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^{0020-1693/\$ -} see front matter @ 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2004.07.064

in 1995 Munakata et al. [20] described three complexes with HL^2 , two of Ag(I) and one of Cu(II), and in 2003 Catalano et al. [21] described Ru(II) complexes with these ligands.

Here, we study the synthesis and structural determination of the Pd(II) and Pt(II) complexes of the ligands 3-phenyl-5-(2-pyridyl)pyrazole (HL^1) [8], 3,5-bis(2pyridyl)pyrazole (HL^2) [9,10], 3-methyl-5-(2-pyridyl)pyrazole (HL^3) [22], and 3-methyl-5-phenylpyrazole (HL^4) [23]. The crystal structure of [PdCl₂(HL¹)] is described and compared with those of closely related structures.

2. Experimental

2.1. General methods

All reactions were performed under a nitrogen atmosphere with the use of vacuum line and standard Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled under N_2 by standard methods just before use.

Elemental analyses (C, N, H) were carried out by the staff of the Chemical Analyses Services 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} DMSO, employing a CyberScan CON 500 (Euthech Instruments) conductimeter. 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. ¹H NMR spectra were recorded on a NMR-FT Bruker 250 MHz spectrometer in DMSO or CDCl₃ solutions at room temperature. All chemical shifts values (δ) are given in ppm.

Samples of $[PdCl_2(CH_3CN)_2]$ [24], $[PtCl_2(CH_3CN)_2]$ [25] and $[PdCl_2(cod)]$ [26] were prepared as described in the literature. The compounds 3-phenyl-5-(2-pyridyl)pyrazole (**HL**¹) [8], 3,5-bis(2-pyridyl)pyrazole (**HL**²) [9,10], 3-methyl-5-(2-pyridyl)pyrazole (**HL**³) [22], and 3-methyl-5-phenylpyrazole (**HL**⁴) [23] were prepared according to the published methods (Fig. 1).



\mathbf{HL}^{1} : R= Py,	R': Ph
\mathbf{HL}^2 : R= Py	R'= Py
HL ³ : R=Py,	R'= Me
HL^4 : R= Ph,	R'=Me

Fig. 1. Pyrazole derived ligands.

2.2. Synthesis

2.2.1. $[MCl_2(HL)]$ (M = Pd(II), $HL = HL^1$ 1, HL^2 2, HL^3 3)

A solution of 0.29 mmol of $\{PdCl_2(CH_3CN)_2: 0.075 g; PdCl_2(cod): 0.082 g\}$ in 75 ml of CH₃CN was treated with a solution of 0.29 mmol of the corresponding ligand (HL¹: 0.064 g; and HL²: 0.064 g; HL³: 0.046 g) in 10 ml of CH₃CN. After 14 h of stirring, the solution was concentrated until a crystalline precipitate appeared, which was filtered off, washed with CH₃CN (5 ml), and dried in vacuo.

2.2.1.1. Compound 1. Yield: 85%. $C_{14}H_{11}N_3Cl_2Pd$: Anal. Calc. C, 42.17; H, 2.76; N, 10.54. Found: C, 42.17; H, 2.64, N, 10.38%. Conductivity (Ω^{-1} cm² mol⁻¹, 8.5 × 10⁻⁴ M in DMSO): 21. IR: (KBr, cm⁻¹) 3237 v(N–H), 3125–3050 v(C–H)_{ar}, 1615–1547 (vC=C, vC=N), 1467–1450 (δ C=C, δ C=N), 1030 δ (C–H)_{ip}, 767 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 483 v(Pd–N), 360, 342 v(Pd–Cl). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 9.55 [1H, s, N *H*], 8.93 [1H, d, ³*J* = 5.9 Hz, Py], 8.31 [1H, t, ³*J* = 8.0 Hz, Py], 8.22 [1H, d, ³*J* = 8.0 Hz, Py], 7.90 [2H, d, ³*J* = 7.7 Hz, Ph], 7.73 [1H, s, Pz], 7.68 [1H, m, Py], 7.50 [3H, m, Ph].

2.2.1.2. Compound 2. Yield: 78%. $C_{13}H_{10}N_4Cl_2Pd$: Anal. Calc. C, 39.06; H, 2.50; N, 14.02. Found: C, 39.08; H, 2.44, N, 13.82%. Conductivity (Ω^{-1} cm² mol⁻¹, 9.1 × 10⁻⁴ M in DMSO): 35. IR: (KBr, cm⁻¹) 3325 ν (N–H), 3000 ν (C–H)_{ar}, 1610–1565 (ν C=C, ν C=N), 1442 (δ C=C, δ C=N), 1099 δ (C–H)_{ip}, 772 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 474 ν (Pd–N), 359, 340 ν (Pd–Cl). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 10.25 [1H, s, N *H*], 9.83 [1H, d, ³*J* = 5.9 Hz, Py], 8.93 [1H, ³*J* = 5.2 Hz, Py], 8.62 [1H, d, ³*J* = 4.8 Hz, Py], 8.50 [1H, d, ³*J* = 4.4 Hz, Py], 8.35 [1H, t, ³*J* = 7.9 Hz, Py], 8.25 [1H, d, ³*J* = 7.9 Hz, Py], 7.85 [1H, m, Py], 7.43 [1H, s, Pz], 7.28 [1H, m, Py].

2.2.1.3. Compound 3. Yield: 90%. C₉H₉N₃Cl₂Pd: Anal. Calc. C, 32.11; H, 2.68; N, 12.48. Found: C, 32.28; H, 2.40, N, 12.33%. Conductivity (Ω^{-1} cm² mol⁻¹, 8.6×10⁻⁴ M in DMSO): 28. IR: (KBr, cm⁻¹) 3438 ν (N–H), 3069 ν (C–H)_{ar}, 2959–2851 ν (C–H)_{al}, 1614– 1569 (ν C=C, ν C=N), 1444 (δ C=C, δ C=N), 1040 δ (C–H)_{ip}, 779 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 473 ν (Pd–N), 348, 329 ν (Pd–Cl). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 13.78 [1H, s, N H], 8.85 [1H, ddd, ³J = 7,3, 5.8 Hz, Py], 8.23 [1H, ddd, ³J = 7.3 Hz, Py], 8.13 [1H, d, ³J = 7.3 Hz, Py], 7.62 [1H, m, Py], 7.05 [1H, s, N H], 7.05 [1H, s, Pz], 2.34 [3H, s, CH₃].

2.2.2. $[MCl_2(HL^4)_2]$ (M = Pd(II) 4, Pt(II) 5)

A solution of 0.58 mmol (0.092 g) of HL^4 in 10 ml of CH₃CN was treated with a solution of 0.29 mmol of

 $[MCl_2(CH_3CN)_2]$ (Pd(II): 0.075 g; Pt(II) 0.101 g) dissolved in 75 ml of CH₃CN. After 12 h of stirring at room temperature, the solution was concentrated until a crystalline precipitate appeared. This precipitate was filtered off, washed twice with CH₃CN (10 ml), and dried in vacuo.

2.2.2.1. Compound 4. Yield: 82%. $C_{20}H_{20}N_4Cl_2Pd$: Anal. Calc. C, 48.64; H, 4.05; N, 11.36. Found: C, 48.52; H, 3.98, N, 11.16%. Conductivity (Ω^{-1} cm² mol⁻¹, 8.6×10⁻⁴ M in DMSO): 28. IR: (KBr, cm⁻¹) 3196 v(N-H), 3055 $v(C-H)_{ar}$, 2989–2863 $v(C-H)_{al}$, 1570– 1502 (vC=C, vC=N), 1477 ($\delta C=C$, $\delta C=N$), 1065 $\delta(C-H)_{ip}$, 762 $\delta(C-H)_{oop}$; (polyethylene, cm⁻¹) 463 v(Pd-N), 336 v(Pd-Cl). ¹H NMR (CDCl₃ solution, 250 MHz) δ : 7.65 [1H, s, *NH*], 7.40 [2H, m, Ph], 7.30 [3H, m, Ph], 5.86 [1H, s, Pz], 2.64 [3H, s, CH₃].

2.2.2.2. Compound 5. Yield: 63%. $C_{20}H_{20}N_4Cl_2Pt$: Anal. Calc. C, 41.23; H, 3.43; N, 9.62%. Found: C, 41.59; H, 3.25, N, 9.23%. Conductivity (Ω^{-1} cm² mol⁻¹, 1.03 × 10⁻³ M in DMSO): 21. IR: (KBr, cm⁻¹) 3194 ν (N–H), 3039 ν (C–H)_{ar}, 2891–2851 ν (C–H)_{al}, 1560– 1502 (ν C=C, ν C=N), 1470–1417 (δ C=C, δ C=N), 1063 δ (C–H)_{ip}, 760 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 452 ν (Pt–N), 318 ν (Pt–Cl). ¹H NMR (CDCl₃ solution, 250 MHz) δ : 7.58 [2H, m, Ph], 7.32 [1H, s, N *H*], 7.30 [3H, m, Ph], 6.06 [1H, s, Pz], 2.48 [3H, s, CH₃].

2.2.3. $[Pt(L)_2]$ $(L = L^1 6, L^2 7, L^3 8)$

The appropriate ligand (0.58 mmol: HL^1 : 0.128 g; HL^2 : 0.129 g; HL^3 : 0.092 g) dissolved in CH_3CN (15 ml) was added to a solution of $[PtCl_2(CH_3CN)_2]$ (0.29 mmol; 0.101 g) in 75 ml of CH_3CN . The resulting solution was stirred at room temperature for 10 h and concentrated on a vacuum line to one-fifth of the initial volume; crystalline solids were obtained which were filtered off, washed with CH_3CN (10 ml), and dried in vacuo.

2.2.3.1. Compound 6. Yield: 60%. $C_{28}H_{20}N_6Pt$: Anal. Calc. C, 52.90; H, 3.15; N, 13.23. Found: C, 52.64; H, 3.05, N, 13.12%. Conductivity (Ω^{-1} cm² mol⁻¹, 8.8 × 10⁻⁴ M in DMSO): 16. IR: (KBr, cm⁻¹) 3062– 3016 v(C–H)_{ar}, 1611–1556 (vC=C, vC=N), 1462–1444 (δ C=C, δ C=N), 1002 δ (C–H)_{ip}, 759 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 467 v(Pt–N). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 8.67 [1H, d, ³J = 5.3 Hz, Py], 8.10 [1H, m, Py], 7.85 [1H, d, ³J = 7.6 Hz, Py], 7.52 [2H, d, ³J = 7.1 Hz, Ph], 7.50 [3H, m, Ph], 7.42 [1H, s, Pz], 7.36 [1H, m, Py].

2.2.3.2. Compound 7. Yield: 53%. $C_{28}H_{20}N_6Pt$: Anal. Calc. C, 48.98; H, 2.82; N, 17.58. Found: C, 48.53; H, 2.95, N, 17.47%. Conductivity (Ω^{-1} cm² mol⁻¹, 9.6 × 10⁻⁴ M in DMSO): 23. IR: (KBr, cm⁻¹) 3085– 3025 $v(C-H)_{ar}$, 1611–1526 (vC=C, vC=N), 1478–1460 ($\delta C=C$, $\delta C=N$), 989 $\delta(C-H)_{ip}$, 777 $\delta(C-H)_{oop}$; (polyethylene, cm⁻¹) 473 v(Pt-N). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 9.74 [2H, d, ³*J* = 5.2 Hz, Py], 8.30 [4H, m, Py], 8.14 [1H, s, Pz], 7.72 [1H, m, Py].

2.2.3.3. Compound 8. Yield: 48%. $C_{18}H_{16}N_6Pt$: Anal. Calc. C, 42.27; H, 3.13; N, 16.44, Found: C, 42.53; H, 3.01, N, 16.47%. Conductivity (Ω^{-1} cm² mol⁻¹, 9.6 × 10⁻⁴ M in DMSO): 29. IR: (KBr, cm⁻¹) 3072– 3012 v(C–H)_{ar}, 2981 v(C–H)_{al}, 1612–1548 (vC=C, vC=N), 1452 (δ C=C, δ C=N), 1022 δ (C–H)_{ip}, 761 δ (C–H)_{oop}; (polyethylene, cm⁻¹) 471 v(Pt–N). ¹H NMR (DMSO-d₆ solution, 250 MHz) δ : 8.43 [1H, d, ³J = 5.1 Hz, Py], 8.01 [1H, t, ³J = 7.4 Hz, Py], 7.98 [1H, d, ³J = 7.4 Hz, Py], 7.42 [1H, m, Py], 6.81 [1H, s, Pz], 2.25 [3H, s, CH₃].

2.3. X-ray crystal structure

Suitable crystals for X-ray diffraction of compound $[PdCl_2(HL^1)]$ (1) were obtained through crystallisation from a DMSO. One crystal was mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Intensities were collected at room temperature with monochromatised Mo K α radiation ($\lambda = 0.71069$ Å), using $\omega/2\theta$ scantechnique. The structure was solved by direct methods (SHELXS-90) [27] and refined by full-matrix least-squares methods (SHELXL-94) [28]. 15 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 14 H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The weigh was $\omega = [\sigma^2(I) + (0.0516P)^2]^{-1}$, where $P = (|F_0|^2 + 2|F_C|^2)/3$. 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 structure are gathered in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

The reaction of the ligands HL^1 , HL^2 and HL^3 with $[PdCl_2(CH_3CN)_2]$ or $[PdCl_2(cod)]$ gives complexes $[PdCl_2(HL)]$ ($HL = HL^1$, HL^2 , HL^3), whereas these same ligands with $[PtCl_2(CH_3CN)_2]$ yield complexes $[Pt(L)_2]$ ($L = L^1$, L^2 , L^3). The reaction of the ligand HL^4 and $[MCl_2(CH_3CN)_2]$ (M = Pd(II), Pt(II)) gives complexes with stoichiometry $[MCl_2(HL^4)_2]$. Stoichiometries of all complexes are not dependent of the M/L molar ratio (1M:1L or 1M:2L). All characterised complexes in this publication are unpublished except $[PdCl_2(HL^3)]$, which has already been published [29].

Table 1 Crystallographic data for [PdCl₂(HL¹)] (1)

Formula	C ₁₄ H ₁₁ Cl ₂ N ₃ Pd
М	398.56
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.421(7)
b (Å)	21.523(8)
<i>c</i> (Å)	8.699(6)
α (°)	90
β (°)	116.92(7)
γ <u>(</u> °)	90
$U(\text{\AA}^3)$	1405.8(16)
Ζ	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.883
$\mu \ (\mathrm{mm}^{-1})$	1.691
<i>F</i> (000)	784
Crystal size	$0.1 \times 0.1 \times 0.2$
θ Range (°)	2.71–30.17°
Index range	-11 < h < 10, 0 < k < 30,
	0 < <i>l</i> < 12
Reflections collected/unique [R _{int}]	4389/4125 [0.0422]
Completeness to $2\theta = 30.17$	96.7%
Data/restraints/parameters	4125/0/202
Goodness-of-fit	0.986
Final $R_1, \omega R_2$	0.0390, 0.1072
R_1 (all data), ωR_2	0.0720, 0.1234
Residual electron density (e $Å^{-3}$)	0.291 and -0.525

Elemental analysis and conductivity measurements confirm the named stoichiometries of all complexes. Conductivity measurements in 10^{-3} M DMSO (between 16 and 35 Ω^{-1} cm² mol⁻¹) show the non-ionic behaviour of the complexes (conductivity values for a nonelectrolyte are below 50 Ω^{-1} cm² mol⁻¹ in DMSO solution) [30,31]. The IR spectra in the range 4000-400 cm^{-1} , show that the ligand is coordinated to the Pd(II) and Pt(II) ions. The most striking bands of the pyridine and pyrazolic ligands (v(C=C), v(C=N))_{ar} and δ (C-H)_{oop} increase their frequency when they are part of the complexes [32,33]. In the complexes **6–8** the pyrazole is deprotonated because the band v(N-H) is not observed, whereas in the complexes 1-5 the v(N-H) band is observed between 3438 and 3194 cm^{-1} [32]. In the IR spectra in the region 600–100 cm⁻¹, the v(M-N)(M = Pd(II), Pt(II)) bands are observed (483–463 cm⁻¹ for Pd(II) and $473-452 \text{ cm}^{-1}$ for Pt(II)). Moreover, the spectra of the complexes 1-3 display two bands (360- 348 cm^{-1} and $342-329 \text{ cm}^{-1}$) corresponding to stretching v(Pd-Cl), which are typical of compounds with a cis disposition of the chloro ligands around the Pd(II), whereas the complexes 4 and 5 display one band v(M-Cl) (M = Pd(II), Pt(II)) (336–318 cm⁻¹), which is typical of compounds with a trans disposition of the chloro ligands around the metal [34].

¹H NMR spectra of complexes 1–3, 6–8 were recorded in DMSO-d₆ and for complexes 4 and 5 in $CDCl_3$, and show the signals of the coordinated ligands. ¹³C NMR spectra could not be recorded for either complex owing to the very low solubility in common solvents. NMR data are reported in Section 2.

The ¹H NMR spectra of complexes 1-5 present one broad signal between 13.78 and 7.32 ppm assigned to the protons N*H*(pz) [32]. This signal is not observed in complexes **6–8**.

In complex 2 chemical shifts of H_{α} pyridyl protons are consistent with the presence of both N-uncoordinated ($\delta = 8.93$ ppm) and N-coordinated ($\delta = 9.83$ ppm) pyridyl groups. This same behaviour is observed in complex [Pd(L^{1'})₂] (L^{1'} = 3-phenyl-5-(6-methyl-2-pyridyl)pyrazolate) [15]. In contrast, the complex 7 chemical shifts of two-H_{\alpha} pyridyl protons displayed at 9.74 ppm are consistent with the presence of coordinated pyridyl groups.

3.2. Crystal and molecular structure of complex 1

The crystal structure of complex 1 consists of monomeric *cis*-[PdCl₂(HL¹)] molecules (Fig. 2). The palladium centre has typical square planar geometry (with a slight tetrahedral distortion), in which the largest deviation from the mean coordination plane is -0.065(4) Å (in N2), very similar to that of $[PdCl_2(HL')]$ (HL' = 2-(3pyrazolyl)pyridine) [35]. There is a significant pseudoaxial interaction between the Pd atom and a Cl atom of an adjacent complex unit (non-bonded Pd···Cl separation 3.63(4) A), and hydrogen bonding between the pyrazolyl NH proton and a Cl atom of an adjacent complex unit $(H \cdots Cl \text{ separation } 2.40(3) \text{ Å})$. The metal atom is coordinated to one HL¹ ligand, via one pyrazole nitrogen and one pyridine nitrogen, and to two chlorides in cis disposition. HL¹ behaves as a bidentate ligand and uses only two of its three donor nitrogen atoms, forming a fivemembered metallocycle, which has a planar configuration.

The selected bond lengths and angles of the molecules are listed in Table 2. The bond distances $Pd-N_{py}$ (2.041(3) Å) are clearly longer than those of $Pd-N_{Pz}$ (1.979(3) Å). Both distances are consistent with previously described values (1.960–2.125 Å) [15,35–40] and (1.968–2.153 Å) [15,35,38–40], respectively. The Pd–Cl bond lengths (2.2763(14), 2.2842(19) Å) can be regarded as normal compared with the distances found in the literature (2.276–2.326 Å) [15,35,41–45].

The N(2)–Pd(1)–N(1) bite angle, 79.16(14)°, is similar to those found in related [PdCl(HL')] (HL' = 2-(3-pyrazolyl)pyridine) (79.82°) [35], [PdCl₂(HL")] (HL" = 2-(2'-pyridyl)quinoxaline) (80.0°) [46] and [Pd(L^{1'})₂] (L^{1'} = 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole) (79.2, 80.2) [15].

The HL¹ ligand is not completely planar. The pyridyl and phenyl groups are slightly twisted with respect to the pyrazole. The angles between rings are py-pz 1.43(4)° and ph-pz 0.48(3)° in this complex. These values are lower than the other published data [8,11,14,16,17].



Fig. 2. ORTEP drawing of the complexe [PdCl₂(HL¹)] (1) showing the numbering scheme (ellipsoides are shown at the 50% probability level).

Table 2 Selected bond lenghts (Å) and angles (°) for $[PdCl_2(HL^1)]$ (1) with estimated standard deviations (e.s.d.s) in parentheses

Pd(1) - N(2)	1.979(3)
Pd(1) - N(1)	2.041(3)
Pd(1)-Cl(2)	2.2763(14)
Pd(1)-Cl(1)	2.2842(19)
N(2)-Pd(1)-N(1)	79.16(14)
N(2)-Pd(1)-Cl(2)	173.56(10)
N(1)-Pd(1)-Cl(2)	94.75(11)
N(2)-Pd(1)-Cl(1)	93.76(11)
N(1)-Pd(1)-Cl(1)	171.60(10)
Cl(2)–Pd(1)–Cl(1)	92.47(6)

4. Conclusions

The ligands HL^1 , HL^2 , HL^3 (HL) and HL^4 react with Pd(II) and Pt(II) ions to give new pyrazole-derived compounds.

The study of the coordination of (HL) ligands to Pd(II) has only revealed the formation of $[PdCl_2(HL)]$ compounds in contrast with Pt(II) complexes, which display $[Pt(L)_2]$ stoichiometries.

Elemental analyses, conductivity measurements and spectroscopic data for the complexes of Pd(II) data are consistent with mononuclear structures where neutral (HL) pyrazole ligands coordinate the metal centre in a bidentate form. Whereas for the complexes of Pt(II), they are consistent with mononuclear structures where ionic (L^-) pyrazolate ligands coordinate the metal centre in a bidentate form.

The X-ray structure of the compound $[PdCl_2(HL^1)]$ indicates that the coordination of metal in $[PdCl_2(HL)]$ complexes is square planar with one bidentate HL^1 neutral ligand and two chloro ligands in a *cis* disposition. In summary, the ligands (HL) when complexed to Pd(II) and Pt(II) can act as in neutral or anionic forms depending on the metallic centre, in contrast with the behaviour of the ligand (HL⁴) which is not dependent of the metallic centre [MCl₂(HL⁴)].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 244281 for compound [PdCl₂(HL¹)] (1). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: htpp://www.ccdc.cam.ac.uk).

Acknowledgement

Support by the Spanish *Ministerio de Educación y Cultura* (Project BQU 2003-03582) is gratefully acknowledged.

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