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## Palladium(II) complexes of 2-pyridylmethylamine and 8-aminoquinoline: A crystallographic and DFT study



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#### HIGHLIGHTS

- Two *cis*-dichloropalladium(II) chelates were synthesised.
- The chelates were studied by single crystal X-ray crystallography.
- Two different supramolecular structures were formed.
- DFT simulations were used to understand the H-bonding.

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#### GRAPHICAL ABSTRACT



#### ABSTRACT

Two nominally square planar palladium(II) chelates: dichloro-(2-aminomethylpyridine-*N*,*N*')-palladium(II) ([Pd(L1)Cl<sub>2</sub>]) and dichloro-(8-aminoquinoline)-palladium(II) ([Pd(L2)Cl<sub>2</sub>]) have been synthesised and studied by X-ray crystallography and DFT methods. [Pd(L1)Cl<sub>2</sub>] crystallised in the monoclinic space group *C2*/*c*. In the solid state this compound exists as a one-dimensional supramolecular structure supported by N–H···Cl hydrogen bonds and metallophilic Pd···Pd interactions. The same hydrogen bonding motif leads to a two-dimensional supramolecular structure in the case of [Pd(L2)Cl<sub>2</sub>]; this structure is devoid of metallophilic interactions. DFT simulations show that the planar geometry of [Pd(L1)Cl<sub>2</sub>] in the solid state is not the lowest energy conformation. An out-of-plane distortion of the methylene group leads to a structure *ca*. 11 kJ mol<sup>-1</sup> lower in energy. The NBO partial charges provide insight into the stability of the hydrogen bonding motif. TD-DFT calculations were used to delineate the experimental UV-visible spectra.

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#### Introduction

The bidentate *N,N'*-donor ligands 2-pyridylmethylamine (amp) and 8-aminoquinoline (amq) have been coordinated to a variety of metal centres including, but not restricted to, Pt(II), Cu(II), Zn(II), Fe(II), Ru(II), Sn(II), Cd(II), Hg(II), Cr(III) and Co(III) [1–14]. Various metal to ligand ratios have been used in the synthesis of

these compounds i.e. 1:1, 1:2 and 1:3. These variable ratios lead to a range of coordination geometries. These ligands have been favoured as the nitrogen donors stabilise the metal centres and the aromatic rings yield complexes with many desirable fluores-cent and structural properties [5]. The coordination complexes of these ligands have therefore found application in a variety of interesting studies.

Much of the coordination chemistry research into these ligands was fuelled by the discovery of the anti-tumour effects of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> [15]. Despite the initial success of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>,



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various Pt(II) and Pd(II) complexes with *N*-donor and *cis*-chloro ligands were synthesised in order improve drug efficacy and overcome drug resistance [1,2]. Coordination complexes of amp and amq formed part of these studies. The ligand amp has been coordinated to Pt(II) to form [PtCl<sub>2</sub>(amp)] to compare the anti-tumour activity of the complex with [*cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)(2-methylpyridine)] which has been effective in clinical trials for the treatment of ovarian cancers, which are resistant to other platinum-based drugs [16,17]. The amq ligand has also been coordinated to Pt(II) and Pd(II), forming complexes with the general formula [ML<sub>2</sub>X<sub>2</sub>] (where X = Cl or Br) to investigate their interaction with calf thymus DNA in an attempt to better understand their biological mode of action [2].

Additionally, amp has been coordinated to Cu(II) in a variety of metal to ligand ratios yielding a range of complexes with various coordination geometries. These coordination compounds have been characterised by X-ray crystallography and used in studies to correlate structural and magnetic properties [18–24]. The Ru(II) chelates of this ligand have been used as a pre-catalyst for the reduction of acetophenone in transfer-hydrogenation conditions [8].

The amq ligand has also been previously reported coordinated to Co(II), Ni(II) and Cu(II) to investigate the compounds' thermal behaviour and to study decomposition pathways [11]. The amq ligand was similarly coordinated to Ru(II) as part of an electrochemistry study as the aromatic rings were found to stabilize the target oxidation intermediates [7].

Despite the extensive research into the coordination complexes of 2-pyridylmethylamine and 8-aminoquinoline ligands, a detailed crystallographic and computational study of the Pd(II) chelates has not been reported. Herein, we report the solid-state structures of the *cis*-dichloropalladium(II) chelates of 2-pyridylmethylamine and 8-aminoquinoline (Scheme 1). The complexes have been fully characterised by NMR, IR and UV-visible spectroscopy as well as mass spectrometry and X-ray crystallography. DFT simulations have been used to further understand the solid-state and electronic structures of the metal chelates.

#### Experimental

#### Materials and methods

All starting materials used in the syntheses were purchased from Sigma–Aldrich (Germany) and used as received. Organic solvents were purchased from Merck (South Africa) and were of spectroscopic grade. All solvents were dried using a Puresolv<sup>™</sup> MD 7 purification system from Innovative Technologies prior to use.

NMR spectra were recorded with a Bruker Avance III 400 spectrometer equipped with a Bruker magnet (9.395 T) using a 5 mm TBIZ probe at frequencies of 400 MHz and 100 MHz for the <sup>1</sup>H and <sup>13</sup>C spectra, respectively. The spectra were recorded at 30 °C. All NMR experiments were conducted using Bruker Topspin 2.1, patch level 6 [25]. All proton and carbon chemical shifts are quoted



**Scheme 1.** Structure and naming scheme of the Pd(II) chelates synthesised in this work.

relative to DMSO- $d_6$ : <sup>1</sup>H, 2.50 ppm and <sup>13</sup>C, 39.51 ppm. FTIR spectra were recorded using a Bruker Alpha FTIR spectrometer equipped with an ATR platinum Diamond 1 reflectance accessory. The machine acquired the information in 32 scans with a spectral resolution of 1.0 cm<sup>-1</sup>. The abbreviations used in the text are as follows; br, broad; s, strong; m, medium and w, weak signals. Electronic spectra were recorded using a Shimadzu UVPC-1800 double beam UV-vis scanning spectrometer (1.0 cm path length cuvette). Spectra were recorded from 700 to 280 nm in DMSO. High resolution masses were determined with a Waters Acquity-LCT Premier coupled high performance liquid chromatographmass spectrometer (time-of-flight) using electrospray ionization in positive mode.

The X-ray data were recorded on a Bruker Apex Duo diffractometer equipped with an Oxford Instruments Cryoiet operating at 100(2) K and an Incoatec microsource operating at 30 W power. Crystal and structure refinement data are given in Table 1. Selected bond lengths and angles are reported in Table 2. For both structures, the data were collected with Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation at a crystal-to-detector distance of 50 mm. The data collections were performed using omega and phi scans with exposures taken at 30 W X-ray power and 0.50° frame widths using APEX2 [26]. The data were reduced with the program SAINT [26] using outlier rejection, scan speed scaling, as well as standard Lorentz and polarization correction factors. A SADABS semi-empirical multi-scan absorption correction [26] was applied to the data. Direct methods, SHELXS-97 [27] and WINGX [28] were used to solve both structures. All non-hydrogen atoms were located in the difference density map and refined anisotropically with SHELXL-97 [27]. The amine hydrogen atoms were located in the difference density map and allowed to refine isotropically. The remaining hydrogen atoms were included as idealized contributors in the least squares process. Their positions were calculated using a standard riding model with C–H<sub>aromatic</sub> distances of 0.95 Å and  $U_{iso} = 1.2 U_{eq}$  and C—H<sub>methylene</sub> distances of 0.99 Å and U<sub>iso</sub> = 1.2 U<sub>eq</sub>.

Table 1										
Crvstal	data	and	structure	refinement	details	for	[Pd(L1)Cl <sub>2</sub> ]	and	[Pd(L2)	Clal

Crystal data	$[Pd(L1)Cl_2]$	$[Pd(L2)Cl_2]$		
Chemical formula	C <sub>6</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> Pd	C <sub>9</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> Pd		
Molar mass (g mol $^{-1}$ )	285.44	321.47		
Crystal system, space group	Monoclinic, C2/c	Monoclinic, P2 <sub>1</sub> /n		
Temperature (K)	100	100		
a, b, c (Å)	9.7497(7),	4.7287(3),		
	17.2465(16),	17.9637(12),		
	10.2923(7)	11.5934(7)		
β, (°)	98.868(3)	97.208(3)		
V (Å)	1709.9(2)	977.02(11)		
Ζ	8	4		
Radiation type	Μο Κα	Μο Κα		
$\mu$ (mm <sup>-1</sup> )	2.73	2.40		
Crystal size (mm)	$0.28\times0.25\times0.20$	$0.18 \times 0.04 \times 0.02$		
Data collection				
Diffractometer	Bruker APEXII CCD	diffractometer		
Absorption correction	Multi-scan, SADABS	, Bruker 2012		
T <sub>min</sub> , T <sub>max</sub>	0.516, 0.612	0.672, 0.954		
No. of measured, independent and	13517, 1641, 1631	8373, 1911, 1835		
observed $[I > 2\sigma(I)]$ reflections				
R <sub>int</sub>	0.021	0.020		
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.029, 0.073, 1.29	0.018, 0.043, 1.12		
No. of reflections	1641	1911		
No. of parameters	108	135		
No. of restraints	1			
H-atom treatment	H atoms treated by a mixture of			
	independent and co	onstrained		
	refinement			
$\Delta ho_{ m max}$ , $\Delta ho_{ m min}$ (e Å $^{-3}$ )	1.82, -0.77	0.70, -0.45		

#### Table 2

Selected bond lengths (Å) and bond angles (°) for  $[Pd(L1)Cl_2]$  and  $[Pd(L2)Cl_2]$ , standard uncertainties are given in parentheses.

	$[Pd(L1)Cl_2]$	$[Pd(L2)Cl_2]$
Bond		
Pd-Cl <sup>a</sup>	2.310(1)	2.301(9)
Pd—N <sub>pyridine</sub>	2.017(4)	2.016(2)
Pd—N <sub>amine</sub>	2.030(4)	2.045(2)
Angles		
Cl—Pd—Cl	91.16(4)	92.18(2)
cis-Cl—Pd—N <sub>amine</sub>	90.9(1)	90.20(6)
cis-Cl-Pd-N <sub>pyridine</sub>	95.2(1)	94.84(6)
N <sub>pyridine</sub> —Pd—N <sub>amine</sub>	82.9(2)	83.12(8)
trans-Cl-Pd-N <sub>amine</sub>	175.6(1)	175.63(7)
trans-Cl—Pd—N <sub>pyridine</sub>	173.0(1)	171.44(6)

<sup>a</sup> Mean bond length.

#### General procedure for the synthesis of $[Pd(L1)Cl_2]$ and $[Pd(L2)Cl_2]$

[Pd(L1)Cl<sub>2</sub>] and [Pd(L2)Cl<sub>2</sub>] were synthesised using the same general procedure. The metal precursor, palladium(II) chloride (100 mg, 0.564 mmol), was refluxed in acetonitrile (20 mL) for 1 h to form the bis(acetonitrile)dichloropalladium(II) complex. The respective ligands; 2-pyridylmethylamine (61.0 mg, 0.564 mmol) or 8-aminoquinoline (70.4 mg, 0.564 mmol), were added to the reaction mixture. A yellow precipitate formed immediately and the solution was refluxed for an additional 20 min. The yellow precipitate was collected by centrifugation, washed with two portions of diethyl ether and dried under a stream of nitrogen.

#### Dichloro-(2-aminomethylpyridine-N,N')-palladium(II)

[Pd(L1)Cl<sub>2</sub>] was synthesised as described above, yield 135 mg (84%). Brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the reaction mixture.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 303 K) [δ, ppm]: 4.10 (t, 2H, *CH*<sub>2</sub>), 5.59 (br, 2H, N*H*<sub>2</sub>), 7.50 (t, 1H, NCH*CH*), 7.61 (d, 1H, NC*CH*), 8.05 (td, 1H, NCC*HCH*), 8.76 (d, 1H, NC*H*). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 303 K) [δ, ppm]: 52.35 (*CH*<sub>2</sub>), 122.12 (NCH*CH*), 124.12 (NC*CH*), 140.22 (NCCH*CH*), 149.22 (NCH), 166.19 (N*C*). IR [cm<sup>-1</sup>]: 423.83 (m, Pd–Cl stretch), 783.71 (s, C–H out-of-plane bend), 1284.76 (m, C–N stretch), 1556.32 (m, C=C stretch), 1610.42 (m, NH<sub>2</sub> scissoring), 3214.76 (m, NH<sub>2</sub> stretch). M.p.t. > 260 °C (decomposition). ES<sup>+</sup>: 326.9541 [M – Cl + DMSO]<sup>+</sup>. UV–vis:  $\lambda_{max}$  (nm) [ $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)] 370 [3.60 × 10<sup>2</sup>].

#### Dichloro-(8-aminoquinoline)-palladium(II)

[Pd(L2)Cl<sub>2</sub>] was synthesised using the general procedure described above, yield 161 mg (89%). Brown crystals suitable for X-ray diffraction were obtained by slow liquid diffusion of ethanol into a DMSO solution of [Pd(L2)Cl<sub>2</sub>].

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 303 K) [δ, ppm]: 7.69–7.81 (m, 3H, NH<sub>2</sub>CCHCHCH), 7.85 (br, 2H, NH<sub>2</sub>), 8.03 (d, 1H, NCHCH), 8.76 (d, 1H, NCHCHCH), 9.12 (d, 1H, NCH). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 303 K) [δ, ppm]: 123.54 (NH<sub>2</sub>CCH), 127.09 (NH<sub>2</sub>CCHCHCH), 128.16 (NCHCH), 129.09 (NH<sub>2</sub>CCHCHCHC), 130.20 (NH<sub>2</sub>CCHCH), 140.11 (NC; NCHCHCH), 148.02 (NH<sub>2</sub>C), 151.26 (NCH). IR [cm<sup>-1</sup>]: 436.61 (w, Pd–Cl stretch), 773.18 (s, C–H out-of-plane bend), 1215.06 (m, C–N stretch), 1565.36 (s, C=C stretch), 1571.64 (m, NH<sub>2</sub> scissoring), 3044.50 (m, NH<sub>2</sub> stretch). M.p.t. > 287 °C (decomposition). ES<sup>+</sup>: 362.9539 [M – Cl + DMSO]<sup>+</sup>. UV–vis: λ<sub>max</sub> (nm) [ε (M<sup>-1</sup> cm<sup>-1</sup>)] 307 [5.85 × 103], 363 [1.06 × 103], 505 [5.80 × 10<sup>2</sup>].

#### **Results and discussion**

#### Synthesis and spectroscopic characterisation

The Pd(II) chelates were both synthesised using a simple onepot, two stage reaction. The palladium(II) chloride starting material was firstly converted to the bis(acetonitrile)dichloropalladium(II) complex by refluxing in acetonitrile. We found that omitting this step lead to the formation of a black precipitate (likely palladium colloids) upon addition of the bidentate ligands. The addition of one equivalent of the bidentate ligands to the refluxing acetonitrile solution of bis(acetonitrile)dichloropalladium(II) resulted in the immediate formation of a yellow/tan precipitate of the desired product in high yields. The 1:1 metal to ligand ratio renders a neutral metal chelate with two chloride ligands coordinated in the third and fourth positions. Spectroscopic grade acetonitrile was used for the reaction, but no further measures were required to shield the reaction from moisture or oxygen.

The characterisation (NMR, IR and UV/visible spectroscopy and mass spectrometry) of the chelates was routine, no unusual results were noted. The fully assigned <sup>1</sup>H and <sup>13</sup>C NMR and IR spectra are available in the electronic supplementary information.

#### X-ray crystallography

[Pd(L1)Cl<sub>2</sub>] and [Pd(L2)Cl<sub>2</sub>] were studied by single crystal X-ray diffraction. The compounds both crystallised in the monoclinic crystal system. [Pd(L1)Cl<sub>2</sub>] crystallised in the C2/c spacegroup while [Pd(L2)Cl<sub>2</sub>] crystallised in the  $P2_1/n$  spacegroup, each structure contains one molecule in the asymmetric unit (Z = 8 and 4, respectively). The structures, [Pd(L1)Cl<sub>2</sub>] and [Pd(L2)Cl<sub>2</sub>], show that the Pd(II) ion has adopted a square planar coordination geometry with chelation of the bidentate 2-pyridylmethylamine and 8-aminoquinoline ligands, respectively. The third and fourth coordination sites are occupied by chloride ligands in a *cis*-configuration (Fig. 1). This square planar coordination geometry is expected due to the d<sup>8</sup> electronic configuration of Pd(II) and is consistent with reported structures of this class of *cis*-chloro Pd(II) compounds [29–31].

 $[Pd(L1)Cl_2]$  is largely planar with the pyridyl ring lying at an angle of 2.3° relative to the coordination sphere. The N–C–C–N torsion angle of the chelation ring measures  $7.1(7)^\circ$  illustrating that this complex deviates less from planarity than a previously reported platinum(II) analogue for which the equivalent torsion angle measures  $-22.2(9)^\circ$  [1].  $[Pd(L2)Cl_2]$  exhibits a similar, nominally planar geometry with an N–C–C–N torsion angle of  $-1.5(3)^\circ$ . The most notable deviation from the ideal square planar geometry of  $[Pd(L2)Cl_2]$  is a slight rotation of the chloride ligands out of the 8-aminoquinoline mean plane. The mean plane of the 8-aminoquinoline ligand (non-H atoms) subtends an angle of *ca*. 7° relative to the mean plane defined by the chloride ligands and Pd(II) ion.

A Mogul [32] structural search shows that the Pd—Cl and Pd—N bond lengths are within the ranges of previously reported structures. The Cl—Pd—Cl bond angles for  $[Pd(L1)Cl_2]$  and  $[Pd(L2)Cl_2]$  measure 91.16(4)° and 92.18(2)°, respectively. The N<sub>pyridine</sub>—Pd—N<sub>amine</sub> angles for both complexes are considerably more acute, measuring 82.9(2)° and 83.12(8)°, respectively. This smaller bond angle is attributed to the fixed bite angle of the bidentate ligands. The chloride ligands have a larger degree of freedom and can adopt a more obtuse bond angle, which will minimise non-bonded repulsion. Selected bond lengths and bond angles for the structures are available in Table 2.

Both complexes exhibit a number of intermolecular interactions including hydrogen-bonding (the NH<sub>2</sub> groups acting as hydrogen-



**Fig. 1.** Thermal ellipsoid plot (50% probability surfaces) showing the atom numbering scheme of (A)  $[Pd(L1)Cl_2]$  and (B)  $[Pd(L2)Cl_2]$ . Hydrogen atoms have been rendered as spheres of arbitrary radius.

bond donors and the chloride ligands of the adjacent molecules acting as hydrogen-bond acceptors) and metallophilic interactions. In  $[Pd(L1)Cl_2]$  there is complementary hydrogen bonding between the amine group and the chloride ligand of an adjacent molecule. The amine group therefore bridges two molecules. This hydrogen bonding pattern propagates a one-dimensional column, which runs transversely across the *ac* plane (Fig. 2). This hydrogen-bonded column is further stabilised by Pd…Pd interactions. The Pd…Pd interactions within the supramolecular structure alternate between longer 3.4388(4) Å and shorter 3.4105(4) Å contacts. These metallophilic interactions are comparable in length to related, neutral *cis*-chloro Pd(II) chelates and are shorter than the sum of the van der Waals radii indicating an attractive interaction [33]. Adjacent one-dimensional columns of molecules are not linked by any significant intermolecular interactions.

 $[Pd(L2)Cl_2]$  employs the same hydrogen bonding motif as  $[Pd(L1)Cl_2]$  i.e. N—H···Cl, however, each molecule is hydrogenbonded to four adjacent molecules (Fig. 2). This hydrogen bonding pattern leads to a two-dimensional hydrogen-bonded network coplanar with the *ac* plane. The two-dimensional supramolecular structure can be considered to comprise one-dimensional columns which are cross-linked by hydrogen bonds, leading to the



**Fig. 2.** (A) One-dimensional hydrogen-bonded network of  $[Pd(L1)Cl_2]$  formed in the solid state. (B) Repeating unit of the two-dimensional hydrogen-bonded network of  $[Pd(L2)Cl_2]$ . Both supramolecular structures are supported by N–H···Cl hydrogen bonds (illustrated as dashed purple tubes). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

two-dimensional structure. The consequence of this alternative hydrogen bonding pattern is that the metallophilic interactions have seemingly been eliminated with the separation between adjacent Pd(II) ions measuring 4.7287(4) Å, substantially longer than the sum of the van der Waals radii. It would appear that the stability gained through the alternative hydrogen bonding pattern outweighs any stability gained from potential metallophilic interactions. The hydrogen bond parameters for  $[Pd(L1)Cl_2]$  and  $[Pd(L2)Cl_2]$  are summarised in Table 3.

The hydrogen bond lengths summarised in Table 3 are significantly shorter than the sum of the van der Waals radii of the interacting atoms. Although hydrogen bond length may not necessarily correlate linearly with bond strength due to packing constraints in the lattice [34], it is likely that these short interactions are moderately strong. This statement is further supported by the fact that the bond angles do not deviate significantly from ideality (180°).

able 3	
hydrogen bond lengths (Å) and bond angles (°) for $[Pd(L1)Cl_2]$ and $[Pd(L2)Cl_2]$ .	

	D—H (Å)	$H \cdots A(Å)$	$D{\cdots}A~({\AA})$	D−H···A (°)	
$[Pd(L1)Cl_2]$ N1—H102···Cl1 <sup>i</sup>	0.87(5)	2.44(5)	3.273(4)	162(4)	
N1—H101 $\cdots$ Cl2 <sup>n</sup> [Pd(L2)Cl <sub>2</sub> ]	0.85(6)	2.50(6)	3.347(4)	171(5)	
N1—H101 $\cdots$ Cl2 <sup>iii</sup>	0.86(4)	2.52(3)	3.368(2)	171(3)	
	0.85(5)	2.34(3)	3.333(2)	108(3)	

Symmetry codes: <sup>i</sup> – x, y, 1.5 – z; <sup>ii</sup> ½ – x, ½ – y, 2 – z; <sup>iii</sup> –1/2 + x, 1.5 – y, -1/2 + z; and <sup>iv</sup> –1 + x, y, z.

#### DFT simulations

Density functional theory (DFT) simulations were used to gain a deeper understanding of the solid-state structures and electronic configuration of the square planar Pd(II) complexes; [Pd(L1)Cl<sub>2</sub>] and [Pd(L2)Cl<sub>2</sub>]. The simulations were performed using Gaussian 09 W [35] using the PBE hybrid functional [36,37]. A split basis set was applied in the simulations, this split basis set specified the 6-311G level of theory [38,39] for the C, H, Cl and N atoms and the LanL2DZ (which makes use of effective core potentials) basis set for the palladium(II) ion [40-43]. The LanL2DZ basis set also takes into account relativistic effects, which can be significant in heavy metal ions [44]. The X-ray coordinates of the metal chelates were used for input structures. Normal geometry convergence criteria were applied and no symmetry constraints imposed. Transition energies and oscillator strengths were calculated for 18 excited singlet states using the TD-DFT method [45–51] using the same split basis set applied to the geometry optimizations. The molecular orbitals were assigned by studying the spatial distributions of their isosurfaces. To account for solvent effects, a Polarizable Continuum Model (PCM) was included in the calculation of the transition energies and oscillator strengths [52–54]. The input files were prepared using GaussView 5.0 [55]; the same program was used to analyse the output files. Structural overlays were performed using Mercury 3.1 [56].

The geometry optimisation simulations were run at the above mentioned level of theory. The resulting structures were concluded to be the true lowest energy conformations on the global potential energy surface by the lack of negative vibrational frequencies. The geometrical parameters of the experimental (solid-state) and simulated (*in vacuo*) structures are compared in Table 4. The data in Table 4 show that the structures are in good agreement; this would suggest that the level of theory applied to the simulations is appropriate and the bulk of the results are therefore likely to be reliable. The largest difference in the calculated bond angles is the Cl—Pd—Cl bond angle. In the absence of lattice constraints, it would seem that the chloride ligands have moved further apart to relieve non-bonded repulsion.

The similarity of the calculated and experimental structures is further illustrated by the structural overlays (least squares fits). The similarity of the structures is measured by the root-meansquare deviations (RMSDs, measured in Å units). The RMSDs show that the structures are in good agreement, refer to Fig. 3. The RMSD for [Pd(L1)Cl<sub>2</sub>] is significantly larger than that of [Pd(L2)Cl<sub>2</sub>]. The difference lies predominantly in the methylene group for which the carbon atom, in the lowest energy conformation, sits below the plane defined by the coordination sphere. This is in contrast

# Table 4 Comparison of DFT-calculated and experimental bond lengths (Å) and bond angles (°) of [Pd(L1)Cl2] and [Pd(L2)Cl2].

	[Pd(L1)Cl <sub>2</sub> ] (DFT)	% Diff <sup>a</sup>	[Pd(L2)Cl <sub>2</sub> ] (DFT)	% Diff <sup>a</sup>
Bond Pd—Cl Pd—Namestra	2.316	0.26	2.315	0.61
Pd—N <sub>amine</sub>	2.091	3.00	2.099	2.64
Angles	04.20	2 2 2	0417	2.10
cis-Cl—Pd—N <sub>amine</sub>	94.20 89.36	-1.69	94.17 88.72	-1.64
cis-Cl—Pd—N <sub>pyridine</sub>	95.19	-0.01	94.95	0.11
N <sub>pyridine</sub> —Pd—N <sub>amine</sub> trans-Cl—Pd—N <sub>amine</sub> trans-Cl—Pd—N <sub>pyridine</sub>	81.26 176.42 170.57	-1.98 0.47 -1.40	82.16 177.11 170.88	-1.15 0.84 -0.56

<sup>a</sup> Difference between DFT-calculated and experimental bond parameters  $\left(\frac{\text{DFT-EXP}}{\text{FXP}} \times 100\%\right)$ .



**Fig. 3.** Least-squares fit of DFT-calculated (blue) and X-ray crystal structures (yellow) of (A) [Pd(L1)Cl<sub>2</sub>] and (B) [Pd(L2)Cl<sub>2</sub>]. Root mean square deviations (RMSDs, Å units) for all non-hydrogen atoms for each structure are indicated on the diagram. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to the experimental structure which can be considered to be fundamentally planar (C<sub>methylene</sub> atom in the plane defined by the coordination sphere). This out-of-plane distortion of the carbon atom allows the methylene group to adopt an angle closer to ideality for an sp<sup>3</sup> hybridised carbon, this is illustrated by the C-C<sub>methylene</sub>-N<sub>amine</sub> bond angle which measures 110.7° and 112.5(4)° in the calculated and experimental structures, respectively. The geometry optimised structure (with the out of plane methylene group) is *ca*. 11 kJ mol<sup>-1</sup> lower in energy than the planar structure. This is a modest energy difference and seemingly the stability gained through the more favourable packing of the planar molecule in the solid state is sufficient to offset this energy difference. The energy of the planar structure was calculated by fixing the N<sub>pyridine</sub>—C<sub>pyridine</sub>—C<sub>methylene</sub>—N<sub>amine</sub> torsion angle of the input structure during the geometry optimisation. This planar configuration exhibits a single negative vibrational frequency, indicating that it is a saddle point on the potential energy surface. The more rigid ligand of [Pd(L2)Cl<sub>2</sub>] is less likely to be distorted in the solid state by packing forces and therefore the solid-state and gas phase structures are in better agreement. The hydrogen bonding in the solid state does not seem to have resulted in a significant distortion from the lowest energy conformation, as has been reported for other hydrogen-bonded supramolecular structures [57].

Natural Bond Orbital (NBO) analysis was used to better understand the hydrogen bonding in the solid-state structure, the partial charge distribution (NBO charges, measured in electrons) of the molecules were calculated; refer to Fig. 4. These clearly show that the amine hydrogen atoms carry the largest partial positive charge and the chloride ligands the largest partial negative charge. If a hydrogen bond can be generally considered an electrostatic interaction then the NBO charges clearly explain the stability of this hydrogen bonding motif.

The experimental UV–visible spectrum of [Pd(L1)Cl<sub>2</sub>] shows just a single broad peak in the spectral window of 280–700 nm with a wavelength of maximum absorption at 370 nm. The poor solubility of the chelates necessitated the use of DMSO for spectroscopic characterisation and hence the high energy UV transitions (200–280 nm) are obscured by the solvent. The additional aromaticity afforded by the 8-aminoquinoline ligand of [Pd(L2)Cl<sub>2</sub>] results in a more complex spectrum with peaks at 307, 363 and 505 nm. The absorption spectra were calculated using the TD-DFT method with the same split basis set applied to the geometry optimisations. A DMSO solvent continuum was included in the simulations to account for solvent effects. Table 5 summarises the main transitions, as determined by the magnitude of the oscillator strength, for [Pd(L1)Cl<sub>2</sub>]. A superposition plot of the



**Fig. 4.** NBO partial charges (e) for [Pd(L1)Cl<sub>2</sub>] illustrating the partial negative and positive charges on the chloride ligands and amine hydrogen atoms, respectively. A similar plot for [Pd(L2)Cl<sub>2</sub>] is available in the ESI.

#### Table 5

Summary of the calculated electronic transitions for [Pd(L1)Cl<sub>2</sub>] and the corresponding molecular orbitals.

Wavelength	Molecular	Oscillator	Assignment <sup>c</sup>
(nm) <sup>a</sup>	orbitals <sup>b</sup>	strength	
358.64 375.48 391.47	$53 \rightarrow 57$ $54 \rightarrow 57$ $51 \rightarrow 56$ $54 \rightarrow 57$ $55 \rightarrow 57$	0.0879 0.0070 0.0071	$\begin{array}{l} Pd[dxz]L\pi \rightarrow \pi^{*}(pyridine)\\ Pd[dz^{2}]Cl\pi \rightarrow \pi^{*}(pyridine)\\ \sigma Cl \rightarrow Pd[d(x^{2}-y^{2})]L\sigma^{*}\\ Pd[dz^{2}]Cl\pi \rightarrow \pi^{*}(pyridine)\\ Pd[dz^{2}] \rightarrow \pi^{*}(pyridine) \end{array}$

<sup>a</sup> Three of the 18 calculated excited states are listed.

<sup>b</sup> The highest occupied molecular orbital (HOMO) is orbital 55, the lowest unoccupied molecular orbital (LUMO) is 56.

<sup>c</sup>  $Pd[d(xz)]L\pi$  refers to an orbital which comprises predominantly mixed metalligand  $\pi$  bonding character.



**Fig. 5.** Superposition of the TD-DFT calculated (DMSO solvent continuum) and experimental UV-visible spectra of  $[Pd(L1)Cl_2]$ . A similar superposition plot for  $[Pd(L2)Cl_2]$  is available in the ESI. Extinction coefficients of calculated spectra have been scaled.

experimental and calculated UV–visible spectra is shown in Fig. 5. This plot shows that there is reasonable agreement between the spectra and therefore an analysis of the orbitals involved in the calculated transitions should provide insight into the experimental transitions. A schematic diagram showing the spatial distributions and calculated energies of the molecular orbitals (MOs) involved in the highest intensity transitions between occupied and unoccupied orbitals, alluded to in Table 5, is shown in Fig. 6.



Fig. 6. Schematic MO diagram of  $[Pd(L1)Cl_2]$ . The energy gap between the HOMO and LUMO is 2.36 eV (227.7 kJ mol<sup>-1</sup>, 525.4 nm).

The simulated data show one dominant transition at 358.64 nm with additional, less significant transitions at 375.48 and 391.47 nm; this is consistent with the single broad peak observed in the experimental spectrum.

The data in Table 5 show that the majority of the transitions can be considered to originate in occupied, metal-based orbitals. The transitions are mostly to  $\pi^*$  orbitals located on the pyridine ring. The transitions could therefore be loosely classified as metal-to-ligand charge transfer (MLCT) bands. Similar data for [Pd(L2)Cl<sub>2</sub>] is available in the electronic supplementary information.

A possible avenue for further development of this work is the inclusion of spin orbit coupling (SOC) effects in the simulations. These effects can be particularly significant for heavy metal ions such as palladium(II). The work by Minaev *et al.* [58,59] has shown that by including non-diagonal SOC, which allows for the mixing of singlet and triplet states, UV–visible spectroscopic features and other physico-chemical properties can be further explained.

#### Conclusions

Coordination of 2-methylaminopyridine and 8-aminoquinoline to Pd(II) yielded two nominally square planar coordination compounds. The bidentate ligands occupy two of the coordination sites; two chloride ligands in a *cis* configuration complete the coordination sphere. [Pd(L1)Cl<sub>2</sub>] and [Pd(L2)Cl<sub>2</sub>] formed one and two-dimensional hydrogen-bonded networks in the solid state, respectively. The supramolecular structures were both supported by N–H···Cl hydrogen bonds; [Pd(L1)Cl<sub>2</sub>] was further stabilised by metallophilic Pd···Pd interactions. DFT simulations showed that *in vacuo* the lowest energy conformation of [Pd(L1)Cl<sub>2</sub>] was not planar; the methylene group showed an out-of-plane distortion. This non-planar configuration is *ca*. 11 kJ mol<sup>-1</sup> lower in energy than the planar Xray structure. The calculated NBO charges clearly explained the stability of the solid-state hydrogen bonding. TD-DFT was used to better understand the experimental spectroscopic results.

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

The CCDC contains the supplementary crystallographic data of [Pd(L1)Cl2] and [Pd(L2)Cl2] (CCDC 1043743 and 1043742, respectively). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ; fax:+44 1223 336 033; or email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.molstruc.2015.02.077.

#### References

- [1] V.P. Munk, C.I. Diakos, L.T. Ellis, R.R. Fenton, B.A. Messerle, T.W. Hambley, Inorg. Chem. 42 (2003) 3582–3590.
- [2] P. Umapathy, R.A. Harnesswala, C.S. Dorai, Polyhedron 9 (1985) 1592-1602.
- [3] H.A. Hudali, J.V. Kingston, H.A. Tayim, Inorg. Chem. 18 (1979) 1391-1394.
- [4] M.E. Quiroz-Castro, G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 297 (2000) 129–133.
- [5] L. Canovese, F. Visentin, G. Chessa, C. Levi, P. Nikolov, Inorg. Chim. Acta 362 (2009) 3925–3933.
- [6] K.W. Törnroos, D. Chernyshov, M. Hostettler, Hans-Beat Bürgi, Acta Cryst. C61 (2005) m450–m452.
- [7] M.K. O'Neill, A.F. Trappey, P. Battle, C.L. Boswell, D.N. Blauch, Dalton Trans. (2009) 3391–3394.
- [8] D.A. Cavarzan, F.D. Fagundes, O. Fuganti, C.W.P. da Silva, C.B. Pinheiro, D.F. Back, A. Barison, A.L. Bogado, M.P. de Araujo, Polyhedron 62 (2013) 75–82.
- [9] C. Niu, X. Wan, X. Zheng, H. Zhang, B. Wu, Y. Niu, H. Hou, J. Coord. Chem. 61 (2008) 1997–2007.
- [10] M. Mirzaei, H. Eshtiagh-Hosseini, M. Mohammadi Abadeh, M. Chahkandi, A.
- Fronterac, A. Hassanpoor, Cryst. Eng. Comm. 15 (2013) 1404–1413.
- [11] A.M. Donia, H.A. El-Boraey, J. Therm. Anal. 48 (1997) 1325-1336.
- [12] D.J. Ayres, D.A. House, W.T. Robinson, Inorg. Chim. Acta 277 (1998) 177-185.
- [13] A. Hazell, K.F. Thong, J. Oyanc, L.E. Khoo, Acta Cryst. C53 (1997) 1226-1228.
- [14] M.K. Paira, J. Dinda, T.-H. Lu, A.R. Paital, C. Sinha, Polyhedron 26 (2007) 4131– 4140.
- [15] B. Rosenberg, L. Van Camp, J.E. Trosko, V.H. Mansour, Nature 222 (1969) 385– 386.
- [16] F.I. Raynaud, F.E. Boxall, P.M. Goddard, M. Valenti, M. Jones, B.A. Murrer, M. Abrams, L.R. Kelland, Clin. Cancer Res. 3 (1997) 22063–22074.
- [17] L.R. Kelland, S.Y. Sharp, C.F. O'Neill, F.I. Raynaud, P.J. Beale, I.R. Judson, J. Inorg. Biochem. 77 (1999) 111–115.
- [18] C.J. O'Connor, E.E. Eduok, F.R. Fronczek, O. Kahn, Inorg. Chim. Acta 105 (1985) 107-113.
- [19] H.M. Hu, D.-L. Long, H.-Y. Zeng, W.-D. Cheng, J.-S. Huang, Acta Cryst. C55 (1999) IUC9900049.
- [20] H.M. Helis, W.H. Goodman, R.B. Wilson, J.A. Morgan, D.J. Hodgson, Inorg. Chem. 16 (1977) 2412–2416.
- [21] A.W. Maverick, M.L. Ivie, F.R. Fronczek, J. Coord. Chem. 21 (1990) 315-322.
- [22] A.G. Hatzidimitriou, M. Uddin, Polyhedron 16 (1997) 1651–1654.
- [23] C.J. O'Connor, E.E. Eduok, J.W. Owens, E.D. Stevens, C.L. Klein, Inorg. Chim. Acta 117 (1986) 175–181.

- [24] H. Kooijman, A.L. Spek, D. Rehorst, W.L. Driessen, J. Reedijk, Acta Cryst. C53 (1997) 1596–1598.
- [25] Bruker Topspin 2.1 (pl6) from Bruker BioSpin, 2010.
- [26] Bruker APEX2, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- [27] G.M. Sheldrick, Acta Cryst. A64 (2008) 112-122.
- [28] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849–854.
- [29] E. Tomas-Mendivil, J. Diez, V. Caderno, Polyhedron 59 (2013) 69–75.
- [30] C. Luque, J. Pons, T. Calvet, M. Font-Bardia, J. Garcia-Anton, J. Ros, Inorg. Chim. Acta 367 (2011) 35–43.
- [31] S. Hanesa, Organometallics 26 (2007) 6551-6555.
- [32] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Cryst. 41 (2008) 466–470.
- [33] I.M. Sluch, A.J. Miranda, O. Elbjeirami, M.A. Omary, L.M. Slaughter, Inorg. Chem. 51 (2012) 10728–10746.
- [34] T. Steiner, Chem. Commun. 8 (1997) 727-734.
- [35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision D.01, Gaussian Inc., Wallingford CT, 2009.
- [36] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [37] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
- [38] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639-5648.
- [39] K. Raghavachari, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650-654.
- [40] T.H. Dunning Jr., P.J. Hay, in: Modern Theoretical Chemistry, in: H.F. Schaefer III (Ed.), vol. 3, Plenum, New York, 1976, pp. 1–28.
- [41] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270–283.
- [42] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299-310.
- [43] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284-298.
- [44] C.E. Check, T.O. Faust, J.M. Bailey, B.J. Wright, T.M. Gilbert, L.S. Sunderlin, J. Phys. Chem. A 105 (2001) 8111–8116.
- [45] R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. 256 (1996) 454-464.
- [46] M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahub, J. Chem. Phys. 108 (1998) 4439-4449.
- [47] R.E. Stratmann, G.E. Scuseria, M.J. Frisch, J. Chem. Phys. 109 (1998) 8218-8224.
- [48] C. Van Caillie, R.D. Amos, Chem. Phys. Lett. 308 (1999) 249-255.
- [49] C. Van Caillie, R.D. Amos, Chem. Phys. Lett. 317 (2000) 159–164.
- [50] F. Furche, R. Ahlrichs, J. Chem. Phys. 117 (2002) 7433-7447.
- [51] G. Scalmani, M.J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, V. Barone, J. Chem. Phys. 124 (094107) (2006) 1–15.
- [52] S. Miertuš, E. Scrocco, J. Tomasi, Chem. Phys. 55 (1981) 117-129.
- [53] S. Miertuš, J. Tomasi, Chem. Phys. 65 (1982) 239–245.
- [54] J.L. Pascual-Ahuir, E. Silla, I. Tuñón, J. Comp. Chem. 15 (1994) 1127–1138.
- [55] R. Dennington, T. Keith, J. Millam, GaussView, Version 5, Semichem Inc., Shawnee Mission KS, 2009.
- [56] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Cryst. 41 (2008) 466–470.
- [57] M.P. Akerman, V.A. Chiazzari, J. Mol. Struct. 1058 (2014) 22–30.
- [58] B.F. Minaev, Phys. Chem. Chem. Phys. 2 (2000) 2851–2856.
- [59] C. Daniel, D. Guillaumont, C. Ribbing, B.F. Minaev, J. Phys. Chem. A 103 (1999) 5766–5772.