Pd(II) and Pt(II) Complexes of 1,2-Bis(pyridin-2-yl)ethane-*N,N'*

A. McFarlane, J. R. Lusty

Department of Chemistry, University of Central Lancashire, Preston, PR1 2HE, U.K.

J. J. Fiol, A. Terrón

Departament de Química, Universitat de les Illes Balears, 07071 Palma de Mallorca, Spain

E. Molins, C. Miravitlles

Institut de Ciència de Materials de Barcelona, CSIC, Bellaterra, 08193, Cerdanyola, Spain

V. Moreno*

Departament de Química Inorgànica, Universitat de Barcelona, Avgda Diagonal,
647.08028 Barcelona, Spain

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Pyridine Pt(II) Compounds, Complexes of Pt(II) and Pd(II)

X-ray crystal structures and properties of the two Pd(II) and Pt(II) complexes $[bpeH_2][PdCl_4]$ and $[Pt(bpe)Cl_2]$, [bpe = 1,2-bis(pyridin-2-yl)ethane] are described and correlated with the IR and ^1H NMR/^{13}C NMR spectroscopic data. In the case of the Pt(II) complex, the 1,2-bis(pyridin-2-yl)ethane is bound to the metal by the heterocycle nitrogen atoms but no direct bond is found in the case of the Pd(II) complex. The ligand exhibits low energy geometries in both compounds: the *cis*-conformation in the Pt(II) complex, and the *trans*-conformation in the Pd(II) complex.

I. Introduction

The interactions of platinum group metal complexes with constituents of the nucleic acids have been reported in recent years [5]. The main aim of these studies was the investigation of the mechanisms related to the antitumoral properties of *cis*-$Pt(NH_3)_2Cl_2$ and analogues [6–8]. We now describe the synthesis of some new compounds of Pd(II) and Pt(II) with nitrogen bases related to heterocycles such as 1,2-bis(pyridin-2-yl)ethane or 1,2-bis(pyridin-2-yl)methane. Reedijk *et al.* [9–10] reported the structure of the products of the interaction of Pt(II) with 1,2-bis(pyridin-2-yl)ethane and other N-donor ligands such as the hypoxanthine derivative. Previous work [11] on X-ray crystal structures of $[PdCl_4]^{2-}$ salts containing the N–N'-dimethyl-4-4'-bipyridylium cation have shown that the Pd(II) ion remains uncoordinated to the nitrogen base. However, coordination of bipyridine to palladium is easier when the metal is in the highest oxidation state Pd(IV) [12]. Recently, A. Baker [13] described the crystal structure of a Pd(II) complex with a similar ligand: 1,2-bis(6-methylpyridin-2-yl)ethane. In this case, the metal ion is coordinated to the N atoms and forms a chelate complex.

The reaction of $K_2[PdCl_4]$ with 1,2-bis(pyridin-2-yl)ethane in methanol yields brown needles which can be studied by X-ray diffraction. The reaction of $K_2[PtCl_4]$ with 1,2-bis(pyridin-2-yl)ethane in water yields pale-yellow needles which could be studied in the same way. We now report the structures and spectral properties of these compounds.

II. Experimental

Materials and methods

The complexes were prepared using $K_2[PdCl_4]$ and $K_2[PtCl_4]$ Johnson Matthey and 1,2-bis(pyridin-2-yl)ethane (bpe) synthesized at the University of Central Lancashire Organic Laboratory.

The analyses of carbon, hydrogen, nitrogen and chlorine were carried out using a Carlo Erba model 1106 microanalyzer at the Institut de Bio-Orgànica del CSIC at Barcelona. The infrared spectra were recorded in solid state (KBr pellets) on a Perkin Elmer 683 IR spectrometer with an IR data station PE 1600 and on a FT-IR Nicolet 5 DZ spectrometer. ^1H and ^{13}C NMR spectra were obtained

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* Reprint requests to Prof. Dr. V. Moreno.

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on a Varian 200 Gemini spectrometer. Chemical shifts were measured relative to TMS.

Crystals suitable for X-ray diffraction experiments were mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from 25 reflections and refined by the least-squares method. Intensity data were collected using graphite monochromated MoK_α radiation. Three standard reflections were monitored each hour during data collection showing a decay of 0.47% for the Pd(II) complex and 0.72% for the Pt(II) complex. Three reflections were measured every 50 to test for crystal misorientation. Lorentz and polarization corrections were applied. The absorption was corrected using the DIFABS program [14]. Trans. max./min.: 1.237/0.726.

Both structures were solved by locating the metal atoms by direct methods using the MULTAN 11/84 program [15]. The positions of the remaining non-hydrogen atoms were determined by weighted Fourier synthesis. Both C7 and C8 were found to be disordered on two sites with half occupancy each. In the case of the Pd(II) compound, hydrogen atoms were located by difference Fourier syntheses and introduced in the refinement with a global isotropic temperature factor after the convergence of the anisotropic thermal parameters for non-H atoms. For the Pt(II) complex the hydrogen atoms were introduced in calculated positions. Refinement was carried out using the SHELX-76 program [16]. A summary of the crystal data and data collection and refinement parameters shown in Table II.*

Syntheses of the complexes

a) $[bpeH_2][PdCl_4]$ (**1**). 1 mmol of $K_2[PdCl_4]$ and 1 mmol of finely powdered 1,2-bis(pyridin-2-yl)ethane (bpe) were mixed and about 20 ml of ethanol with a few drops of HCl were added. The solution was stirred for 3 h at 20 °C and after 2 d bright brownish needles were formed.

Analysis for $C_{12}H_{14}N_2Cl_4Pd$ *(434.4 g/mol)*

Calcd	C 33.15	H 3.22	N 6.44	Cl 32.68%,
Found	C 33.32	H 3.01	N 6.40	Cl 33.12%.

b) $[Pt(bpe)Cl_2]$ (**2**). 0.5 mmol of $K_2[PdCl_4]$ was dissolved in 10 ml of H_2O, and an aqueous suspension of 1,2-bis(pyridin-2-yl)ethane (0.5 mmol in 5 ml of H_2O) was added. The mixture was stirred for 2 h at 60 °C. After the solution was concentrated to 10 ml, a crude, yellow product was isolated, which, on recrystallization from water gave **2** as yellow needles.

Analysis for $C_{12}H_{12}N_2Cl_2Pt$ *(459.1 g/mol)*

Calcd	C 32.07	H 2.67	N 6.24	Cl 15.59%,
Found	C 31.93	H 2.61	N 6.21	Cl 15.54%.

III. Results and Discussion

IR spectra

The infrared spectra of the obtained compounds were recorded down to 200 cm^{-1} and compared with that of the ligand 1,2-bis(pyridin-2-yl)ethane (bpe). The assignment was carried out according to the literature [17–18]. The most important bands are recorded in Table I.

In both spectra there are important changes in frequency and intensity on the ν ring bands of the bpe ligand as a consequence of protonation or metalation. The 1594 cm^{-1} band related to $\nu(C{=}N)$ + $\nu(C{=}C)$ of the heterocyclic ring shifts to a higher frequency in the two cases with splitting in the spectrum of the N-protonated system. Other bands due to $\delta(C-H)$ and $\gamma(C-H)$ are also shifted. In the lower frequency region of the spectrum of **2**, two weak intensity bands appear at 479 and 463 cm^{-1} assignable to Pt–N stretching vibrations which are absent in the spectrum of **1.** The strong absorptions at 325 (**1**) and 331 (**2**) are assigned to $\nu(M-Cl)$. The broad character of the

Table I. Characteristic IR bands (cm^{-1}) for the bpe ligand and complexes.

Compound	ν_{ring}, $\nu C{=}N + \nu C{=}C$			$\delta C-H$			$\gamma C-H$		$\nu M-N$		$\nu M-Cl$
bpe	1594 s	1570 s	1476 s	1310 m		1153 m	787 s	752 s			
$[bpeH_2][PdCl_4]$	1629 s 1616 s	1539 s	1463 s	1314 m	1273 m	1173 m	797 s	752 s			325 s, sp
$[Pt(bpe)Cl_2]$	1611 s	1570 m	1484 s	1315 m	1286 m	1161 m	792 s	777 s	479 w	463 m	331 s, br

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* Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry-No. CSD 58152, the names of the authors and the journal citation.

Table II. Crystal data and summary of data collection and refinement.

Complex	[bpeH_2][PdCl_4]	[Pt(bpe)Cl_2]
Composition	$PdC_{12}H_{14}N_2Cl_4$	$PtC_{12}H_{12}N_2Cl_2$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	8.647(8)	8.410(1)
b (Å)	7.293(1)	14.591(2)
c (Å)	12.581(4)	10.858(2)
β (°)	105.21(4)	99.92(1)
V (Å^3)	766(8)	1312.4(1)
Z	2	4
Mol.wt.	434.4	452.25
F(000)	428	848
D_c(g cm^{-3})	1.88	2.29
Crystal size (mm)	0.14×0.28×0.47	0.24×0.35×0.36
μ (cm^{-1})	18.9	111.9
Radiation	MoK_α($\lambda = 0.71069$ Å)	
Scan method	ω-2θ	ω-2θ
Data collection range (2θ)	2–50°	2–50°
Range of hkl	$-10<h<10$, $0<k<8$, $0<l<14$,	$-10<h<10$, $-17<k<17$, $0<l<12$
N. of refl. measured	1538	4850
N. of unique refl.	1336	2295
N. of obs. refl. ($I \geq 2\sigma(I)$)	1200	1600
N. of variables	110	153
R	0.037	0.040
R_w	0.044	0.044

ν(Pt–Cl) band is indicative of the *cis*-configuration. The *cis*-position of chloride atoms was also confirmed by the Kurnakov reaction.

X-ray study

A perspective view of the two molecules, including the atom labeling, is presented in Fig. 1 and 2. Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Tables III and IV for **1** and **2** respectively. Tables V and VI contain important bond distances and angles.

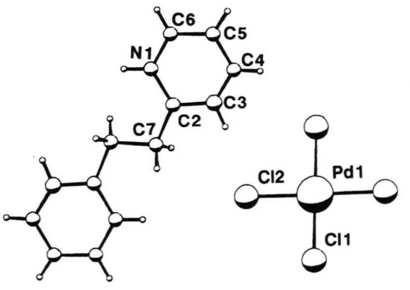

Fig. 1. Molecular structure of [bpeH_2][PdCl_4].

Table III. Fractional atomic coordinates (×10^4) with equivalent temperature factors for [bpeH_2][PdCl_4].

Atom	x/a	y/b	z/c	B_{eq}
Pd1*	5000	0	0	2.72
Cl1	7500(1)	958(2)	−96(1)	3.97
Cl2	5807(2)	117(2)	1891(1)	4.19
N1	2602(5)	515(7)	2750(3)	3.30
C2	3098(5)	540(6)	3861(3)	2.81
C3	1948(6)	1004(7)	4408(4)	3.88
C4	416(6)	1443(8)	3823(4)	4.50
C5	−21(5)	1381(7)	2684(4)	4.14
C6	1120(5)	933(7)	2164(4)	4.02
C7	5186(7)	−25(5)	5618(5)	2.98

* Fixed at the special position.

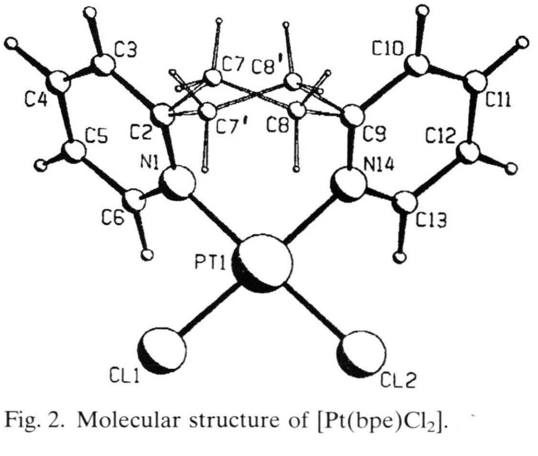

Fig. 2. Molecular structure of [Pt(bpe)Cl_2].

Table IV. Fractional atomic coordinates (×10^4) with equivalent temperature factors for [Pt(bpe)Cl$_2$].

Atom	x/a	y/b	z/c	B_{eq}
Pt1	9569.6(5)	1152.4(3)	6864.8(4)	4.72
Cl1	11432(4)	9(3)	7334(4)	7.08
Cl2	11587(4)	2227(3)	6948(3)	6.78
N1	7753(9)	230(6)	6670(8)	4.74
C2	6642(11)	174(6)	7431(9)	4.40
C3	5458(11)	– 495(7)	7223(11)	5.99
C4	5382(15)	–1098(8)	6424(12)	6.31
C5	6514(15)	–1036(8)	5446(11)	6.04
C6	7691(13)	– 363(8)	5699(11)	5.61
C7	6286(37)	848(13)	8362(23)	6.46
C8	7077(32)	1785(13)	8435(15)	5.12
C9	6795(12)	2304(7)	7223(11)	5.37
C10	5699(12)	3027(8)	6924(13)	6.72
C11	5740(18)	3594(10)	5907(13)	7.40
C12	6891(19)	3399(10)	5158(14)	8.40
C13	7961(16)	2672(9)	5453(11)	6.92
N14	7902(10)	2152(7)	6482(9)	5.09
C7′	7035(30)	783(12)	8533(15)	4.39
C8′	6418(45)	1743(16)	8264(26)	8.69

Table V. Bond lengths (in Å) and bond angles (in degrees) with their e.s.d.'s for [bpeH$_2$][PdCl$_4$].

Cl1–Pd1	2.305(1)	Cl2–Pd1–Cl1	90.5(1)
Cl2–Pd1	2.298(1)	Cl2–Pd1–Cl2	180.0(1)
N1–C2	1.350(5)	N1–C2–C3	116.1(4)
N1–C6	1.335(6)	N1–C6–C5	120.1(4)
C7–C7′	1.51(1)	C6–N1–C2	124.6(4)

Table VI. Selected bond lengths (in Å) and bond angles (in degrees) with their e.s.d.'s for [Pt(bpe)Cl$_2$].

Cl1–Pt1	2.285(3)	Cl2–Pt1–Cl1	90.9(1)
Cl2–Pt1	2.301(3)	N1–Pt1–Cl1	90.8(3)
N1–Pt1	2.019(9)	N1–Pt1–Cl2	176.2(2)
N14–Pt1	2.016(9)	N14–Pt1–Cl1	178.7(3)
C2–N1	1.353(12)	N14–Pt1–Cl2	89.8(3)
C6–N1	1.358(13)	N14–Pt1–N1	88.5(4)
C7–C2	1.478(9)	C2–N1–Pt1	124.5(7)
C7′–C2	1.481(9)	C6–N1–Pt1	115.7(7)
C8–C7	1.515(10)	C6–N1–C2	119.8(9)
C8′–C7′	1.504(10)	C3–C2–N1	119.8(9)
C9–N14	1.349(13)	C7–C2–N1	128.3(12)
C13–N14	1.358(15)	C7–C2–C3	110.9(12)
C8–C9	1.502(9)	C7′–C2–N1	112.0(12)
C8′–C9	1.474(10)	C7′–C2–C3	127.5(13)
		C5–C6–N1	122.4(10)
		C8–C7–C2	119.8(18)
		C8′–C7′–C2	112.4(19)
		C9–N14–Pt1	121.5(7)
		C13–N14–Pt1	116.8(8)
		C13–N14–C9	121.7(10)
		C10–C9–N14	118.7(10)
		C8–C9–N14	114.7(13)
		C8–C9–C10	125.5(14)
		C8′–C9–N14	128.8(14)
		C8′–C9–C10	112.1(14)
		C12–C13–N14	120.1(13)
		C9–C8–C7	114.1(18)
		C9–C8′–C7′	123.6(20)

In the structure of [bpeH$_2$][PdCl$_4$] the tetrachloropalladate anion crystallizes with the dipronated ligand, 1,2-bis(pyridin-2-ylium)ethane, in the *trans* conformation. In [Pt(bpe)Cl$_2$], the crystal structure shows the neutral ligand in the *cis*-conformation coordinated to the metal as a bidentate ligand by the two nitrogens atoms of the heterocycle. The other two coordination sites in the square plane geometry of the Pt(II) are occupied by chloride anions. The Pt–N and Pt–Cl bond distances are as expected. The torsion angles $Cl_1Pt_1N_1C_2 = 113.6°$, $Cl_2Pt_1N_{1'}C_{6'} = 57.6°$ indicates the relative conformation between the pyridine rings and the platinum coordination plane.

Table VII. ^1H NMR and ^{13}C NMR chemical shifts.

^1H NMR chemical shifts [ppm] for bpe and [Pt(bpe)Cl$_2$]^a.

Compound	H(6)	H(4)	H(3), H(5)	CH_2
bpe	8.42(d)	7.41(t)	7.00, 6.97	3.11
[Pt(bpe)Cl$_2$]	9.02(d)	7.59(t)	7.14, 7.08	4.82(q), 3.34(q)^b

^{a} $CDCl_3$ as solvent; ^{b} AB quartet pattern centered at the values given.

^{13}C NMR chemical shifts [ppm] for bpe and the complexes

Compound	C(2)	C(6)	C(3)	C(5)	C(4)	C(7)
bpe^c	160.00	148.20	135.38	127.15	121.99	36.82
[bpeH$_2$][PdCl$_4$]^d	154.65	147.37	142.43	128.03	126.27	32.41
[Pt(bpe)Cl$_2$]^a	159.68	153.36	138.36	126.30	123.46	33.14

^{c} In $CDCl_3$/DMSO-d_6(6:4); ^{d} In DMSO-d_6.

^1H and ^{13}C NMR study

The ^1H and ^{13}C NMR data are summarized in Table VII. Unfortunately, solvent conditions were not the same owing to solubility problems. The spectra of **1** was registered in DMSO-d_6 solution and the spectra of **2** and that of the ligand were registered in a mixture of $CDCl_3$ with DMSO-d_6 (6:4).

In the ^1H spectrum of $[Pt(bpe)Cl_2]$ the downfield shift of H(6) from 8.42 ppm to 9.02 ppm and of H(3) from 7.00 to 7.14 ppm can be observed. The signal corresponding to the CH_2 group appears as an AB quartet centered at 4.82 and 3.34 indicating the loss of equivalency of the two H of each CH_2 group as the Pt(II) atom is bound to the ligand.

By comparison of the complex **2** and bpe spectra (which are recorded in the same solvent) it can be observed that the signals corresponding to the C(6) and $C(CH_2)$ are considerably modified. The signal of C(6) in the bpe spectrum (148.20 ppm) is shifted downfield by about 5 ppm, and the $C(CH_2)$ signal is shifted upfield by *ca.* 4 ppm. These changes are consistent with Pt–N binding and the *cis*-configuration of the coordinated ligand. By contrast, the C(6) signal in the spectrum of **1** remains almost unaltered.

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