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Studies on the Metal–Amide Bond. XV*. The Molecular Structure of Chloro{[N-methyl-N-(2′-pyridinecarboxamide)-N′-(2′-pyridinecarboxamido)]-1,2-ethane}palladium(II) Determined by X-ray Diffraction and High-Resolution NMR Studies

MOH'D MULQI, FREDERICK S. STEPHENS and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

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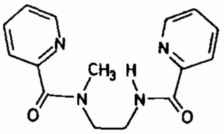
Chloro{[N-methyl-N-(2′-pyridinecarboxamide)-N′-(2′-pyridinecarboxamido)]-1,2-ethane}palladium(II), $C_{15}H_{15}N_4O_2ClPd$, is tetragonal, space group $I4_1/a$ *with* $a = 14.340(8)$, $c = 31.226(10)$ Å, $Z = 16$. *The crystal structure was refined to* $R = 0.078$ *for 1886 photographic reflexions by least-squares calculations. The ligand acts as an N_3-tridentate to the Pd atom via the two pyridine and one deprotonated amide nitrogen atoms [Pd–N(amide) 1.98(1) Å; average Pd–N(pyridine) 2.05(1) Å]. The N-methylated amide group is not coordinated but forms part of an unusual eight-membered chelate ring. A square-planar coordination is completed by the chlorine atom [Pd–Cl 2.293(4) Å]. The coordinated picolinamide unit is almost co-planar with the coordination plane, whereas the N-methyl picolinamide unit is non-planar. The plane of this amide group is approximately perpendicular to the plane of the pyridine ring, the latter making an angle of 64.9° with the coordination plane. This unusual molecular geometry is shown to be retained in solution. The complex proton n.m.r. spectrum of the compound in $CDCl_3$ only may be simulated assuming a rigid structure similar to that found in the solid state. The hydrogen atoms of the central ethane link are closely eclipsed; observed vicinal coupling constants for the protons show a close correlation with those calculated using the H–C–C–H torsion angles derived from the X-ray analysis. Observed chemical shifts are explained in terms of close intramolecular contacts in the structure as determined.*

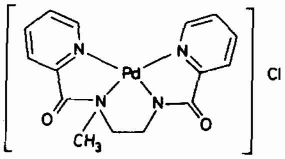
Introduction

The ligand N-methyl-N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane, bpenMeH (I), was synthesised as part of an attempt to enforce coordination of an N-substituted amide nitrogen atom through a multidentate effect involving an N_4-tetradentate function [1]. Analogous unsubstituted ligands [2–5] commonly act as tetradentates when both amide nitrogen atoms are deprotonated, particularly stable square-planar chelates forming with bivalent palladium [2–4]. The sole deprotonated chelate obtained with this ligand is Pd(bpenMe)Cl [1], and a possible structure for this compound is represented in (II) below.



bpenMeH

(I)



(II)

This article details an investigation of the molecular structure of this compound in both solution and solid state using high-resolution proton n.m.r. and X-ray diffraction methods.

Experimental

The complex crystallises from chloroform/ethanol [1] as yellow-orange octahedra elongated along [001] with [100] parallel to an edge.

Crystal Data: $C_{15}H_{15}N_4O_2ClPd$, M_r = 425.3, Tetragonal, a = 14.340(8), c = 31.226(10) Å, U =

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*Part XIV is reference [1].

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6421.2 Å^3, D_m = 1.77 (by flotation), Z = 16, D_c = 1.760 Mg m^{-3}, $F(000)$ = 3392, μ(Mo-K$_\alpha$) = 1.32 mm^{-1}. Systematic absences: hkl if $h + k + l \neq 2n$, $hk0$ if $h \neq 2n$ and $00l$ if $l \neq 4n$; space group $I4_1/a$ (no. 88).

X-ray Diffraction Analysis

Cell parameters were determined from precession photographs using Mo-K$_\alpha$ radiation. 2760 non-zero reflexions were recorded on the layers 0–4 about [100] and 0–5 about [110] from precession photographs using Mo-K$_\alpha$ radiation. Intensities were estimated visually and corrected for Lorentz and polarization effects but not for extinction or absorption. The observed structure factors were placed on a common scale by internal correlation. The unique data set generated contained 1886 reflexions.

The structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations in which the function minimized was $\Sigma w\Delta^2$. The weight, w, for each reflexion was initially unity, and in the final cycles of refinement $w = (1.0 + 0.001|F_o| + 0.0001|F_o|^2)^{-1}$ was used. After isotropic refinement a difference map was calculated which gave the approximate positions of hydrogen atoms other than those of the methyl group and these positions were optimised assuming C–H to be 1.0 Å. They were included in subsequent calculations with a thermal parameter of B = 6.0 Å^2 but their parameters were not refined. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms, and terminated when the maximum shift in any parameter was <0.01 σ. The final value for R, based on 1886 reflexions, was 0.078 and for R' [$=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}$] was 0.095. A final difference map showed no positive electron density >0.9e Å^{-3}, and also gave no indication of the positions of the methyl hydrogen atoms which therefore were excluded from the model.

All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S. Scattering factors used were taken from *International Tables for X-ray Crystallography* [6].

Proton Magnetic Resonance Studies

P.m.r. spectra for both the ligand and the palladium complex were recorded on a Varian XL-200 spectrometer at 25 °C using deuterated chloroform as solvent. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane with traces of $CHCl_3$ (δ 7.25) [7] used as internal reference. Computer simulation spectra were generated using the programme LAOCN3 of Bothner-By and Castellano [8].

Results

The final atomic coordinates for non-hydrogen atoms taken from the X-ray analysis are given in Table I. Anisotropic thermal parameters for non-hydrogen atoms are given in Table II and hydrogen atomic coordinates in Table III. A list of observed and calculated structure factors has been deposited with the Editor.

TABLE I. Final Atomic Coordinates (fractional × 10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x	y	z
Pd	1693.8(8)	1112.5(8)	−302.1(3)
Cl	1154(3)	1753(4)	−928(1)
O(1)	1602(11)	501(10)	964(4)
O(2)	3456(7)	2955(6)	−248(4)
N(11)	448(8)	1203(8)	8(4)
N(21)	2959(9)	945(9)	−596(4)
N(1)	2093(10)	663(9)	268(5)
N(2)	3666(10)	1895(10)	282(4)
C(1)	3000(17)	280(18)	365(8)
C(2)	3820(12)	939(12)	426(5)
C(N)	3561(16)	2608(14)	628(5)
C(11)	520(10)	1006(9)	425(4)
C(12)	−240(12)	1057(11)	690(5)
C(13)	−1106(10)	1324(12)	530(6)
C(14)	−1160(10)	1514(12)	93(5)
C(15)	−357(12)	1432(10)	−164(5)
C(21)	3720(10)	1390(10)	−461(4)
C(22)	4583(11)	1249(12)	−656(6)
C(23)	4635(12)	605(13)	−994(5)
C(24)	3864(11)	129(12)	−1125(4)
C(25)	3013(11)	311(11)	−913(5)
C(01)	1472(12)	735(10)	594(5)
C(02)	3613(11)	2124(11)	−138(5)

Bond lengths and angles together with estimated standard deviations are given in Table IV. A perspective drawing [9] of the molecule is given in Fig. 1 together with the atomic labelling scheme.

The ligand functions as an N_3-tridentate and coordinates to the palladium atom through the two pyridine and the deprotonated-amide nitrogen atoms. An irregular square plane is completed by coordination of the chloride ion [Pd–Cl 2.293(4) Å] with the two pyridine nitrogens occupying *trans* positions (Table V, plane 1). A small tetrahedral distortion of 5.2° is evident in this coordination plane (Table V, planes 2–5). The average Pd–N-(*pyridine*) bond distance of 2.05(1) Å is slightly longer than the Pd–N(*amide*) distance of 1.98(1) Å. As a consequence of this bonding mode an unusual eight-membered chelate ring is generated in the molecular structure.

Generally the ligand structure may be defined by three intersecting planes which, together with the N_3Cl coordination plane, are shown in Fig. 1. The least-squares planes defined by N(11), C(11)–C(15),

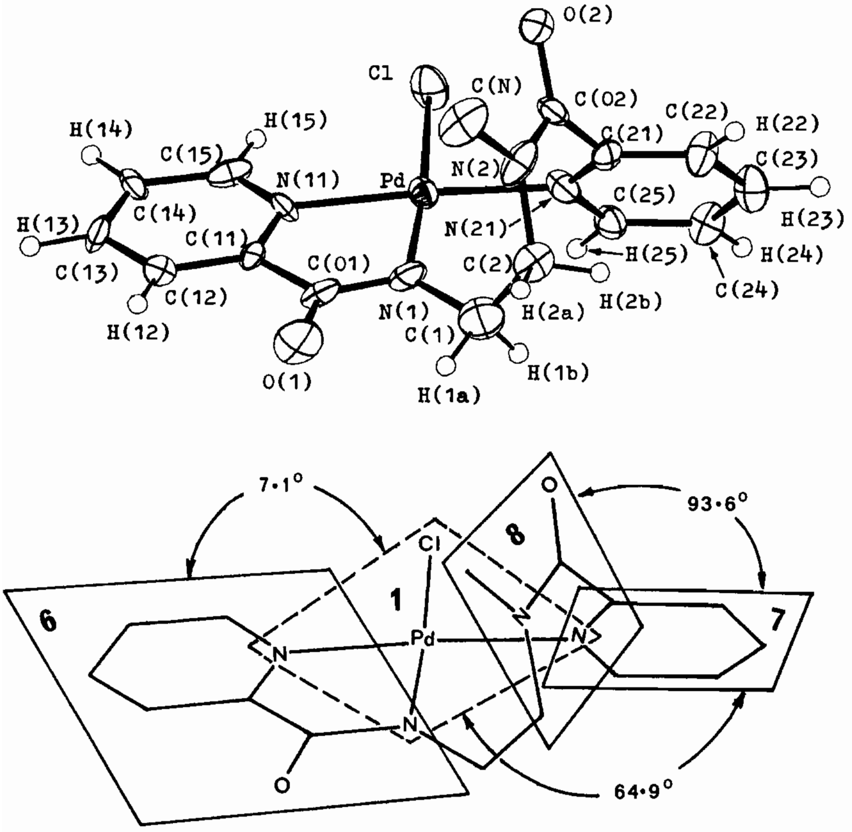


Fig. 1. A perspective drawing of the molecule showing the atomic labelling scheme, and a trigonometric projection illustrating the four major least-squares planes of the molecule numbered according to Table V. Thermal ellipsoids are scaled to include 35% probability. Hydrogen atoms have been included with a thermal parameter of $B = 1.0$ Å^2.

TABLE II. Final Anisotropic Thermal Parameters ($\times 10^4$) in the form exp $-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$, with Estimated Standard Deviations in Parentheses.[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pd	32.4(6)	28.6(6)	6.0(1)	−5.5(5)	3.3(2)	−1.9(2)
Cl	53(3)	73(3)	5.6(4)	−1(2)	2.4(8)	2.3(9)
O(1)	87(10)	78(9)	7(1)	26(8)	−3(3)	7(3)
O(2)	51(7)	39(6)	10(1)	8(5)	6(3)	2(2)
N(11)	23(6)	33(6)	6(1)	−10(5)	3(2)	4(2)
N(12)	45(8)	33(7)	7(1)	−12(6)	5(3)	−1(2)
N(1)	39(8)	31(7)	14(2)	14(6)	−2(3)	6(3)
N(2)	47(8)	48(8)	9(2)	18(7)	−4(3)	−11(3)
C(1)	70(15)	82(17)	20(4)	23(13)	5(6)	19(6)
C(2)	37(9)	42(9)	9(2)	−2(7)	−7(3)	−4(3)
C(N)	92(15)	58(12)	7(2)	19(11)	−4(4)	−15(4)
C(11)	35(8)	20(7)	6(1)	7(6)	5(3)	−3(2)
C(12)	48(10)	33(9)	10(2)	5(8)	8(4)	4(3)
C(13)	26(8)	38(9)	12(2)	15(7)	5(3)	−3(4)
C(14)	21(8)	40(9)	12(2)	−7(7)	5(3)	9(4)
C(15)	55(11)	19(7)	10(2)	3(7)	−7(4)	−2(3)
C(21)	25(7)	33(8)	6(1)	6(6)	−2(3)	2(3)
C(22)	27(8)	47(10)	13(2)	−2(7)	0(3)	−12(4)

(continued overleaf)

TABLE II. *(continued)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(23)	42(10)	71(13)	5(1)	3(9)	0(3)	−2(3)
C(24)	43(9)	52(10)	5(1)	7(8)	−3(3)	−7(3)
C(25)	41(9)	36(8)	7(2)	−4(7)	4(3)	−1(3)
C(01)	50(10)	24(7)	7(2)	15(7)	−4(3)	0(3)
C(02)	36(8)	30(8)	7(1)	−9(7)	4(3)	3(3)

[a] For all hydrogen atoms $B = 6.0$ Å^2.

TABLE III. Hydrogen Atomic Coordinates (fractional × 10^3).

	x	y	z
H(1a)	311	−25	17
H(1b)	287	−1	65
H(2a)	433	68	24
H(2b)	402	89	73
H(12)	−16	94	100
H(13)	−167	134	72
H(14)	−177	172	−3
H(15)	−40	155	−48
H(22)	515	157	−55
H(23)	525	51	−114
H(24)	390	−32	−137
H(25)	244	−5	−100

C(01), O(1) and N(1) and pyridine ring 2 (Table V, planes 6 and 7) have the palladium atom displaced by 0.13 and 0.06 Å respectively. The carbonyl carbon C(01) is distorted significantly (16%) from planarity (Table V, planes 16–18) with the average dihedral angle between the three-atom planes at C(01) being 9.3°. A further distortion in this amide carbon is demonstrated by the larger external angle of 126.6° compared with 120.2° about the other amide carbon atom C(02). Both amide nitrogen atoms N(1) and N(2) and the carbonyl carbon C(02) have the expected trigonal-planar geometry (Table V, planes 10–15 and 19–21).

Pyridine ring 2 is rotated by 64.9° out of the coordination plane, and the uncoordinated tertiary amide group (Table V, plane 8) has a *cis*-planar geometry, which contrasts with a *trans*-arrangement

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

(a) Distances (Å)

Pd–Cl	2.293(4)	Pd–N(1)	1.98(1)
C(1)–C(2)	1.52(3)	C(N)–N(2)	1.50(2)

	n = 1	n = 2
Pd–N(n1)	2.04(1)	2.05(1)
N(n1)–C(n5)	1.31(2)	1.34(2)
C(n5)–C(n4)	1.41(2)	1.41(2)
C(n4)–C(n3)	1.39(2)	1.36(2)
C(n3)–C(n2)	1.39(2)	1.41(2)
C(n2)–C(n1)	1.37(2)	1.39(2)
C(n1)–N(n1)	1.34(2)	1.33(2)
C(n1)–C(On)	1.51(2)	1.47(2)
C(On)–O(n)	1.22(2)	1.26(2)
C(On)–N(n)	1.36(2)	1.35(2)
N(n)–C(n)	1.44(3)	1.46(2)

(b) Angles (°)

N(1)–Pd–Cl	174.2(3)	N(11)–Pd–N(21)	176.5(3)
N(1)–Pd–N(11)	81.2(3)	N(1)–Pd–N(21)	96.2(3)

(continued on facing page)

TABLE IV. *(continued)*

C(01)–N(1)–Pd	117.4(8)	C(02)–N(2)–C(N)	121.9(9)
C(1)–N(1)–Pd	125.1(8)	C(2)–N(2)–C(N)	115.8(9)
N(1)–C(1)–C(2)	119.1(16)	N(2)–C(2)–C(1)	115.4(15)

	n = 1	n = 2
N(n1)–Pd–Cl	94.8(3)	87.9(3)
C(n)–N(n)–C(On)	117.6(10)	122.3(13)
C(n5)–N(n1)–Pd	126.4(9)	117.4(8)
C(n1)–N(n1)–Pd	112.4(6)	121.8(6)
C(n5)–N(n1)–C(n1)	121.2(10)	120.6(7)
C(n1)–C(On)–N(n)	110.6(14)	119.2(14)
C(n1)–C(On)–O(n)	122.6(13)	120.6(14)
O(n)–C(On)–N(n)	126.2(14)	120.2(14)
C(n2)–C(n1)–N(n1)	121.0(13)	121.4(15)
C(n2)–C(n1)–C(On)	121.4(13)	119.8(14)
N(n1)–C(n1)–C(On)	117.6(14)	118.4(14)
C(n3)–C(n2)–C(n1)	120.5(15)	118.0(15)
C(n4)–C(n3)–C(n2)	117.1(14)	120.8(14)
C(n5)–C(n4)–C(n3)	119.7(15)	117.9(14)
N(n1)–C(n5)–C(n4)	120.5(15)	121.3(14)

TABLE V. Least-Squares Planes Data.

(a) Least-squares planes and their equations given by $lX + Y + nZ - p = 0$. Deviations (Å) of relevant atoms from the planes are given in square brackets.

		l	m	n	p
Plane (1):	N(11), N(1), N(21), Cl	0.2519	0.9208	0.2978	1.8171
	[N(11) –0.060; N(1) 0.064; N(21) –0.055; Cl 0.052; Pd –0.02]				
Plane (2):	N(1), Cl, N(11)	0.1947	0.9278	0.3183	1.7328
	[Pd –0.08]				
Plane (3):	N(1), N(21), Cl	0.2994	0.9137	0.2746	1.9972
	[Pd –0.07]				
Plane (4):	N(11), N(21), Cl	0.2692	0.9021	0.3372	1.7368
	[Pd 0.04]				
Plane (5):	N(11), N(1), N(21)	0.2251	0.9431	0.2448	1.7770
	[Pd 0.04]				
Plane (6):	N(11), C(11)–(15), C(01), O(1), N(1)	0.2233	0.9576	0.1823	1.7714
	[N(11) 0.028; C(11) 0.019; C(12) –0.004; C(13) –0.006; C(14) –0.011; C(15) –0.013; C(01) 0.047; O(1) –0.021; N(1) –0.038; Pd 0.13; Cl 0.48; C(1) –0.22]				
Plane (7):	N(21), C(21)–(25)	0.1963	0.7272	–0.6578	1.3604
	[N(21) 0.017; C(21) –0.011; C(22) –0.002; C(23) 0.008; C(24))0.003; C(25) –0.010; Pd –0.06; C(2) 0.12]				
Plane (8):	C(2), N(2), C(N), C(02), O(2), C(21)	0.9863	0.1642	–0.0182	5.6097
	[C(2) –0.011; N(2) 0.006; C(N) 0.005; C(02) 0.009; O(2) –0.013; C(21) 0.004; Pd –2.94]				
Plane (9):	N(1), C(1), C(2), N(2)	–0.2120	0.2081	0.9548	0.3255
	[N(1) 0.035; C(1) –0.065; C(2) 0.064; N(2) –0.033; Pd –1.41]				

(continued overleaf)

TABLE V. *(continued)*

		l	*m*	*n*	*p*
Plane (10):	N(1), Pd, C(1) [C(01) 0.02]	0.3348	0.9153	0.2238	2.0624
Plane (11);	N(1), Pd, C(01) [C(1) 0.02]	0.3521	0.9106	0.2165	2.1036
Plane (12):	N(1), C(1), C(01) [Pd 0.03]	0.3401	0.9177	0.2053	2.0652
Plane (13):	N(2), C(2), C(02) [C(N) −0.01]	0.9881	0.1523	−0.0189	5.5923
Plane (14):	N(2), C(2), C(N) [C(02) −0.01]	0.9878	0.1555	−0.0092	5.6077
Plane (15):	N(2), C(N), C(02) [C(2) −0.01]	0.9865	0.1627	−0.0162	5.6145
Plane (16):	C(01), C(11), N(1) [O(1) −0.15]	0.2343	0.9662	0.1077	1.7119
Plane (17):	C(01), C(11), O(1) [N(1) −0.19]	0.1767	0.9528	0.2471	1.8346
Plane (18):	C(01), N(1), O(1) [C(11) −0.22]	0.3443	0.9153	0.2092	2.0786
Plane (19):	C(02), C(21), N(2) [O(2) −0.03]	0.9871	0.1593	−0.0172	5.6072
Plane (20):	C(02), C(21), O(2) [N(2) −0.03]	0.9836	0.1766	−0.0357	5.6502
Plane (21):	C(02), N(2), O(2) [C(21) −0.03]	0.9829	0.1837	−0.0108	5.6574
Plane (22):	N(1), C(1), C(2)	−0.2040	0.0578	0.9773	0.2600
Plane (23):	N(2), C(1), C(2)	0.3414	−0.2426	−0.9081	0.3359

(b) Dihedral angles (°) between relevant planes

1–6	7.1	2–3	6.6	10–11	1.1	16–17	8.7
1–7	64.9	2–4	4.6	10–12	1.0	16–18	9.1
1–8	66.8	2–5	4.6	11–12	1.1	17–18	10.1
1–9	65.0	3–4	4.0	13–14	0.6	19–20	1.5
		3–5	4.9	13–15	0.6	19–21	1.5
6–8	68.0	4–5	6.3	14–15	0.6	20–21	1.5
7–8	93.6					22–23	13.8

for the coordinated amide group. The dihedral angle between the plane of pyridine ring 2 and its corresponding amide group is 93.6° and hence there would be no π-conjugation in this picolinamide unit. The shortest intramolecular contact from the uncoordinated amide group to the palladium atom is Pd····C(02) at 3.15(2) Å. Steric strain present in the eight-membered ring is demonstrated by out of plane distortions at N(21) and C(21) of 8.3 and 12.7% respectively compared with planar arrangements around N(11) and C(11) in the other ring. These deviations, as measured by the average dihedral angle

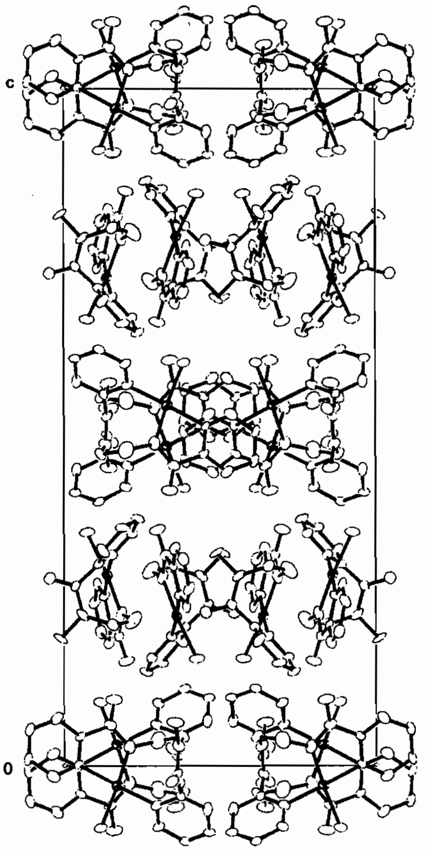


Fig. 2. The packing of the molecules in the unit cell, viewed down *b*.

TABLE VI. Interatomic Distances < 3.50 Å*.

O(1) . . . . . . .C(13^{I})	3.45(2)
O(1) . . . . . . .C(24^{II})	3.31(2)
O(1) . . . . . . .C(25^{II})	2.99(2)
O(2) . . . . . . .C(1^{III})	3.42(3)
O(2) . . . . . . .C(22^{IV})	3.29(2)
N(11). . . . . . .C(14^{V})	3.44(2)
N(11). . . . . . .C(15^{V})	3.44(2)
C(15). . . . . . .C(15^{V})	3.23(2)

*Roman numeral superscripts refer to the following equivalent positions relative to x, y, z:

I	$\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$
II	$\frac{1}{4} + y, \frac{1}{4} - x, \frac{1}{4} + z$
III	$x, \frac{1}{2} + y, -z$
IV	$1 - x, \frac{1}{2} - y, z$
V	$-x, \frac{1}{2} - y, z$

TABLE VII. Nuclear Magnetic Resonance Parameters for bpenMeH and [Pd(bpenMe)Cl].

a) Chemical shift (ppm)^{a}:

	bpenMeH	[Pd(bpenMe)Cl]
H(amide)	9.59(brs)	–
H(12)	8.16(d)	7.52(d)^{b}
H(13)	7.84(t)	8.05(t)
H(14)	7.38(t)^{b}	7.46(t)^{b}
H(15)	8.70(d)	9.09(d)
H(22)	7.57(d)^{b}	7.50(d)^{b}
H(23)	7.72(t)	7.90(t)
H(24)	7.38(t)^{b}	7.46(t)^{b}
H(25)	8.55(d)	8.92(d)
H(1a)	3.76(s) 3.83(s)	2.21(m)
H(1b)		4.21(m)
H(2a)		3.28(m)
H(2b)		3.50(m)
$-CH_3$	3.13(s) 3.15(s)	3.22(s)

(b) Coupling constants (Hz) of pyridyl and methylene protons in the spectrum of [Pd(bpenMe)Cl]

$J_{(12,13)}$	6.98	$J_{(22,23)}$	7.70
$J_{(12,14)}$	1.88	$J_{(22,24)}$	1.15
$J_{(13,14)}$	7.47	$J_{(23,24)}$	7.75
$J_{(13,15)}$	1.13	$J_{(23,25)}$	1.08
$J_{(14,15)}$	5.42	$J_{(24,25)}$	5.65
$J_{(1a,1b)}$	14.05	$J_{(2a,2b)}$	15.00
$J_{(1a,2a)}$	7.75	$J_{(1b,2b)}$	8.55
$J_{(1a,2b)}$	7.75	$J_{(1b,2a)}$	4.55

^{a}m = multiplet; t = triplet; d = doublet; s = singlet; brs = broad singlet. ^{b}These peaks partially overlapped in spectrum; relative positions in multiplet determined from decoupling experiments.

between the three-atom planes about each atom, are 5.0 and 7.5° respectively. A steric interaction between amide oxygen O(2) and the methyl group is evidenced by the short O(2)···C(N) contact distance of 2.78(2) Å, which is 0.6 Å less than the sum of their van der Waals radii [10].

The $N-CH_2-CH_2-N$ molecular fraction is almost planar (Table V, plane 9) with the methylene hydrogen atoms thus adopting a closely eclipsed configuration, the torsion angle N(1)–C(1)–C(2)–N(2) being 13.8° (Table V, planes 22 and 23).

Figure 2 illustrates the arrangement of the chelate molecules in the unit cell. Intermolecular contacts less than 3.5 Å are listed in Table VI and indicate that only van der Waals forces are present between molecules.

Table VII gives the proton n.m.r. chemical shifts for both the free ligand and the deprotonated palladium complex. The spectrum of the free ligand shows the amide proton resonance to be at 9.59 ppm, which is 1.03 ppm further downfield than that of the unsubstituted ligand bpenH$_2$ [3]. In D_2O this amide proton signal disappears indicating a rapid exchange. The chemical shifts of the pyridine and

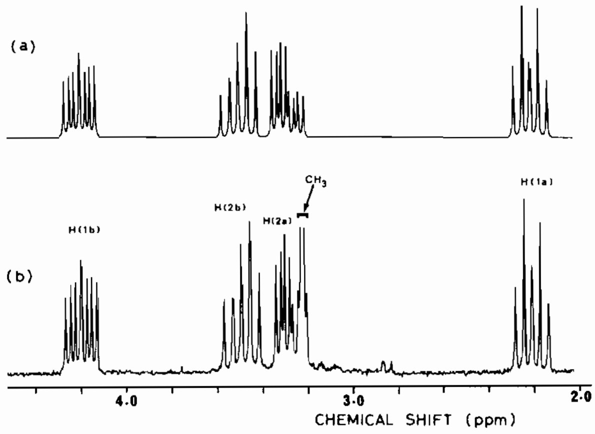


Fig. 3. Computer simulation of signals for methylene protons in [Pd(bpenMe)Cl]. (a) Simulated spectrum using coupling constants and chemical shifts given in Table VII. (b) Observed spectrum.

methylene protons in both ligands are comparable. The spectrum of bpenMeH shows the signals of both the methyl and methylene protons as two asymmetric doublets each with an approximate 2:1 ratio. Variations in temperature give no change in these splitting patterns. Unlike bpenH_2 [3], decoupling of the amide proton does not affect the methylene signals.

The spectrum of the palladium complex is more complicated. The four individual methylene protons are magnetically nonequivalent indicating different environments in a rigid structure on coordination. The assignment of these protons, together with the pyridyl protons, was assisted by resonance decoupling experiments. Figure 3 shows the spectrum observed for the methylene protons, together with a computer simulation using the coupling constants indicated in Table VII and assuming restricted rotation about both the ethane link and the N–CH_2 bonds.

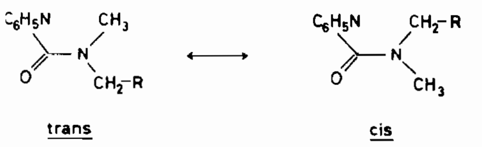
Discussion

The most striking feature of the molecular structure of this palladium complex is the unusual N_3-tridentate function of the ligand. Unlike the deprotonated nickel [11] and copper [12] complexes of bpenH_2, and like ligands [2–5], the two pyridine nitrogen atoms in this structure bond in a *trans* arrangement in the coordination plane. The eight-membered chelate ring which forms is a consequence of the tertiary amide nitrogen atom remaining uncoordinated.

Complexes of first row transition metals with seven-membered or larger chelate rings are quite rare. On the other hand palladium complexes containing such relatively large chelate rings are a little more common. Amide-deprotonation of glutamine complexes, for example, has been observed with palladium [13] resulting in a seven-membered ring system.

Some other interesting structural features are apparent in [Pd(bpenMe)Cl]. The Pd–N(*pyridine*) bonds [average 2.05(1) Å] are slightly longer than the average 1.99–2.04 Å reported for Pd^{II}–N distances in square-planar Pd(II) complexes [14, 15]. The Pd–Cl bond length of 2.293(4) Å is in accord with literature values which range between 2.294–2.422 Å [16, 17]. The bond dimensions of the coordinated amide group are comparable with similar deprotonated amide and peptide complexes [11, 12, 18]. That the coordinated amide group is co-planar with its corresponding pyridine ring would permit electronic delocalization over the whole picolinamide unit. This planarity may enforce a weak steric interaction between the chlorine atom and the pyridyl hydrogen in the 6-position indicated by the short Cl···H(15) contact distance of 2.64 Å, compared with 3.0 Å for the sum of their van der Waals radii [10], and a small 'leaning' of the Pd–Cl bond towards pyridine ring 2. The Pd–N(11)–C(11) angle of 112.4° is significantly smaller than the Pd–N(11)–C(15) angle of 126.4° imposed by the coordination of the deprotonated amide group.

The appearance of two unequal resonances for both the methyl group and methylene protons in the p.m.r. spectrum of the free ligand may be taken as indicating the presence of the two rotamers shown in (III) below.



(III)

That this splitting is not affected by varying the temperature indicates that there is a large energy barrier to rotation in these *cis* and *trans* forms of the free ligand, which obviously are present in solution in an approximate 1:2 ratio.

The palladium complex, which shows only one sharp singlet for the methyl protons, contains the ligand in the *cis* form alone, as evidenced by the crystal structure. Both protons in the 6-pyridyl positions show a down-field shift, compared with the free ligand, which is much larger than was observed in the analogous deprotonated palladium complex of bpenH_2 [3]. This may be explained by the deshielding capability of the chlorine atom in the present complex.

The closely eclipsed configuration of the central ethane link observed in the crystal structure analysis can be shown to be retained in solution. The computer simulation spectrum of these proton signals (Fig. 3) employs coupling constants of 7.75 Hz and 8.55 Hz respectively between the two eclipsed vicinal proton pairs H(1a)H(2a) and H(1b)H(2b). Using the Karplus equation [19], and torsion angles derived from the methylene proton positions in the crystal structure, the calculated coupling constants for those pairs would be 8.20 Hz and 8.19 Hz respectively. In addition a Johnson–Bovey analysis [20] based on these atomic positions shows proton H(1a) to be the most magnetically shielded by the ring current of pyridine 2. Conversely, the close equatorial proximity of H(1b) to the adjacent carbonyl group [H(1b)·····O(1) 2.18 Å; H(1b)·····C(O1) 2.28 Å] would lead to its low-field resonance position in the p.m.r. spectrum.

In both the planar complexes Pd(bpen) [3] and Pd(6-mebpen) [4] the signals for the methylene protons are observed as singlets, and their chemical shifts are little removed from those of each respective parent ligand molecule. In the title complex however, the structural parameters used to simulate the complex pattern of the methylene signals in its p.m.r. spectrum show a high correlation with the rigid molecular structure determined in the solid state. Notwithstanding both the degree of uncertainty of the hydrogen positions in the crystal structure and the empirical nature of the Karplus equation, this correlation may be taken as further evidence for the high stability and inflexibility of square-planar palladium complexes [22].

Generally, the study has confirmed [18] that coordination of a tertiary or non-deprotonated amide group via the nitrogen atom is energetically unfavourable [23]. Rather than act as a tetradentate the ligand bpenMeH has accepted a lower degree of multidentate behaviour, resulting in a loss of planarity in the chelate molecule as a whole and in one picolinamide unit in particular. Some N,N′-dialkylated bispicolinamide ligands have been synthesised also, and their coordination chemistry will be reported in the near future.

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