

Palladium and platinum complexes with vitamin B₆ compounds

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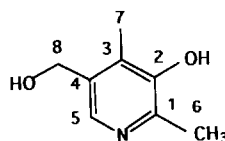
Abstract

cis- and *trans*-[PdCl₂(PN)₂], *cis*-[PdCl₂(PL)₂], [PdCl₂(PM)], [PtCl₂(PM)]·H₂O, (PMH₂)[PdCl₄]·H₂O and (PLH)₂[PtCl₆]·2H₂O were synthesized, where PM, PN and PL are the B₆ vitamins pyridoxamine, pyridoxine and pyridoxal, respectively. The structures were deduced by single crystal X-ray methods and IR spectroscopic techniques. *cis*- and *trans*-[PdCl₂(PN)₂] and *cis*-[PdCl₂(PL)₂] contain pyridoxine and pyridoxal ligands coordinated through the pyridine nitrogen. [PdCl₂(PM)] and [PtCl₂(PM)]·H₂O have pyridoxamine chelated in the usual manner through the phenolate oxygen and the amine group, while (PMH₂)[PdCl₄]·H₂O and (PLH)₂[PtCl₆]·2H₂O contain protonated, uncomplexed ligands. ¹³C NMR chemical shifts in the complexes are correlated to changes in the tautomeric form of the vitamin and to the coordination site. [PtCl₂(PM)]·H₂O crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *a* = 7.028(1), *b* = 12.788(1), *c* = 13.435(2) Å, *Z* = 4, *R* = 0.029 for 3382 observed reflections. Distances include Pt–N 2.032(5), Pt–O 2.015(4), Pt–Cl(1) 2.313(2) and Pt–Cl(2) 2.286(2) Å. (PLH)₂[PtCl₆]·2H₂O crystallizes in the triclinic space group *P*1̄ with *a* = 7.355(2), *b* = 8.534(2), *c* = 11.555(2) Å, *α* = 71.73(2); *β* = 74.10(2), *γ* = 66.79(2)°, *Z* = 1, *R* = 0.059 for 3487 observed reflections. The octahedral [PtCl₆]²⁻ ion lies on a centre of symmetry, and the pyridoxal cation is in the expected hemiacetal form.

Introduction

Pyridoxal phosphate is involved in many enzymatic transformations of α -amino and α -keto acids [1], and much research has been carried out since Metzler *et al.* proposed that the metal-ion catalyzed reactions of pyridoxal with amino acids involve complexation of the pyridoxal to the metal ion prior to Schiff base formation [2]. The compounds comprising the vitamin B₆ complex, including pyridoxal (PL), pyridoxamine (PM) and pyridoxine (PN), display a variety of coordination sites with different charges and hard/soft character, thus giving them a rich coordination chemistry. X-ray crystal structures have shown that chelation through the phenolate oxygen and the adjacent hydroxymethyl or aminomethyl group are common for pyridoxamine and pyridoxine [3–8]. Other bonding modes noted for pyridoxine include coordination solely through the pyridine nitrogen [9], chelation plus bonding through the pyridine nitrogen [10], and chelation plus bridging through the coordinated phenolate or hydroxyl group [11, 12].

This paper continues our work on structures and spectra of vitamin B₆ and its complexes [3–5, 13–16]. The structures and numbering scheme adopted for this paper are as follows.



PL: 7 = CHO; PM: 7 = CH₂NH₂; PN: 7 = CH₂OH

Experimental

General

Potassium tetrachloropalladate and potassium tetrachloroplatinate were obtained from Alfa Products, and palladium(II) chloride from Matheson, Coleman and Bell. Pyridoxal hydrochloride and pyridoxamine dihydrochloride were purchased from Sigma Chemicals, and pyridoxine hydrochloride was purchased from Eastman Kodak. Neutral pyridoxamine, pyridoxine and pyridoxal were prepared by neutralizing aqueous solutions of the acid forms of the ligands and recrystallizing the precipitate from water.

Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN; Guelph Chemical Laboratories, Guelph, Ont.; and Mikroanalytisches Laboratorium, Bonn, Germany. IR spectra were recorded from 200–4000 cm⁻¹ on a Perkin-Elmer 225 grating infrared spectrophotometer. The samples were prepared as mulls in Nujol. The proton-decoupled ¹³C NMR

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spectra were obtained at 15.08 MHz on a Bruker WP-60 FT NMR spectrometer at ambient temperature and a flip angle of 30° using 0.5 Hz of line broadening. A sweep width of 3759 Hz and a 1.1 s acquisition time were used. Samples were prepared in DMSO- d_6 . The internal standard was either TMS or DMSO.

Synthesis of the complexes

$[PtCl_2(PM)] \cdot H_2O$

$PM \cdot 2H_2O$ (0.25 g, 1.2 mmol) was dissolved in 30 ml warm water and added dropwise to a solution of 0.25 g K_2PtCl_4 (0.6 mmol) in 10 ml water. The pH was adjusted to 7 with dilute NaOH. Evaporation yielded yellow needles in 2–3 days. *Anal.* Calc. for $C_8H_{14}Cl_2N_2O_3Pt$: C, 21.25; H, 3.72; N, 6.19; Cl, 15.68. Found: C, 21.28; H, 3.11; N, 6.20; Cl, 16.32%. IR spectrum (cm^{-1}): 1515 (pyridinium NH^+), 342, 334 (*cis*- $PtCl_2$).

$[PdCl_2(PM)]$

A solution of 0.2 g (0.6 mmol) K_2PdCl_4 in 20 ml water was stirred into 60 ml 0.5 M sodium metasilicate solution whose pH had been adjusted to 7.5. The resulting solution was divided among four large test tubes. After the gel set, 5 ml of a $PM \cdot 2H_2O$ solution (0.15 g, 0.75 mmol, in 20 ml water) was carefully layered above the gel. Yellow needles 3 mm long were produced in 2 weeks. *Anal.* Calc. for $C_8H_{12}Cl_2N_2O_2Pd$: C, 27.81; H, 3.50; N, 8.11; Cl, 20.52. Found: C, 27.60; H, 3.74; N, 7.72; Cl, 19.91%. ^{13}C NMR spectrum: 148.1 (C(1)), 160.4 (C(2)), 135.6 (C(3)), 134.1 (C(4)), 133.0 (C(5)), 19.5 (C(6)), 58.7 (C(8)). IR spectrum (cm^{-1}): 1540 (pyridinium NH^+); 328 broad (*cis*- $PdCl_2$).

$trans-[PdCl_2(PN)_2]$

A solution of PN (0.4 g, 2.4 mmol) in 20 ml water was stirred into a solution of K_2PdCl_4 (0.3 g, 0.9 mmol) in 20 ml water. The pH was adjusted to 7.0 with dilute NaOH. Evaporation yielded yellow needles in a day. *Anal.* Calc. for $C_{16}H_{22}Cl_2N_2O_6Pd$: C, 37.27; H, 4.30; N, 5.43; Cl, 13.75. Found: C, 36.90; H, 4.44; N, 5.40; Cl, 12.89%. ^{13}C NMR spectrum: 148.0, 147.8 (C(1)); 150.8 (C(2)); 141.5, 141.2 (C(3)); 135.1 (C(4)); 133.5, 133.7 (C(5)); 21.3, 20.3 (C(6)); 57.9 (C(7)), 55.8 (C(8)). IR spectrum (cm^{-1}): 1558, 1240 (coordinated pyridine); 345 (*trans*- $PdCl_2$). The structure of this isomer was confirmed by its X-ray crystal structure (Table 1), which is identical to the one previously reported by El-Ezaby and co-workers [9].

$cis-[PdCl_2(PN)_2]$

Stirring a solution of 0.6 g PN (3.5 mmol) in 20 ml water into a solution of 0.8 g (2.5 mmol) K_2PdCl_4 in 20 ml water gave a solution with pH 6. Slow evaporation yielded yellow parallelepipeds. *Anal.* Calc. for

$C_{16}H_{22}Cl_2N_2O_6Pd$: C, 37.27; H, 4.30; N, 5.43. Found: C, 37.47; H, 4.49; N, 5.57%. ^{13}C NMR spectrum: 148.0 (C(1)); 150.7 (C(2)); 141.6 (C(3)); 135.2 (C(4)); 133.8 (C(5)); 21.4, 20.4 (C(6)), 57.9 (C(7)); 55.7 (C(8)). IR spectrum (cm^{-1}): 1562, 1245 (coordinated pyridine); 352, 335 (*cis*- $PdCl_2$).

$cis-[PdCl_2(PL)_2]$

A solution of PL (0.4 g, 2.4 mmol) in 20 ml water was stirred into a solution of K_2PdCl_4 (0.4 g, 1.2 mmol) in 20 ml water. The pH was adjusted to 7.0 with dilute NaOH whereupon a yellow precipitate appeared. *Anal.* Calc. for $C_{16}H_{18}Cl_2N_2O_6Pd$: C, 37.56; H, 3.55; N, 5.48. Found: C, 37.39; H, 4.23; N, 5.43%. ^{13}C NMR spectrum: 148.0 (C(1)); 148.3 (C(2)); 147.2 (C(3)); 136.2 (C(4)); 135.7 (C(5)); 20.1, 21.0 (C(6)); 98.2 (C(7)); 68.6 (C(8)). IR spectrum (cm^{-1}): 1580 (coordinated pyridine); 358, 330 (*cis*- $PdCl_2$).

$(PLH)_2(PtCl_6) \cdot 2H_2O$

K_2PtCl_4 (0.5 g, 1.2 mmol) and PLHCl (0.5 g, 2.5 mmol) were heated with stirring in 30 ml water. The resulting solution gave orange plates of $(PLH)_2[PtCl_6] \cdot 2H_2O$ upon evaporation. *Anal.* Calc. for $C_{16}H_{24}Cl_6N_2O_8Pt$: C, 24.63; H, 3.10; N, 3.59; Cl, 27.27; Pt, 25.01. Found: C, 24.34; H, 3.17; N, 3.45; Cl, 25.74; Pt, 22.76. IR spectrum (cm^{-1}): 1540 (pyridinium NH^+); 335 (Pt–Cl).

$(PMH_2)[PdCl_4] \cdot H_2O$

Addition of 0.2 g (0.5 mmol) of $PdCl_2$ to 10 ml 0.1 M HCl and 10 ml benzene, followed by addition of 0.2 g PM (0.6 mmol), gave large yellow–brown needles of $(PMH_2)[PdCl_4] \cdot H_2O$ upon evaporation. *Anal.* Calc. for $C_8H_{16}Cl_4N_2O_3Pd$: C, 22.02; H, 3.70; N, 6.42; Cl, 32.49; Pd, 24.38. Found: C, 21.93; H, 3.79; N, 6.38; Cl, 32.40; Pd, 23.10. IR spectrum (cm^{-1}): 2040 ($-NH_3^+$); 1560 (pyridinium NH^+); 325 (Pd–Cl).

Molecular modelling

Molecular mechanics calculations were performed with Allinger's MM2 force field [17], as implemented in the software program Chem3D Plus (Cambridge Scientific Computing, Cambridge, MA). Parameters involving the metal–ligand bonds are listed in Table 2; standard values were employed for the parameters involving the organic groups.

Structure determinations

Unit cell dimensions were determined from the angular setting of 25 reflections measured with graphite-monochromatized Mo $K\alpha$ radiation. Intensities were measured by the ω – 2θ technique at room temperature (293–298 K) with an Enraf-Nonius CAD4 single-crystal diffractometer and corrected for Lorentz and polari-

TABLE 1. Crystal data, data collection and structure refinement parameters

Compound	[PtCl ₂ (PM)]·H ₂ O	[PLH] ₂ [PtCl ₆]·2H ₂ O	<i>trans</i> -[PdCl ₂ (PN) ₂]
Formula	C ₈ H ₁₄ Cl ₂ N ₂ O ₃ Pt	C ₁₆ H ₂₄ Cl ₆ N ₂ O ₈ Pt	C ₁₆ H ₂₂ Cl ₂ N ₂ O ₆ Pd
Molecular weight	452.21	780.18	515.7
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Cell dimensions determined from 25 reflections with:	14 < θ < 25°	8 < θ < 21°	12 < θ < 19°
<i>a</i> (Å)	7.028(1)	7.355(2)	5.271(2)
<i>b</i> (Å)	12.788(1)	8.534(2)	17.263(2)
<i>c</i> (Å)	13.435(2)	11.555(2)	10.269(1)
α (°)	90.00	71.73(2)	90.00
β (°)	90.00	73.10(2)	95.41(2)
γ (°)	90.00	66.79(2)	90.00
<i>V</i> (Å ³)	1207.46	621.26	930.25
<i>Z</i>	4	1	2
<i>D</i> _{obs} (g cm ⁻³)	2.46	2.03	1.78
<i>D</i> _x (g cm ⁻³)	2.49	2.08	1.84
μ (mm ⁻¹)	12.67	6.61	1.303
<i>F</i> (000)	848	378	520
Maximum value of θ (°)	30	30	25
Range in <i>h</i> , <i>k</i> and <i>l</i>	<i>hkl</i> + Friedel equiv.	$\pm h$, $\pm k$, $\pm l$	$\pm h$, $\pm k$, $\pm l$
Standard reflection	2, 4, 3	-2, -3, 3	-2, 1, -1
Interval, standard reflection measured (s)	7200	3600	7200
Total no. reflections	4115	3803	1823
No. unique reflections	3514	3493	1637
No. observed reflections (<i>I</i> > 3 σ (<i>I</i>))	3382	3487	1335
Parameters refined	151	162	138
<i>p</i> in weights	0.0004	0.0075	0.0006
<i>R</i>	0.029	0.059	0.030
<i>R</i> _w	0.031	0.056	0.034
Max. height in final $\Delta\rho$ map	2.4 (near Pt)	6.3 (near Pt)	0.47 (near C(8))

TABLE 2. Additional molecular mechanics parameters for [PdCl₂(PN)₂]

Bond	Equil. value	<i>K</i> _s
Pd-N	2.000 Å	3.5 mdyn Å ⁻¹
Pd-Cl	2.315 Å	2.5 mdyn Å ⁻¹
C-N-Pd	120°	0.4 mdyn Å rad ⁻²
X-Pd-Y	90 or 180°	0.3 mdyn Å rad ⁻²
C-C-N-Pd	0 or 180°	<i>V</i> ₂ = 15.00 kcal
C-N-Pd-Y		<i>V</i> ₁ = <i>V</i> ₂ = <i>V</i> ₃ = 0

zation effects. The structures were solved by Patterson methods and refined by full-matrix least-squares, with anisotropic displacement parameters for all atoms except hydrogen. Scattering factors, including the real and imaginary parts of the anomalous scattering, were taken from the International Tables for X-ray Crystallography [18]. The form of the anisotropic displacement parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*)]$. The weighting scheme was $w = [\sigma^2(F) + pF^2]^{-1}$ with a value of *p* assigned to minimize the variance as a function of reflection intensity. The correct handedness of the chiral space group *P*2₁2₁2₁ for [PtCl₂(PM)]·H₂O was determined by least-squares minimization after inverting all of the coordinates; the resulting higher value of *R* (0.0480) showed that the

original handedness was correct. Programs used included SHELX-76 [19] and ORTEP [20]. The crystal data and experimental details are listed in Table 1. The final parameters are given in Tables 3 and 4.

Results and discussion

Syntheses

The complex obtained depends on a delicate balance of kinetic and thermodynamic factors, which in turn are functions of the solvent, the starting materials, the pH, and the general reaction conditions. Thus, we obtained *trans*-[PdCl₂(PN)₂] at pH 7 with an excess of pyridoxine, but the *cis* complex at pH 6 and a deficiency of pyridoxine. Pneumatikakis *et al.* obtained 1:1 Pd:PN and Pd:PL complexes from DMF, as well as a dimeric palladium complex containing deprotonated pyridoxamine from aqueous solution [21]. Others too have noted the variety of complexes obtainable, especially given the protonation equilibria of the B₆ vitamins [3, 10, 11, 16].

Crystal structures

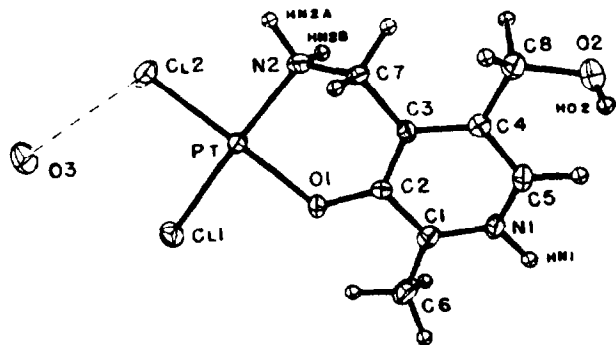
[PtCl₂(PM)]·H₂O contains square-planar platinum(II) with the pyridoxamine ligand chelated through

TABLE 3. Positional parameters ($\times 10^4$) and anisotropic displacement coefficients ($\times 10^4$) for $[\text{PtCl}_2(\text{PM})]\cdot\text{H}_2\text{O}$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Pt	2047.8(3)	2030.4(2)	869.4(2)	218.2(11)	150.3(10)	161.1(10)	17.4(8)	−18.7(8)	−8.5(9)
Cl(1)	1317(3)	3005(1)	2269(1)	406(8)	254(7)	212(6)	−48(6)	30(6)	−76(7)
Cl(2)	2245(3)	525(1)	1781(1)	515(10)	220(7)	315(8)	103(6)	−39(8)	14(8)
O(1)	1949(8)	3383(3)	101(3)	412(26)	199(19)	137(18)	31(15)	32(21)	12(22)
O(2)	950(9)	2526(4)	−4350(3)	516(33)	387(27)	195(22)	2(20)	−52(24)	46(26)
O(3)	2603(10)	1230(5)	4231(4)	656(40)	483(33)	234(25)	−27(23)	39(27)	−18(30)
N(1)	2388(9)	4650(4)	−2212(4)	383(32)	203(23)	174(22)	53(19)	−15(21)	−31(22)
N(2)	2706(9)	1227(4)	−389(4)	326(28)	189(24)	241(25)	−20(20)	−15(23)	86(23)
C(1)	2377(9)	4501(5)	−1228(5)	243(30)	196(26)	248(28)	49(23)	8(24)	−5(23)
C(2)	2017(9)	3459(4)	−894(4)	233(26)	173(24)	187(24)	0(21)	24(29)	67(22)
C(3)	1767(8)	2643(5)	−1585(4)	168(25)	229(27)	144(24)	24(20)	23(20)	33(21)
C(4)	1683(9)	2888(5)	−2601(4)	265(27)	207(27)	180(24)	−5(22)	0(21)	23(23)
C(5)	1997(12)	3930(5)	−2883(5)	531(42)	235(28)	171(25)	41(23)	34(32)	17(36)
C(6)	2769(15)	5382(5)	−527(5)	598(51)	189(28)	310(33)	44(26)	−96(39)	−31(35)
C(7)	1533(9)	1525(4)	−1265(5)	327(33)	116(23)	206(26)	3(21)	−27(24)	25(22)
C(8)	1278(12)	2085(5)	−3376(5)	509(41)	205(28)	210(27)	13(24)	−31(28)	−26(33)

TABLE 4. Positional parameters ($\times 10^4$) and anisotropic displacement coefficients ($\times 10^4$) for $(\text{PLH})_2[\text{PtCl}_6]\cdot 2\text{H}_2\text{O}$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Pt	0	0	0	247(2)	233(2)	217(2)	−75(1)	−61(1)	−71(1)
Cl(1)	200(3)	1267(2)	−2106(1)	383(8)	400(8)	256(6)	−40(6)	−77(6)	−106(6)
Cl(2)	2943(3)	−2297(3)	−410(2)	417(9)	407(9)	372(9)	−105(7)	−60(7)	57(7)
Cl(3)	1942(4)	1509(4)	102(2)	637(13)	765(15)	479(11)	−251(10)	−19(9)	−487(12)
O(1)	3467(8)	2271(7)	5333(5)	335(24)	337(23)	391(25)	−173(19)	−146(20)	4(19)
O(2)	−595(8)	5987(7)	5976(5)	317(22)	412(26)	316(24)	−142(20)	−116(18)	−14(19)
O(3)	1321(11)	7748(7)	5712(7)	555(36)	284(24)	525(34)	−118(22)	−196(28)	−60(23)
O(4)	1551(16)	4422(10)	1558(7)	1097(66)	485(38)	405(34)	−110(28)	−68(37)	−267(40)
N(1)	5517(10)	2619(10)	7631(6)	318(28)	518(35)	398(31)	−119(26)	−159(23)	−60(24)
C(1)	5151(10)	1915(9)	6879(7)	274(28)	312(30)	303(28)	−71(23)	−80(22)	−51(22)
C(2)	3766(9)	3016(8)	6087(6)	258(25)	304(27)	266(24)	−108(20)	−50(19)	−63(20)
C(3)	2890(9)	4757(8)	6154(6)	264(26)	303(27)	281(25)	−117(20)	−74(20)	−56(21)
C(4)	3368(11)	5414(10)	6940(7)	296(29)	365(32)	377(33)	−165(26)	−73(24)	−77(24)
C(5)	4707(12)	4303(12)	7711(8)	371(36)	548(43)	418(37)	−231(32)	−126(29)	−107(31)
C(6)	6208(14)	21(10)	6876(9)	403(40)	319(33)	579(46)	−88(30)	−211(34)	30(28)
C(7)	1290(11)	6231(8)	5494(6)	361(31)	281(26)	259(26)	−96(21)	−96(22)	−23(22)
C(8)	2240(12)	7337(10)	6765(8)	435(36)	367(34)	487(39)	−230(30)	−105(30)	−86(27)

Fig. 1. Structure of $[\text{PtCl}_2(\text{PM})]\cdot\text{H}_2\text{O}$. The dotted line indicates the proposed hydrogen bond between the water molecule and Cl(2).

the phenolate oxygen and amino nitrogen (Fig. 1). Although hydrogen positions could not be determined accurately because of the overwhelming scattering ability of the platinum, the presence of a protonated nitrogen in the pyridine ring is shown by the expansion of the C(1)–N(1)–C(5) angle from *c.* 120 to 125.2(6)° and by the shortness of the C(2)–O(1) bond [3, 5, 13, 15, 22]. Distances and angles within the ligand (Table 5) compare to those reported in other pyridoxamine complexes in which the ligand is chelated to the metal ion [3, 5], and those involving the metal are within the ranges for other square planar Pt(II) complexes with similar ligands [23].

During the attempted synthesis of $[\text{PtCl}_2(\text{PL})_2]$, Pt(II) oxidized to Pt(IV) and $(\text{PLH})_2[\text{PtCl}_6]\cdot 2\text{H}_2\text{O}$ was produced. The hexachloroplatinate ion displays an almost regular octahedral structure (Table 6). The protonated

TABLE 5. Bond distances and angles for [PtCl₂(PM)]·H₂O with e.s.d.s in parentheses

Distances (Å)			
Pt–Cl(1)	2.313(2)	C(3)–C(4)	1.402(8)
Pt–Cl(2)	2.286(2)	C(4)–C(8)	1.489(8)
Pt–O(1)	2.015(4)	C(8)–O(2)	1.444(8)
Pt–N(2)	2.032(5)	C(4)–C(5)	1.402(8)
O(1)–C(2)	1.342(7)	C(5)–N(1)	1.318(8)
C(2)–C(3)	1.408(8)	N(1)–C(1)	1.335(8)
C(3)–C(7)	1.501(8)	C(1)–C(6)	1.494(9)
C(7)–N(2)	1.487(8)	C(1)–C(2)	1.429(8)
Angles (°)			
Cl(1)–Pt–Cl(2)	91.8(1)	C(1)–C(2)–C(3)	120.4(5)
Cl(1)–Pt–O(1)	86.9(1)	C(2)–C(3)–C(4)	118.8(5)
Cl(1)–Pt–N(2)	177.8(2)	C(2)–C(3)–C(7)	122.1(5)
Cl(2)–Pt–N(2)	90.4(2)	C(4)–C(3)–C(7)	119.2(5)
Cl(2)–Pt–O(1)	177.8(2)	C(3)–C(4)–C(5)	118.0(6)
O(1)–Pt–N(2)	90.9(2)	C(3)–C(4)–C(8)	122.3(5)
C(5)–N(1)–C(1)	125.2(5)	C(5)–C(4)–C(8)	119.7(5)
C(2)–C(1)–N(1)	116.4(6)	N(1)–C(5)–C(4)	120.8(6)
C(6)–C(1)–N(1)	121.1(6)	C(3)–C(7)–N(2)	114.2(5)
C(6)–C(1)–C(2)	122.5(6)	C(4)–C(8)–O(2)	113.3(5)
C(1)–C(2)–O(1)	112.8(5)	C(2)–O(1)–Pt	124.9(4)
C(3)–C(2)–O(1)	126.8(5)	C(7)–N(2)–Pt	113.8(4)
X...Y distances in X–H...Y hydrogen bonds			
O(3)–H(O3A)...O(2) ⁱⁱ	2.781(8)	O(3)–H(O3B)...Cl(2)	3.421(6)
O(2)–H(O2)...O(3) ⁱ	2.844(8)	N(1)–H(N1)...Cl(1) ^{iv}	3.210(5)
N(2)–H(N2A)...O(3) ⁱⁱⁱ	3.190(8)	N(2)–H(N2B)...O(1) ^v	3.048(7)

Symmetry codes: (i) $-0.5+x, 0.5-y, -z$; (ii) $x, y, 1+z$; (iii) $0.5-x, -y, -0.5+z$; (iv) $0.5-x, 1-y, -0.5+z$; (v) $0.5+x, 0.5-y, -z$.

pyridoxal cation (Fig. 2) exists in the hemiacetal form. The C(1)–N–C(5) angle of 126.3(2)° confirms that the pyridine nitrogen atom is protonated, and the lengthening of the C(2)–O(1) bond distance by 0.044 Å compared to free pyridoxal [15] shows that the phenol group is unionized.

In each structure, the IR spectra in the 3000–3600 cm^{−1} region show that all available hydroxyl, amino and pyridinium groups are engaged in hydrogen bonding. Thus, even though hydrogen positions are not very accurate in these structures, sensible hydrogen-bonding interactions can be proposed on the basis of close contacts between the X and Y atoms in an X–H...Y hydrogen bond. These are listed in Tables 5 and 6.

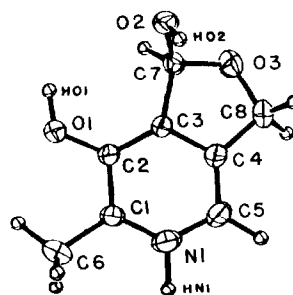
IR and NMR spectra

IR spectra allow the prediction of coordination site when the X-ray structure is not available. Peaks characteristic for $-\text{NH}_3^+$ in the stable pyridoxamine tautomer appear near 2000 cm^{−1}; their disappearance, and the appearance of a band near 1540 cm^{−1} characteristic of pyridinium cations [24, 25], is diagnostic for chelation of pyridoxamine [4]. Coordination of pyridine is accompanied by shifts in the ring breathing frequencies in the 1400–1600 cm^{−1} region and the

TABLE 6. Bond distances and angles for (PLH)₂[PtCl₆]·2H₂O with e.s.d.s in parentheses

Distances (Å)			
Pt–Cl(1)	2.320(1)	N–C(1)	1.334(10)
Pt–Cl(2)	2.322(2)	C(1)–C(6)	1.493(10)
Pt–Cl(3)	2.314(2)	C(2)–O(1)	1.334(7)
C(1)–C(2)	1.416(9)	C(3)–C(7)	1.517(8)
C(2)–C(3)	1.384(8)	C(7)–O(2)	1.408(9)
C(3)–C(4)	1.387(9)	C(7)–O(3)	1.404(8)
C(4)–C(5)	1.381(10)	O(3)–C(8)	1.443(10)
C(5)–N	1.344(11)	C(4)–C(8)	1.496(10)
Angles (°)			
Cl(1)–Pt–Cl(2)	90.6(1)	C(2)–C(3)–C(4)	121.9(6)
Cl(1)–Pt–Cl(3)	89.5(1)	C(3)–C(4)–C(8)	109.1(6)
Cl(2)–Pt–Cl(3)	88.7(1)	C(5)–C(4)–C(8)	131.2(7)
C(2)–C(1)–N	118.2(6)	C(3)–C(4)–C(5)	119.7(7)
C(6)–C(1)–N	120.0(6)	C(4)–C(5)–N	116.9(7)
C(2)–C(1)–C(6)	121.8(7)	C(1)–N–C(5)	126.3(2)
C(1)–C(2)–O(1)	116.4(6)	C(3)–C(7)–O(2)	110.3(5)
C(3)–C(2)–O(1)	126.6(6)	O(2)–C(7)–O(3)	112.6(6)
C(1)–C(2)–C(3)	117.1(6)	C(3)–C(7)–O(3)	104.1(5)
C(2)–C(3)–C(7)	130.0(6)	C(7)–O(3)–C(8)	111.2(5)
C(4)–C(3)–C(7)	108.0(5)	C(4)–C(8)–O(3)	103.8(5)
X...Y distances in X–H...Y hydrogen bonds			
O(1)–H(O1)...O(2) ⁱ	2.633(10)	O(2)–H(O2)...O(4) ⁱ	2.673(10)
N–H(N)...Cl(1) ⁱⁱ	3.247(8)	O(4)...Cl(2) ⁱⁱⁱ	3.312(9)
O(4)...Cl(3)	3.297(9)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1+x, y, 1+z$; (iii) $x, 1+y, z$.

Fig. 2. Structure of the pyridoxal cation in (PLH)₂[PtCl₆]·2H₂O.

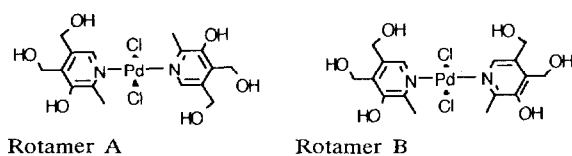
appearance of a weak band between 1235 and 1250 cm^{−1} [26]. *cis*- and *trans*-PdCl₂ groups are readily distinguished by the number of peaks near 340 cm^{−1}, there being one peak for *trans* and two for *cis* [27]. Thus, we assigned the structure of [PdCl₂(PM)] as a four-coordinate monomer with chelated pyridoxamine, and concluded that *cis*-[PdCl₂(PN)₂] and *cis*-[PdCl(PL)₂] are square planar with ligands coordinated through the pyridine nitrogens. The IR spectrum of *trans*-[PdCl₂(PN)₂] is as expected from its crystal structure, which showed that pyridoxine coordinates through the pyridine nitrogen [9].

¹³C NMR spectra were readily obtainable for the palladium complexes, but the platinum complexes were not sufficiently soluble for good spectral acquisition.

Peak assignments were made in accordance with previous work on vitamin B₆ complexes of transition metals [16].

Two resonances of nearly equal intensity are observed for C(1), C(3), C(5) and C(6) in the ¹³C NMR spectrum of *trans*-[PdCl₂(PN)₂]. It is unlikely that they are due to a mixture of *cis* and *trans* isomers, as has been observed for a number of other palladium complexes [28], since *cis*-[PdCl₂(PN)₂] does not exhibit similar behavior (although both *cis*-[PdCl₂(PN)₂] and *cis*-[PdCl₂(PL)₂] show two peaks for C(6)). A further possibility is that the DMSO solvent displaces the vitamin B₆, and the observed peaks are due to the free ligand. This appears to be ruled out since the peaks for solutions of the complex are different from those for solutions of the ligand alone in DMSO. Furthermore, the spectra were time-independent: spectra taken after several hours displayed peak positions and peak heights identical to those obtained immediately upon dissolution.

We propose that the double peaks are due to rotamers of the complexes. *trans*-[PdCl₂(PN)₂] has the ligand rings nearly perpendicular to the PdCl₂N₂ plane [9], so that two rotamers are possible: rotamer A (the observed structure) has the ligands disposed so that the C(6) methyl groups are on opposite sides of the PdCl₂N₂ plane, and rotamer B has one of the ligands rotated 180° about the Pd–N bond to give a configuration with methyl groups on the same side of the PdCl₂N₂ plane.

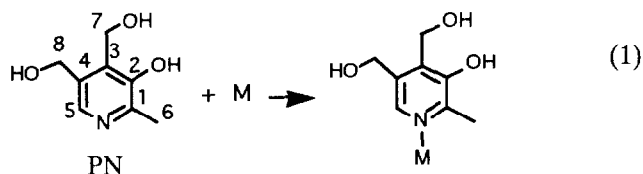


The relative energies of these conformers, and thus their relative stabilities, can be estimated by molecular mechanics methods [29]. The steric energy calculated by molecular mechanics gives the energy involved in distorting the bonds from ideal values, and includes terms for van der Waals interactions. Steric energies of 17.7 and 17.9 kcal/mol, respectively, were obtained for rotamers A and B of *trans*-[PdCl₂(PN)₂]. The corresponding rotamers of *cis*-[PdCl₂(PN)₂] have steric energies of 18.0 and 18.8 kcal. These energies should be in the correct relative order, since the metal–ligand stretching, bending and torsional parameters were chosen to mimic the structure of *trans*-[PdCl₂(PN)₂]. Thus both isomers, and both major rotamers of each isomer, are similar in energy, and ought to be observed under appropriate circumstances.

The activation energy for intramolecular rotamerization can also be estimated, albeit crudely, from molecular mechanics. The minimized steric energy (30.3

kcal) of *trans*-[PdCl₂(PN)₂] with one ligand rotated 90° into the PdCl₂N₂ plane as the starting point for minimization gives *c.* 12 kcal for this barrier. The calculated value of the activation energy depends strongly on the molecular mechanics parameters as well as on the form of the potential function, since considerable distortions occur about the palladium coordination center in order to relieve the van der Waals repulsions when the ligand is in the PdCl₂N₂ plane. Even so, the barrier is not a large one and intramolecular rotation to give both rotamers of *trans*-[PdCl₂(PN)₂], with a rate that is slow on the NMR time scale, is a possible explanation for the multiple peaks seen in the ¹³C NMR spectrum. Similar arguments apply to *cis*-[PdCl₂(PN)₂] and to *cis*-[PdCl₂(PL)₂]. The fact that rotamers exist does not, of course, guarantee that the chemical shifts of the atoms in each rotamer will be different; hence not all peaks in the spectra are multiple.

The ¹³C NMR spectra of the complexes show that the resonance positions are shifted compared to the free ligands in the same solvent (Table 7). The shift differences, Δ*C_i*, can be interpreted in terms of the structure changes that occur upon complexation. In *cis*- and *trans*-[PdCl₂(PN)₂], the only change that occurs for the ligand is that the metal becomes coordinated at the pyridine nitrogen (eqn. (1)). Shifts of *c.* 2 ppm for the *o*- and *p*-carbons C(1), C(3) and C(5) result, along with small shifts of the other carbons.



In contrast, cadmium complexes of pyridoxine, which contain the ligand chelated through the phenolate and hydroxymethyl group [11], display quite different Δ*C_i* [11, 16] compared to the N-coordinated pyridoxine complex of palladium. Thus ¹³C NMR spectra are a valuable tool for determining structures in solution, as Kelusky and Hartman suggested [16].

For *cis*-[PdCl₂(PL)₂] Δ*C₃* and Δ*C₅* are quite large, due to the change in tautomeric form for the ligand and replacement of the pyridinium proton by palladium (eqn. (2)). The phenolate oxygen becomes protonated, affecting not only Δ*C₂* but reducing Δ*C₁* relative to the shifts seen for the other *o*- and *p*-carbons in this complex.

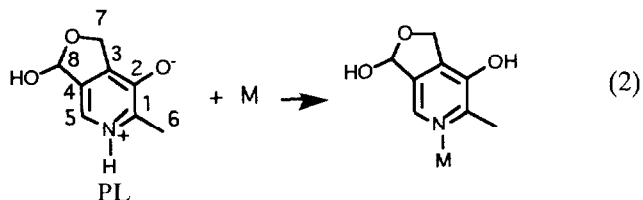
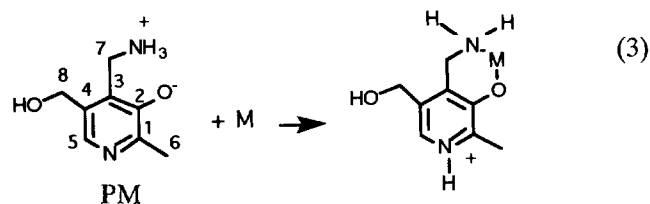


TABLE 7. Differences (ΔC_i) between the ^{13}C NMR chemical shifts of atom C_i in the complex and the free ligand

Complex	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
<i>trans</i> -[PdCl ₂ (PN) ₂]	1.9	0.8	2.6	0.9	2.1	2.1	-1.0	-1.0
	1.7		2.3		2.3	1.1		
<i>cis</i> -[PdCl ₂ (PN) ₂]	1.9	0.8	2.7	1.0	2.4	2.2	-1.0	-1.2
						1.2		
<i>cis</i> -[PdCl ₂ (PL) ₂]	3.6	1.7	10.0	-0.2	7.7	2.9	-1.7	-2.0
						2.1		
[PdCl ₂ (PM)]	2.7	7.1	-1.8	2.0	4.0	1.0		-0.3

In pyridoxamine, the ammonium group loses a proton and the pyridine nitrogen gains one upon chelation through the phenolate oxygen and amino group (eqn. (3)). The C(2) carbon is most affected by this change, showing a ΔC_2 of 7.1 ppm, and the resonance position of C(7) is shifted into the region occupied by the DMSO peaks. As in the case of the other complexes, ΔC_8 is relatively unaffected since C(8) lies well away from the coordination locus and has no π -connection with the rest of the system.



Supplementary material

Tables of the hydrogen positions and the structure factor tables for [PtCl₂(PM)]·H₂O and (PLH)₂·[PtCl₆]·2H₂O are available from M.F.R.

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