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## Key indicators

Single-crystal X-ray study  
 $T = 123\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.031\text{ \AA}$   
 $R$  factor = 0.067  
 $wR$  factor = 0.226  
Data-to-parameter ratio = 17.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**cyclo-Tetrakis[4-(aminomethyl)-5-(hydroxy-  
methyl)-2-methylpyridin-3-olato- $\kappa N^1$ : $\kappa^2 N^4, O^3$ ]-  
tetrakis[chloropalladium(II)] nonahydrate**

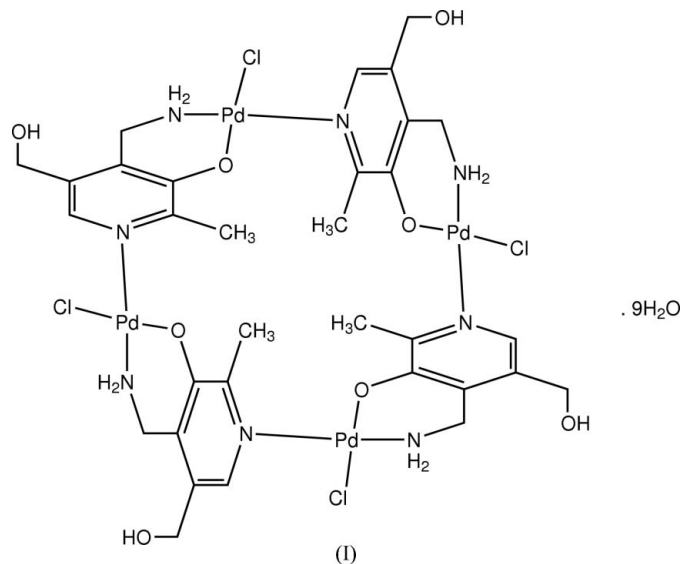
The title compound,  $[\text{Pd}_4(\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2)_4\text{Cl}_4] \cdot 9\text{H}_2\text{O}$ , is a cyclic tetramer. The  $\text{Pd}^{\text{II}}$  atom shows distorted square-planar coordination arising from chelation by the phenolate O atom and the pyridoxamine ligand; the metal atom is also linked to the pyridyl N atom from an adjacent ligand and a Cl atom. A twofold axis, which is parallel to the  $c$  axis, is located at the center of a tetramer. The crystal packing is stabilized by hydrogen bonding among neighboring complex molecules *via* the solvent water molecules.

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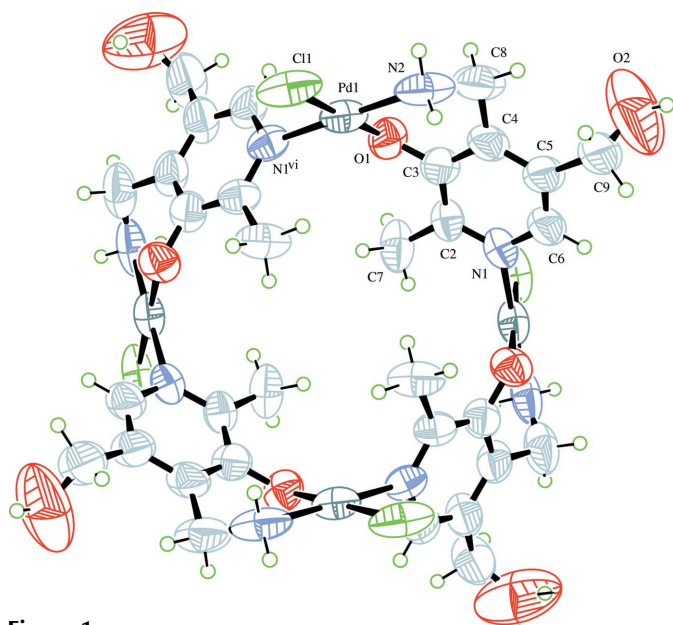
Accepted 29 August 2006

## Comment

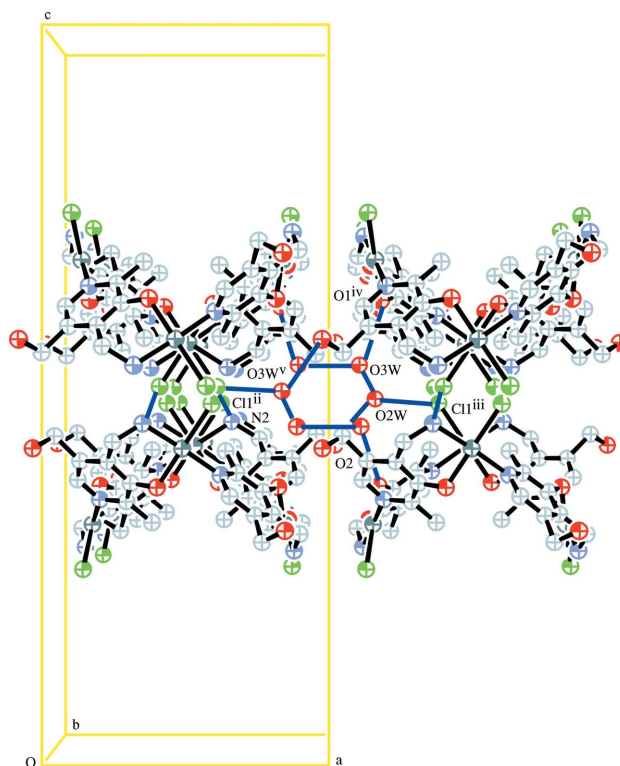
Pyridoxamine (PM) is a member of the vitamin B6 family including pyridoxal and pyridoxine (PN). The crystal structures of metal complexes of B6 vitamins have been studied; the phenolate O, and 4-hydroxymethyl O or 4-aminomethyl N atoms are, in general, the sites involved in chelation (Mosset *et al.*, 1978; Franklin & Richardson, 1978, 1980; Thompson *et al.*, 1980; Sabirov *et al.*, 1982, 1983, 1984, 1993, 1997; Rao *et al.*, 1986; Mathews & Manohar, 1991; Acquaye & Richardson, 1992; Mathews *et al.*, 1992; Casas *et al.*, 1997, 2000, 2004; Sakagami *et al.*, 1999). In other crystal structures, chelation also involves the 5-hydroxymethyl O atom (Franklin & Richardson, 1980; Casas *et al.*, 1997). On the other hand, for PN-metal complexes, the site is the pyridyl N atom (Sabirov *et al.*, 1983; Makhyoun *et al.*, 1986; Acquaye & Richardson, 1992; Dey *et al.*, 2003).



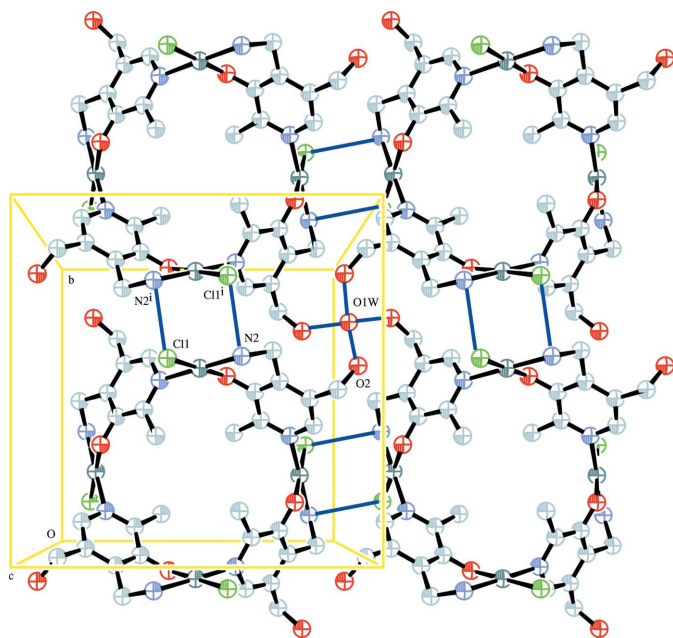
The title compound, (I), is a nonhydrated cyclic tetramer (Fig. 1), which is rarely found among B6 vitamin-metal



**Figure 1**  
A view of the structure of the PM-Pd<sup>II</sup> complex compound of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (vi)  $\frac{3}{4} - y, -\frac{1}{4} + x, \frac{3}{4} - z$ .]



**Figure 3**  
A view of the hydrogen bonding (blue lines) between the complex layers. [Symmetry codes: (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $1 + x, y, z$ ; (iv)  $\frac{7}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$ ; (v)  $2 - x, \frac{3}{2} - y, z$ .]



**Figure 2**  
A view of the hydrogen bonding (blue lines) stabilizing the complex layer. [Symmetry code: (i)  $1 - x, \frac{3}{2} - y, z$ .]

complexes. A twofold axis, which is parallel to the *c* axis, is located at the center of a tetramer. The Pd atom is coordinated by one phenolate O atom and one 4-aminomethyl N atom from the PM ligand, one pyridine N atom from an adjacent PM ligand and one Cl atom. This is the first crystal structure of a PM-metal complex having these chelation sites along with the pyridyl N atom. The coordinating atoms form a square

plane around the Pd atom. The coordination geometry is similar to those found in PM-Pt<sup>II</sup> complexes (Acquaye & Richardson, 1992) in which the Pt atom is coordinated by the chelating atoms along with two Cl atoms.

In (I), the pyridyl plane C1–C5/N1 is tilted by 44.7 (2)° from the coordination plane O1/N2/Cl1/N1<sup>vi</sup>/Pd [symmetry code: (vi)  $\frac{3}{4} - y, -\frac{1}{4} + x, \frac{3}{4} - z$ ]; the tilt is larger than that in PM-Pt<sup>II</sup> (approximately 23.35°). The tilt seems to be necessary for the formation of the cyclic tetramer. The pyridyl plane is tilted by 46.3 (2)° from the mean plane of the tetramer defined by Cl1/Cl1<sup>vi</sup>/Cl1<sup>viii</sup>/Cl1<sup>viii</sup> [symmetry codes: (vii)  $1 - x, \frac{1}{2} - y, z$ ; (viii)  $\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} - z$ ], with the 2-methyl group on the inside of the tetramer and with 5-hydroxymethyl group outside. As a result, the inside of the tetramer is hydrophobic, whereas the outside is hydrophilic.

In the crystal packing, PM-Pd<sup>II</sup> lies in a layer parallel to the *ab* plane, stabilized by N–H...Cl hydrogen bonding between 4-aminomethyl N and Cl atoms, and between 5-hydroxymethyl groups *via* O1W. The layers are stabilized by N–H...Cl hydrogen bonding and the hydrogen-bond network *via* O2W and O3W (Table 2, and Figs. 2 and 3).

## Experimental

Pyridoxamine dihydrochloride (5 mg, 0.02 mmol) was dissolved in 20% (*v/v*) EtOH/H<sub>2</sub>O (2 ml), and to this was added potassium

tetrachloropalladate(II) (6 mg, 0.02 mmol) dissolved in 20% (v/v) EtOH/H<sub>2</sub>O (3 ml). Red needle-like crystals appeared from the mixture after one month.

#### Crystal data

[Pd <sub>4</sub> (C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>4</sub> Cl <sub>4</sub> ]·9H <sub>2</sub> O	$D_x = 1.953 \text{ Mg m}^{-3}$
$M_r = 1398.38$	Mo $K\alpha$ radiation
Tetragonal, $I4_1/a$	$\mu = 1.79 \text{ mm}^{-1}$
$a = 12.26 (2) \text{ \AA}$	$T = 123 \text{ K}$
$c = 31.65 (4) \text{ \AA}$	Needle, red
$V = 4757 (13) \text{ \AA}^3$	$0.20 \times 0.20 \times 0.15 \text{ mm}$
$Z = 4$	

#### Data collection

Rigaku R-AXIS RAPID diffractometer	21727 measured reflections
$\omega$ scans	2736 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1659 reflections with $F^2 > 2\sigma(F^2)$
$T_{\min} = 0.206$ , $T_{\max} = 0.670$	$R_{\text{int}} = 0.048$
(expected range = 0.235–0.765)	$\theta_{\max} = 27.5^\circ$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1218P)^2 + 4.0653P]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.226$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.13$	$\Delta\rho_{\max} = 1.53 \text{ e \AA}^{-3}$
2736 reflections	$\Delta\rho_{\min} = -1.15 \text{ e \AA}^{-3}$
154 parameters	
All H-atom parameters refined	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pd1—O1	1.997 (13)	Pd1—N1 <sup>vi</sup>	2.020 (15)
Pd1—N2	2.019 (19)	Pd1—Cl1	2.295 (6)
O1—Pd1—N2	90.8 (7)	O1—Pd1—Cl1	179.5 (4)
O1—Pd1—N1 <sup>vi</sup>	86.5 (5)	N2—Pd1—Cl1	89.4 (6)
N2—Pd1—N1 <sup>vi</sup>	177.4 (7)	N1 <sup>vi</sup> —Pd1—Cl1	93.3 (4)

Symmetry code: (vi)  $-y + \frac{3}{4}, x - \frac{1}{4}, -z + \frac{3}{4}$ .

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A $\cdots$ Cl1 <sup>i</sup>	0.90	2.44	3.276 (16)	155
O1W—H1W $\cdots$ O2	0.85	1.65	2.50 (5)	180
N2—H2B $\cdots$ Cl1 <sup>ii</sup>	0.90	2.64	3.448 (19)	149
O2W—H2W $\cdots$ Cl1 <sup>iii</sup>	0.88	1.99	2.88 (4)	179
O2W—H3W $\cdots$ O3W	0.81	1.86	2.67 (4)	179
O3W—H5W $\cdots$ O1 <sup>iv</sup>	0.86	1.97	2.84 (2)	179
O3W—H6W $\cdots$ O3W <sup>v</sup>	0.88	2.04	2.92 (5)	180
O3W—H7W $\cdots$ O2W	0.81	1.86	2.67 (4)	179
O2—H2 $\cdots$ O1W	0.76	1.74	2.50 (4)	177
O2—H3 $\cdots$ O2W	0.87	1.91	2.78 (4)	179

Symmetry codes: (i)  $-x + 1, -y + \frac{3}{2}, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x + 1, y, z$ ; (iv)  $-y + \frac{7}{4}, x + \frac{1}{4}, z + \frac{1}{4}$ ; (v)  $-x + 2, -y + \frac{3}{2}, z$ .

For water molecules, H atoms were included in the riding-model approximation, with O—H = 0.81–0.88  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

All other H atoms were included in the riding-model approximation with C—H = 0.95–0.99  $\text{\AA}$ , N—H = 0.90  $\text{\AA}$  and O—H = 0.76–0.87  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The highest maximum residual electron density is 1.63  $\text{\AA}^{-3}$  from H6W and the deepest hole is 0.94  $\text{\AA}^{-3}$  from Pd1.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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