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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
Some non-H atoms missing
Disorder in main residue
 R factor = 0.046
 wR factor = 0.120
Data-to-parameter ratio = 17.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.***trans*-Bis(1*H*-benzimidazol-2-ylmethyl- κ N³ diethyl phosphate)dichloropalladium(II) monohydrate**

The title compound, *trans*-[PdCl₂(2-bimOpe)₂] \cdot H₂O, where 2-bimOpe is 1*H*-benzimidazol-2-ylmethyl diethyl phosphate (C₁₂H₁₇N₂O₄P), crystallizes as a monohydrate. The most satisfactory structure refinement was obtained by eliminating the solvent contribution from the intensity data and the solvent-free model was employed for the final refinement. The Pd atom possesses a square-planar geometry in a centrosymmetric *trans* configuration.

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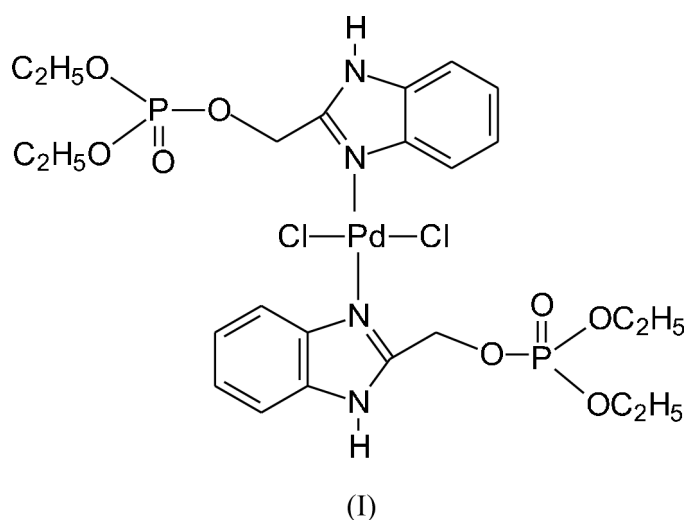
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Comment

Although only a few platinum compounds, *viz.* cisplatin [*cis*-diamminedichloroplatinum(II)], carboplatin, oxaliplatin and nedaplatin, have been used as antitumor agents in clinical treatments, a variety of studies in this field have been carried out (Jakupec *et al.*, 2003; Wong & Giandomenico, 1999). The utility of these drugs is limited by severe side effects, *e.g.* gastrointestinal toxicity, and neuro- and nephrotoxicity, the narrow range of tumors in which they are efficient, and low bioavailability (Ferguson & Pearson, 1996).

Platinum(II) and palladium(II) complexes that carry nitrogen-containing ligands are the subject of intensive biological evaluation in the search for antitumor agents with a superior therapeutic index to cisplatin. Palladium(II) complexes with dialkyl α -anilinobenzylphosphonates (Tušek-Božić *et al.*, 1995; Curić *et al.*, 1996), quinolylmethylphosphonates (Tušek-Božić *et al.*, 1991), coumarin-derived ligands (Budzisz *et al.*, 2004), pyrazoles and β -carboline alkaloids (Al-Allaf & Rashan, 2001) have been tested against tumor cell lines, and in some cases exhibited remarkable activity. Recently, platinum(II) complexes with 2-substituted benzimidazole ligands have been described and shown to be cytotoxically and mutagenically active (Gumus, Algul *et al.*, 2003; Gumus, Demirci *et al.*, 2003; Gumus, Pamuk *et al.*, 2003).

The above-mentioned results encouraged us to synthesize the palladium(II) complex of 1*H*-benzimidazol-2-ylmethyl diethyl phosphate, [PdCl₂(2-bimOpe)₂], (I). We have chosen phosphate derivatives of benzimidazole as ligands, because the benzimidazole residue is found in a variety of naturally occurring compounds such as vitamin B₁₂ and its derivatives, and it is structurally similar to purine bases. Our interest in benzimidazoles has also been stimulated by their promising pharmacological properties, such as anticancer activity (Hawash *et al.*, 1999) and inhibition of nucleic acid synthesis (Bucknall & Carter, 1967). On the other hand, many phosphate derivatives show various biological properties (Sigel & Kapinos, 2000).



Compound (I) crystallizes as a monohydrate. The water molecule appears to be highly disordered, and it was difficult to model its position and distribution reliably. Therefore, the SQUEEZE function of *PLATON* (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement (see Experimental section).

The molecular structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The Pd atom is coordinated by the two N atoms of the benzimidazole ring and two Cl atoms in a centrosymmetric *trans* configuration. The Pd–N distance in (I) compares well with the reported value of 2.005 (4) Å, but the Pd–Cl bond is significantly shorter than the value of 2.307 (3) Å reported for *trans*-dichlorobis(2-methylimidazole)palladium(II) (Navarro-Ranninger *et al.*, 1983).

The mean plane of the benzimidazole ring is nearly perpendicular to the Pd coordination plane, PdCl₂N₂, forming a dihedral angle of 80.1 (1)°. The bond distances and angles within the heterocyclic ring are in good agreement with literature values (Orpen *et al.*, 1989).

In the phosphate group of (I), a deformation from the ideal tetrahedral shape is observed, especially in the O2–P–O4 and O3–P–O4 angles. Disorder was identified in both ethoxy groups of the phosphonic fragment. Atoms C31 and C32, and C41 and C42, were refined with equal site occupancies (see *Experimental*).

Atom N2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* atom H2, to atom O2 in the molecule at (1 – *x*, *y*, *z*), so generating a C(11)[R₂²(14)] chain of rings (Bernstein *et al.*, 1995) running parallel to the [011] direction (Fig. 2). The complete analysis of the hydrogen-bonding interaction is not possible because of the omission of the water molecule in the refinement of (I). The crystal packing of (I) is additionally stabilized by π – π stacking interactions between partially overlapping benzimidazole rings across the inversion center at ($\frac{1}{2}$, 0, $\frac{1}{2}$). The perpendicular distance between the

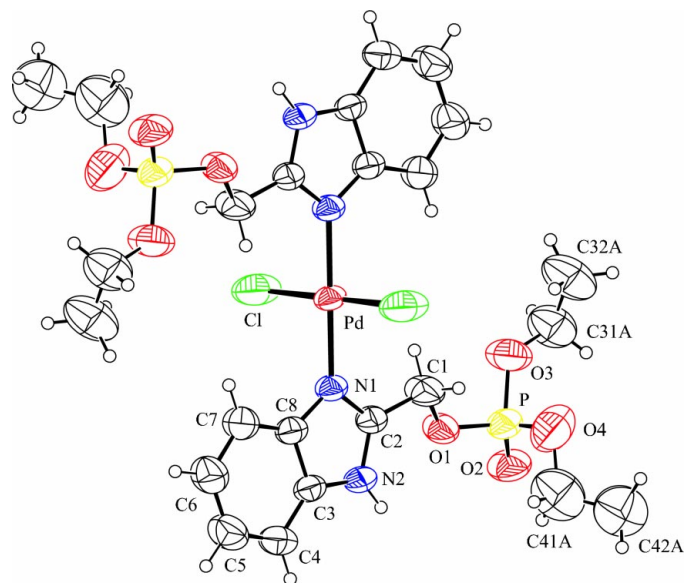


Figure 1

The structure of the title compound, with the atom-numbering scheme. The second component of the disordered atoms (C31*B*, C32*B*, C41*B* and C42*B*) has been omitted for clarity. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are related by the symmetry operator (1 – *x*, 1 – *y*, 1 – *z*).

centroid of the five-membered imidazole ring and the plane of the benzene ring is 3.420 Å, whereas the intercentroid distance is 3.822 (4) Å. A view of the stacking is shown in Fig. 3.

Experimental

The title compound was prepared by the reaction of two molecular equivalents of phosphoric acid 1*H*-benzimidazol-2-ylmethyl ester diethyl ester with one equivalent of K₂PdCl₄ in methanol–water solution. The yellow product was recrystallized from ethanol, yielding single transparent crystals of (I)·H₂O.

Crystal data

[PdCl₂(C₁₂H₁₇N₂O₄P)₂]*·*H₂O
M_r = 763.81
 Triclinic, *P* $\bar{1}$
a = 9.463 (5) Å
b = 9.638 (2) Å
c = 10.908 (3) Å
 α = 100.31 (2)°
 β = 115.10 (3)°
 γ = 100.64 (4)°
V = 847.6 (6) Å³

Z = 1
D_x = 1.496 Mg m^{−3}
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 15.3–24.7°
 μ = 0.85 mm^{−1}
T = 293 (2) K
 Prism, yellow
 0.50 × 0.25 × 0.10 mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: analytical
 (de Meulenaer & Tompa, 1965)
 T_{\min} = 0.723, T_{\max} = 0.905
 4131 measured reflections
 3898 independent reflections
 1608 reflections with $I > 2\sigma(I)$

R_{int} = 0.029
 θ_{max} = 27.5°
 h = −12 → 12
 k = 0 → 12
 l = −14 → 13
 3 standard reflections
 every 150 reflections
 intensity decay: none

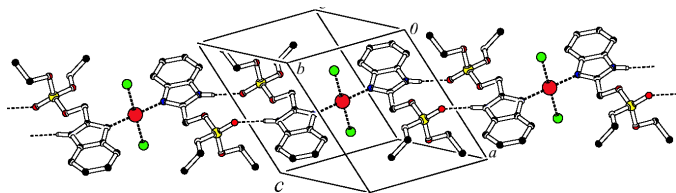


Figure 2
Part of the crystal structure, showing the $C(11)[R_2^2(14)]$ chain of rings parallel to the $[011]$ direction. The B component of disordered atoms and H atoms not participating in the hydrogen-bonding have been omitted for clarity.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.120$
 $S = 0.90$
 3898 reflections
 223 parameters
 H-atom parameters constrained

$$w = \{ \exp[3(\sin\theta/\lambda)^2] / [\sigma^2(F_o^2) + (0.0494P)^2] \}$$

$$P = (F_o^2 + 2F_c^2) / 3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.51 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

Pd—N1	1.998 (3)	P—O4	1.527 (6)
Pd—Cl	2.278 (2)	P—O3	1.553 (4)
C2—C1	1.492 (7)	P—O1	1.555 (4)
P—O2	1.440 (4)		
N1—Pd—Cl	90.22 (13)	O2—P—O1	110.3 (2)
O1—Cl—C2	107.6 (4)	O4—P—O1	108.6 (3)
O2—P—O4	117.7 (3)	O3—P—O1	101.9 (2)
O2—P—O3	116.8 (3)	Cl—O1—P	120.9 (3)
O4—P—O3	100.1 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots O2^i$	0.86	1.90	2.749 (6)	171

Symmetry codes: (i) $1-x, -y, -z$.

There is a potential solvent-accessible volume of 39.3 Å^3 per unit cell. The symmetry-unique cavity is centered at (0.0, 0.5, 0.5). Satisfactory refinement results were obtained when the disordered O atom was defined, but large displacement parameters of this O atom were observed. As an alternative strategy, the SQUEEZE function of PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data. The use of this strategy and the subsequent solvent-free model produced slightly better refinement results than the attempt to model the solvent atoms. Therefore, the solvent-free model and intensity data were used for the final results reported here. During the refinement of (I), the ethoxy groups revealed large atomic displacement parameters. Four atoms (C31, C32, C41 and C42), appeared to be disordered over two orientations with equal site occupancies (0.5). Similarity restraints were used in the refinement of the atomic displacement parameters of those disordered atoms. Moreover, bond-length restraints were applied to all C—C bonds involving the disordered atoms. All H atoms were

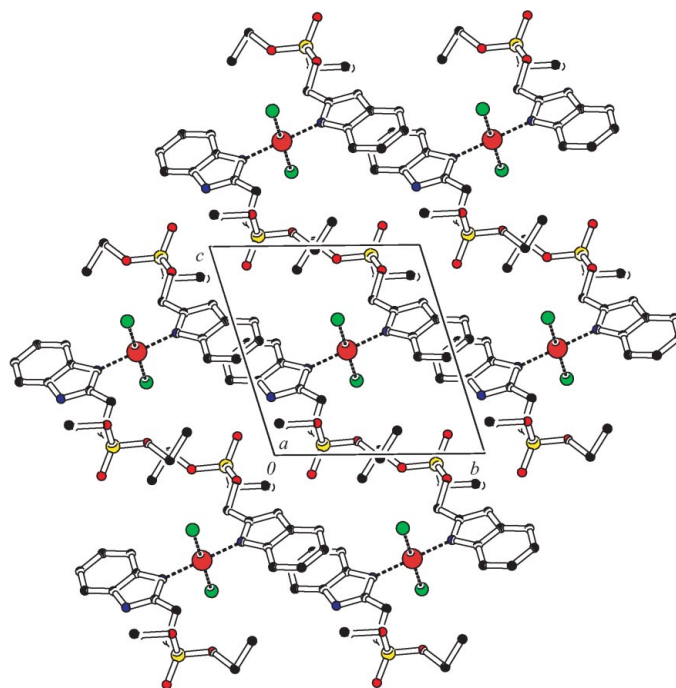


Figure 3

A view of the molecules of (I), showing the partial overlapping of the rings due to intermolecular stacking.

placed in idealized positions ($C-H = 0.93-0.97 \text{ Å}$ and $N-H = 0.86 \text{ Å}$) and constrained to ride on their parent atoms, with $U_{\text{iso}} = 1.2U_{\text{eq}}(C,N)$ (or $1.5U_{\text{eq}}$ for methyl C atoms). The low ratio of observed to unique reflections (41%) is the result of the poor quality of the crystals obtained.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *PLATON*.

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