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(Adeninato-N^9)[*N*-(2-aminoethyl)salicylideneiminato]palladium(II) 3.5-hydrate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.026
wR factor = 0.070
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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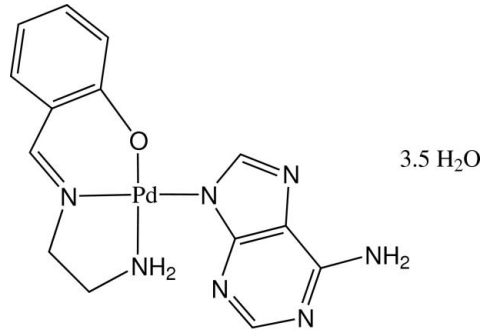
In the title compound, {[(2-aminoethyl)iminomethyl]phenolato-κ^3N,N',O}(9*H*-purine-6-aminato-κN^9)palladium(II) 3.5-hydrate, $[Pd(C_5H_4N_5)(C_9H_{11}N_2O)]\cdot 3.5H_2O$, the Pd^{II} ion is coordinated by the N9 atom of the adeninate ligand, two N atoms and one O atom of the *N*-(2-aminoethyl)-salicylideneiminate in a square-planar coordination. The crystal structure is stabilized by centrosymmetric stacking interactions between neighbouring complexes, and by hydrogen bonds involving adeninate and *N*-(2-aminoethyl)-salicylideneiminate ligands, and non-coordinated water molecules.

Comment

Since the discovery of the antitumour Pt^{II} complex cisplatin (Rosenberg *et al.*, 1965, 1969), it has been important to analyse the interaction of metal ions with nucleic acids and nucleobases. Some studies have revealed interactions between Pt^{II} group metal ions and nucleobases (Brüning *et al.*, 2002; Amantia *et al.*, 2003; Zhang *et al.*, 2005). In addition, some complexes of transition metal ions with salen-type Schiff base ligands [salen is *N*,*N*′-ethylenebis(salicylideneaminato)] have been tested as DNA reactive agents (Rokita & Burrows, 2003).



(I)

The aim of this study was to determine the binding function to nucleobases of a Pt^{II} group metal ion, Pd^{II}, coordinated by a salen-type ligand. Therefore, we synthesized an adeninato-Pd^{II}–SalEn [SalEn is *N*-(2-aminoethyl)salicylideneiminato] complex, (I), and analyzed its structure.

The title compound, (I), is shown in Fig. 1. The Pd^{II} ion is coordinated by atom N9 of the adeninate ligand, and atoms N11, N12 and O11 of the SalEn ligand, forming a square-planar coordination around the metal centre. Coordination through atom N9 of the adeninate ligand [Pd—N9 = 2.037 (2) Å] also occurs in the crystal structure of *trans*-$(n\text{-}Bu_3P)_2Pd(adeninato)_2\cdot 4CH_3OH$ [Pd—N9 = 2.015 (3) Å; Beck

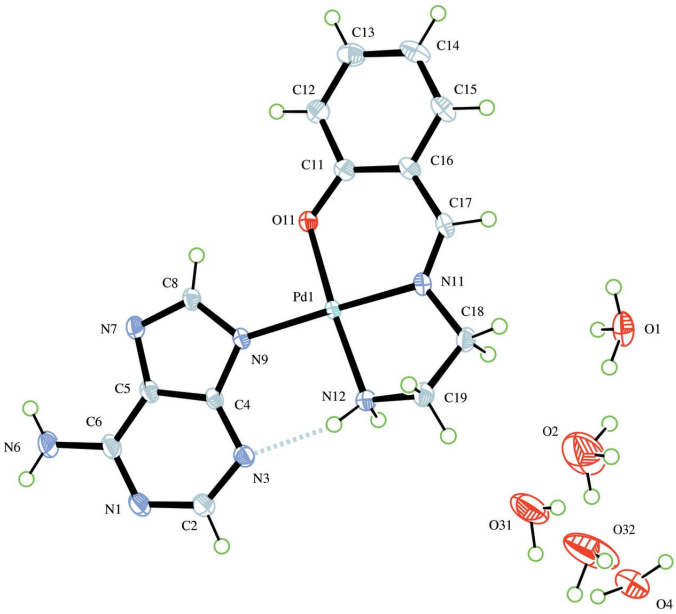


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. A dashed line indicates the intramolecular hydrogen bond. All disorder components are shown.

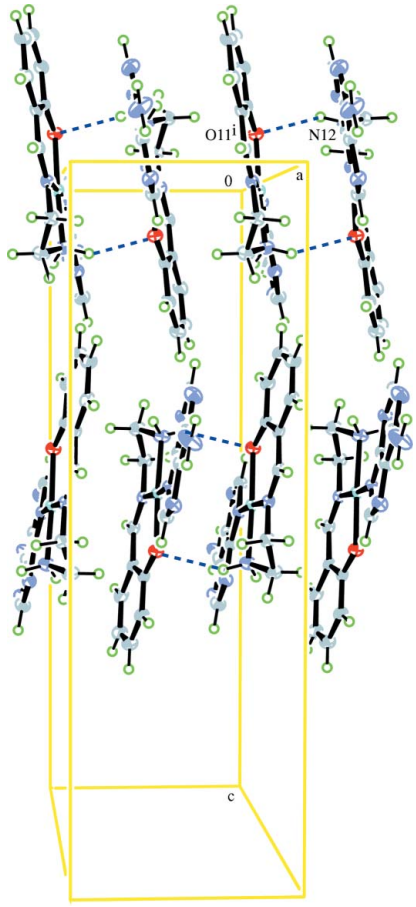


Figure 2
A view of the crystal packing of (I), showing the centrosymmetric stacking interactions between neighbouring complexes. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.]

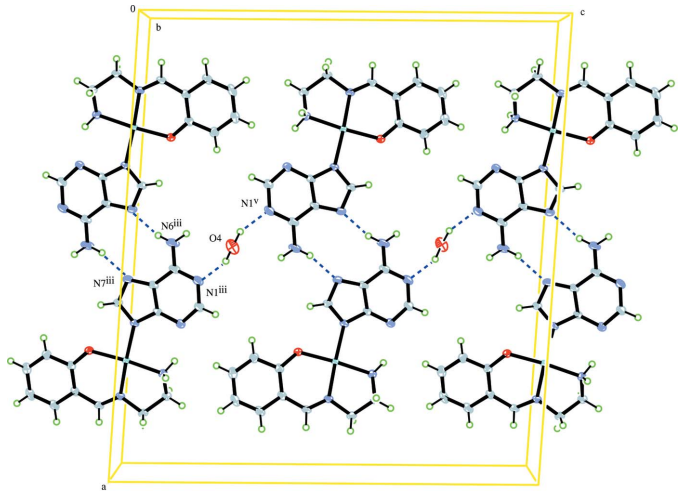


Figure 3
A view of the hydrogen bonds (dashed lines) between adeninate ligands, and hydrogen-bond bridges formed by O4 water molecules. [Symmetry codes: (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

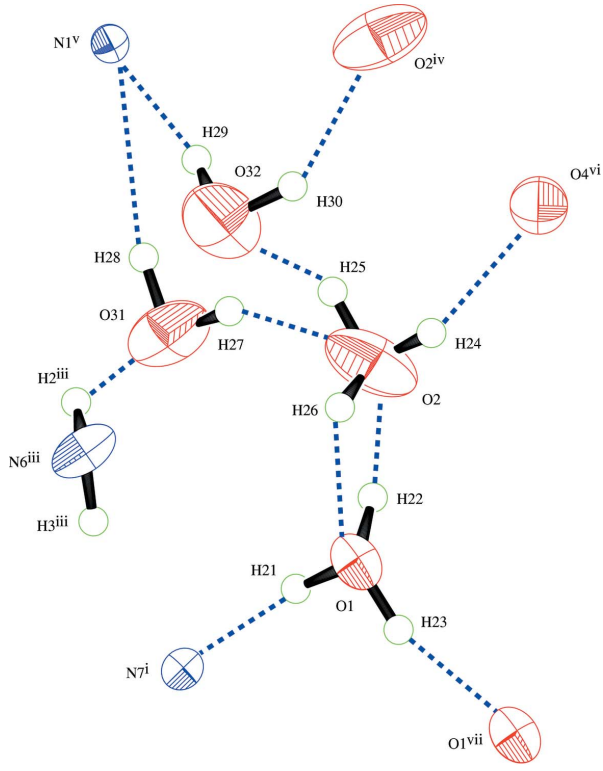


Figure 4
A view of the hydrogen-bond network (dashed lines) involving the disordered water molecules. All disorder components are shown. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iv) $1 - x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $x, 1 + y, z$; (vii) $1 - x, 2 - y, -z$.]

et al., 1979], in agreement with the fact that N9 is the most basic of the four available N atoms on the adeninate anion (Hodgson, 1977; Beck *et al.*, 1979). While the Pd^{II} ion and its coordinated atoms lie almost in a plane (r.m.s. deviation of fitted atoms = 0.056 Å), the overall structure of the complex is not planar. The dihedral angle between the adeninate ligand

and salicylidene plane (O11/C11–C17/N11) is 12.23 (6)°. An intramolecular hydrogen bond is observed between the amino group of SalEn and the adeninate ligand (N12—H14···N3; Fig. 1 and Table 2).

The crystal packing is stabilized by centrosymmetric stacking interactions between neighbouring complexes (Fig. 2), the separations ranging from 3.2642 (2) (Pd1···Pd1^{i}) to 3.457 (3) Å [C4···C17^{i}; symmetry code: (i) $\frac{1}{2}-x,\frac{3}{2}-y,-z$], and by hydrogen bonds involving SalEn ligands (N12—H15···O11^{i}; Table 2). The crystal structure is also stabilized by hydrogen bonds between neighbouring adeninate ligands [N6—H3···N7^{ii}; symmetry code: (ii) $-x,2-y,-z$] (Fig. 3 and Table 2), hydrogen-bond bridging of two symmetry-related adeninate ligands *via* a water molecule [N1^{iii}—O4···N1^{v}; symmetry codes: (iii) $\frac{1}{2}+x,-\frac{1}{2}+y,+z$; (*v*) $\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z$] (Fig. 3 and Table 2), and a complex network of hydrogen bonds involving adeninate ligands and disordered water molecules (Fig. 4 and Table 2).

Experimental

N,*N*′-Ethylenebis(salicylideneamine) dissolved in EtOH–H_2O (40% *v*/*v*) was reacted with adenine and sodium tetrachloropalladium(II) trihydrate dissolved in water at 298 K (molar ratio = 2:1:2). This mixture was diluted with 50% KCl solution. Light-brown crystals appeared from this mixture after one month of evaporation at 298 K.

Crystal data

$[Pd(C_5H_4N_5)(C_9H_{11}N_2O)]\cdot3.5H_2O$
M_r = 466.81
Monoclinic, $C2/c$
a = 23.75 (2) Å
b = 6.869 (5) Å
c = 21.65 (2) Å
β = 93.46 (3)°
V = 3526 (5) Å^3
Z = 8
D_x = 1.759 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14802 reflections
θ = 3.1–27.5°
μ = 1.09 mm^{-1}
T = 123 (1) K
Plate, brown
0.50 × 0.15 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.682, T_{max} = 0.947
17133 measured reflections
4009 independent reflections
3440 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.014
θ_{max} = 27.5°
$h = -30 \rightarrow 30$
$k = -8 \rightarrow 8$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.070
S = 1.07
4009 reflections
283 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 7.5219P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—O11	1.993 (2)	Pd1—N11	1.968 (2)
Pd1—N9	2.037 (2)	Pd1—N12	2.038 (2)
O11—Pd1—N9	88.73 (7)	N9—Pd1—N11	175.49 (7)
O11—Pd1—N11	93.97 (7)	N9—Pd1—N12	94.88 (7)
O11—Pd1—N12	175.05 (7)	N11—Pd1—N12	82.65 (8)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H14···N3	0.90	2.22	2.845 (4)	126
N12—H15···O11^{i}	0.90	2.39	3.175 (3)	145
N6—H3···N7^{ii}	0.86	2.24	3.040 (3)	155
O4—H31···N1^{iii}	0.99	2.00	2.920 (3)	154
O4—H31^{iv}···N1^{v}	0.99	2.00	2.920 (3)	154
O1—H21···N7^{i}	0.93	2.04	2.960 (3)	170
O1—H22···O2	0.94	1.86	2.783 (4)	167
O2—H24···O4^{vi}	0.95	1.97	2.752 (4)	137
O2—H25···O32	0.96	1.59	2.473 (8)	151
O32—H29···N1^{v}	0.96	1.92	2.804 (6)	154
O32—H30···O2^{iv}	0.96	2.25	3.095 (8)	146
O1—H23···O1^{vii}	0.95	1.88	2.793 (4)	163
O2—H26···O1	0.95	1.99	2.783 (4)	139
O31—H27···O2	0.96	1.98	2.811 (8)	144
O31—H28···N1^{v}	0.96	2.30	3.260 (7)	179
N6^{iii}—H2^{iii}···O31	0.86	2.16	2.877 (6)	140

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

One water molecule was found to be disordered over two sites, O31 and O32; the occupancies were refined and then fixed at 0.5. For water molecules O1, O2, O31 and O32, H atoms were found in difference maps with some disordered over two sites. Occupancies were refined and fixed in the last cycles: H22, bonded to O1, is disordered with H23 (0.56/0.54); H25, bonded to O2, is disordered with H26 (0.22/0.78); H27 and H28 are bonded to O31 with occupancies 0.5; H29 and H30 are bonded to O32, with occupancies 0.5. In the last cycles, the coordinates of H atoms of water molecules were fixed and their isotropic displacement parameters were fixed at U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were placed in idealized positions and refined as riding, with U_{iso}(H) = 1.5U_{eq}(carrier atom). Constrained distances: 0.93 Å for aromatic CH; 0.97 Å for methylene CH_2; 0.90 Å for coordinated amine; 0.86 Å for uncoordinated amine. The maximum electron density appears near atom O32.

Data collection: *RAPID-AUTO* (Rigaku, 1998; cell refinement: *PROCESS-AUTO* (Rigaku/MSC, 2005); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2005).

References

Amantia, D., Price, C., Shipman, M. A., Elsegood, M. R. J., Clegg, W. & Houlton, A. (2003). *Inorg. Chem.* **42**, 3047–3056.
Beck, W. M., Calabrese, J. C. & Kottmair, N. D. (1979). *Inorg. Chem.* **18**, 176–182.
Brüning, W., Ascaso, I., Freisinger, E., Sabat, M. & Lippert, B. (2002). *Inorg. Chim. Acta*, **339**, 400–410.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Hodgson, D. J. (1977). *Prog. Inorg. Chem.* **23**, 211–254.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
Rigaku/MSC (2005). *PROCESS-AUTO* and *CrystalStructure* (Version 3.7). Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Rokita, S. E. & Burrows, C. J. (2003). *Small Molecule DNA and RNA Binders*, Vol. 1, edited by M. Demeunynck, C. Bailly & W. D. Wilson, pp. 126–145. Weinheim: Wiley-VCH.
Rosenberg, B., Camp, L. V. & Krigas, T., (1965). *Nature (London)*, **205**, 698–699.
Rosenberg, B., Camp, L. V., Trosko, J. E. & Mansour, V. H. (1969). *Nature (London)*, **222**, 385–386.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Zhang, Z. Q., Zhou, L. X., He, Q. & Zhao, Y. Y. (2005). *Jiegou Huaxue*, **24**, 114–120. (In Chinese.)