Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Platinum complexes of oxopurines: *cis*-bis(theophyllinato-N^7)bis(triphenylphosphine)platinum(II) and *cis*-chloro(theobrominato-N^1)bis(triphenylphosphine)platinum(II) ethanol hemisolvate

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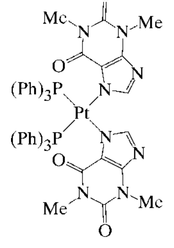
Received 13 September 2001
Accepted 28 November 2001
Online 23 January 2002

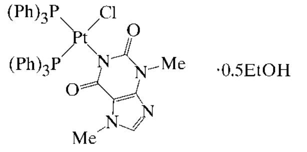
The syntheses and structures of two mixed-ligand complexes of platinum(II) with deprotonated oxopurine bases and triphenylphosphine are reported, namely the theophyllinate complex *cis*-bis(1,2,3,6-tetrahydro-1,3-dimethylpurine-2,6-dionato-κN^7)bis(triphenylphosphine-κP)platinum(II), $[Pt(C_7H_7N_4O_2)_2(C_{18}H_{15}P)_2]$, (I), and the theobrominate complex *cis*-chloro(1,2,3,6-tetrahydro-3,7-dimethylpurine-2,6-dionato-κN^1)bis(triphenylphosphine-κP)platinum(II) ethanol hemisolvate, $[PtCl(C_7H_7N_4O_2)(C_{18}H_{15}P)_2]\cdot 0.5C_2H_5OH$, (II). In (I), the coordination geometry of Pt is square planar, formed by the two coordinating N atoms of the theophyllinate anions in a *cis* arrangement and two P atoms from the triphenylphosphine groups. In (II), there are two crystallographically independent molecules. They both exhibit a square-planar coordination geometry around Pt involving one Cl atom, the coordinating N atom of the theobrominate anion and two P atoms from the triphenylphosphine groups. The two triphenylphosphine groups are arranged in a *cis* configuration in both structures. The heterocyclic rings are rotated with respect to the coordination plane of the metal by 82.99 (8) and 88.09 (8)° in complex (I), and by 85.91 (16) and 88.14 (18)° in complex (II). Both structures are stabilized by intramolecular stacking interactions involving the purine rings and the phenyl rings of adjacent triphenylphosphine moieties.

Comment

Transition metal complexes of nucleobase derivatives may serve as models for the coordination of metals to nucleic acids. The methylated oxopurines theophylline and theobromine are of additional interest in view of their pharmacological properties. Theophylline exhibits anti-asthmatic effects, theobromine is in current clinical use as a vasodilator and a bronchodilator, and both oxopurines are also used as cardiac stimulants or muscle relaxants. Pt complexes of these oxopurines may be worthy of additional attention because of the potential antitumour activity of such complexes (Bloemink & Reedijk, 1996; Whitehead & Lippard, 1996). Here, we report the synthesis and structure of two molecular platinum(II) complexes involving triphenylphosphine and the anions of theophylline (TP) and theobromine (TB) as ligands, respectively, namely *cis*-$[Pt(TP^-)_2(PPh_3)_2]$, (I), and *cis*-$[PtCl(TB^-)(PPh_3)_2]\cdot 0.5EtOH$, (II).



(I)



(II)

In metal complexes synthesized in non-alkaline media, theophylline binds as a neutral ligand, whereas complexes crystallized from alkaline solutions show the presence of theophyllinate anions (Madarasz *et al.*, 2000), usually deprotonated at N7, the atom where the H atom is located in the crystal structure of neutral theophylline (Ebisuzaki *et al.*, 1997), and single-crystal data for many metal complexes prove that theophylline moieties are normally bonded to the metal centre through N7 (Madarasz *et al.*, 2000). There are, however, some rare examples of other coordination modes of unsubstituted theophylline or theophyllinate anions. N7 coordination including a balanced metal–O6 chelation has been found in a titanium cyclopentadienyl complex, with a Ti—O6 distance of 2.28 Å (Cozak *et al.*, 1986), whereas some weak N7/O6-chelating interactions have been established, for example, in copper(II) complexes, with a Cu—O6 distance of 2.92 Å (Szalda *et al.*, 1976) or 3.34 Å (Kistenmacher *et al.*, 1978; Madarasz *et al.*, 2000). N9 coordination of theophyllinate anions, in spite of steric hindrance by the neighbouring methyl group at N3, has been established in a dimeric rhodium(II) complex (Aoki & Yamazaki, 1980), whereas neutral theophylline also bonds through N9 in a chloroplatinum(II) complex (Griffith & Amma, 1979). N7/N9 bridging theophyllinate anions, including a weak Pt—O6 interaction of 2.34 Å, have been observed in a hexameric trimethylplatinum complex (Lorberth *et al.*, 1988). Finally, in a mixed-ligand Pd^{II} complex, theophyllinate anions are linked to the metal through C8 (Romerosa *et al.*, 1997).

The molecular structure of (I) is shown in Fig. 1. Two theophyllinate monoanions coordinate to Pt^{II} *via* the N7 atoms. Compound (I) exhibits a slightly distorted square-planar coordination geometry around Pt, with two N7-coordinating theophyllinate anions [Pt—N71 2.069 (3) Å and Pt—N72 2.071 (3) Å] and two P atoms from the triphenylphosphine groups [Pt—P1 2.2792 (11) Å and Pt—P2 2.2685 (11) Å] in a *cis* arrangement (Fig. 1). Weak C—H···O

DOI: 10.1107/S0108270101020364

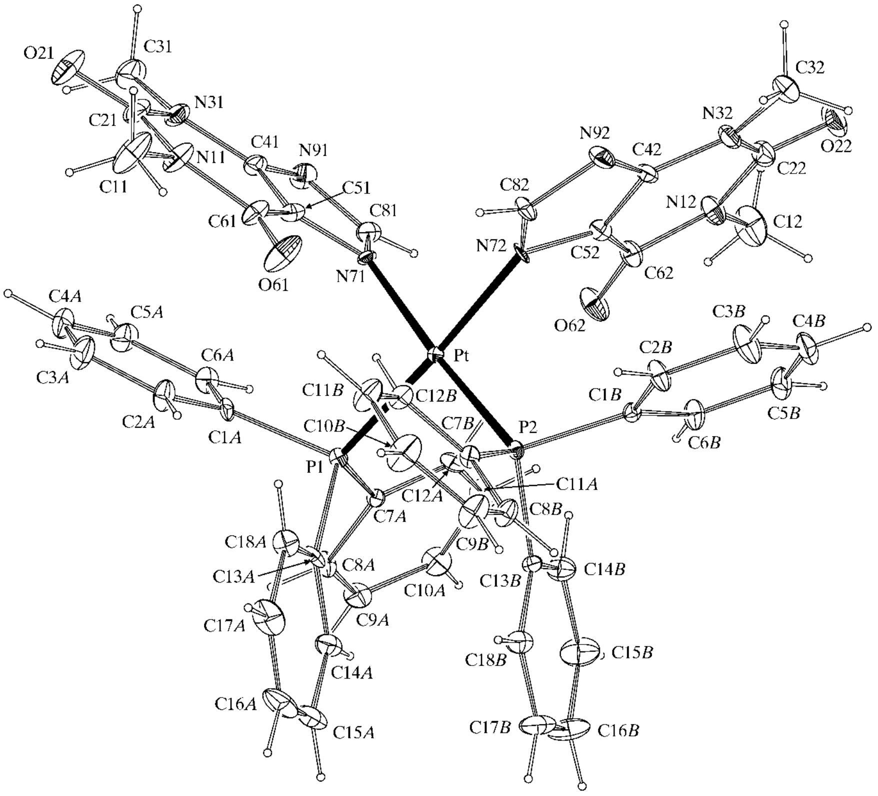


Figure 1
A view of the molecule of (I) shown with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

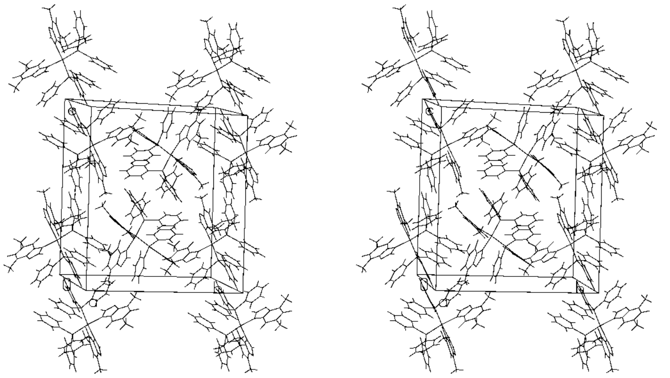


Figure 2
A stereoview of (I), showing the intramolecular stacking interactions involving the purine and phenyl rings.

hydrogen-bonding interactions are observed involving O2, with donor–acceptor distances of 3.065 (6) and 3.184 (6) Å. Two rather close contacts are observed between Pt and atoms O61 and O62 adjacent to N71 and N72, with Pt···O61 and Pt···O62 distances of 3.234 (4) and 3.284 (4) Å, respectively.

In theobromine, in contrast with theophylline, the N7 coordination site is blocked by a methyl group, and therefore N9 is expected to be the preferred coordination site. Such a coordination is found in the only theobromine metal complex structure reported to date, $K[Pt^{II}(TB)Cl_3]$ (Crowston *et al.*, 1986). In complex (II), however, we have now established a structure involving theobrominate anions coordinating to Pt through N1 in both crystallographically independent molecules. In addition, one Cl^- anion and two *cis* P atoms from triphenylphosphine groups are coordinated to Pt, forming a slightly distorted square-planar coordination geometry (Fig. 3). The metal–ligand distances in molecules 1 and 2, respectively, are Pt1—N11 2.079 (5) and Pt2—N12 2.097 (5) Å, Pt1—Cl1 2.340 (2) and Pt2—Cl2 2.349 (2) Å, Pt1—P1 2.239 (2) and Pt1—P2 2.2697 (18) Å, and Pt2—P3 2.251 (2) and Pt2—P4 2.2898 (17) Å. The Pt—P distances in (II) *trans* to the purine ligands are significantly longer (by about 0.04 Å) than the corresponding values *trans* to the Cl atoms in both crystallographically independent molecules; the purine base obviously exhibits a stronger *trans* influence than the Cl atom.

In both complexes, the Pt—N(purine) distances are significantly longer than in corresponding complexes without triphenylphosphine ligands. This may be explained by a lengthening of the Pt—N bonds due to the relatively high *trans* influence of PPh_3.

The heterocyclic oxopurine rings are rotated with respect to the coordination plane of the metal by 82.99 (8) and 88.09 (8)° in complex (I), and by 85.91 (16) and 88.14 (18)° in complex (II). The maximum deviation of individual purine-ring atoms from the least-squares plane through the nine ring atoms is 0.040 (4) Å for N12 in (I) and 0.077 (8) Å for C52 in (II),

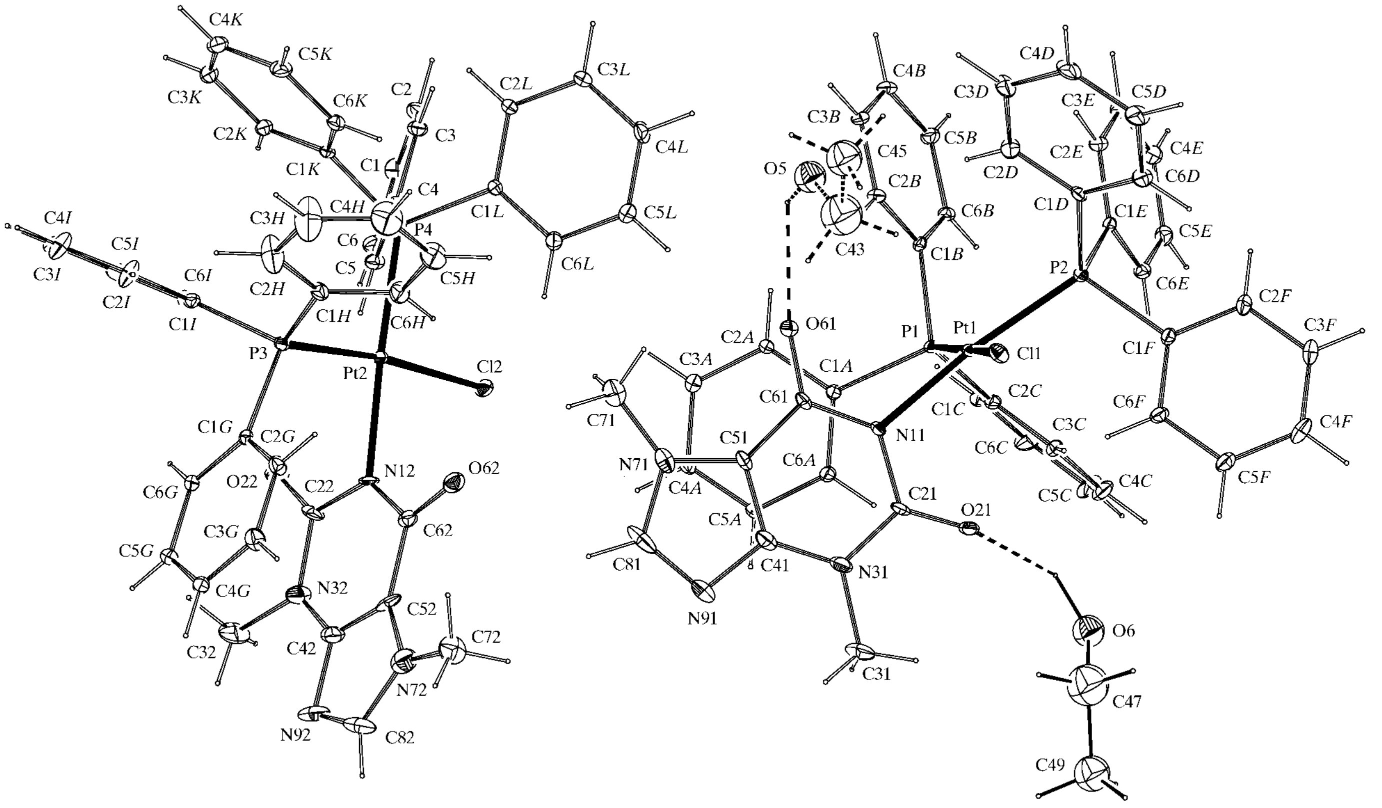


Figure 3

Views of the two independent molecules of (II) shown with 10% probability displacement ellipsoids and the atom-numbering schemes. H atoms are drawn as small spheres of arbitrary radii and hydrogen-bonding contacts of the disordered ethanol molecules are indicated by dashed lines.

whereas the corresponding maximum deviation for ring-substituent atoms is 0.256 (7) Å for C32 in (I) and 0.17 (1) Å for O22 in (II).

In both complexes, the structures are stabilized by intramolecular stacking interactions between the purine rings and a phenyl ring of an adjacent triphenylphosphine group (Figs. 2 and 4). The corresponding stacking distances (calculated as the mean distance of all ring atoms of one molecule from the least-squares planes through the stacking molecule) and stacking angles are 3.26 Å and 10.0°, respectively, for molecule 1, and 3.32 Å and 13.7°, respectively, for molecule 2 in the theophylline complex, (I) (see Fig. 1). In the theobromine complex, (II), the corresponding values are 3.31 Å and 19.9°, respectively, for molecule 1, and 3.32 Å and 12.0°, respectively, for molecule 2. The hydrogen-bonding contacts for (II) are shown in Fig. 3 and Table 4.

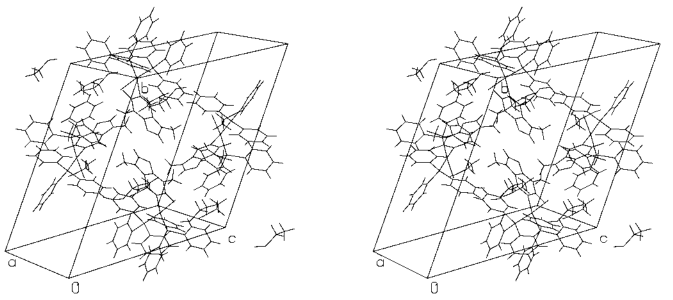


Figure 4

A stereoview of (II), showing the intramolecular stacking interactions involving the purine and phenyl rings.

Experimental

Complex (I) was crystallized by adding a suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (119 mg, 0.15 mmol) in ethanol (50 ml) to a solution of theophylline (54 mg, 0.3 mmol) in water (5 ml) containing NaOH (0.3 mmol). The reaction mixture was heated to give a clear solution. After slow evaporation at room temperature over a period of one month, colourless plates of (I) were formed. Elemental analysis, found: C 55.40, H 4.27, N 9.99%; calculated for $C_{50}H_{44}N_8O_4P_2Pt$: C 55.71, H 4.11, N 10.39%. A molecular peak corresponding to [Pt(TP$^-$)$_2$(PPh$_3$)$_2$]H$^+$ at *m*/*z* 1078 (2%) and a peak corresponding to [Pt(TP$^-$)(PPh$_3$)$_2$]$^+$ at *m*/*z* 898 (43%) were found in the FAB-MS spectrum. Complex (II) was obtained by adding a suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (119 mg, 0.15 mmol) in ethanol (50 ml) to a solution of theobromine (27 mg, 0.15 mmol) in water (5 ml) containing NaOH (0.3 mmol). The reaction mixture was heated to give a clear solution. After slow evaporation over a period of one month at 323 K and subsequent slow addition of a solution of excess NaBF$_4$ in 100 µl of the main solution, colourless plates of (II) formed. Elemental analysis, found: C 54.93, H 3.99, N 5.83%, calculated for $C_{44}H_{40}ClN_4O_{2.5}P_2Pt$: C 55.20, H 4.21, N 5.85%. A molecular peak corresponding to [Pt(TB$^-$)(PPh$_3$)$_2$]$^+$ at *m*/*z* 898 (67%) and a peak corresponding to [PtCl(TB$^-$)(PPh$_3$)$_2$]Na$^+$ at *m*/*z* 957 (4%) were found in the FAB-MS spectrum.

Table 1
Selected geometric parameters (Å, °) for (I).

Pt—N71	2.069 (3)	N71—C81	1.315 (6)
Pt—N72	2.071 (3)	C81—N91	1.341 (6)
Pt—P2	2.2685 (11)	N12—C22	1.402 (7)
Pt—P1	2.2792 (11)	N12—C62	1.412 (6)
N11—C21	1.401 (6)	N12—C12	1.482 (6)
N11—C61	1.412 (6)	C22—O22	1.226 (6)
N11—C11	1.476 (7)	C22—N32	1.374 (6)
C21—O21	1.225 (6)	N32—C42	1.390 (6)
C21—N31	1.377 (7)	N32—C32	1.460 (6)
N31—C41	1.391 (6)	C42—N92	1.356 (6)
N31—C31	1.462 (6)	C42—C52	1.370 (6)
C41—N91	1.349 (6)	C52—N72	1.390 (5)
C41—C51	1.378 (6)	C52—C62	1.423 (6)
C51—N71	1.395 (5)	C62—O62	1.231 (6)
C51—C61	1.415 (6)	N72—C82	1.326 (5)
C61—O61	1.233 (6)	C82—N92	1.375 (6)
N71—Pt—N72	87.05 (14)	C21—N31—C41	119.2 (4)
N71—Pt—P2	174.37 (10)	C81—N71—C51	104.0 (3)
N72—Pt—P2	87.88 (10)	C81—N91—C41	102.0 (4)
N71—Pt—P1	87.60 (10)	C22—N12—C62	126.9 (4)
N72—Pt—P1	174.04 (11)	C22—N32—C42	118.9 (4)
P2—Pt—P1	97.57 (4)	C82—N72—C52	104.8 (3)
C21—N11—C61	126.1 (4)	C42—N92—C82	101.7 (4)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4B—H4$B\cdots$O21$^{\rm i}$	0.95	2.42	3.065 (6)	125
C10A—H10$A\cdots$O22$^{\rm ii}$	0.95	2.51	3.184 (6)	128

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

Compound (I)

Crystal data

$[Pt(C_7H_7N_4O_2)_2(C_{18}H_{15}P)_2]$
M_r = 1077.96
Monoclinic, $P2_1/c$
a = 9.7839 (5) Å
b = 20.7991 (10) Å
c = 22.0788 (12) Å
β = 99.172 (6)°
V = 4435.5 (4) Å^3
Z = 4
D_x = 1.614 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.7–30.3°
μ = 3.29 mm^{-1}
T = 183 (2) K
Plate, colourless
0.27 × 0.16 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ rotation scans
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\rm min}$ = 0.470, $T_{\rm max}$ = 0.779
52 916 measured reflections
13 203 independent reflections
9092 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.067
$\theta_{\rm max}$ = 30.3°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 31$
50 to 200 standard reflections
frequency: 5.8 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
S = 1.01
13 203 reflections
585 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.003
$\Delta\rho_{\rm max}$ = 1.42 e Å^{-3}
$\Delta\rho_{\rm min}$ = −3.35 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Pt1—N11	2.079 (5)	Pt2—N12	2.097 (5)
Pt1—P1	2.239 (2)	Pt2—P3	2.251 (2)
Pt1—P2	2.2697 (18)	Pt2—P4	2.2898 (17)
Pt1—Cl1	2.340 (2)	Pt2—Cl2	2.349 (2)
N11—C61	1.369 (7)	N12—C62	1.362 (8)
N11—C21	1.406 (7)	N12—C22	1.401 (8)
C21—O21	1.235 (8)	C22—O22	1.213 (9)
C21—N31	1.395 (7)	C22—N32	1.407 (8)
N31—C41	1.341 (8)	N32—C42	1.331 (9)
N31—C31	1.509 (8)	N32—C32	1.524 (10)
C41—N91	1.376 (8)	C42—N92	1.392 (9)
C41—C51	1.401 (8)	C42—C52	1.397 (10)
C51—N71	1.346 (8)	C52—N72	1.343 (9)
C51—C61	1.439 (7)	C52—C62	1.453 (8)
C61—O61	1.248 (7)	C62—O62	1.243 (8)
N71—C81	1.394 (8)	N72—C82	1.395 (10)
N71—C71	1.433 (8)	N72—C72	1.417 (10)
C81—N91	1.356 (9)	C82—N92	1.327 (11)
N11—Pt1—P1	89.67 (19)	N12—Pt2—P3	88.52 (18)
N11—Pt1—P2	170.62 (17)	N12—Pt2—P4	174.13 (19)
P1—Pt1—P2	98.54 (7)	P3—Pt2—P4	96.96 (7)
N11—Pt1—Cl1	86.84 (19)	N12—Pt2—Cl2	84.79 (18)
P1—Pt1—Cl1	175.07 (8)	P3—Pt2—Cl2	173.03 (7)
P2—Pt1—Cl1	85.24 (7)	P4—Pt2—Cl2	89.79 (7)
C61—N11—C21	125.7 (5)	C62—N12—C22	127.2 (5)
C41—N31—C21	119.5 (6)	C42—N32—C22	117.5 (7)
C51—N71—C81	106.0 (7)	C52—N72—C82	105.2 (7)
C81—N91—C41	101.7 (6)	C82—N92—C42	99.0 (7)

Compound (II)

Crystal data

$[PtCl(C_7H_7N_4O_2)(C_{18}H_{15}P)_2]\cdot 0.5C_2H_6O$
M_r = 957.28
Triclinic, $P\overline{1}$
a = 11.4777 (9) Å
b = 19.3276 (13) Å
c = 20.5946 (17) Å
α = 62.565 (8)°
β = 81.354 (10)°
γ = 89.019 (9)°
V = 4001.7 (5) Å^3
Z = 4
D_x = 1.589 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.7–29.3°
μ = 3.70 mm^{-1}
T = 183 (2) K
Plate, colourless
0.36 × 0.18 × 0.06 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\rm min}$ = 0.350, $T_{\rm max}$ = 0.809
43 394 measured reflections
19 993 independent reflections
8805 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.096
$\theta_{\rm max}$ = 29.3°
$h = -15 \rightarrow 15$
$k = -23 \rightarrow 25$
$l = 0 \rightarrow 28$
50 to 200 standard reflections
frequency: 5 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.092
S = 0.69
19 993 reflections
839 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 1.40 e Å^{-3}
$\Delta\rho_{\rm min}$ = −2.62 e Å^{-3}

The abnormalities of the displacement parameters of N72 in (I) may be related to systematic errors that probably occurred during the

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O61	1.1 (2)	2.1 (2)	2.74 (2)	112 (19)
O6—H6···O21	1.12 (8)	2.44 (13)	3.089 (17)	115 (13)
C3*A*—H3*A*···Cl2	0.95	2.83	3.549 (4)	133
C3*G*—H3*G*···O21$^{\rm i}$	0.95	2.54	3.469 (7)	167
C5*E*—H5*E*···Cl2$^{\rm ii}$	0.95	2.81	3.511 (5)	131
C5*I*—H5*I*···O22$^{\rm iii}$	0.95	2.21	3.129 (8)	162
C6*L*—H6*L*···Cl2	0.95	2.73	3.428 (5)	131
C49—H49*C*···O61$^{\rm iv}$	0.98	2.38	2.94 (3)	116
C72—H72*B*···Cl1$^{\rm i}$	0.98	2.78	3.571 (13)	138

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $2-x, 1-y, -z$; (iv) $x-1, y, z$.

indexing of crystal faces and measurement of the face-to-face distances of the tiny crystal with the aid of a video camera. Four anisotropic displacement parameters of (II) showed max/min ratios larger than 3.0, with a maximum value of 3.70 for atom C3*H*. This may be explained by the low diffracting power and small size of the crystal used, resulting in only 44% observed reflections. For the phenyl rings of (II), rigid-group constraints (*AFIX* 66 in *SHELXL*97; Sheldrick, 1997) were used. Ten 1,2- and two 1,3-distance restraints (*DFIX*) were applied for the purine-ring system of molecule 1. Similarity restraints were used for the purine-ring system of molecule 2 with the *SAME* instruction. The ethanol solvent of (II) appeared to be disordered, with very large displacement parameters. Therefore, the site occupancy was started at 0.5 and the atoms were refined with the *PART* instruction. The isotropic displacement parameters of the corresponding C and O atoms were equated using *EADP* constraints. The 1,2- and 1,3-distance restraints which were applied for the ethanol molecules were based on theoretical calculations. Attempts to localize the hydroxy H5 and H6 atoms using *AFIX* 87/*AFIX* 83 options, and also using extended difference electron-density calculations that could lead to the expected hydrogen-bonding contacts, were unsuccessful. Therefore, the calculated positions of H5 and H6 (*AFIX* 83) were used as a starting set for restraint models of the O5—H5···O61 and O6—H6···O21 hydrogen-bond contacts using 1,2- and 1,3-distance restraints (*DFIX*). Many cycles of refinement were necessary for convergence, using the shift-limiting *DAMP* option. The last cycle of refinement was calculated separately (*DAMP* 0 0) to obtain the correct standard uncertainties. The final disorder ratio of the ethanol molecules was 60:40. All H-atom positions were calculated [except for H5 and H6 in (II)] after each cycle of refinement with *SHELXL*97, using a riding model in both structures, with C—H distances in the range 0.95–0.99 Å and $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(C) for phenyl and $1.5U_{\rm eq}$(C) for methyl C atoms.

For both compounds, data collection: *IPDS* (Stoe & Cie, 1999); cell refinement: *IPDS*; data reduction: *XRED* in *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *PLUTON* (Spek, 1991); software used to prepare material for publication: *SHELXL*97.

The authors are grateful to the Swiss National Science Foundation for research grants. We thank Dr Heiko Jacobsen for providing us with the theoretical structural data of the ethanol, which were used for 1,2- and 1,3-restraints in the refinement.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1480). Services for accessing these data are described at the back of the journal.

References

Aoki, K. & Yamazaki, H. (1980). *J. Chem. Soc. Chem. Commun.* pp. 186–188.

Bloemink, M. J. & Reedijk, J. (1996). *Met. Ions Biol. Syst.* **32**, 641–685.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cozak, D., Mardhy, A., Olivier, M. J. & Beauchamp, A. L. (1986). *Inorg. Chem.* **25**, 2600–2606.

Crowston, E. H., Goodgame, D. M. L., Hayman, P. B., Slawin, A. M. Z. & Williams, D. J. (1986). *Inorg. Chim. Acta*, **122**, 161–168.

Ebisuzaki, Y., Boyle, P. D. & Smith, J. A. (1997). *Acta Cryst.* C**53**, 777–779.

Griffith, E. H. & Amma, E. L. (1979). *J. Chem. Soc. Chem. Commun.* pp. 322–324.

Kistenmacher, T. J., Szalda, D. J., Chiang, C. C., Rossi, M. & Marzilli, L. G. (1978). *Inorg. Chem.* **17**, 2582–2584.

Lorberth, J., El-Essawi, M., Massa, W. & Lahib, L. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 1160–1161.

Madarasz, J., Bombicz, P., Czugler, M. & Pokol, G. (2000). *Polyhedron*, **19**, 457–463.

Romerosa, A., Suarez-Varela, J., Hidalgo, M. A., Avila-Roson, J. C. & Colacio, E. (1997). *Inorg. Chem.* **36**, 3784–3786.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Spek, A. L. (1991). *PLUTON*. University of Utrecht. The Netherlands.

Stoe & Cie (1999). *IPDS*. Version 2.92. Stoe & Cie, Darmstadt, Germany.

Szalda, D. J., Kistenmacher, T. J. & Marzilli, L. G. (1976). *J. Am. Chem. Soc.* **98**, 8371–8377.

Whitehead, J. P. & Lippard, S. J. (1996). *Met. Ions Biol. Syst.* **32**, 687–726.