Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dichloro(propane-1,3-diamine-κ^2N,N')platinum(II), dichloro(propane-1,3-diamine-κ^2N,N')palladium(II) and μ-4,9-diazadodecane-1,12-diamine-κ^2N^1,N^4:-κ^2N^9,N^{12}-bis[dichloroplatinum(II)]

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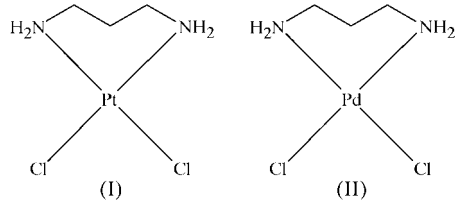
Received 11 January 2006
Accepted 20 February 2006
Online 18 March 2006

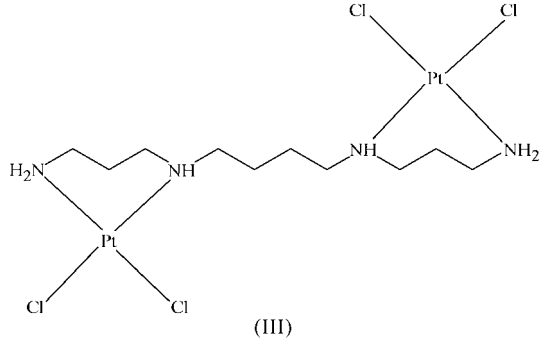
In the title compounds, $[PtCl_2(C_3H_{10}N_2)]$, (I), $[PdCl_2(C_3H_{10}N_2)]$, (II), and $[Pt_2Cl_4(C_{10}H_{26}N_4)]$, (III), each metal atom lies in a distorted *cis*-square coordination geometry. Compounds (I) and (II) are isostructural, and each complex has a mirror plane through the metal atom and the middle C atom of the propane-1,3-diamine ligand. In (III), the binuclear complex $[Pt_2Cl_4(spn)]$ has an inversion center at the middle of the 4,9-diazadodecane-1,12-diamine (spermine, spn) ligand. The six-membered chelate rings in (III) adopt a chair form, which is unsymmetrical and less flattened than those in (I) and (II). In all three crystal structures, there are intermolecular N—H$\cdots$Cl hydrogen bonds.

Comment

cis-Diamminedichloroplatinum(II) (cisplatin) is known as an anticancer agent active against a wide variety of human tumors, especially testicular and ovarian cancers (Siddik, 2003; Zhang & Lippard, 2003). However, its use is limited because of toxic side effects and the development of resistance in tumor cells. Therefore, it is important to design new Pt^{II} compounds with improved pharmacological properties and a broader range of anticancer activity.

On the other hand, it is known that polyamines play an important role in the syntheses of nucleic acids and protein, in the structure of the cell membrane, and in the modulation of neurophysiological function in mammalian systems (Morgan, 1999). Numerous derivatives and analogs of the biogenic polyamines spermidine [*N*-(3-aminopropyl)butane-3,4-diamine, spd] and spermine [*N*,*N*′-bis(3-aminopropyl)butane-1,4-diamine or 4,9-diazadodecane-1,12-diamine, spn] have been synthesized with the aim of generating a new type of anticancer drug (Seiler, 2005). The Pt^{II} or Pd^{II} complexes of these ligands have also been synthesized, their anticancer properties tested (Teixeira *et al.*, 2004; Marques *et al.*, 2002; McGregor *et al.*, 2002; Hegmans *et al.*, 2001; Amo-Ochoa *et al.*, 1996; Navarro-Ranninger *et al.*, 1992, 1994) and their crystal structures analyzed (Codina *et al.*, 1999). Among them, Pt^{II} complexes of spn have been investigated for their antiproliferative and cytotoxic effects, and have been demonstrated to display irreversible anticancer properties against Hera and HSC-3 cell lines, and growth inhibition properties against THP-1 and MOLT-3 cell lines (Teixeira *et al.*, 2004).





The Pt^{II} and Pd^{II} complexes of propane-1,3-diamine (tn) have also been used as model anticancer agents to study the interaction with DNA (Akdi *et al.*, 2005; Alvarez-Valdes *et al.*, 2002; Marzilli *et al.*, 1980). In the present study, we report the crystal structures of the title compounds, namely $[PtCl_2(tn)]$, (I), $[PdCl_2(tn)]$, (II), and $[Pt_2Cl_4(spn)]$, (III).

Compounds (I) and (II) are isostructural (Fig. 1). In each complex, the M^{II} atom (Pt^{II} or Pd^{II}) and atom C2 of the tn ligand lie on a mirror plane. The metal atom is coordinated by two N atoms from the tn ligand and two Cl atoms, which form a slightly distorted *cis*-square coordination geometry. The M^{II} atom and the four coordinated atoms are coplanar [the r.m.s. deviation of the fitted atoms is 0.016 Å for (I) and 0.022 Å for

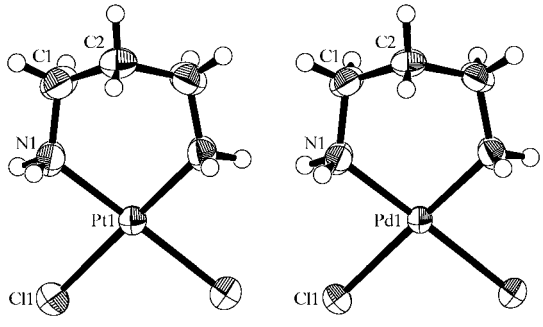


Figure 1
A view of the structures of (I) (left) and (II) (right), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level.

  DOI: 10.1107/S010827010600610X

(II)]. The metal atom and the tn ligand form a six-membered chelate ring, which adopts a chair conformation.

The M^{II}—Cl and M^{II}—N bond lengths in (I) and (II) (Tables 1 and 3) are comparable to those in $[PtCl_2(en)]$ and $[PdCl_2(en)]$ (en is ethylenediamine; Iball *et al.*, 1975), and in *cis*-$[PtCl_2(NH_3)_2]$ (Milburn & Truter, 1966) [M^{II}—Cl = 2.288 (8)–2.333 (9) Å and M^{II}—N = 1.95 (3)–2.08 (3) Å], although the five-membered chelate rings of the en ligands have smaller N—M^{II}—N bond angles [73 (2)–87 (2)°] than those of (I) and (II). The shortest intermolecular distance between the metal atoms is 3.646 (4) Å in (I) and 3.586 (3) Å in (II), which are considerably longer than those of the en complexes cited above (3.37–3.41 Å); this difference may be due to the steric hindrance of the propane groups of the tn ligand.

In the crystal packing of (I) and (II), centrosymmetrically related complexes are aligned along the *b* axis (Fig. 2). The crystal structures are stabilized by N—H···Cl hydrogen bonds (Tables 2 and 4) between the amine groups of the tn ligands and the Cl atoms of neighboring complexes along the *b* and *c* axes (Figs. 2 and 3), forming lattice-like networks.

In (III), the spn ligand coordinates to the two Pt^{II} atoms to form a binuclear complex (Fig. 4). Compound (III) is iso-

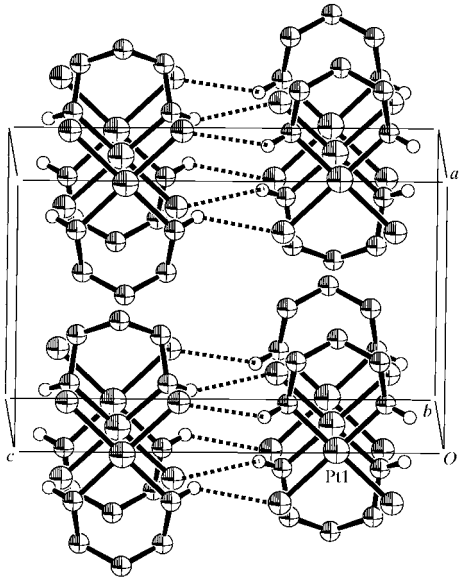


Figure 2
A view of the crystal packing of (I), showing the centrosymmetric stacking along the *b* axis. Dashed lines indicate N—H···Cl hydrogen bonds.

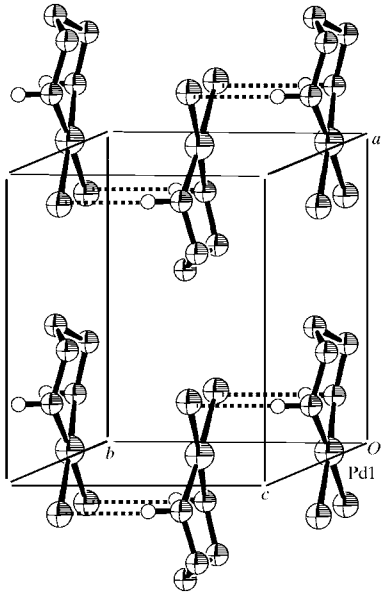


Figure 3
A view of the crystal packing of (II), showing the N—H···Cl hydrogen bonds along the *b* axis as dashed lines.

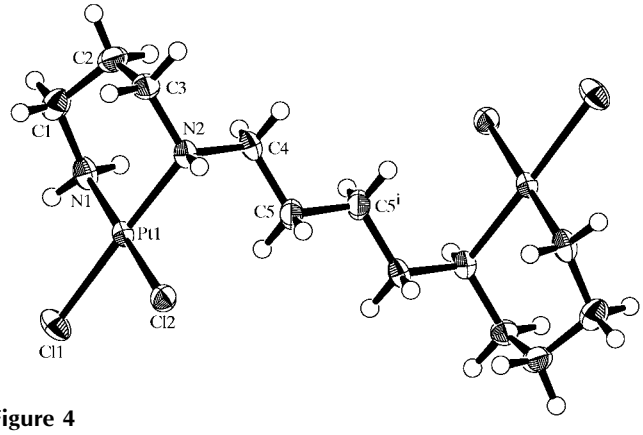


Figure 4
A view of the structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (vi) $-x, -y+1, -z+2$.]

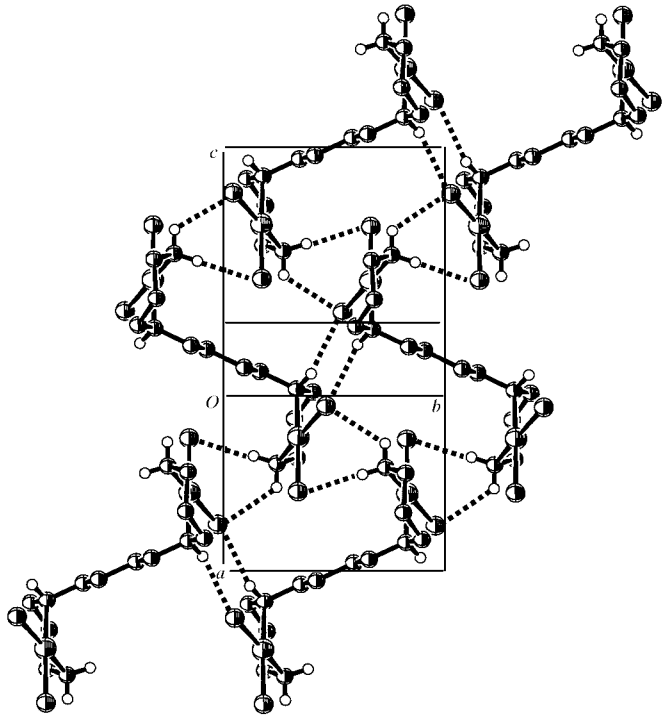


Figure 5
A view of the crystal packing of (III), showing the N—H···Cl hydrogen bonds as dashed lines.

structural with the corresponding Pd^{II} complex, *viz*. $[Pd_2Cl_4(spn)]$ (Codina *et al.*, 1999). A crystallographic inversion center is located at the middle of the butane chain of the spn ligand. The Pt^{II} atom is in a slightly distorted *cis*-square coordination geometry formed by two N and two Cl atoms. The Pt^{II} atom and the four coordinated atoms are coplanar (the r.m.s. deviation is 0.046 Å). The coordination bond lengths and bond angles (Table 5) are similar to those of (I). The Pt^{II} atom and the tn group of the spn ligand form a six-membered chelate ring, which adopts a chair form as in (I) and (II). However, the dihedral angles of the Pt1/N1/N2 and C1/C2/C3 planes with respect to the N1/C1/N2/C3 plane are 46.4 (2) and 57.9 (4)°, respectively, indicating a less flattened conformation than those in (I) and (II). The corresponding dihedral angles are 24.3 (2) and 62.1 (5)° for (I), and 22.2 (1) and 62.1 (3)° for (II), respectively. In addition, the torsion angles of the chelate rings (Table 5) show an unsymmetrical conformation around the Pt^{II} atom.

In the crystal packing of (III), there are intermolecular N—H···Cl hydrogen bonds (Table 6) between the primary amine groups of the spn ligand and the Cl atoms of neighboring complexes along the *b* axis, and between the secondary amine groups and the Cl atoms of neighboring complexes along the *c* axis, forming a three-dimensional network (Fig. 5).

Experimental

For the preparation of (I), propane-1,3-diamine dihydrochloride (5 mg) was dissolved in 90% (*v*/*v*) dimethylformamide (DMF)/water (5 ml) and added to a solution of $K_2[PtCl_4]$ (14 mg) in DMF (0.1 ml). Colorless crystals appeared after three months on evaporation of this mixture. For the preparation of (II), propane-1,3-diamine dihydrochloride (5 mg) was dissolved in water (5 ml), and $PdCl_2$ (6 mg) in a 2 *M* NaCl aqueous solution (0.1 ml) and $AgNO_3$ (5.8 mg) dissolved in water (0.1 ml) were added. Brown needle-like crystals appeared from this mixture within one week. For the preparation of (III), spermine phosphate (5 mg) dissolved in a 50% (*v*/*v*) DMF/1 *M* NaCl aqueous solution (5 ml) was added to $K_2[PtCl_4]$ (2.6 mg) dissolved in water (0.1 ml). Colorless platelet crystals appeared after five months on evaporation of this mixture.

Compound (I)

Crystal data

$[PtCl_2(C_3H_{10}N_2)]$
M_r = 340.11
Orthorhombic, *Pbcm*
a = 8.36 (1) Å
b = 7.292 (8) Å
c = 12.950 (5) Å
V = 789.5 (13) Å^3
Z = 4
D_x = 2.861 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4958 reflections
θ = 3.1–27.4°
μ = 18.36 mm^{-1}
T = 296 K
Platelet, colorless
0.20 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.152, T_{max} = 0.401
7821 measured reflections
945 independent reflections
573 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.020
θ_{max} = 27.4°
h = −10 → 10
k = −9 → 9
l = −16 → 16

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.042
S = 1.10
945 reflections
41 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.2145P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

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

Pt1—N1	2.040 (3)	Pt1—Cl1	2.3295 (17)
N1—Pt1—N1^{i}	93.0 (2)	Cl1—Pt1—Cl1^{i}	92.99 (9)
N1—Pt1—Cl1	86.98 (13)		
N1^{i}—Pt1—N1—C1	28.3 (4)	Pt1—N1—C1—C2	−50.5 (5)

Symmetry code: (i) $x, y, -z+\frac{1}{2}$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1^{ii}	0.90	2.65	3.369 (5)	138
N1—H1*B*···Cl1^{iii}	0.90	2.48	3.349 (6)	164

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

Compound (II)

Crystal data

$[PdCl_2(C_3H_{10}N_2)]$
M_r = 251.45
Orthorhombic, *Pbcm*
a = 8.386 (7) Å
b = 7.167 (5) Å
c = 12.88 (1) Å
V = 774.1 (10) Å^3
Z = 4
D_x = 2.158 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5562 reflections
θ = 3.2–27.4°
μ = 3.00 mm^{-1}
T = 296 K
Needle, brown
0.15 × 0.05 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.645, T_{max} = 0.861
7656 measured reflections
923 independent reflections
650 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.022
θ_{max} = 27.5°
h = −10 → 10
k = −9 → 8
l = −16 → 16

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

Pd1—N1	2.036 (2)	Pd1—Cl1	2.3296 (15)
N1—Pd1—N1^{i}	93.52 (13)	N1—Pd1—Cl1^{i}	177.09 (5)
N1—Pd1—Cl1	86.42 (9)	Cl1—Pd1—Cl1^{i}	93.49 (8)
N1^{i}—Pd1—N1—C1	26.0 (2)	Pd1—N1—C1—C2	−49.0 (2)

Symmetry code: (i) $x, y, -z+\frac{1}{2}$.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.043$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
923 reflections	$\Delta\rho_{min} = -0.60$ e Å^{-3}
41 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1^{ii}	0.90	2.61	3.359 (3)	141
N1—H1B···Cl1^{iii}	0.90	2.47	3.334 (3)	162

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

Compound (III)

Crystal data

$[Pt_2Cl_4(C_{10}H_{26}N_4)]$	$D_x = 2.657$ Mg m^{-3}
$M_r = 734.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8101 reflections
$a = 8.86$ (1) Å	$\theta = 3.1$–$27.5°$
$b = 8.018$ (6) Å	$\mu = 15.80$ mm^{-1}
$c = 12.93$ (1) Å	$T = 123$ K
$\beta = 92.09$ (4)°	Platelet, colorless
$V = 917.9$ (14) Å^3	0.10 × 0.10 × 0.05 mm
$Z = 2$	

Data collection

Rigaku R-AXIS RAPID diffractometer	2105 independent reflections
	1725 reflections with $F^2 > 2\sigma(F^2)$
ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$
	$h = -11 \rightarrow 11$
$T_{min} = 0.089$, $T_{max} = 0.455$	$k = -10 \rightarrow 10$
9030 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.3492P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.029$	
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 2.61$ e Å^{-3}
2105 reflections	$\Delta\rho_{min} = -2.71$ e Å^{-3}
92 parameters	
H-atom parameters constrained	

Table 5
Selected geometric parameters (Å, °) for (III).

Pt1—N1	2.013 (5)	Pt1—Cl1	2.310 (3)
Pt1—N2	2.047 (5)	Pt1—Cl2	2.312 (2)
N1—Pt1—N2	91.0 (2)	N2—Pt1—Cl2	86.94 (15)
N1—Pt1—Cl1	88.44 (14)	Cl1—Pt1—Cl2	93.69 (7)
N2—Pt1—N1—C1	−53.6 (4)	Pt1—N1—C1—C2	65.1 (5)
N1—Pt1—N2—C3	49.7 (3)	Pt1—N2—C3—C2	−60.3 (5)

All H atoms were located in difference Fourier maps, and were then placed at idealized positions and treated as riding, with C—H distances of 0.97 Å, N—H distances for the primary amine groups of 0.90 Å and for the secondary amine groups of 0.91 Å, and U_{iso}(H) values of $1.2U_{eq}$(carrier atom).

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1^{iv}	0.90	2.48	3.376 (5)	177
N1—H1B···Cl2^{iv}	0.90	2.78	3.261 (5)	115
N2—H2···Cl2^{v}	0.91	2.58	3.309 (6)	138

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

For all compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Watkin *et al.*, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) for (I) and (II), and *SHELXS97* (Sheldrick, 1997) for (III); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1247). Services for accessing these data are described at the back of the journal.

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