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Key indicators

[Bis(diphenylphosphino)amine-κ^2P,P'][1,3-bis(diphenylphosphino)propane-κ^2P,P']platinum(II) dichloride dichloromethane solvate

The title complex, $[Pt(C_{24}H_{21}NP_2)(C_{27}H_{26}P_2)]Cl_2 \cdot CH_2Cl_2$ or $[Pt(dppa)(dppp)]Cl_2 \cdot CH_2Cl_2$, where dppa is bis(diphenylphosphino)amine and dppp is 1,3-bis(diphenylphosphino)propane, has two different chelate rings. The Pt^{II} atom has a distorted square-planar geometry. The six-membered chelate ring of dppp has a chair conformation. There is a hydrogen bond between the dppa N—H group and a Cl^- counter-ion.

Comment

Diphosphinoamine ligands have proved very versatile, because substituents on both P and N atoms can be varied, introducing changes in the P—N—P bond angle and the conformation around the phosphorus centres (Balakrishna *et al.*, 1994). Diphosphinoamines can bind to metals in several modes, namely monodentate, bidentate, chelating and bridging. Bis(diphenylphosphino)amine (dppa) has generated much interest since its discovery. One or two phosphorus atoms of dppa can be readily oxidized by oxygen, sulfide and selenium, to give $[Ph_2P(E)NHP(E')Ph_2]$ and $[Ph_2P(E)NHPPh_2]$ (E or E'= O, S and Se). Several metal complexes of dppa and these derivatives have been prepared (Uson *et al.*, 1989; Browning *et al.*, 1998; Smith *et al.*, 1996). All of these ligands are readily deprotonated to give $[Ph_2PNPPh_2]^-$, $[Ph_2P(E)NP(E')Ph_2]^-$ and $[Ph_2P(E)NPPh_2]^-$ ligands which coordinate with the metals to give chelate compounds. The chemistry of these imidodiphosphinate anions have been reported extensively (Balazs *et al.*, 1999; Slawin *et al.*, 1994; Novasad *et al.*, 1999). They are widely used in catalysis, metal extraction and bioinorganic chemistry (Ly & Woollins, 1998). There are only a limited number of studies in the literature related to the mixed bis(chelate) complexes which contain dppa and diphosphine ligands (Balakrishna *et al.*, 1994; Bhattacharyya *et al.*, 1993).

(I)
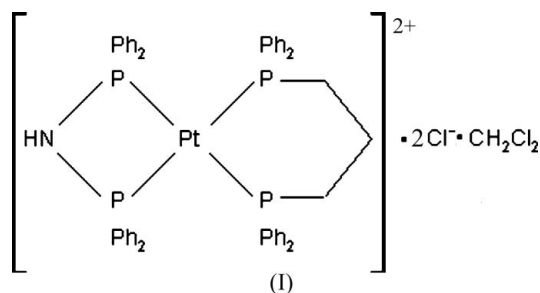
We describe here the preparation and characterization of a new ionic mixed platinum complex which has dppa and 1,3-bis(diphenylphosphino)propane (dppp) chelating ligands. The reaction of $PtCl_2$(dppp) with dppa (molar ratio 1:1) in CH_2Cl_2 yielded $[Pt(dppa)(dppp)]Cl_2 \cdot CH_2Cl_2$, (I). A perspective view
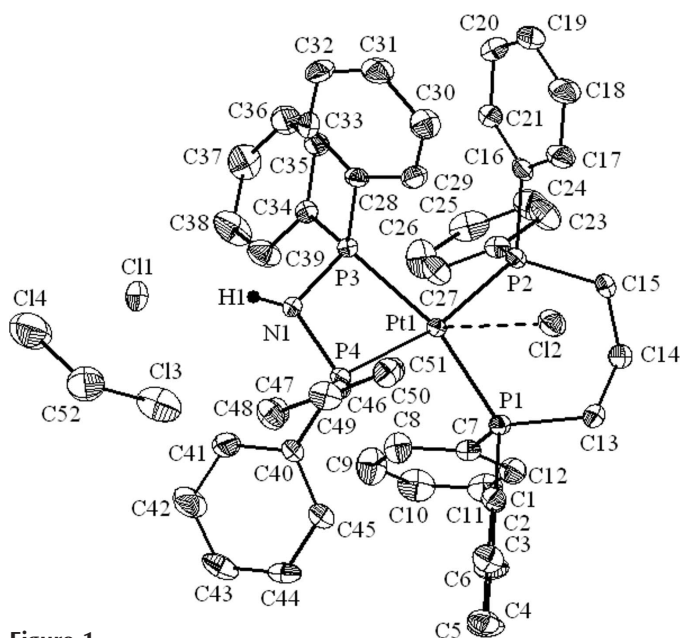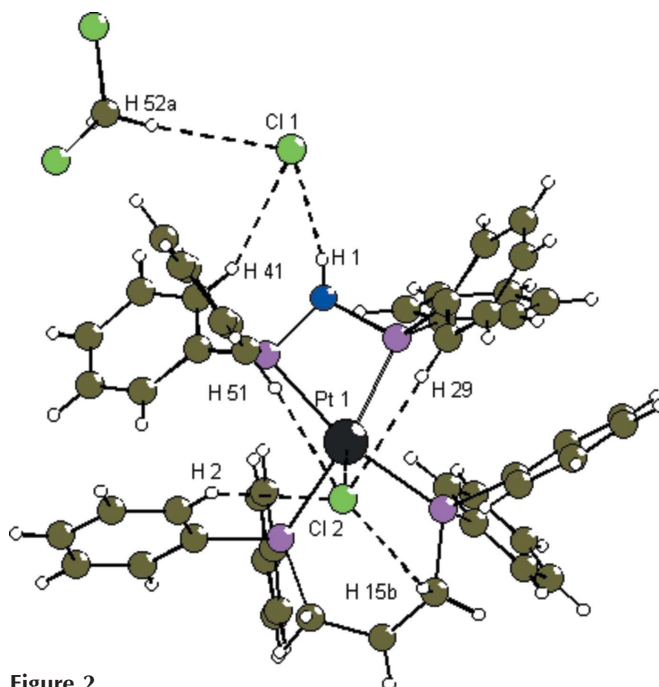
Figure 1
A perspective view of complex (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

of complex (I) is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

In complex (I), the dppa ligand is coordinated to Pt in a bidentate manner. The Pt is coordinated by four P atoms of dppp and dppa ligands in a distorted square-planar arrangement with *trans* P1—Pt1—P3 [161.70 (6)°] and P2—Pt1—P4 [167.56 (6)°] angles. Within the dppa chelate ring the Pt—P distances are slightly different from each other [Pt1—P3, 2.3161 (15) Å and Pt1—P4, 2.3431 (15) Å]. These values are longer than those of the relatively strain-free five-membered chelate of PtCl2[Ph2PN(Et)P(S)Ph2] [2.197 (2) Å; Balakrishna *et al.*, 1993]. The Pt—P bond lengths of dppp are Pt1—P1 = 2.3421 (16) Å and Pt1—P2 = 2.3288 (16) Å. These values are consistent with the literature (Güneş *et al.*, 2001).

The considerable strain in the PtP2N ring of (I) is also reflected in the P3—Pt1—P4 bond angle of 69.10 (5)°. This value is consistent with those of chelate complexes [Cu(CN)(dppa)PPh3]·CH3OH [71.4 (1)°; Ellermann *et al.*, 1992] and Cp[Ru(dppa)Cl] [69.12 (3)°; Geicke *et al.*, 1998]. The P3—N1—P4 bond angle [104.8 (3)°] is smaller than the angle in free bis(phosphino)amine ligands, which have a trigonal environment (Bhattacharyya *et al.*, 1996; Rösler *et al.*, 1998). The four-membered chelate ring of the complex (I) deviates from planarity with the torsion angles of N1—P4—Pt1—P3 = 7.42 (19)°; N1—P3—Pt1—P4 = −7.42 (19)°. This result supports the large upfield shift of dppa on complexation [δ(P) = 7.5 p.p.m. for complex (I), δ(P) = 42.9 p.p.m. for free dppa]. The P—N bond length [1.668 (5) Å] reflects the partial double-character of this bond.

The resulting six-membered Pt1/P1/P2/C13–C15 ring in complex (I) has a chair conformation, with Pt1—P1—C13—C14 and Pt1—P2—C15—C14 torsion angles of −52.8 (5)° and 62.1 (5)°, respectively.

Figure 2
Intermolecular hydrogen-bonding interactions (dashed lines) of complex (I).

The crystal structure of this complex includes one molecule of CH2Cl2 per complex molecule. The N-bound H atom in the dppa ligand is hydrogen bonded [2.33 (7) Å] to the Cl1 ion. This same chloride ion is situated 2.81 Å from the H atom of the solvent molecule. There are other inter- and intramolecular interactions, summarized in Table 2 and shown in Fig. 2. The other Cl⁻ ion (Cl2) interacts with Pt1 at a distance of 3.3134 (2) Å in a direction approximately perpendicular to the coordination plane.

Experimental

The reaction was carried out under an argon atmosphere by use of Schlenk techniques. All solvents were dried prior to use. A solution of dppa (0.12 g, 0.30 mmol) in CH2Cl2 (15 ml) was added to a solution of PtCl2dppp (0.20 g, 0.30 mmol) in CH2Cl2 (15 ml) and stirred for 24 h at room temperature. The solution was concentrated and then Et2O was added. Cooling of the solution to 273 K gave a colourless microcrystalline product. The product was recrystallized from CH2Cl2/Et2O. Yield 58%, m.p. 533–537 K. Analysis found: C 55.10, H 4.32, P 12.47%; calculated for C52H49Cl4NP4Pt: C 54.32, H 4.27, P 10.79%. IR: 3215 (νN–H), 886 (NP—N) cm⁻¹; ³¹P{¹H} NMR (CDCl3, p.p.m.): δ −13.6 [¹J(Pt—P) = 2441 Hz (dppp)], 7.5 [¹J(Pt—P) = 2137 Hz (dppa)].

Crystal data

[Pt(C24H21NP2)(C27H26P2)]Cl2·CH2Cl2	$D_x = 1.572$ Mg m⁻³
$M_r = 1148.69$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3963 reflections
$a = 12.2069 (11)$ Å	$\theta = 2.2–19.7°$
$b = 22.302 (2)$ Å	$\mu = 3.28$ mm⁻¹
$c = 17.8300 (16)$ Å	$T = 297 (2)$ K
$\beta = 91.049 (2)°$	Block, colourless
$V = 4853.3 (8)$ Å³	0.16 × 0.16 × 0.08 mm
$Z = 4$	

The maximum and minimum residual densities are located 0.89 Å from atom Pt1 and 1.04 Å from P4, respectively.. The H atoms were positioned geometrically and refined with a riding model, with C—H = 0.93–0.97 Å and with U_{iso} constrained to $1.2U_{eq}(C)$. The hydrogen atom bonded to N1 was freely refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

Data collection

Bruker SMART CCD area-detector diffractometer	9916 independent reflections
φ and ω scans	8258 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker 2001)	$R_{int} = 0.074$
	$\theta_{max} = 26.4°$
$T_{min} = 0.622$, $T_{max} = 0.779$	$h = -15 \rightarrow 15$
38986 measured reflections	$k = -27 \rightarrow 27$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 2.9082P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{max} = 0.015$
$S = 1.14$	$\Delta\rho_{max} = 1.33$ e Å^{-3}
9916 reflections	$\Delta\rho_{min} = -1.76$ e Å^{-3}
563 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

N1—P3	1.668 (5)	P2—Pt1	2.3288 (16)
N1—P4	1.668 (5)	P3—Pt1	2.3161 (15)
P1—Pt1	2.3421 (16)	P4—Pt1	2.3431 (15)
P3—N1—P4	104.8 (3)	P3—Pt1—P4	69.10 (5)
P3—Pt1—P2	98.48 (6)	P2—Pt1—P4	167.56 (6)
P3—Pt1—P1	161.70 (6)	P1—Pt1—P4	102.83 (6)
P2—Pt1—P1	88.78 (6)		
C14—C13—P1—Pt1	−52.8 (5)	N1—P3—Pt1—P4	−7.42 (19)
C14—C15—P2—Pt1	62.1 (5)	N1—P4—Pt1—P3	7.42 (19)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl1^i	0.79 (7)	2.33 (7)	3.101 (5)	167 (7)
C2—H2$\cdots$Cl2	0.93	2.77	3.601 (6)	149
C15—H15$B\cdots$Cl2	0.97	2.76	3.497 (7)	133
C41—H41$\cdots$N1	0.93	2.62	3.064 (9)	110
C42—H42$\cdots$Cl1^{ii}	0.93	2.78	3.622 (9)	151
C51—H51$\cdots$Cl2	0.93	2.59	3.520 (6)	175
C52—H52$A\cdots$Cl1^{iii}	0.97	2.81	3.763 (10)	169

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

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