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Key indicators

Single-crystal X-ray study  
 T = 297 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.020 \text{ \AA}$   
 R factor = 0.076  
 wR factor = 0.162  
 Data-to-parameter ratio = 17.4

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

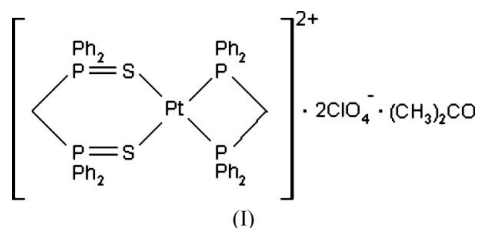
[Bis(diphenylphosphino)methane- $\kappa^2P,P'$ ]-  
 [bis(diphenylthiophosphiny)methane- $\kappa^2S,S'$ ]-  
 platinum(II) bis(perchlorate) acetone solvate

The title complex,  $[\text{Pt}(\text{C}_{25}\text{H}_{22}\text{P}_2)(\text{C}_{25}\text{H}_{22}\text{P}_2\text{S}_2)](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_6\text{O}$  or  $[\text{Pt}(\text{dppm})(\text{dppmS}_2)](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_6\text{O}$ , where  $\text{dppmS}_2$  is bis(diphenylthiophosphiny)methane and  $\text{dppm}$  is bis(diphenylphosphino)methane, is the first example of a platinum(II) complex containing both  $\text{dppm}$  and  $\text{dppmS}_2$  ligands. In the cation, the  $\text{dppm}$  ligand forms a non-planar four-membered chelate ring, while the  $\text{dppmS}_2$  ligand forms a six-membered chelate ring with twist-boat conformation.

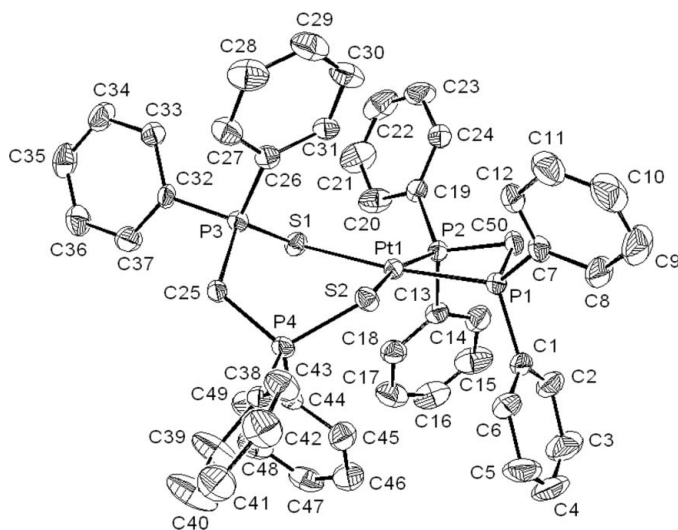
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Comment

There has been considerable interest in studying metal complexes with bidentate tertiary phosphine chalcogenides. Complexes have been studied mainly with the bidentate ligands  $\text{Ph}_2\text{P}(E)(\text{CH}_2)_n\text{P}(E)\text{Ph}_2$  ( $E = \text{S}, \text{O}$  and  $\text{Se}; n = 1, 2$  and  $3$ ). The derivatives of  $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$  exhibit monodentate  $S$  and bidentate or bridging  $S,S$  coordination of the neutral ligand, and bidentate  $S,S$  and  $C,S$  coordination of the monoanion. A large number of complexes of different metals have been reported for these chalcogenide ligands (Browning *et al.*, 1992; Berry *et al.*, 1992; Schumann, 1987; Bond *et al.*, 1989). The lability of the chalcogen-metal bonds can give rise to dynamic processes and thus renders these ligands appropriate for catalytic applications (Alvarez *et al.*, 1998). As a matter of fact, the complexes of bis(phosphine chalcogenide) ligands with 'soft' transition metals [rhodium(I), palladium(II) and ruthenium(II)] are found to be effective catalysts. For example, the complexes of rhodium are used for hydroformylation of alkenes and aldehydes (Choopani *et al.*, 1995; Abu-Gnim & Amer, 1994). The rhodium complex of the diphenylphosphino-substituted compound  $\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$  was found to be an effective catalyst for carbonylation of methanol (Wegman *et al.*, 1987). The palladium complex of the  $\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$  ligand has been tested as catalyst in the alternating copolymerization of ethylene and carbon monoxide (Suranna *et al.*, 2000).



There are only a limited number of studies in the literature related to mixed bis(chelate) complexes that contain bis(diphenylthiophosphiny)methane ( $\text{dppmS}_2$ ) and diphosphine ligands (İrişli & Alkan, 2004; İrişli & Yanar, 2005).



**Figure 1**

A perspective view of the cation in (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms, the solvent molecule and  $\text{ClO}_4^-$  anions have been omitted for clarity.

We report here the crystal structure of the first example of a mixed bis(chelate) platinum(II) complex containing the dppmS<sub>2</sub> and diphosphine neutral ligands, in which dppmS<sub>2</sub> coordinates to the metal in a bidentate manner. The reaction of  $\text{PtCl}_2\text{dppm}$  [dppm is bis(diphenylphosphino)methane] with dppmS<sub>2</sub> (molar ratio 1:1) in  $\text{CH}_2\text{Cl}_2/\text{acetone}$  in the presence of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  gives  $[\text{Pt}(\text{dppmS}_2)(\text{dppm})](\text{ClO}_4)_2 \cdot (\text{CH}_3)_2\text{CO}$ , (I). A perspective view of (I) is shown in Fig. 1. Selected geometric parameters are listed in Table 1.

In complex (I), Pt is coordinated by two P atoms of the dppm ligand and two S atom of the dppmS<sub>2</sub> ligand in a distorted square-planar arrangement with *trans* P1–Pt1–S1 [165.03 (8)°] and P2–Pt1–S2 [166.33 (8)°]. In the dppm chelate ring, the Pt–P bond lengths are slightly different from each other [Pt1–P1 = 2.251 (2) Å; Pt1–P2 2.260 (2) Å]. These values are shorter than that of 2.330 Å found in  $[\text{Pt}(\text{dppm})(\text{dppp})]\text{Cl}_2$  (Güneş *et al.*, 2001). The shortening of the mean Pt–P distance in (I) may be related to the different bidentate bite angles in the two complexes {72.51 (9)° for (I) and 69.84 (14)° for  $[\text{Pt}(\text{dppm})(\text{dppp})]\text{Cl}_2$ }. Thus, in the relatively strain-free five-membered chelate ring of  $\text{PtCl}_2\text{PPh}_2\text{N}(\text{Ph})\text{P}(\text{S})\text{Ph}_2 \cdot \text{H}_2\text{O}$  (Balakrishna *et al.*, 1993), the Pt–P bond length is 2.197 Å (the S–Pt–P angle is 90.49°). The  $\text{PtP}_2\text{C}$  four-membered chelate ring deviates from planarity, as indicated by the values of the torsion angles C50–P1–Pt1–P2 [16.4 (3)°] and C50–P2–Pt1–P1 [–16.5 (3)°].

The six-membered dppmS<sub>2</sub> chelate ring (Pt1/S1/P3/C25/P4/S2) has a twist-boat conformation, with Pt1–S1–P3–C25 and Pt1–S2–P4–C25 torsion angles of –69.2 (3) and –79.3 (3)°, respectively. The ring-puckering parameters for this ring [ $\theta = 86.22$  (19)° and  $\Phi = 275.5$  (3)° (Cremer & Pople, 1975)] support a twist-boat conformation. The Pt–S distances are slightly different from each other [Pt1–S1 = 2.394 (2) Å and Pt1–S2 = 2.407 (2) Å]. These values are longer than that of 2.043 Å observed in *trans*- $[\text{PtCl}(\text{PEt}_3)]_2[\text{Ph}_2\text{PCH}_2\text{P}(\text{S})-$

$\text{Bu}'_2]\text{ClO}_4$  (Berry *et al.*, 1988), where the shortening may be ascribed to the *trans* influence of the  $\text{Cl}^-$  anion. The Pt–S bond lengths are comparable to the value of 2.390 Å found in  $[\text{PtCl}(\text{PEt}_3)]_2[\text{Ph}_2\text{P}(\text{S})_2\text{CH}]$  (Browning *et al.*, 1983), in which the dppmS<sub>2</sub> ligand is present as an anion.

In the simple phosphorus compound  $\text{P}_4\text{S}_{10}$ , the P–S bond lengths are 2.097 Å (single) and 1.908 Å (double) (Berry *et al.*, 1988). Thus, the observed P3–S1 and P4–S2 lengths [2.021 (3) Å and 2.023 (3) Å, respectively] are rather closer to single bond than double bond lengths.

In the crystal packing, some C–H···O interactions are present, involving H atoms of the phenyl rings and O atoms of the  $\text{ClO}_4^-$  anion and acetone solvent molecule (Table 2).

## Experimental

The title complex was prepared according to the method given in the literature (İrişli & Alkan, 2004). Recrystallization from acetone/diethyl ether yielded colourless crystals suitable for X-ray analysis.

### Crystal data

$[\text{Pt}(\text{C}_{25}\text{H}_{22}\text{P}_2)(\text{C}_{25}\text{H}_{22}\text{P}_2\text{S}_2)](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_6\text{O}$	$Z = 4$
$M_r = 1284.92$	$D_x = 1.564 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 20.888$ (2) Å	Cell parameters from 6151 reflections
$b = 11.8633$ (14) Å	$\theta = 2.3\text{--}25.1^\circ$
$c = 23.109$ (3) Å	$\mu = 2.92 \text{ mm}^{-1}$
$\beta = 107.686$ (2)°	$T = 297$ (2) K
$V = 5455.7$ (11) Å <sup>3</sup>	Block, colourless
	$0.45 \times 0.39 \times 0.34 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	11149 independent reflections
$\varphi$ and $\omega$ scans	10211 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.300$ , $T_{\text{max}} = 0.371$	$\theta_{\text{max}} = 26.4^\circ$
42618 measured reflections	$h = -25 \rightarrow 26$
	$k = -14 \rightarrow 14$
	$l = -28 \rightarrow 28$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 42.6288P]$
$R[F^2 > 2\sigma(F^2)] = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.162$	$(\Delta\rho)_{\text{max}} = 0.002$
$S = 1.25$	$\Delta\rho_{\text{max}} = 2.95 \text{ e } \text{Å}^{-3}$
11149 reflections	$\Delta\rho_{\text{min}} = -2.96 \text{ e } \text{Å}^{-3}$
642 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

Pt1–P1	2.251 (2)	Pt1–S2	2.407 (2)
Pt1–P2	2.260 (2)	P3–S1	2.021 (3)
Pt1–S1	2.394 (2)	P4–S2	2.023 (3)
P1–Pt1–P2	72.51 (9)	P1–Pt1–S2	93.96 (8)
P1–Pt1–S1	165.03 (8)	P2–Pt1–S2	166.33 (8)
P2–Pt1–S1	92.69 (8)	S1–Pt1–S2	100.90 (8)
C25–P3–S1–Pt1	–69.2 (3)	C25–P4–S2–Pt1	–79.3 (3)
P2–Pt1–P1–C50	16.4 (3)	P1–Pt1–P2–C50	–16.5 (3)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C17—H17···O3 <sup>i</sup>	0.93	2.59	3.34 (2)	137
C24—H24···O7 <sup>ii</sup>	0.93	2.49	3.26 (2)	140
C27—H27···O1 <sup>iii</sup>	0.93	2.45	3.376 (17)	176
C28—H28···O9 <sup>iv</sup>	0.93	2.41	3.27 (3)	153
C37—H37···O4	0.93	2.51	3.284 (18)	141
C43—H43···S2	0.93	2.85	3.335 (12)	114
C50—H50B···O6 <sup>iii</sup>	0.97	2.59	3.433 (18)	145
C53—H53A···O2	0.96	2.57	3.21 (4)	124
C53—H53C···O4 <sup>i</sup>	0.96	2.50	3.22 (4)	131

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

The maximum and minimum residual densities are located at 0.92 Å from Pt1 and 1.23 Å from S1, respectively. The H atoms were positioned geometrically and refined with a riding model, with C—H = 0.93–0.97 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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

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## References

- Abu-Gnim, C. & Amer, I. (1994). *J. Chem. Soc. Chem. Commun.* **1**, 115–117.
- Alvarez, B., Fernandez, E. J., Gimeno, M. C., Jones, P. G., Laguna, A. & Lopez-de-Luzuriaga, J. M. (1998). *Polyhedron*, **17**, 2029–2035.
- Balakrishna, M. S., Klein, R., Uhlenbrock, S., Pinkerton, A. A. & Cavell, R. G. (1993). *Inorg. Chem.* **32**, 5676–5681.
- Berry, D. E., Browning, J., Dixon, K. R. & Hiltz, R. W. (1988). *Can. J. Chem.* **66**, 1272–1282.
- Berry, D. E., Browning, J., Dixon, K. R., Hiltz, R. W. & Pidcock, A. (1992). *Inorg. Chem.* **31**, 1479–1487.
- Bond, A. M., Colton, R., Ebner, J. & Ellis, S. R. (1989). *Inorg. Chem.* **28**, 4509–4516.
- Browning, J., Bushnell, G. W., Dixon, K. R. & Hiltz, R. W. (1992). *J. Organomet. Chem.* **434**, 241–252.
- Browning, J., Bushnell, G. W., Dixon, K. R. & Pidcock, A. (1983). *Inorg. Chem.* **22**, 2226–2228.
- Bruker (2001). *SAINTE* (Version 6.26a), *SMART* (Version 5.625), *SHELXTL* (Version 6.12) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Choopani, S., Davis, R., Smith, K. & Tebby, J. (1995). *XIIIth International Conference on Phosphorus Chemistry*, ICPC, p. 223, Jerusalem, Israel.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Güneş, B., Nergiz, E., Ide, S., Şahin, E. & İrişli, S. (2001). *Acta Cryst.* **C57**, 1282–1284.
- İrişli, S. & Alkan, L. (2004). *Synth. React. Inorg. Met.-Org. Chem.* **34**, 1817–1823.
- İrişli, S. & Yanar, S. (2005). *Polyhedron*. In the press. [Paper reference POLY 5853].
- Schumann, H. (1987). *J. Organomet. Chem.* **320**, 145–162.
- Suranna, G. P., Mastroilli, P., Nobile, C. F. & Keim, W. (2000). *Inorg. Chim. Acta*, **305**, 151–156.
- Wegman, R. W., Abatjoglou, A. G. & Harrison, A. M. (1987). *J. Chem. Soc. Chem. Commun.* **24**, 1891–1892.