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[Bis(2-diphenylphosphinoethyl) sulfide-κ^3P,S,P'](triphenylphosphine-κP)platinum(II) diperchlorate acetone solvate

Lars V. Andreasen,[a] Alan Hazell[b]* and Ole Wernberg[a]

[a]Department of Chemistry, University of Southern Denmark, Odense Campus, Campusvej 55, DK-5230 Odense M, Denmark, and [b]Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark
Correspondence e-mail: ach@chem.au.dk

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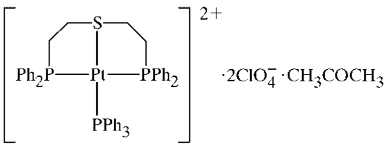
In the title compound, $[Pt(C_{18}H_{15}P)(C_{28}H_{28}P_2S)](ClO_4)_2\cdot C_3H_6O$ or $[Pt(PPh_3)(PSP)](ClO_4)_2\cdot CH_3COCH_3$, where PSP is the potentially tridentate chelate ligand bis(2-diphenylphosphinoethyl) sulfide, all three donor groups of the PSP ligand are coordinated to the central Pt atom, with Pt—P = 2.310 (1) Å and Pt—S = 2.343 (1) Å. The fourth coordination site is occupied by the P donor of the triphenylphosphine ligand [Pt—P = 2.289 (1) Å]. The complex cation has exact mirror symmetry, with the S atom, the Pt atom and the P atom of the PPh_3 ligand in the mirror plane. The Pt atom has a distorted square-planar coordination geometry. A π–π interaction is present between the phenyl rings of the PPh_3 ligand and the terminal $-PPh_2$ group of the PSP chelate.

Comment

A range of platinum metal complexes of phosphinothioether chelate ligands have been found to serve as efficient catalysts in homogeneous hydrogenation, carbonylation and asymmetric allylic alkylation reactions (Bayón *et al.*, 1999; Dilworth *et al.*, 1995; Sugama *et al.*, 2001). In addition, the synthesis and characterization of Pt^{II} complexes of mixed *P*,*S*-polydentate chelate ligands, which are acyclic or macrocyclic ligands, have attracted significant attention (Andreasen *et al.*, 1999; Connolly *et al.*, 1997; Kyba *et al.*, 1987; Siah *et al.*, 1994). The systematic geometric variation of the respective P and S donors within these ligands has provided insight into the *trans* influence of chelated phosphines on chelated thioethers and *vice versa*.

In our current investigation of the relationship between structure and reactivity of tridentately chelated Pt^{II} complexes, several complexes of the tridentate phosphinothioether chelate ligand bis(2-diphenylphosphinoethyl) sulfide (PSP) have been prepared and characterized (Andreasen *et al.*, 1999; Andreasen, 2000). Two of these Pt^{II}–PSP complexes, *i.e.* $[Pt(PSP)Cl]ClO_4$ and $[Pt(PSP)I]I$, have been characterized by X-ray diffraction (Andreasen *et al.*, 1999). We present here the X-ray structure of a third such complex, the title compound, (I).



$$[Pt(PPh_3)(PSP)]^{2+}\cdot 2ClO_4^-\cdot CH_3COCH_3$$

(I)

Complex (I) contains PPh_3 *trans* to the central thioether chelate donor; the molecular structure of the cation of (I) is shown in Fig. 1. The three donors of the PSP chelate ligand, namely the S and the two tertiary phosphine P atoms, are all coordinated to the Pt atom, forming two five-membered chelate rings, with the PPh_3 donor occupying the fourth coordination site. The $[Pt(PPh_3)(PSP)]^{2+}$ cation has exact mirror symmetry, with atoms S and Pt, and P1 of the PPh_3 ligand in the mirror plane.

The coordination sphere of the $[Pt(PPh_3)(PSP)]^{2+}$ cation is tetrahedrally distorted from planar geometry, with the two PSP P atoms (P2 and P2′) deviating by 0.075 Å on one side of the least-squares plane through the S- and P-donor atoms, while the remaining two donors, *i.e.* the PSP S and the PPh_3 P1 atoms, are located on the opposite side of this plane at 0.085 and 0.064 Å, respectively. The Pt atom is 0.04 Å from the plane on the same side as the S and PPh_3 P atoms. This tetrahedral distortion is, however, less pronounced than that in the $[PtCl(PSP)]^+$ and $[PtI(PSP)]^+$ complexes.

In addition to the two ClO_4^- counter-anions, which are centred 4.950 (2) and 6.422 (2) Å from the closest Pt atom, a

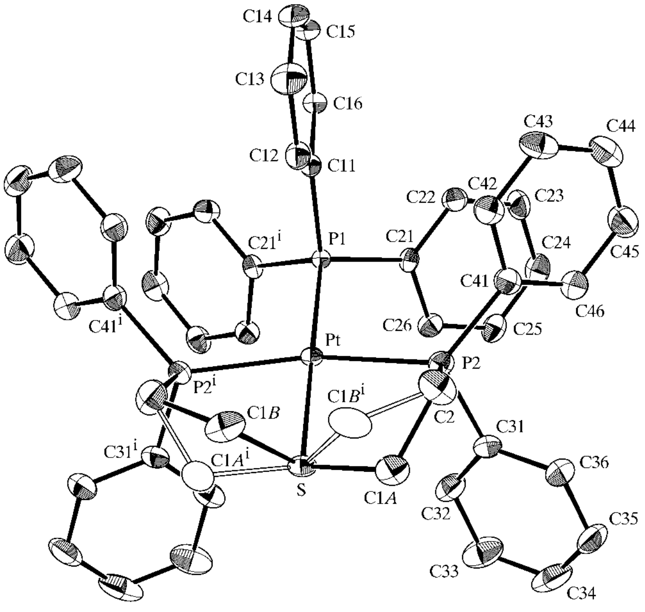


Figure 1
A view of the cation of (I), showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity [symmetry code: (i) $x, \frac{1}{2} - y, z$].

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molecule of acetone has cocrystallized in (I). This acetone solvate is located close to the PPh_3 group, with the shortest distance to a phenyl-ring C atom being 3.293 (5) Å for O7···C26.

The P1—Pt—S bond angle of 178.29 (4)° is close to the ideal value of 180°, while the P2—Pt—P2′ angle of 161.57 (5)° is significantly bent. The large steric demand of the PPh_3 group is indicated by the large *cis* P—Pt—P angles between the $-PPh_2$ and PPh_3 groups; P1—Pt—P2 is 98.79 (2)°, exceeding the reported *cis* P—Pt—I angles in the $[PtI(PSP)]^+$ cation, in spite of the fact that I is likewise a sterically demanding ligand. The *cis* P—Pt—P angles for (I) are, however, not unusual in complexes having two non-chelated mutually *cis* phosphine ligands (Battan *et al.*, 2001). This steric crowding is illustrated further by the smallest P—Pt—S angles [P2—Pt—S = 81.30 (2)°] yet observed in the five-membered chelate ring of a Pt^{II}–PSP complex.

The mirror plane of the cation in (I) results in equal Pt—P bond lengths [Pt—P2 = 2.310 (1) Å] and this Pt—P distance is within the normal range observed for two mutually *trans* $-PPh_2$ donors (Andreasen *et al.*, 1999; Siah *et al.*, 1994). The Pt—S bond length in (I) [Pt—S = 2.343 (1) Å] is approximately 0.09 Å longer than the Pt—S bonds in the Pt^{II}–PSP salts $[PtCl(PSP)]ClO_4$ and [PtI(PSP)]I, which is in line with the larger *trans* influence of the PPh_3 donor compared with Cl or I. Only scant information is available on bond distances in Pt^{II} complexes having the *trans* S—Pt—PPh_3 motif, with S being both a monodentate thioether ligand and part of a chelate system; one example is $[Pt(\{^iPrS(CH_2)_3\}_2S)(PPh_3)](BF_4)_2$ [$\{^iPrS(CH_2)_3\}_2S$ is 2,12-dimethyl-3,7,11-trithiatridecane, $C_{12}H_{26}S_3$; Loeb & Mansfield, 1996]. The Pt—S distance in (I) is similar to the values for chelated thioether donors in the *trans* position both to PPh_3 in $[Pt(\{^iPrS(CH_2)_3\}_2S)(PPh_3)]^{2+}$ (Loeb & Mansfield, 1996) or intra-ligand $-PPh_2$ donors (Connolly *et al.*, 1997).

The Pt—P bond length in (I) to the coordinated PPh_3 ligand [Pt—P1 = 2.289 (1) Å] is significantly shorter than the reported Pt—PPh_3 distance of 2.332 (2) Å in $[Pt(\{^iPrS(CH_2)_3\}_2S)(PPh_3)]^{2+}$, where the PPh_3 donor is also positioned *trans* to a chelated thioether group. The latter distance, however, is longer than the Pt—P distance in *trans*-$[PtI_2(PPh_3)_2]$ [2.318 (2) Å; Boag *et al.*, 1991]. This is remarkable, since it is generally accepted that the *trans* influence of PPh_3 is greater than that of a thioether group (Connolly *et al.*, 1997).

In (I), the PPh_3 phenyl ring, C21–C26, and the C41–C46 phenyl ring of PSP are positioned so that they are approximately slipped-parallel and only tilted by 3°, with a C21···C41 separation of 3.370 (5) Å for the two C_{ipso} atoms. This value is similar to the calculated optimum distance of 3.5 Å obtained for slipped-parallel benzene dimers, as reported in a recent computational calculation by Tsuzuki *et al.* (2002). This indicates that a *π–π* interaction may exist between the phenyl rings of PPh_3 and PSP, and the C21···C41 distance is in the range reported for overlap between arene moieties (Breu *et al.*, 1997; Fanizzi *et al.*, 1994).

Experimental

Compound (I) was prepared as reported previously by Andreasen *et al.* (1999). Colourless crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow diffusion of diethyl ether into an acetone–methanol (1:1) solution.

Crystal data

$[Pt(C_{18}H_{15}P)(C_{28}H_{28}P_2S)](ClO_4)_2\cdot C_3H_6O$
$M_r = 1172.84$
Orthorhombic, *Pnma*
$a = 15.698$ (3) Å
$b = 15.337$ (3) Å
$c = 19.957$ (4) Å
$V = 4804.9$ (16) Å^3
$Z = 4$
$D_x = 1.621$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.0$–30.4°
$\mu = 3.23$ mm^{-1}
$T = 120$ K
Octahedral, colourless
0.26 × 0.24 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: by integration (*XPREP*; Siemens, 1995)
$T_{min} = 0.448$, $T_{max} = 0.594$
41 330 measured reflections
7613 independent reflections
5723 reflections with $I > 3\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 30.5°$
$h = -16 \rightarrow 21$
$k = -22 \rightarrow 22$
$l = -27 \rightarrow 24$

Refinement

Refinement on F
$R = 0.032$
$wR = 0.036$
$S = 0.99$
5723 reflections
329 parameters
H-atom parameters constrained
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.3$ (2) e Å^{-3}
$\Delta\rho_{min} = -1.5$ (2) e Å^{-3}
Extinction correction: B–C type 1, Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 88 (9)

Table 1
Selected geometric parameters (Å, °).

Pt—P1	2.289 (1)	S—C1*A*	1.810 (9)
Pt—P2	2.310 (1)	S—C1*B*	1.834 (8)
Pt—S	2.343 (1)		
P1—Pt—P2	98.79 (2)	S—Pt—P2	81.30 (2)
P2—Pt—P2^i	161.57 (5)	S—Pt—P2^i	81.30 (2)
S—Pt—P1	178.29 (5)		

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

The H atoms were kept fixed in calculated positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}$ of the atoms to which they were attached. Refinement of (I) in the centrosymmetric space group *Pnma* gave very elongated displacement ellipsoids for atom C1. This elongation could result either from disorder or from a wrong choice of space group. Solving and refining the structure in the polar space group $Pna2_1$ gave many non-positive definite displacement ellipsoids, and refinement of the polarity gave a Rogers (1981) factor close to zero instead of ±1, indicating that the structure was non-polar. The structure was therefore refined in *Pnma* with C1 split over two sites, C1*A* and C1*B*, each with 50% site occupancy.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1116). Services for accessing these data are described at the back of the journal.

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