Cis- and trans-influences in [PtCl₂(SPh₂)₂]

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Both *cis-* and *trans-*dichlorobis(diphenyl sulfide)platinum(II), [PtCl₂(C₁₂H₁₀S)₂], crystallize as mononuclear pseudo-square-planar complexes. In the *cis* compound, the Pt—Cl distances are 2.295 (2) and 2.319 (2) Å, and the Pt—S distances are 2.280 (2) and 2.283 (2) Å. In the *trans* compound, Pt is located on a centre of inversion and the Pt—Cl and Pt—S distances are 2.2786 (15) and 2.3002 (12) Å, respectively.

Comment

In square-planar platinum(II) complexes, the *trans*-influence is a well known phenomenon which has been widely studied for a large number of complexes, such as *cis/trans*-[PtCl₂(dms)₂] (dms is dimethyl sulfide; Horn *et al.*, 1990; Johansson *et al.*, 2001), *cis*-[PtCl₂(dmso)₂] (dmso is diemethyl sulfoxide; Melanson & Rochon, 1975; Shibaeva, 1983) and *cis/trans*-[PtCl₂(tioxane)₂] (Bugarcic *et al.*, 1993). The *trans*-influence is larger for thioether sulfur than for chloride, but the substituents on the S atom are expected to modulate the influence. In light of this, we have investigated the structures of *cis-* and *trans*-dichlorobis(diphenyl sulfide)platinum(II), (I) and (II), respectively.


(I)   (II)
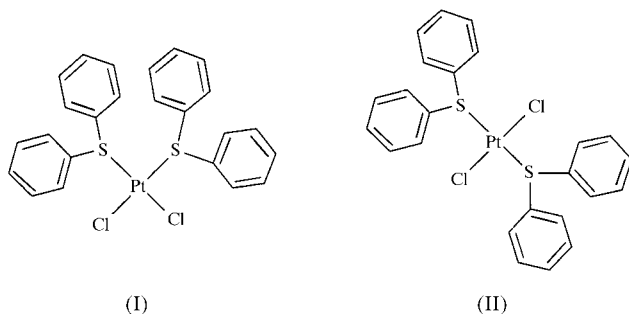
In *cis*-[PtCl₂(SPh₂)₂] (Fig. 1), the coordination around Pt is distorted square planar, with angles ranging from 83.68 (7) to 93.06 (7)°. The r.m.s. deviation from the Cl₂PtS₂ plane is 0.0550 Å, where S2 shows the largest deviation

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[−0.0652 (11) Å]. The closest non-bonding contact to Pt is intramolecular to H226 at a distance of 2.92 Å, where H226 is approximately situated at an octahedral position of the coordination sphere of platinum. On the other side of the coordination plane, the closest contact in the octahedral position is intermolecular to H116 at (2 − x, 1 − y, −z) at a distance of 3.43 Å, too long to be a Pt···H interaction. The two closest Cl1···H interactions are 2.84 and 2.97 Å to H113 at ($\frac{1}{2}$ − x, $\frac{1}{2}$ + y, z) and H224 at (−$\frac{1}{2}$ + x, y, $\frac{1}{2}$ − z), respectively. The closest Cl2···H interaction is 2.93 Å to H225 at (−$\frac{1}{2}$ + x, y, $\frac{1}{2}$ − z). The S—Pt—S—C torsion angles show that for each ligand one S—C bond is fairly close to the coordination plane, while the other S—C bonds are close to being perpendicular to this plane (Table 1).

In *trans*-[PtCl₂(SPh₂)₂] (Fig. 2), the coordination is pseudo-square planar, with Pt at a centre of inversion and bond angles of 84.80 (5) and 95.20 (5)° around platinum. Atoms H112 are located in an approximate octahedral site on both sides of the platinum, at a distance of 2.90 Å, which is the closest non-bonding contact (intramolecular) with platinum. The closest non-bonding interaction to chloride is intermolecular to H114 at (1 + x, $\frac{1}{2}$ − y, $\frac{1}{2}$ + z), at a distance of 2.73 Å. The Cl—Pt—S—C torsion angles show that one S—C bond in the ligand is fairly close to the coordination plane, while the other S—C bonds are close to being perpendicular to this plane (Table 2).

The Cambridge Structural Database (CSD; Allen & Kennard, 1993) has been searched for compounds of the types [PtCl₂R₂], [PtS₄]²⁺ and [PtCl₄]²⁻, where R represents a ligand with a sulfur-donor atom connected to two C atoms. 31 *cis*- and seven *trans*-[PtCl₂R₂] examples were found. From the CSD search, a mean value of 2.319 (12) Å was calculated for the distances in ten [PtS₄]²⁺ complexes (no chelating ligands) and this value may be used as a reference value for a discussion of the *cis/trans* influence. The *cis*-[PtCl₂R₂] compounds have a mean Pt—S distance of 2.24 (2) Å (62 distances), while the similar *trans* compounds have a mean of 2.301 (9) Å (14
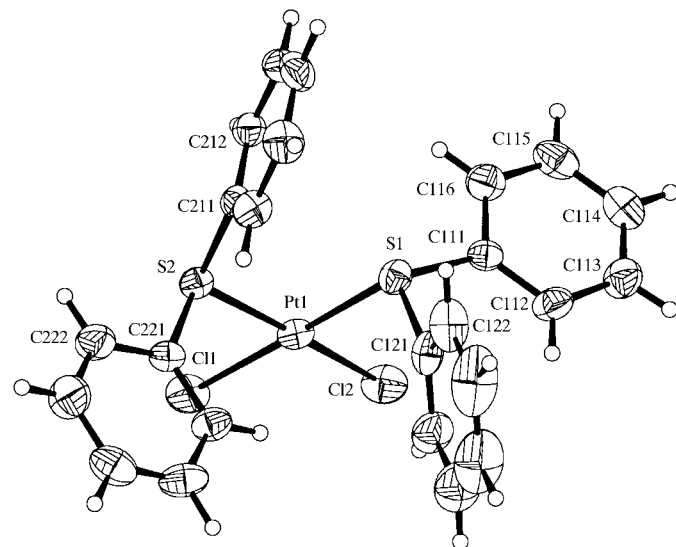
Figure 1
The structure of the *cis* isomer showing the atom-numbering scheme and displacement ellipsoids (30% probability).

1053

distances). The Pt—S distances in cis-[PtCl$_2$(SPh$_2$)$_2$] are 2.280 (2) and 2.283 (2) Å, which are significantly longer than the mean value in other cis compounds. These are similar to the distances found in cis-[PtCl$_2${S(C$_6$H$_4$Cl)$_2$}$_2$], 2.292 (6) and 2.278 (7) Å (Spofford et al., 1971), and shorter than distances in [PtS$_4$]$^{2+}$ complexes. Thus, the combined cis(Cl/S)- and trans(Cl)-influence may shorten the Pt—S bond, by 0.04 Å compared to [PtS$_4$]$^{2+}$, but not as much as in other analogous
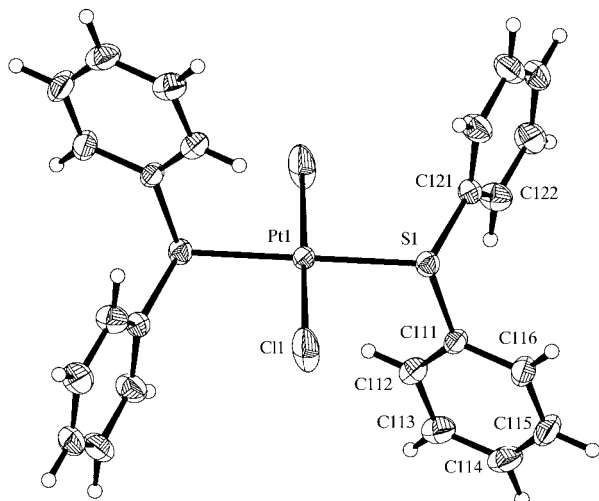
Figure 2
The structure of the trans isomer showing the atom-numbering scheme and displacement ellipsoids (30% probability).

compounds (Table 3). In trans-[PtCl$_2$(SPh$_2$)$_2$], the Pt—S distances are 2.3002 (12) Å, which is in the normal range for such bonds [mean 2.301 (9) Å]. The cis(Cl/Cl)-influence shortens it by 0.02 Å compared to [PtS$_4$]$^{2+}$ compounds. The mean Pt—Cl distance found in 33 [PtCl$_4$]$^{2-}$ complexes, 160 distances, is 2.302 (16) Å. The Pt—Cl distances in cis-[PtCl$_2$(SPh$_2$)$_2$], 2.295 (2) and 2.319 (2) Å, are in good agreement with distances found for related cis compounds, mean of 2.312 (11) for 62 distances, while the Pt—Cl distance in trans-[PtCl$_2$(SPh$_2$)$_2$], 2.2786 (15) Å, is shorter than in related trans compounds, mean of 2.299 (5) Å for 14 distances. The cis(S/S)-influence of SPh$_2$ shortens the Pt—Cl bond in trans-[PtCl$_2$(SPh$_2$)$_2$] by 0.02 Å compared to [PtCl$_4$]$^{2-}$, but also compared to analogous trans-[PtCl$_2$R$_2$] compounds.

The reduced overlap population (ROP) may be used as a measure of the bond strength. We have calculated the ROP in the Pt–ligand bonds using the crystallographically observed geometries (Table 3) at the Extended Hückel (EH) level using the program CACAO (Maelli & Prosperpio, 1990). The Pt—S bonds have higher ROP values than the Pt—Cl bonds. This is true even in the trans compounds where the Pt—S bonds are equal to or slightly longer than the Pt—Cl bonds. All the cis complexes, except cis-[PtCl$_2$(thioxane)$_2$], have larger ROP values for the Pt—S bonds than the corresponding trans compounds, thus following the trends in the Pt—S distances. However, in the thioxane compounds, the ROP for the trans compound is the larger one, in spite of the fact that the Pt—S distance is 2.298 (2) Å, compared with 2.273 (2) Å in the cis compound.

The total energy for trans-[PtCl$_2$(SPh$_2$)$_2$] was also calculated at 20° intervals for a 360° rotation around the Pt—S bond, keeping all other geometric parameters constant. It is interesting to note that the observed conformation of trans-[PtCl$_2$(SPh$_2$)$_2$] is the one with the lowest energy. It is well known that EH calculations are reasonably successful in calculating conformational energies (Jolly, 1991) and it is concluded that the packing has small effects, not only on bond distances and angles as normally observed (Johansson et al., 2000), but also on the conformation in this case.

Experimental

[PtCl$_2$(SPh$_2$)$_2$] was prepared according to Tayim & Bailar (1967). To prepare the cis compound, [PtCl$_2$(SPh$_2$)$_2$] (0.2 g, 3.13 mmol) was dissolved in 10 ml of benzene to give a clear solution. Ph$_3$SnH (0.109 g, 3.195 mmol) dissolved in 2 ml benzene was added and the reaction mixture was left stirring overnight and then filtered. Benzene was removed to give a brown solid which was dissolved in CH$_2$Cl$_2$/ benzene and MeOH. A dirty white solid was removed by filtration and yellow crystals were obtained from the filtrate. The trans compound was prepared by adding SnCl$_2$ (0.04 g, 2.35 mmol) to a 10 ml acetone solution of [PtCl$_2$(SPh$_2$)$_2$] (0.15 g, 2.35 mmol). The clear solution became dark and was left overnight. The solution was filtered and dark-orange crystals were obtained by slow evaporation.

Compound (I)

Crystal data

[PtCl$_2$(C$_{12}$H$_{10}$S)$_2$]	Mo Kα radiation
M_r = 638.51	Cell parameters from 5997
Orthorhombic, Pbca	reflections
a = 10.281 (2) Å	θ = 2–29°
b = 17.244 (3) Å	μ = 6.42 mm^{-1}
c = 26.382 (5) Å	T = 293 (2) K
V = 4676.9 (16) Å^3	Plate, yellow
Z = 8	0.15 × 0.13 × 0.03 mm
D_x = 1.814 Mg m^{-3}	

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

Pt1—S1	2.2801 (19)	S1—C111	1.787 (7)
Pt1—S2	2.2832 (18)	S1—C121	1.785 (8)
Pt1—Cl1	2.319 (2)	S2—C211	1.785 (6)
Pt1—Cl2	2.295 (2)	S2—C221	1.776 (7)
S1—Pt1—S2	92.39 (6)	C111—S1—C121	103.3 (3)
S1—Pt1—Cl1	175.16 (7)	C211—S2—C221	103.4 (3)
S1—Pt1—Cl2	93.06 (7)	S1—C111—C112	123.3 (6)
S2—Pt1—Cl1	83.68 (7)	S1—C111—C116	116.0 (6)
S2—Pt1—Cl2	173.62 (7)	S1—C121—C122	115.4 (8)
Cl1—Pt1—Cl2	91.03 (8)	S1—C121—C126	121.9 (6)
Pt1—S1—C111	113.7 (2)	S2—C211—C212	115.7 (5)
Pt1—S1—C121	106.2 (3)	S2—C211—C216	123.0 (6)
Pt1—S2—C211	110.5 (2)	S2—C221—C222	117.2 (6)
Pt1—S2—C221	110.3 (2)	S2—C221—C226	122.2 (6)
S1—Pt1—S2—C211	17.8 (2)	Pt1—S1—C111—C112	−100.3 (6)
S1—Pt1—S2—C221	−95.9 (3)	Pt1—S1—C121—C122	−143.9 (5)
S2—Pt1—S1—C111	−152.6 (3)	Pt1—S2—C211—C212	73.4 (5)
S2—Pt1—S1—C121	94.5 (3)	Pt1—S2—C221—C222	−165.1 (5)

Data collection

Bruker SMART CCD diffractometer	5802 independent reflections
ω scans	4144 reflections with $I > 2\sigma(I)$
Absorption correction: empirical	$R_{int} = 0.064$
($SADABS$; Sheldrick, 1996)	$\theta_{max} = 28.3°$
$T_{min} = 0.446$, $T_{max} = 0.831$	$h = -12 \rightarrow 13$
32 399 measured reflections	$k = -22 \rightarrow 22$
	$l = -33 \rightarrow 35$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 15.3500P]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} = 0.001$
5802 reflections	$\Delta\rho_{max} = 1.71$ e Å^{-3}
262 parameters	$\Delta\rho_{min} = -1.08$ e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

$[PtCl_2(C_{12}H_{10}S)_2]$	$D_x = 1.830$ Mg m^{-3}
$M_r = 638.51$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5997
$a = 5.8742 (12)$ Å	reflections
$b = 16.980 (3)$ Å	$\theta = 2$–$30°$
$c = 11.733 (2)$ Å	$\mu = 6.47$ mm^{-1}
$\beta = 97.99 (3)°$	$T = 293 (2)$ K
$V = 1158.9 (4)$ Å^3	Plate, orange
$Z = 2$	$0.35 \times 0.19 \times 0.08$ mm

Data collection

Bruker SMART CCD diffractometer	3583 independent reflections
ω scans	2811 reflections with $I > 2\sigma(I)$
Absorption correction: empirical	$R_{int} = 0.046$
($SADABS$; Sheldrick, 1996)	$\theta_{max} = 31.8°$
$T_{min} = 0.177$, $T_{max} = 0.383$	$h = -6 \rightarrow 8$
9455 measured reflections	$k = -24 \rightarrow 21$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 2.6752P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
3583 reflections	$\Delta\rho_{max} = 1.27$ e Å^{-3}
133 parameters	$\Delta\rho_{min} = -2.07$ e Å^{-3}
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Pt1—Cl1	2.2786 (15)	S1—C111	1.783 (5)
Pt1—S1	2.3002 (12)	S1—C121	1.789 (5)
Cl1—Pt1—S1	84.80 (5)	S1—C111—C116	117.5 (4)
Cl1^i—Pt1—S1	95.20 (5)	C111—S1—C121	102.4 (2)
Pt1—S1—C111	107.32 (16)	S1—C121—C122	124.2 (4)
Pt1—S1—C121	111.79 (16)	S1—C121—C126	115.4 (4)
S1—C111—C112	122.0 (4)		
Cl1—Pt1—S1—C111	−76.55 (18)	Pt1—S1—C111—C112	−23.1 (4)
Cl1—Pt1—S1—C121	171.97 (19)	Pt1—S1—C121—C122	96.5 (5)

Symmetry code: (i) $-x, -y, -z$.

Table 3
Comparison of Pt—Cl and Pt—S distances in analogous *cis/trans* complexes together with their ROP values.

Compound	Pt—Cl (Å)	ROP	Pt—S (Å)	ROP
cis-[PtCl₂{S(C₆H₅)₂}₂][a]	2.295 (2)	0.449	2.280 (2)	0.539
	2.319 (2)	0.416	2.283 (2)	0.518
trans-[PtCl₂{S(C₆H₅)₂}₂][a]	2.2786 (15)	0.446	2.3002 (12)	0.507
cis-[PtCl₂(dms)₂][b]	2.315 (1)	0.440	2.269 (1)	0.531
	2.319 (1)	0.434	2.272 (1)	0.536
trans-[PtCl₂(dms)₂][c]	2.288 (2)	0.448	2.303 (2)	0.517
cis-[PtCl₂(thioxane)₂][d]	2.321 (2)	0.439	2.273 (2)	0.512
	2.327 (2)	0.438	2.273 (2)	0.520
trans-[PtCl₂(thioxane)₂][d]	2.300 (2)	0.441	2.298 (2)	0.534

Notes: (*a*) this study; (*b*) Horn *et al.* (1990), dms is SMe₂; (*c*) Johansson *et al.* (2001); (*d*) Bugarcic *et al.* (1993), thioxane is SC₄H₈O.

H atoms were treated as riding with a C—H distance of 0.93 Å. In (I), the maximum and minimum residual electron densities were located 0.87 and 0.78 Å from Pt1, respectively. The corresponding values in (II) were 0.89 Å from Cl1 and 0.81 Å from Pt1.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL*97.

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