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Cis- and *trans*-influences in $[PtCl_2(SPh_2)_2]$

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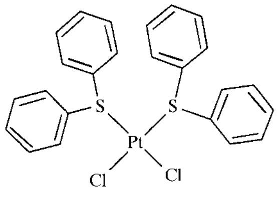
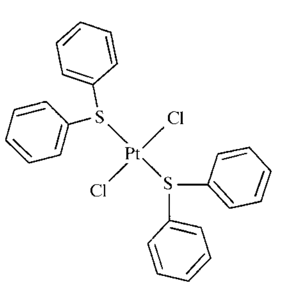
Both *cis*- and *trans*-dichlorobis(diphenyl sulfide)platinum(II), $[PtCl_2(C_{12}H_{10}S)_2]$, crystallize as mononuclear pseudo-square-planar complexes. In the *cis* compound, the Pt—Cl distances are 2.295 (2) and 2.319 (2) Å, and the Pt—S distances are 2.280 (2) and 2.283 (2) Å. In the *trans* compound, 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*-$[PtCl_2(dms)_2]$ (dms is dimethyl sulfide; Horn *et al.*, 1990; Johansson *et al.*, 2001), *cis*-$[PtCl_2(dmso)_2]$ (dmso is diemethyl sulfoxide; Melanson & Rochon, 1975; Shibaeva, 1983) and *cis*/*trans*-$[PtCl_2(tioxane)_2]$ (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*-$[PtCl_2(SPh_2)_2]$ (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 Cl_2PtS_2 plane is 0.0550 Å, where S2 shows the largest deviation [−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*-$[PtCl_2(SPh_2)_2]$ (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 $[PtCl_2R_2]$, $[PtS_4]^{2+}$ and $[PtCl_4]^{2-}$, where R represents a ligand with a sulfur-donor atom connected to two C atoms. 31 *cis*- and seven *trans*-$[PtCl_2R_2]$ examples were found. From the CSD search, a mean value of 2.319 (12) Å was calculated for the distances in ten $[PtS_4]^{2+}$ complexes (no chelating ligands) and this value may be used as a reference value for a discussion of the *cis*/*trans* influence. The *cis*-$[PtCl_2R_2]$ 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

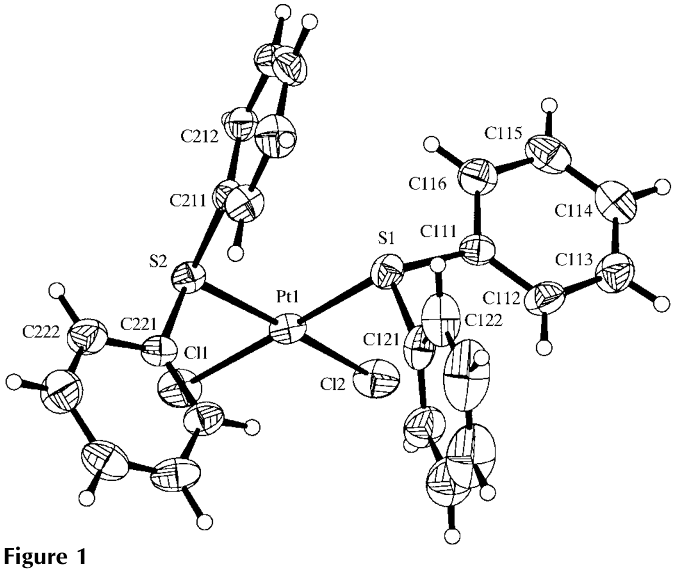


Figure 1
The structure of the *cis* isomer showing the atom-numbering scheme and displacement ellipsoids (30% probability).

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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*-$[PtCl_2\{S(C_6H_4Cl)_2\}_2]$, 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 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*-$[PtCl_2R_2]$ compounds.

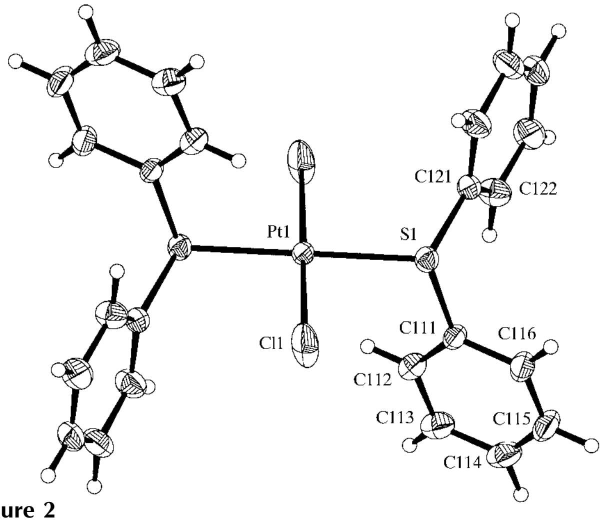

Figure 2
The structure of the *trans* isomer showing the atom-numbering scheme and displacement ellipsoids (30% probability).

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*-$[PtCl_2(\text{thioxane})_2]$, 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_3SnH (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_2Cl_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

$[PtCl_2(C_{12}H_{10}S)_2]$
$M_r = 638.51$
Orthorhombic, *Pbca*
$a = 10.281 (2)$ Å
$b = 17.244 (3)$ Å
$c = 26.382 (5)$ Å
$V = 4676.9 (16)$ Å^3
$Z = 8$
$D_x = 1.814$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5997 reflections
$\theta = 2–29°$
$\mu = 6.42$ mm^{-1}
$T = 293 (2)$ K
Plate, yellow
0.15 × 0.13 × 0.03 mm

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
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.446$, $T_{\max} = 0.831$
32399 measured reflections
5802 independent reflections
4144 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 28.3°$
$h = -12 \rightarrow 13$
$k = -22 \rightarrow 22$
$l = -33 \rightarrow 35$

Refinement

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

Compound (II)

Crystal data

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

Data collection

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

Refinement

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

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-$[PtCl_2\{S(C_6H_5)_2\}_2]^a$	2.295 (2)	0.449	2.280 (2)	0.539
	2.319 (2)	0.416	2.283 (2)	0.518
trans-$[PtCl_2\{S(C_6H_5)_2\}_2]^a$	2.2786 (15)	0.446	2.3002 (12)	0.507
cis-$[PtCl_2(dms)_2]^b$	2.315 (1)	0.440	2.269 (1)	0.531
	2.319 (1)	0.434	2.272 (1)	0.536
trans-$[PtCl_2(dms)_2]^c$	2.288 (2)	0.448	2.303 (2)	0.517
cis-$[PtCl_2(thioxane)_2]^d$	2.321 (2)	0.439	2.273 (2)	0.512
	2.327 (2)	0.438	2.273 (2)	0.520
trans-$[PtCl_2(thioxane)_2]^d$	2.300 (2)	0.441	2.298 (2)	0.534

Notes: (*a*) this study; (*b*) Horn *et al.* (1990), dms is SMe_2; (*c*) Johansson *et al.* (2001); (*d*) Bugarcic *et al.* (1993), thioxane is SC_4H_8O.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1157). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Brandenburg, K. (2000). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bugarcic, Z., Lövqvist, K. & Oskarsson, Å. (1993). *Acta Chem. Scand.* **47**, 554–559.
Horn, G. W., Kumar, R., Maverick, A. W., Fronczek, F. R. & Watkins, S. F. (1990). *Acta Cryst.* C**46**, 135–136.
Johansson, M. H., Giveen, D. & Oskarsson, Å. (2001). In preparation.
Johansson, M. H., Otto, S., Roodt, A. & Oskarsson, Å. (2000). *Acta Cryst.* B**56**, 226–233.
Jolly, W. L. (1991). *Modern Inorganic Chemistry*, pp. 137–140. Singapore: McGraw-Hill Inc.
Maelli, C. & Prosperpio, D. M. (1990). *J. Chem. Educ.* **67**, 399–402.
Melanson, R. & Rochon, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Shibaeva, R. B. (1983). *Koord. Khim.* **11**, 129–131.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spofford, W. A., Amma, E. L. & Senoff, C. V. (1971). *Inorg. Chem.* **10**, 2309–2312.
Tayim, A. T. & Bailar, J. C. Jr (1967). *J. Am. Chem. Soc.* **89**, 4330–4338.