

repulsion between *M* and *C* ligands than between *M* and *T*, with a repulsion ratio $R_c/R_T \approx 1.1$, which corresponds to the averaged bond-length ratio $\langle\langle \text{Mn-L} \rangle_c / \langle \text{Mn-L} \rangle_T \rangle_L > 1$ found for both isomers. Nevertheless, these bond lengths are also supposed to be conditioned by the *cis* and *trans* influences. On the other hand, theoretical force constants for both carbonyls have been calculated using the empirical formulae of Timney (1979), and are listed in Table 4 together with the corresponding X-ray bond distances and the observed IR bands for both *cis-cis* and *cis-trans* isomers. These results show that the predicted force constants do not correspond to the X-ray C=O bond distances; nevertheless, the Mn—C bonds seem to

be more sensible to the environment, and are in agreement with the calculated force constants.

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cis-[*rac-cis*-1,2-Bis(phenylsulphinyl)ethylene]dichloroplatinum(II)

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Abstract. C₁₄H₁₂Cl₂O₂PtS₂, $M_r = 542.26$, orthorhombic, *Pbca*, $a = 22.087$ (4), $b = 12.517$ (2), $c = 11.834$ (2) Å, $U = 3272$ (1) Å³, $Z = 8$, $D_c = 2.20$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 2.15$ mm⁻¹. The structure was refined by least squares to $R = 0.054$ for 1870 intensities. The Pt atom adopts a square-planar coordination geometry, being bonded to two Cl atoms arranged in a *cis* configuration and two S atoms of the bidentate disulphoxide ligand. This ligand forms a five-membered ring with the Pt atom.

Introduction. Platinum(II) forms cyclic systems with bidentate, chelating ligands such as disulphoxides (Cattalini, Michelon, Marangoni & Pelizzi, 1979). The title complex contains a disulphoxide ligand with an unsaturated centre, and the molecular structure was determined to discover whether any further interaction might arise between the carbon–carbon double bond and any of the Pt atoms.

The title complex was prepared by gently heating and stirring an ethanolic solution of *cis*-(C₆H₅)SOCH=CHSO(C₆H₅) with an excess of K₂PtCl₄ for 2 h (Filgueiras, 1981). A beige precipitate was collected and recrystallized from propane. A single crystal with dimensions 0.35 × 0.21 × 0.17 mm was mounted on a

Syntex P₂₁ diffractometer and cell dimensions were determined from the angular measurements of 15 strong reflections in the range 45.0 < 2θ < 55.0°. 2036 intensities were recorded in the range 3.0 < 2θ < 125.0° using graphite-monochromated Cu Kα radiation and a 96-step ω-2θ scan technique. Lp corrections, and empirical absorption corrections based on a pseudo-ellipsoid model were applied, and equivalent reflections were averaged to give 1870 unique observed intensities [$F > 3\sigma(F)$].

The Pt atom was located from a Patterson map, and all the remaining non-hydrogen atoms were located by subsequent electron-density difference syntheses. The positions of the H atoms were calculated geometrically and they were constrained to ride 1.08 Å from the relevant C atom; the ethylene H atoms and the H atoms of each phenyl ring were assigned common isotropic temperature factors which refined to 0.05 (4), 0.08 (4), and 0.03 (2) Å², respectively. The structure was refined to $R = 0.054$ by blocked full-matrix least squares with all the non-hydrogen atoms assigned anisotropic thermal parameters. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and unit weights were employed throughout, since $w\Delta^2$ was fairly independent of

Table 1. Fractional coordinates and equivalent isotropic thermal parameters

E.s.d.'s are given in parentheses and refer to the last decimal position. $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized U matrix.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Pt(1)	0.15783 (4)	0.03315 (7)	0.19045 (7)	0.0450 (3)
Cl(1)	0.0764 (2)	0.0453 (6)	0.3120 (6)	0.073 (2)
Cl(2)	0.1788 (3)	-0.1407 (5)	0.2475 (6)	0.070 (2)
S(1)	0.2337 (2)	0.0279 (4)	0.0707 (4)	0.041 (2)
O(1)	0.2377 (7)	-0.0602 (12)	-0.0102 (13)	0.05 (1)
C(1)	0.2281 (10)	0.1538 (18)	-0.0057 (19)	0.05 (1)
C(11)	0.3038 (8)	0.0434 (15)	0.1391 (15)	0.03 (1)
C(12)	0.3058 (9)	0.0748 (15)	0.2500 (17)	0.04 (1)
C(13)	0.3668 (10)	0.0887 (18)	0.2989 (21)	0.06 (1)
C(14)	0.4172 (10)	0.0688 (16)	0.2365 (19)	0.05 (1)
C(15)	0.4137 (10)	0.0386 (19)	0.1269 (18)	0.05 (1)
C(16)	0.3599 (9)	0.0251 (18)	0.0776 (19)	0.05 (1)
S(2)	0.1379 (2)	0.1974 (4)	0.1350 (5)	0.044 (2)
O(2)	0.1428 (7)	0.2831 (13)	0.2178 (14)	0.07 (1)
C(2)	0.1864 (10)	0.2187 (19)	0.0185 (20)	0.06 (1)
C(21)	0.0666 (8)	0.2019 (15)	0.0678 (17)	0.04 (1)
C(22)	0.0221 (10)	0.2668 (19)	0.1131 (20)	0.06 (1)
C(23)	-0.0334 (11)	0.2686 (21)	0.0622 (22)	0.07 (1)
C(24)	-0.0456 (11)	0.2080 (18)	-0.0292 (20)	0.06 (1)
C(25)	-0.0008 (10)	0.1444 (20)	-0.0727 (21)	0.06 (1)
C(26)	0.0549 (10)	0.1401 (19)	-0.0227 (20)	0.06 (1)

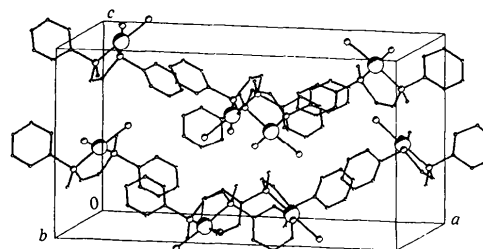


Fig. 1. A packing diagram for the title compound.

$|F_o|$ and $\sin \theta$ with this scheme. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The unit-cell contents are shown in Fig. 1. The shortest intermolecular non-bonded contact distance is 2.545 (7) Å [H(22)···H(25)], and the shortest between two non-hydrogen atoms is 3.001 (7) Å [C(12)···O(1)]. The phenyl rings in adjacent molecules lie approximately parallel to each other with an interplanar distance of *ca* 3.5 (1) Å.

Fig. 2 illustrates a single molecule of the title complex and includes the atom-numbering scheme. The disulphoxide ligand is bonded to the Pt atom at two coordination sites through the S atoms. The average Pt—S distance of 2.198 (5) Å is not significantly different from the values found in *cis*-[PtCl₂(*meso*-PhSOCH₂CH₂SOPh)] [2.217 (2) and 2.209 (2) Å] and *cis*-[PtCl₂(*rac*-PhSOCH₂CH₂SOPh)] [2.192 (4) and 2.188 (4) Å] (Cattalini, Michelson, Marangoni & Pelizzi, 1979). However, these distances are significantly shorter than those in the dimethyl sulphoxide complex *cis*-[PtCl₂(Me₂SO)₂] [2.244 (2) and 2.229 (2) Å] (Melanson & Rochon, 1975). The longer Pt—S distances in the dimethyl sulphoxide complex may be due to ligand–ligand interactions which are absent in the disulphoxide complexes. The difference cannot be due to electronic effects since the S—O bond lengths range from 1.40 (2) Å in *cis*-[PtCl₂(*rac*-PhSOCH₂CH₂SOPh)] to 1.470 (8) Å in *cis*-[PtCl₂(*meso*-PhSOCH₂CH₂SOPh)]. The dimethyl sulphoxide complex has values of 1.469 (6) and 1.454 (9) Å, which are not significantly different from either of the two extreme values. The steric argument is supported by the Cl—Pt—Cl bond angles. In the Me₂SO complex the angle is 87.58 (9)° and in the *cis*-PhSOCH=CHSOPh complex it is 92.1 (3)°, which is significantly larger. Also, in the Me₂SO complex the S—Pt—S angle is 91.03 (8)° and this angle in the *cis*-PhSOCH=CHSOPh complex is 89.3 (2)°, which

Table 2. Bond distances (Å)

E.s.d.'s are given in parentheses.

Pt(1)—Cl(1)	2.308 (6)	Pt(1)—Cl(2)	2.326 (6)
Pt(1)—S(1)	2.195 (5)	Pt(1)—S(2)	2.203 (5)
S(1)—O(1)	1.46 (1)	S(1)—C(1)	1.82 (2)
S(1)—C(11)	1.76 (2)	C(1)—C(2)	1.26 (3)
C(11)—C(12)	1.37 (3)	C(11)—C(16)	1.46 (3)
C(12)—C(13)	1.48 (3)	C(13)—C(14)	1.36 (3)
C(14)—C(15)	1.35 (3)	C(15)—C(16)	1.33 (3)
S(2)—O(2)	1.46 (2)	S(2)—C(2)	1.77 (2)
S(2)—C(21)	1.76 (2)	C(21)—C(22)	1.38 (3)
C(21)—C(26)	1.35 (3)	C(22)—C(23)	1.37 (3)
C(23)—C(24)	1.35 (3)	C(24)—C(25)	1.37 (3)
C(25)—C(26)	1.37 (3)		

Table 3. Bond angles (°)

E.s.d.'s are given in parentheses.

Cl(1)—Pt(1)—Cl(2)	92.1 (3)	Cl(1)—Pt(1)—S(1)	177.4 (2)
Cl(2)—Pt(1)—S(1)	90.4 (2)	Cl(1)—Pt(1)—S(2)	88.2 (2)
Cl(2)—Pt(1)—S(2)	179.5 (2)	S(1)—Pt(1)—S(2)	89.3 (2)
Pt(1)—S(1)—O(1)	119.4 (7)	Pt(1)—S(1)—C(1)	104.0 (8)
O(1)—S(1)—C(1)	109.4 (10)	Pt(1)—S(1)—C(11)	111.8 (7)
O(1)—S(1)—C(11)	109.4 (9)	C(1)—S(1)—C(11)	101.1 (10)
S(1)—C(1)—C(2)	119.6 (18)	C(12)—C(11)—S(1)	120.0 (15)
C(16)—C(11)—S(1)	120.2 (15)	C(16)—C(11)—C(12)	119.8 (18)
C(11)—C(12)—C(13)	115.9 (18)	C(12)—C(13)—C(14)	120.9 (22)
C(13)—C(14)—C(15)	121.6 (23)	C(14)—C(15)—C(16)	120.5 (21)
C(11)—C(16)—C(15)	121.3 (20)	Pt(1)—S(2)—O(2)	118.1 (7)
Pt(1)—S(2)—C(2)	104.6 (7)	Pt(1)—S(2)—C(21)	110.1 (6)
O(2)—S(2)—C(2)	111.6 (10)	O(2)—S(2)—C(21)	110.3 (10)
C(2)—S(2)—C(21)	100.7 (11)	S(2)—C(21)—C(22)	118.6 (17)
S(2)—C(21)—C(26)	120.7 (17)	C(22)—C(21)—C(26)	120.7 (21)
C(21)—C(22)—C(23)	118.5 (23)	C(22)—C(23)—C(24)	121.5 (24)
C(23)—C(24)—C(25)	119.0 (24)	C(24)—C(25)—C(26)	120.7 (25)
C(21)—C(26)—C(25)	119.7 (25)	S(2)—C(2)—C(1)	121.5 (20)

* Lists of structure factors, anisotropic thermal parameters, and parameters associated with the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36509 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

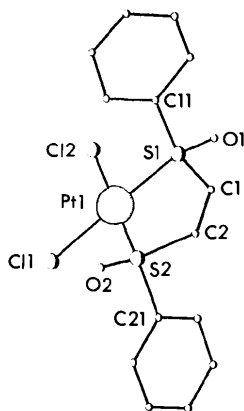


Fig. 2. A molecule of the title complex with the atom-numbering scheme.

Table 4. Deviations (Å) of atoms from the least-squares plane defined by Pt(1), S(1), S(2), Cl(1), Cl(2)

- (a) *cis*-[PtCl₂(*rac-cis*-PhSOCH=CHSOPh)] (this work).
 (b) *cis*-[PtCl₂(*rac*-PhSOCH₂CH₂SOPh)] (Cattalini, Michelon, Marangoni & Pelizzi, 1979).
 (c) *cis*-[PtCl₂(*meso*-PhSOCH₂CH₂SOPh)] (Cattalini, Michelon, Marangoni & Pelizzi, 1979).

	(a)	(b)	(c)
Pt(1)	0.012 (2)	0.011	0.000
S(1)	-0.008 (8)	-0.005	0.130
S(2)	0.002 (9)	-0.001	-0.130
Cl(1)	-0.008 (11)	-0.001	-0.121
Cl(2)	0.002 (12)	-0.005	0.121
C(1)*	-0.237 (41)	0.087	0.136
C(2)*	-0.335 (41)	-0.496	0.670

* Atom not included in the calculation of the least-squares plane.

is significantly smaller. The saturated disulphoxide complexes also show significantly larger Cl—Pt—Cl and smaller S—Pt—S angles than the Me₂SO complex.

The closest approach of a Pt atom to the centre of the C=C double bond is an intramolecular distance of 3.10 (1) Å. This is too long to indicate any interaction between the Pt and the π system of the C=C bond. Presumably the stability of square-planar Pt^{II} is such

that the formation of a five-coordinate complex involving the unsaturated C—C bond is not favoured. Also, the steric constraints of the disulphoxide ligand may prevent the formation of a five-coordinate complex.

The distances of the Pt, S, Cl and C atoms from the least-squares plane defined by the Pt coordination shell in *cis*-[PtCl₂(*rac-cis*-PhSOCH=CHSOPh)], *cis*-[PtCl₂(*rac*-PhSOCH₂CH₂SOPh)] (Cattalini, Michelon, Marangoni & Pelizzi, 1979), and *cis*-[PtCl₂(*meso*-PhSOCH₂CH₂SOPh)] are given in Table 4. In the *meso* complex the coordination about the Pt is tetrahedrally distorted whereas in the other two complexes it is much closer to square planar. The C atoms in the *rac*-PhSOCH₂CH₂SOPh complex are very dissimilar with one close to the plane and the other approximately 0.5 Å out of the plane. The C atoms in the *rac-cis*-PhSOCH=CHSOPh complex are both significantly out of the plane in the same direction, by approximately 0.25 Å. In each case this distortion must occur to relieve strain in the ring. It is possible that the reason for both the C atoms being out of the plane in the unsaturated ring is that the torsional rigidity of the C=C bond is governing the distortion in order to maintain an S—C—C angle which is not significantly different from the ideal angle of 120° [119.6 (18) and 121.5 (20)°].

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