Stereochemistry, and Crystal and Molecular Structure, of *meso*- and *rac*-1,2-Bis(phenylsulphinyl)ethane, *cis*-[*meso*-1,2-Bis(phenylsulphinyl)ethane]dichloroplatinum(II), and *cis*-[*rac*-1,2-Bis(phenylsulphinyl)ethane]dichloroplatinum(II)

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Diastereoisomeric *meso* and *rac* forms of 1,2-bis(phenylsulphinyl)ethane (1) and (2) respectively, have been separated and treated with $K_2[PtCl_4]$ to obtain the title complexes (3) and (4) respectively. The crystal structures of (1) and of the enantiomeric (*S,S*) form of (2), indicated as (2a), as well as of (3) and (4), have been solved by *X*-ray analysis from three-dimensional counter data and refined by block-diagonal least squares to *R* 0.028 and 0.051 for the ligands, and by full-matrix least squares to *R* 0.030 and 0.056 for the complexes, respectively. The co-ordination around platinum, which involves two chlorides and two sulphur atoms of the organic ligand, is quite close to square planar for (4) and only slightly tetrahedrally distorted for (3). The lengths of the Pt–Cl bonds are in fairly good agreement with those found in square-planar platinum(II) complexes, whereas the Pt–S bonds are slightly shorter. The different conformations assumed by the ligand when unco-ordinated or co-ordinated to the metal are compared and discussed. The structural data are related to i.r. and ^{1}H n.m.r. measurements.

THE synthesis, properties, and reactivity of organic sulphoxides, and the resolution of the optical isomers of asymmetric sulphoxides, have been widely studied.[1-6] In particular, the asymmetric oxidation of unsymmetrical sulphides [7] and the reaction of an optically active sulphinate ester with an organomagnesium halide [8,9] have been reported as methods of obtaining sulphoxides of high optical purity. In some cases, the chemical assignments have been confirmed by *X*-ray structure determinations.[10-12]

The related class of organic disulphoxides have been scarcely studied. A synthesis of bis(phenylsulphinyl)methane was first reported by Hinsberg [13] by the oxidation of the parent disulphide. In this and subsequent cases [2,14] no mention was made of the possible stereoisomers, *i.e meso* and (±) *rac*, which were separated later and characterized by n.m.r. spectroscopy.[15,16] Very recently, the preparation of β-disulphoxides in optically and diastereomerically pure states has been achieved by a ready one-step synthesis, starting from arenesulphinic esters and α-sulphinylcarbanions derived from the corresponding methyl-substituted sulphoxides.[17] The configurational assignments were made by a combination of n.m.r. and polarimetric measurements.[18] Some γ-disulphoxides were first prepared by Bell and Bennett,[19] who succeeded also in the separation of different forms of bis(methylsulphinyl)- and bis(phenylsulphinyl)-ethane. The previously arbitrarily named α and β compounds have been recently re-examined and their structures assigned by n.m.r. measurements.[15,20,21] Furthermore, the *X*-ray crystal and molecular structure of *meso*-bis(methylsulphinyl)ethane has now been solved.[22] Unlike dialkyl sulphoxides, which are known to form complexes with a large number of metal ions,[23-30] the co-ordination compounds of disulphoxides have been much less studied.[31,32] The separation and resolution of stereoisomers has not been attempted, nor have *X*-ray structural determinations been carried out.

We report a study of the synthesis, physicochemical characterization, and crystal structure of the diastereoisomeric (*R,S*)- and (*S,S*)-1,2-bis(phenylsulphinyl)ethane, (1) and (2a) respectively, and of *cis*-[*meso*-1,2-bis(phenylsulphinyl)ethane]dichloroplatinum(II) (3) and *cis*-[*rac*-1,2-bis(phenylsulphinyl)ethane]dichloroplatinum(II) (4). A kinetic study of the replacement of chloride by other ions in both these complexes is in progress.

EXPERIMENTAL

Materials.—Reagent-grade thiophenol, ethylene dibromide, and dipotassium tetrachloroplatinate(II) were used without further purification. Commercial ethanol, chloroform, acetone, and dimethylformamide were purified before use as reported in the literature.

Instruments.—Infrared spectra (300—4 000 cm^{-1}) were recorded on a Perkin-Elmer 621 spectrophotometer as Nujol mulls between KBr plates or as KBr pellets. Calibration of the frequency reading was made with polystyrene films. Hydrogen-1 n.m.r. measurements were carried out with Varian T-60 or NV-14 instruments for solutions in deuteriochloroform, carbon tetrachloride, and deuterionitromethane using $SiMe_4$ as internal standard.

Crystal and intensity data were determined by means of a single-crystal Siemens AED diffractometer. Atomic scattering factors were taken from Cromer and Mann for non-hydrogen atoms [33] and from Stewart *et al.*[34] for hydrogen atoms. All the calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario del l'Italia Nord Orientale.

Preparation of the Ligands.—According to the method of Cerniani and Modena [3] for the oxidation of diaryl sulphides to the corresponding sulphoxides, hydrogen peroxide (7.8 cm^3 of a 32% aqueous solution) was added dropwise and with stirring to a solution of 1,2-bis(phenylthio)ethane in a mixture of acetone (100 cm^3) and $HClO_4$ (7 cm^3, 70%) cooled on an ice-bath, so that the temperature did not rise above 25 °C. The solution was stirred for another 2 h before being neutralized with solid $Na[HCO_3]$. After filtration of the solid formed, the solution was concentrated and extracted, after addition of a saturated aqueous solution of NaCl, with several portions of $CHCl_3$. The organic phase was dried over $Na_2[SO_4]$ and the white solid obtained on removing the solvent was washed several times with water, ethanol, and diethyl ether and then dried *in vacuo*. The crude product (8 g) thus obtained was separated by fractional crystallization from $CHCl_3$–light petroleum into the two diastereoisomers (*R*,*S*)-1,2-bis(phenylsulphinyl)ethane (*meso* form) (1) and (±)-1,2-bis(phenylsulphinyl)ethane (*rac* form) (2) respectively, which were recrystallized from ethanol.

TABLE 1

Analytical and physicochemical data

	Analysis (%) [a]						I.r. (cm^{-1})	
Compound	C	H	S	Cl	M.p. (θ_c/°C)	^1H N.m.r. (δ/p.p.m.) CH_2	$\nu(SO)$	$\nu(Pt-Cl)$
(1)	60.2	4.95	22.9		166—167	2.88	1 033	
	(60.4)	(50.5)	(23.05)					
(2)	60.1	5.05	23.0		122—123	2.25—3.53	1.037	
	(60.4)	(5.05)	(23.05)					
(3)	30.8	2.65	11.9	12.95	228—232	(3.3—4.1) [b]	1 158	327—317
	(30.9)	(2.55)	(11.8)	(13.05)	(decomp.)			
(4)	30.75	2.60	11.75	12.9	239—242	(3.3—4.1) [b]	1 153	334—324
	(30.9)	(2.55)	(11.8)	(13.05)	(decomp.)			

[a] Calculated values are given in parentheses. [b] Approximate range.

TABLE 2

X-Ray data

Compound	(1)	(2a)	(3)	(4)
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$Pbca$
a/Å	8.946(9)	16.463(7)	11.923(7)	11.50(1)
b/Å	9.406(9)	14.536(9)	19.040(8)	22.12(2)
c/Å	8.347(8)	5.625(3)	7.322(5)	12.76(2)
β/°	105.3(1)			
U/Å^3	677.5	1 346.1	1 662.3	3 245.9
Z	2	4	4	8
D_c/g cm^{-3}	1.36	1.37	2.17	2.22
Radiation	Mo-K_α	Cu-K_α	Mo-K_α	Mo-K_α
Number of unique reflections	1 329	1 499	2 484	4 313
Number of ' observed ' reflections	788	1 426	2 132	2 068
Solution techniques	heavy atom	direct methods	heavy atom	heavy atom
Refinement	block-diagonal least squares	block-diagonal least squares	full-matrix least squares	full-matrix least squares
Absolute configuration		determined	determined	
Hydrogen atoms	located and refined	located and refined	located and refined	in calculated positions
R	0.028	0.051	0.030	0.056

Preparation of the Platinum(II) *Complexes*.—To an aqueous solution (50 cm^3) of $K_2[PtCl_4]$ (1.35 mmol) at *ca*. 70 °C was slowly added an equimolar solution of the ligand, (1) or (2) respectively, in methanol (30 cm^3) with vigorous stirring. The whitish complexes soon precipitated, *cis*-[*meso*-1,2-bis(phenylsulphinyl)ethane]dichloroplatinum(II) (3) and *cis*-[*rac*-1,2-bis(phenylsulphinyl)ethane]dichloroplatinum(II) (4) respectively, and were carefully washed with water, methanol, and diethyl ether and dried *in vacuo*. Crystals suitable for *X*-ray structure determinations were grown from dimethylformamide–methanol solutions.

Analytical data for both the ligands and complexes are in Table 1.

DISCUSSION

The solution i.r. spectra of the diastereoisomeric forms of the uncomplexed ligands (1) and (2) are very similar and only slight differences are present in the solid-state spectra, the high-melting species (1) showing relatively more complexity. On the other hand the ^1H n.m.r. spectra are very different. Compound (1) shows only a single resonance at δ 2.88 p.p.m. for the methylene protons, while (2) displays a complex multiplet, symmetric with respect to the baricentre and centred at about the same frequency. These features, which indicate magnetic non-equivalence of the methylene protons, have been previously interpreted[21] by considering that the presence of two asymmetric centres of opposite chirality causes a mutual compensation of the magnetic non-equivalence, whereas the presence in the same molecule of two centres of equal chirality enhances the non-equivalence. It was then concluded that (1) is the *meso* compound and (2) the *rac* form. These conclusions have been confirmed by the present *X*-ray structure investigation. It is to be noted that the single crystal of (2) casually chosen for the structure determination was found to be the (*S*,*S*) stereoisomer, which will be indicated as (2a).

Both (1) and (2) readily react with $K_2[PtCl_4]$ to give the corresponding neutral platinum(II) complexes, in which the disulphoxide molecule acts as a bidentate chelating ligand. Investigations of a wide variety of sulphoxide complexes strongly suggest that the i.r. shift of the S–O bond on co-ordination reflects the nature of the donor atom, *i.e.* S or O.[35] This has been directly confirmed by a number of *X*-ray determinations[36-39] and there is no exception to the generalization that an increase in ν(SO) is diagnostic for *S*-co-ordination, and a decrease for *O*-co-ordination. Furthermore, it has been pointed out that in palladium and platinum sulphoxide complexes the sulphur atom is the donor in the absence of special steric requirements.[40] In the present ligand the CH_2CH_2 segment between the two sulphoxide donor sites is less sterically restricting than are, for example, adjacent methyl groups on two dimethyl sulphoxide ligands in *cis*-[Pt(dmso)$_2$Cl$_2$], for which the *cis* sulphur-bonded structure has been demonstrated.[41] In the present complexes the i.r. spectra in the solid state, compared with those of the free ligands, show an increase of more than 100 cm^{-1} in ν(SO) and also a double band in the Pt–Cl region. These features, together with the absence of strong absorptions in the ν(SO) (*O*-bonded) region (880—940 cm^{-1}), clearly indicate *cis* sulphur-bonded structures for both platinum complexes.

TABLE 3

Atomic co-ordinates with estimated standard deviations in parentheses

(*a*) Ligand (1) (× 10^4 for S, O, and C; × 10^3 for H)

	x/*a*	*y*/*b*	*z*/*c*
S	1 211(1)	2 057(1)	35(1)
O	2 467(2)	1 692(2)	1 538(2)
C(1)	1 850(2)	1 510(2)	−1 740(3)
C(2)	3 295(3)	918(3)	−1 504(3)
C(3)	3 819(3)	582(3)	−2 877(3)
C(4)	2 909(3)	836(3)	−4 448(3)
C(5)	1 470(3)	1 430(3)	−4 673(3)
C(6)	921(3)	1 779(3)	−3 320(3)
C(7)	−309(3)	749(2)	−109(3)
H(1)	396(3)	80(3)	−39(3)
H(2)	486(3)	17(3)	−267(3)
H(3)	319(3)	56(3)	−546(3)
H(4)	81(3)	163(3)	−578(3)
H(5)	−17(3)	220(3)	−342(3)
H(6)	−78(2)	102(2)	71(3)
H(7)	−110(3)	89(2)	−122(3)

(*b*) Ligand (2a) (× 10^4 for S, O, and C; × 10^3 for H)

	x/*a*	*y*/*b*	*z*/*c*
S(1)	4 650(1)	4 016(1)	3 132(4)
O(1)	4 433(3)	3 897(4)	5 684(10)
C(1)	4 056(4)	4 955(4)	2 035(12)
C(2)	3 389(4)	5 229(4)	3 316(14)
C(3)	2 945(4)	5 974(5)	2 475(16)
C(4)	3 174(4)	6 435(5)	399(16)
C(5)	3 863(4)	6 127(5)	−838(14)
C(6)	4 285(4)	5 390(4)	−44(13)
C(7)	4 134(4)	3 088(4)	1 563(12)
H(1)	320(4)	486(5)	450(14)
H(2) *	245	620	338
H(3)	285(5)	703(5)	−25(17)
H(4)	408(5)	665(6)	−23(16)
H(5)	473(4)	515(4)	−102(13)
H(6)	420(3)	314(4)	4(11)
H(7)	350(4)	309(4)	163(12)
S(2)	4 115(1)	1 209(1)	738(3)
O(2)	4 225(3)	1 461(4)	−1 817(10)
C(8)	4 473(4)	2 201(4)	2 439(13)
C(9)	3 043(3)	1 308(4)	1 368(11)
C(10)	2 556(4)	1 702(4)	−344(13)
C(11)	1 710(4)	1 725(5)	66(14)
C(12)	1 388(4)	1 348(5)	2 144(15)
C(13)	1 899(4)	952(5)	3 841(13)
C(14)	2 750(4)	928(4)	3 468(12)
H(8)	513(4)	224(4)	247(12)
H(9)	425(3)	210(4)	380(11)
H(10)	280(4)	203(5)	−185(14)
H(11)	133(4)	208(5)	−128(14)
H(12)	82(4)	127(5)	258(14)
H(13)	167(5)	40(6)	510(17)
H(14)	318(4)	60(5)	480(15)

TABLE 3 (*Continued*)

(*c*) Complex (3) (× 10^4 for Pt, Cl, S, O, and C; × 10^3 for H)

	x/*a*	*y*/*b*	*z*/*c*
Pt	480(1)	57(1)	1 726(1)
Cl(1)	−508(3)	649(1)	−525(4)
Cl(2)	585(2)	−959(1)	4(4)
S(1)	585(2)	1 048(1)	3 307(4)
S(2)	1 238(2)	−509(1)	4 052(4)
O(1)	1 206(7)	1 643(4)	2 522(13)
O(2)	2 432(6)	−680(5)	3 993(12)
C(1)	−750(8)	1 348(5)	3 975(15)
C(2)	−1 618(10)	883(6)	4 293(19)
C(3)	−2 654(10)	1 122(7)	4 891(24)
C(4)	−2 802(10)	1 827(7)	5 211(22)
C(5)	−1 965(11)	2 291(7)	4 930(25)
C(6)	−913(10)	2 071(6)	4 247(20)
C(7)	1 269(9)	814(5)	5 431(14)
C(8)	992(8)	59(6)	5 977(13)
C(9)	487(10)	−1 265(5)	4 701(13)
C(10)	−711(11)	−1 265(6)	4 667(18)
C(11)	−1 260(11)	−1 858(7)	5 199(19)
C(12)	−705(14)	−2 431(6)	5 804(19)
C(13)	494(16)	−2 431(6)	5 863(19)
C(14)	1 067(11)	−1 846(5)	5 345(18)
H(1)	−143(10)	35(6)	382(17)
H(2)	−322(12)	80(7)	537(20)
H(3)	−355(11)	205(7)	569(19)
H(4)	−212(10)	291(6)	524(18)
H(5)	−25(10)	248(5)	355(17)
H(6)	216(11)	88(7)	527(20)
H(7)	125(10)	120(6)	653(18)
H(8)	17(9)	−4(6)	658(15)
H(9)	154(9)	−8(6)	706(16)
H(10)	−114(12)	−89(7)	376(20)
H(11)	−216(12)	−185(7)	542(21)
H(12)	−114(9)	−287(6)	630(16)
H(13)	84(11)	−294(7)	635(20)
H(14)	199(11)	−177(7)	576(19)

(*d*) Complex (4) (× 10^4 for Pt, Cl, and S; × 10^3 for O and C)

	x/*a*	*y*/*b*	*z*/*c*
Pt	1 924(1)	3 423(0)	382(1)
Cl(1)	3 143(4)	4 244(2)	426(4)
Cl(2)	2 436(5)	3 220(2)	−1 329(4)
S(1)	1 419(4)	3 626(2)	2 001(3)
S(2)	716(3)	2 639(2)	372(4)
O(1)	231(1)	361(1)	281(1)
O(2)	−8(1)	258(1)	−45(1)
C(1)	69(1)	432(1)	206(1)
C(2)	108(1)	475(1)	276(1)
C(3)	53(2)	531(1)	281(2)
C(4)	−34(2)	545(1)	214(2)
C(5)	−68(2)	502(1)	139(2)
C(6)	−17(2)	447(1)	134(2)
C(7)	44(3)	303(1)	236(2)
C(8)	−18(2)	279(1)	148(2)
C(9)	144(1)	197(1)	56(1)
C(10)	82(2)	142(1)	32(1)
C(11)	137(2)	88(1)	40(2)
C(12)	254(2)	85(1)	77(1)
C(13)	312(2)	137(1)	101(2)
C(14)	258(2)	196(1)	92(2)

* Calculated position.

Hydrogen-1 n.m.r. spectra of the complexes, both in CD_3NO_2 and $CDCl_3$, are not well resolved because of the low solubility and the high complexity of the multiplets due to the magnetically non-equivalent methylene protons. However, complex multiplets are observed centred at δ *ca.* 8.2 and 7.8 (α and $\beta + \gamma$ aromatic protons) and at *ca.* 3.7 p.p.m. (methylene protons). Physicochemical data for the four compounds are summarized in Table 1 while some relevant *X*-ray data are in Table 2. Information on the intensity data and

TABLE 4

Bond distances (Å) and angles (°)

(*a*) Ligand (1)

S–O	1.487(2)	C(7)–C(7$^{\text{I}}$) *	1.507(3)
S–C(1)	1.798(3)	C(2)–H(1)	0.97(2)
S–C(7)	1.814(4)	C(3)–H(2)	0.98(3)
C(1)–C(2)	1.373(4)	C(4)–H(3)	0.98(3)
C(1)–C(6)	1.384(3)	C(5)–H(4)	0.98(2)
C(2)–C(3)	1.385(4)	C(6)–H(5)	1.04(3)
C(3)–C(4)	1.370(4)	C(7)–H(6)	0.93(2)
C(4)–C(5)	1.370(5)	C(7)–H(7)	1.02(2)
C(5)–C(6)	1.385(4)		

O–S–C(1)	107.2(1)	C(1)–C(2)–C(3)	119.0(2)
O–S–C(7)	106.6(1)	C(2)–C(3)–C(4)	120.5(3)
C(1)–S–C(7)	98.5(1)	C(3)–C(4)–C(5)	120.1(2)
S–C(1)–C(2)	119.3(2)	C(4)–C(5)–C(6)	120.5(2)
S–C(1)–C(6)	119.4(2)	C(5)–C(6)–C(1)	118.7(2)
C(2)–C(1)–C(6)	121.1(2)	S–C(7)–C(7$^{\text{I}}$) *	112.4(2)

(*b*) Ligand (2a)

S(1)–O(1)	1.489(6)	C(4)–C(5)	1.404(10)
S(1)–C(1)	1.789(6)	C(5)–C(6)	1.353(9)
S(1)–C(7)	1.822(6)	C(6)–C(1)	1.382(9)
S(2)–O(2)	1.494(6)	C(9)–C(10)	1.378(9)
S(2)–C(9)	1.806(5)	C(10)–C(11)	1.412(9)
S(2)–C(8)	1.828(7)	C(11)–C(12)	1.396(11)
C(7)–C(8)	1.489(9)	C(12)–C(13)	1.397(11)
C(1)–C(2)	1.372(9)	C(13)–C(14)	1.417(9)
C(2)–C(3)	1.390(10)	C(14)–C(9)	1.390(9)
C(3)–C(4)	1.398(12)		

O(1)–S(1)–C(1)	106.9(3)	O(2)–S(2)–C(9)	106.7(3)
O(1)–S(1)–C(7)	105.6(3)	O(2)–S(2)–C(8)	105.7(3)
C(1)–S(1)–C(7)	98.2(3)	O(9)–S(2)–C(8)	98.6(3)
S(1)–C(7)–C(8)	107.8(5)	S(2)–C(8)–C(7)	112.9(5)
S(1)–C(1)–C(2)	118.5(5)	S(2)–C(9)–C(10)	117.7(5)
S(1)–C(1)–C(6)	119.5(4)	S(2)–C(9)–C(14)	118.3(4)
C(2)–C(1)–C(6)	122.0(6)	C(10)–C(9)–C(14)	123.9(5)
C(1)–C(2)–C(3)	117.9(7)	C(9)–C(10)–C(11)	118.0(6)
C(2)–C(3)–C(4)	121.1(7)	C(10)–C(11)–C(12)	120.1(7)
C(3)–C(4)–C(5)	118.6(7)	C(11)–C(12)–C(13)	120.4(6)
C(4)–C(5)–C(6)	120.3(7)	C(12)–C(13)–C(14)	120.3(7)
C(5)–C(6)–C(1)	120.1(6)	C(13)–C(14)–C(9)	117.3(6)

(*c*) Complex (3)

Pt–Cl(1)	2.318(3)	C(2)–C(3)	1.39(2)
Pt–Cl(2)	2.313(2)	C(3)–C(4)	1.37(2)
Pt–S(1)	2.217(2)	C(4)–C(5)	1.35(2)
Pt–S(2)	2.209(3)	C(5)–C(6)	1.41(2)
S(1)–O(1)	1.470(8)	C(6)–C(1)	1.40(2)
S(1)–C(1)	1.76(1)	C(9)–C(10)	1.43(2)
S(1)–C(7)	1.81(1)	C(10)–C(11)	1.36(2)
C(7)–C(8)	1.53(1)	C(11)–C(12)	1.35(2)
S(2)–O(2)	1.461(8)	C(12)–C(13)	1.43(2)
S(2)–C(9)	1.76(1)	C(13)–C(14)	1.36(2)
S(2)–C(8)	1.80(1)	C(14)–C(9)	1.39(2)
C(1)–C(2)	1.38(2)		

Cl(1)–Pt–Cl(2)	92.67(9)	O(2)–S(2)–C(9)	108.8(5)
Cl(1)–Pt–S(1)	89.20(9)	C(8)–S(2)–C(9)	101.4(5)
Cl(1)–Pt–S(2)	173.36(11)	S(1)–C(1)–C(2)	121.1(8)
Cl(2)–Pt–S(1)	173.47(9)	S(1)–C(1)–C(6)	118.9(8)
Cl(2)–Pt–S(2)	89.43(9)	C(2)–C(1)–C(6)	120(1)
S(1)–Pt–S(2)	89.40(9)	C(1)–C(2)–C(3)	121(1)
Pt–S(1)–O(1)	118.7(4)	C(2)–C(3)–C(4)	119(1)
Pt–S(1)–C(1)	111.7(3)	C(3)–C(4)–C(5)	121(1)
Pt–S(1)–C(7)	105.3(3)	C(4)–C(5)–C(6)	121(1)
O(1)–S(1)–C(1)	108.3(5)	C(5)–C(6)–C(1)	118(1)
O(1)–S(1)–C(7)	107.4(5)	S(2)–C(9)–C(10)	120.3(8)
C(1)–S(1)–C(7)	104.4(5)	S(2)–C(9)–C(14)	119.4(9)
S(1)–C(7)–C(8)	111.0(7)	C(10)–C(9)–C(14)	120(1)
C(7)–C(8)–S(2)	109.0(7)	C(9)–C(10)–C(11)	118(1)
Pt–S(2)–O(2)	119.0(4)	C(10)–C(11)–C(12)	122(1)
Pt–S(2)–C(8)	104.1(3)	C(11)–C(12)–C(13)	120(1)
Pt–S(2)–C(9)	113.5(4)	C(12)–C(13)–C(14)	120(1)
O(2)–S(2)–C(8)	108.4(5)	C(13)–C(14)–C(9)	120(1)

TABLE 4 (*Continued*)

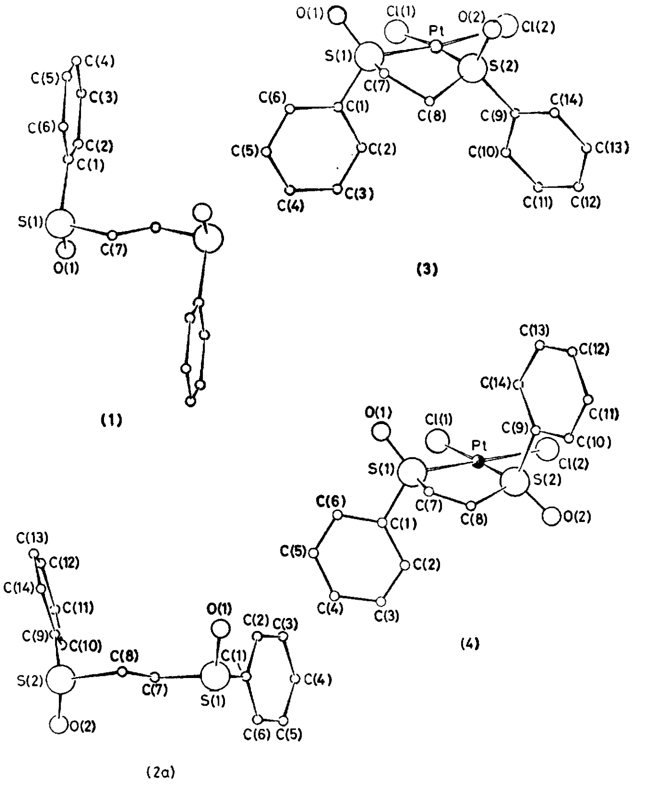
(*d*) Complex (4)

Pt–Cl(1)	2.295(4)	C(2)–C(3)	1.39(3)
Pt–Cl(2)	2.305(5)	C(3)–C(4)	1.35(3)
Pt–S(1)	2.192(4)	C(4)–C(5)	1.40(3)
Pt–S(2)	2.188(4)	C(5)–C(6)	1.35(3)
S(1)–O(1)	1.46(1)	C(6)–C(1)	1.39(2)
S(1)–C(1)	1.75(1)	C(9)–C(10)	1.44(2)
S(1)–C(7)	1.79(2)	C(10)–C(11)	1.36(3)
C(7)–C(8)	1.43(4)	C(11)–C(12)	1.43(3)
S(2)–O(2)	1.40(2)	C(12)–C(13)	1.36(3)
S(2)–C(9)	1.75(2)	C(13)–C(14)	1.45(2)
S(2)–C(8)	1.77(2)	C(14)–C(9)	1.39(2)
C(1)–C(2)	1.38(2)		

Cl(1)–Pt–Cl(2)	91.2(2)	O(2)–S(2)–C(9)	108(1)
Cl(1)–Pt–S(1)	88.7(2)	C(8)–S(2)–C(9)	108(1)
Cl(1)–Pt–S(2)	178.0(2)	S(1)–C(1)–C(2)	118(1)
Cl(2)–Pt–S(1)	179.2(2)	S(1)–C(1)–C(6)	121(1)
Cl(2)–Pt–S(2)	90.4(2)	C(2)–C(1)–C(6)	121(1)
S(1)–Pt–S(2)	89.7(2)	C(1)–C(2)–C(3)	120(2)
Pt–S(1)–O(1)	118.5(7)	C(2)–C(3)–C(4)	121(2)
Pt–S(1)–C(1)	110.3(5)	C(3)–C(4)–C(5)	119(2)
Pt–S(1)–C(7)	104.9(7)	C(4)–C(5)–C(6)	121(2)
O(1)–S(1)–C(1)	109(1)	C(5)–C(6)–C(1)	119(2)
O(1)–S(1)–C(7)	104(1)	S(2)–C(9)–C(10)	118(1)
C(1)–S(1)–C(7)	109(1)	S(2)–C(9)–C(14)	120(1)
S(1)–C(7)–C(8)	113(2)	C(10)–C(9)–C(14)	122(1)
C(7)–C(8)–S(2)	113(2)	C(9)–C(10)–C(11)	120(2)
Pt–S(2)–O(2)	121.0(7)	C(10)–C(11)–C(12)	120(2)
Pt–S(2)–C(8)	103.8(8)	C(11)–C(12)–C(13)	120(2)
Pt–S(2)–C(9)	111.7(5)	C(12)–C(13)–C(14)	122(2)
O(2)–S(2)–C(8)	104(1)	C(13)–C(14)–C(9)	116(2)

* I = $\bar{x}, \bar{y}, \bar{z}$.

structure determination and refinement have already been reported in preliminary communications.[42] Table 3 lists the final positional parameters for the four compounds. A list of observed and calculated structure



Clinographic projections of the four structures factors and thermal parameters is available as Supplementary Publication No. SUP 22201 (43 pp.).*

The molecules of the ligands and the complexes are represented in the Figure in an orientation suitable for comparison. The hydrogen atoms are omitted for clarity. Selected bond distances and angles are in Table 4. The main differences between the two uncomplexed isomers concern the conformation of the molecule, which is acentric in the (*S*,*S*) derivative (2a) and centrosymmetric in the (*R*,*S*) form (1). In (1) the asymmetric unit consists of half of the molecule since the centre of gravity of the central C–C bond lies on a centre of symmetry. A similar situation has recently been found in *meso*-1,2-bis(methylsulphinyl)ethane,[22] and the bond distances and angles agree with those found for the present compound. Unlike most organic sulphoxides which, as indicated by Svinning *et al.*,[22] deteriorate when exposed to *X*-rays, in the present case no significant change was found in the intensity of a reflection periodically measured during data collection. In both the uncomplexed isomers the central C–C bond is significantly shorter than a normal $C(sp^3)$–$C(sp^3)$ bond. This shortening is typical of C–C bonds next to S and can be explained in terms of a secondary rehybridization effect on C atoms caused by the electron-withdrawing properties of the S–O group.[22,43]

TABLE 5

Comparison of the structural parameters (bond lengths in Å, angles in °) of 1,2-bis(phenylsulphinyl)ethane as found in the four compounds

	(1)	(2a)		(3)		(4)	
S–O	1.487(2)	1.489(6)	1.494(6)	1.470(8)	1.461(8)	1.46(1)	1.40(2)
S–$C(sp^3)$	1.814(4)	1.822(6)	1.828(7)	1.81(1)	1.80(1)	1.79(2)	1.77(2)
S–$C(sp^2)$	1.798(3)	1.789(6)	1.806(5)	1.76(1)	1.76(1)	1.75(1)	1.75(2)
$C(sp^3)$–$C(sp^3)$	1.507(3)	1.489(9)		1.53(1)		1.43(4)	
$C(sp^2)$–$C(sp^2)$	1.378(4)	1.39(1)		1.39(2)		1.39(3)	
O–S–$C(sp^3)$	106.6(1)	105.6(3)	105.7(3)	107.4(5)	108.4(5)	104(1)	104(1)
O–S–$C(sp^2)$	107.2(1)	106.9(3)	106.7(3)	108.3(5)	108.8(5)	109(1)	108(1)
$C(sp^2)$–S–$C(sp^3)$	98.5(1)	98.2(3)	98.6(3)	104.4(5)	101.4(5)	109(1)	108(1)
S–$C(sp^3)$–$C(sp^3)$	112.4(2)	107.8(5)	112.9(5)	111.0(7)	109.0(7)	113(2)	113(2)
S–$C(sp^2)$–$C(sp^2)$	119.4(2)	118.5(5)		119.9(8)		119.(1)	
$C(sp^2)$–$C(sp^2)$–$C(sp^2)$	120.0(2)	120.0(6)		120(1)		120(2)	

If one compares the uncomplexed and complexed ligand (Table 5), worthy of note are the conformations assumed by the organic molecule in co-ordinating to metal and the structural parameters involving sulphur. In particular, there is a small but significant shortening in bond distances on going from the uncomplexed to the complexed molecule, while the bond angles have larger values in the complexes, with only one exception. In all the compounds the S–$C(sp^2)$ bond is slightly shorter than the S–$C(sp^3)$ bond, the average values being 1.77 and 1.80 Å respectively. These values are close to those (1.75 and 1.81 Å) obtained by Jones and Power [44] from a survey of several organic sulphides and proposed as characteristic of single bonds of the types S–$C(sp^2)$ and S–$C(sp^3)$ respectively.

The platinum complexes have the following common features: (*i*) square-planar co-ordination around platinum, which involves two chlorides and two sulphur atoms belonging to the organic ligand; {a similar environment has been found for platinum in *cis*-[$PtCl_2(CF_3SCHMeCH_2SCF_3)$].[45]} (*ii*) an envelope conformation of the five-membered chelate ring, in which C(8) is *ca.* 0.6 Å from the plane formed by Pt–S(1)–C(7)–S(2); (*iii*) the presence of two rather short (2.8—3.0 Å) intramolecular Pt · · · H contacts involving the hydrogen atoms of the phenyl rings. {Similar contacts have been recently found in (+)-*trans*-[$PtCl\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2$] (Pt · · · H 2.72 and 2.78 Å).[46]} The bond lengths at platinum are not significantly different in the two complexes even though the values observed in (3) are slightly longer than the corresponding ones found in (4). Moreover, while the Pt–Cl bonds fall in the range usually found for square-planar platinum(II) complexes,[47-50] the Pt–S bonds are slightly shorter [41,50-52] than in platinum(II) complexes containing unidentate sulphoxides. This may be a structural consequence of the stability of the chelate ring.

From an inspection of the Figure, it is easy to see that the different conformation assumed by the organic ligand in co-ordinating to metal involves the exchange of an oxygen atom with a phenyl group. This seems to be the only factor responsible for the small differences observed in the two compounds regarding the bond angles at platinum and the planarity of the ligand atoms. In fact, unlike complex (3), where the two *trans* angles deviate significantly from linearity (173.5 and 173.4°) and the co-ordination is tetrahedrally distorted square planar, in complex (4) the *trans* angles are very close to 180° (178.0 and 179.2°) and the co-ordination around the metal is nearly regular square planar. All the intermolecular contacts less than 3.60 Å have been calculated and none is significantly shorter than the sum of van der Waals radii.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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