Crystal and Molecular Structure of *cis*-[Dichlorobis(methyl phenyl sulphoxide)]platinum(II) and *cis*-[Dichlorobis(benzyl methyl sulphoxide)]platinum(II). An X-Ray and NMR Spectroscopic Study

Luciano Antolini, Ugo Folli, Dario Iarossi, Luisa Schenetti and Ferdinando Taddei
Dipartimento di Chimica, Università di Modena, Via Campi 183, 41100 Modena, Italy

Reactions of (*R,S*)-methyl phenyl sulphoxide and (*R,S*)-benzyl methyl sulphoxide with K_2PtCl_4 give diastereomeric mixtures of *cis*-L_2PtCl_2 complexes. The mixtures isolated from the reactions, change their composition when allowed to stand in solution, to give, at equilibrium, ratios of ± and *meso* forms which differ as a function of the sulphoxide employed. The crystal structure of one of the diastereoisomers isolated in the case of the complex obtained from (*R,S*)-methyl phenyl sulphoxide is built up from racemic pairs of discrete molecules with *R,R* and *S,S* configurations at chiral sulphur atoms. The crystals of the complex prepared from (*S*)-benzyl methyl sulphoxide contain two crystallographically independent but chemically equivalent molecules with *S,S* absolute configuration at sulphur atoms, and one methanol solvate molecule. In both complexes the metal atom shows *cis* square-planar co-ordination geometry of the two chlorine and two sulphur atoms from the organic ligands. The complexes show differences in the orientation of the sulphoxide ligands with respect to the co-ordination plane. The NMR parameters obtained at ^1H, ^{13}C and ^{195}Pt frequencies provide useful indications for recognizing ± and *meso* forms of platinum(II) complexes of sulphoxides and also contain information on the relative conformational patterns of the free and complexed ligands.

Sulphoxides are known to have a pyramidal structure and are intrinsically chiral.[1] Several experimental and theoretical results seem to indicate that the S–O linkage in sulphoxides is best expressed as a semipolar single bond rather than a covalent double bond.[1] Nevertheless a certain degree of π-character of this bond should be attributed to interactions involving p-orbitals on oxygen and 3d-orbitals of the sulphur atom.[2] This property affects the conformational behaviour of the methylsulphinyl group bonded to unsaturated[3] and aromatic[4,5] systems, since, in absence of steric effects, the ground-state conformations for the process of internal rotation around the C–S bond is that in which the S–O bond is almost coplanar with the carbon skeleton of the unsaturated system. The potential energy for the rotational process seems to be regulated mostly by π-conjugation effects. The entity of this interaction is nevertheless small and less operative than in the corresponding ketones.[4,5] Furthermore, the pattern of *ortho* substitution markedly affects the conformational behaviour of methyl phenyl sulphoxides.[4,5]

Complexation of sulphoxides with platinum(II) and palladium(II) involves the sulphur atom as donor, in absence of special steric requirements.[6] In the structure of the square-planar complex, L_2PtCl_2, the ligands L assume, preferentially, a *cis* relationship, when their bulkiness does not create steric crowding.[7–9]

In methyl phenyl sulphoxides the conformation of the methylsulphinyl group dictates conditions for the stereochemical availability of the sulphur lone-pair for complexation. In the absence of *ortho* substituents the lone-pair points out of the plane of the benzene ring, whereas it is almost coplanar when two *ortho* substituents are present.[4,5]

In the light of these structural features we have undertaken an investigation of the effects exerted by the conformational properties of sulphoxides on their complexation behaviour with platinum(II). From a chemical point of view the importance of platinum(II) complexes is also bound up with their potential use as optical resolution agents for sulphoxides.[10] An antitumour activity has been recognized[11] in these complexes and the extent of this property is influenced by the chirality of sulphoxides.

In the present study the structure of the complexes with methyl phenyl sulphoxide and benzyl methyl sulphoxide is dealt with and the conformational behaviour of the free and complexed ligand molecules is examined. The complexes are studied in the solid state and in solution.

Results and Discussion

The complexes of general formula L_2PtCl_2 [**1**, L = (*R,S*)-methyl phenyl sulphoxide; **2**, L = (*R,S*)-benzyl methyl sulphoxide; **3**, L = (*S*)-benzyl methyl sulphoxide] were obtained by reacting the ligand with K_2PtCl_4 as described in the Experimental section. The solid complexes, which, in the case of compounds **1** and **2**, were diastereomeric mixtures of ± and *meso* forms, were either isolated, taken up in an appropriate solvent and subjected to NMR spectroscopy, or, in the case of compounds **1** and **3**, properly crystallized in order to undergo X-ray analysis. The sulphur donor site to platinum(II) and the *cis* configuration in complexes of this type have been detailed in previous studies.[9,12] In the complexes isolated from our reactions the configuration was confirmed from the IR spectra (splitting of the vibrations assigned[13] to the Pt–Cl bond), from NMR features[8,9,14] (^1H, ^{13}C and ^{195}Pt) and from the evidence relating to the X-ray analysis of the compounds.

Crystal Structures.—Selected bond distances and bond angles for compounds **1** and **3** are given in Table 1, the atoms being labelled as shown in Figs. 1 and 2. The crystal structure of compound **1**, Fig. 1, is made up of racemic pairs of discrete molecules with *R,R* and *S,S* configurations at the chiral sulphur atoms. The metal atom shows *cis* square-planar co-ordination geometry of two chlorine and two sulphur atoms. The deviations of the four donor atoms from their mean plane (± *ca.* 0.073 Å) and the *trans* bond angles [176.7(1) and 175.9(1)°] indicate a slight but significant distortion from ideal geometry. The same *cis*-square-planar and slightly distorted environment about the platinum atom, with very close Pt–S and Pt–Cl bond distances, was observed in several platinum complexes containing unidentate sulphoxides.[15] Moreover, as previously

Table 1 Selected bond distances (Å) and bond angles (°) for *cis-rac*[dichlorobis(methyl phenyl sulphoxide)platinum(II) (**1**) and *cis*-(*S*,*S*)[dichlorobis(benzyl methyl sulphoxide)]platinum(II) (**3**)

1 *S*,*S* + *R*,*R* configurations			
Pt–Cl(1)	2.314(2)	Pt–Cl(2)	2.297(2)
Pt–S(1)	2.241(1)	Pt–S(2)	2.245(1)
S(1)–O(1)	1.467(4)	S(2)–O(2)	1.458(4)
S(1)–C(1)	1.783(6)	S(2)–C(8)	1.769(6)
S(1)–C(2)	1.770(5)	S(2)–C(9)	1.785(5)
Cl(1)–Pt–Cl(2)	88.1(1)	Cl(2)–Pt–S(1)	91.7(1)
S(1)–Pt–S(2)	87.6(1)	S(2)–Pt–Cl(1)	92.8(1)
Cl(1)–Pt–S(1)	176.7(1)	Cl(2)–Pt–S(2)	175.9(1)
Pt–S(1)–O(1)	114.0(2)	Pt–S(2)–O(2)	115.0(2)
Pt–S(1)–C(1)	114.4(3)	Pt–S(2)–C(8)	113.0(3)
Pt–S(1)–C(2)	110.0(2)	Pt–S(2)–C(9)	110.9(2)
O(1)–S(1)–C(1)	107.1(3)	O(2)–S(2)–C(8)	107.4(3)
O(1)–S(1)–C(2)	108.5(2)	O(2)–S(2)–C(9)	108.5(2)
C(1)–S(1)–C(2)	102.2(3)	C(8)–S(2)–C(9)	101.1(2)
3 *S*,*S* configuration			
Pt(1)–Cl(1)	2.301(2)	Pt(2)–Cl(3)	2.307(1)
Pt(Cl)–Cl(2)	2.311(2)	Pt(2)–Cl(4)	2.303(2)
Pt(1)–S(1)	2.253(1)	Pt(2)–S(3)	2.239(1)
Pt(1)–S(2)	2.242(1)	Pt(2)–S(4)	2.253(1)
S(1)–O(1)	1.456(6)	S(3)–O(3)	1.462(5)
S(1)–C(1)	1.775(9)	S(3)–C(17)	1.775(8)
S(1)–C(2)	1.811(6)	S(3)–C(18)	1.813(8)
S(2)–O(2)	1.469(4)	S(4)–O(4)	1.466(6)
S(2)–C(9)	1.780(8)	S(4)–C(25)	1.774(8)
S(2)–C(10)	1.784(8)	S(4)–C(26)	1.829(5)
Cl(1)–Pt(1)–Cl(2)	87.2(1)	Cl(3)–Pt(2)–Cl(4)	88.1(1)
Cl(2)–Pt(1)–S(2)	88.1(1)	Cl(4)–Pt(2)–S(3)	88.0(1)
S(2)–Pt(1)–S(1)	92.5(1)	S(3)–Pt(2)–S(4)	92.0(1)
S(1)–Pt(1)–Cl(1)	92.2(1)	S(4)–Pt(2)–Cl(3)	91.8(1)
Cl(1)–Pt(1)–S(2)	174.3(1)	Cl(3)–Pt(2)–S(3)	175.4(1)
Cl(2)–Pt(1)–S(1)	179.1(2)	Cl(4)–Pt(2)–S(4)	179.8(1)
Pt(1)–S(1)–O(1)	116.0(2)	Pt(2)–S(3)–O(3)	117.5(2)
Pt(1)–S(1)–C(1)	107.3(3)	Pt(2)–S(3)–C(17)	111.8(3)
Pt(1)–S(1)–C(2)	112.4(2)	Pt(2)–S(3)–C(18)	109.9(3)
Pt(1)–S(2)–O(2)	118.4(2)	Pt(2)–S(4)–O(4)	114.0(2)
Pt(1)–S(2)–C(9)	111.1(3)	Pt(2)–S(4)–C(25)	110.4(2)
Pt(1)–S(2)–C(10)	108.6(3)	Pt(2)–S(4)–C(26)	112.6(2)
O(1)–S(1)–C(1)	109.4(3)	O(3)–S(3)–C(17)	106.5(4)
O(1)–S(1)–C(2)	107.9(4)	O(3)–S(3)–C(18)	108.6(4)
C(1)–S(1)–C(2)	102.9(4)	C(17)–S(3)–C(18)	101.2(4)
O(2)–S(2)–C(9)	108.2(4)	O(4)–S(4)–C(25)	109.8(3)
O(2)–S(2)–C(10)	108.7(4)	O(4)–S(4)–C(26)	108.7(3)
C(9)–S(2)–C(10)	100.4(4)	C(25)–S(4)–C(26)	100.4(3)

reported for platinum complexes containing phenyl rings,[16,17] there are two short (2.88 and 2.99 Å) intramolecular Pt ••• H contacts between the metal atom and two phenyl protons [those at C(3) and C(14)]. These contacts complete a severely distorted octahedral geometry around the Pt atom. The dimensions of the two crystallographically independent sulphoxide ligands do not significantly differ and compare well with previously reported structural results. Furthermore, these moieties show a rather similar orientation with respect to the co-ordination plane, and the corresponding torsion angles do not differ by more than 4.2° at Pt–S bonds and 9.2° at S–C (phenyl) bonds. As a result, the whole molecule exhibits approximate C_2 symmetry, with the twofold axis bisecting the Cl–Pt–Cl and S–Pt–S bond angles. The crystal packing is characterized by a few (ten) short (less than 3.6 Å) van der Waals contacts; the shortest one (3.172 Å) occurring between the sulphinyl oxygen and phenyl carbon atoms. The structure of **3**, Fig. 2, consists of two crystallographically independent but chemically equivalent $PtCl_2(CH_3SOCH_2C_6H_5)_2$ molecules of *S*,*S* configurations at chiral sulphur atoms, and one methanol solvate molecule. To the presence of the latter molecule, in a 1:2 ratio with the complex, we attribute the loss of crystallographical equivalence between the complex molecules. These display the expected *cis* square-planar and slightly distorted co-ordination geometry about the metal atom with the two sulphoxide ligands acting as S donors, and with two chlorine atoms. The dimensions of the co-ordination polyhedra do not significantly differ, and their individual and mean values compare well with those previously[15] and above reported.

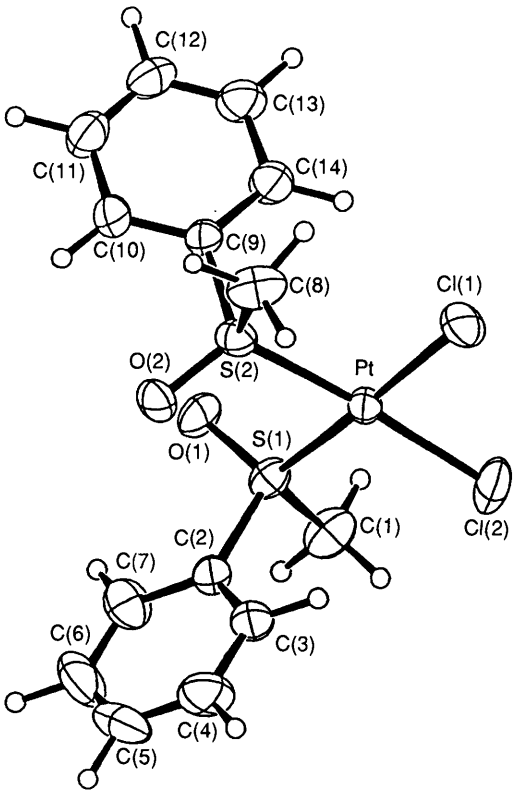

Fig. 1 ORTEP drawing and labelling scheme for non-H atoms of *cis-rac*-[dichlorobis(methyl phenyl sulphoxide)]platinum(II) (**1**) (thermal ellipsoids 40%). Hydrogen atoms are represented as spheres of radius 0.1 Å.

The tetrahedral distortions (atomic deviations from planes to within ±0.038 and ±0.027 Å, respectively) appear slightly less than those observed in compound **1**. A comparison between the orientation of the sulphoxide groups in the two independent complex molecules shows somewhat larger differences (about 18° in a number of corresponding torsion angles), which could be due to crystal packing requirements. The most striking differences between the two compounds examined are in the relative orientations of the two sulphoxide ligands: nearly coincident for the methyl phenyl sulphoxide molecules, and completely different within the $PtCl_2(CH_3SOCH_2C_6H_5)_2$ species, with loss of the approximate C_2 symmetry displayed by the first complex. Furthermore, in compound **3**, the short axial Pt ••• H contacts observed in compound **1**, were not found to be present. It is also interesting to note that one of the two $-CH_2S(O)-CH_3$ fragments, in both crystallographically independent molecules, displays a *trans* planar H–C–S–C–H pattern, with torsion angles at C–S bonds ranging from 167 to 183°.

The crystal packing is determined by a few short van der Waals contacts, and the methanol molecule, the atoms of which show very high thermal motion parameters, appears to be loosely held in lattice holes by weak coulombic forces.

NMR Results.—The spectral features of the complexes **1** and **2**, obtained through the synthetic routes followed by us,

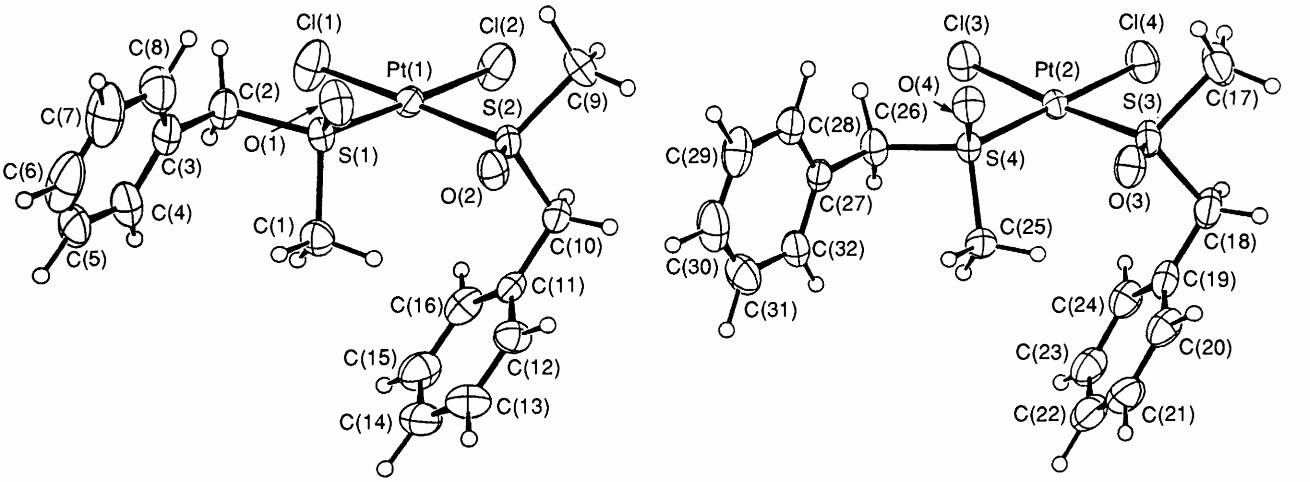

Fig. 2 Atom labelling and thermal ellipsoids (40%) for the two crystallographically independent complex molecules of *cis*-(*S*,*S*)-[dichlorobis(benzyl methyl sulphoxide)]platinum(II) (**3**)

Table 2 Most characteristic NMR parameters of compound **1** in [^{2}H]chloroform solution (6×10^{-2} mol dm^{-3})[a]

	± form	*meso* form
$\delta_H(CH_3)^b$	3.49	3.56
$^3J(CH_3, {}^{195}Pt)$	22.98	22.65
$\delta_C(CH_3)^b$	47.23	46.60
δ_C(C-1)^b	141.15	141.46
δ_C(C-2, C-2′)^b	125.45	125.38
δ_C(C-3, C-3′)^b	129.49	129.11
δ_C(C-4)^b	133.33	132.84
$^2J(CH_3, {}^{195}Pt)^c$	63.24	
^2J(C-1, ^{195}Pt)^c	46.69	
^3J(C-2, ^{195}Pt)^c	7.33	
$\delta_{Pt}{}^d$	-1853.9^e	-1894.1

[a] Equilibrium mixture of ±:*meso* forms in the ratio 1:0.34. Chemical shifts in ppm and coupling constants *J* in Hz. The numbering of the carbon atoms refers to the position of the substituent in the ring. [b] From internal SiMe$_4$. [c] Coupling constants of the *meso* form could not be measured owing to the low solubility of the compound. [d] Referenced to external Na$_2$PtCl$_4$ in D$_2$O. [e] $\Delta\nu_{\frac{1}{2}} = 10$ Hz.

dissolved in [^{2}H]chloroform and allowed to reach the equilibrium between diastereomeric forms, are reported in Tables 2 and 3.

A few minutes after being dissolved in [^{2}H]chloroform at room temperature (23 °C), the NMR spectrum of compound **1** showed the presence of two diastereoisomers, the ± and *meso* forms, in the mole ratio 1:0.13. This ratio slowly changed with time and reached, at equilibrium, the value of 1:0.34 (*ca.* 48 h). Samples resulting from different reaction conditions (varying dilution and reaction times) were found to cover a range of diastereoisomer ratios, yet the equilibrium mixture in [^{2}H]chloroform solution always reached the same final composition. The NMR parameters of Table 2 refer to this mixture.

In the case of compound **2**, obtained under the reaction conditions reported in the Experimental section, the mixture initially contained the ± and *meso* diastereoisomers in the ratio 1:0.25. This composition slowly changed with time and reached the equilibrium value of 0.76:1. The NMR parameters referring to this mixture are reported in Table 3.

Assignment of NMR signals to the diastereoisomers and, consequently, of their amount, was made, in the case of compound **1**, on the basis of the X-ray absolute structure determination of one of the diastereomeric forms, and, for compound **2**, by comparison of the spectra of the diastereomeric mixture with that of the complex obtained from the *S*-enantiomer, compound **3**. The results reported in Table 3 show that the NMR parameters obtained for the latter compound are almost coincident (to within experimental error) with those of the ± form (equimolecular mixture of the enantiomeric complexes of sulphoxide configurations *R*,*R* and *S*,*S*). The ^{1}H spectra were recorded at 80 and 200 MHz, since at higher applied frequencies a broadening of the satellites due to ^{195}Pt (33.79% natural abundance) was observed. This broadening, which caused inaccurate measurements of long-range Pt–H coupling constants at high NMR frequencies, is probably due to a chemical-shift anisotropy effect. This in turn is due[18] to nuclei having a high chemical-shift anisotropy that is not rapidly averaged by Brownian motion, and significantly affects the relaxation time at high applied fields. In the derivatives of Pt^{II} this contribution is likely to be observed,[8] the chemical-shift anisotropy of this nucleus being of the order[19] of *ca.* 10.000 ppm.

The NMR parameters referring to ^{1}H, ^{13}C and ^{195}Pt nuclei, reported in Tables 2 and 3, differ in the ± and *meso* forms of the complexes examined. In particular, the ^{1}H chemical shift of the CH$_3$ group is at lower field in the *meso* form of both compounds. Complexation causes shifts to lower field, with respect to the free ligand, of the ^{1}H resonance of the CH$_3$ group and, in compound **2**, those of the CH$_2$ group as well. For the latter compound, bonding to platinum(II) also increases the shift between the two diastereotopic nuclei: 0.5 ppm in both diastereoisomers of the complex as against 0.13 ppm in the free ligand.

The long-range $^3J(Pt,CH_3)$ coupling constants are slightly larger in the ± form and are of an order of magnitude close to that measured[9] in PtCl$_2$(DMSO)$_2$. A slight difference was observed even for $^2J(Pt,CH_3)$ and $^2J(Pt,CH_2)$ in compound **2**: the latter behaves as $^3J(Pt, CH_3)$ while the former shows the opposite trend in the two diastereoisomers.

An interesting coupling pattern is observed for the two diastereotopic protons of the methylene group of compound **2**, both with the protons of the CH$_3$ group and with the Pt nucleus. The proton at 5.09 ppm of the ± form, labelled H(1), has a ^3J(Pt,H) of 3.76 Hz and $^4J(H,CH_3)$ of 0.52 Hz, while for the other proton, H(2), ^3J(Pt,H) amounts to 16.02 Hz and $^4J(H,CH_3)$ is small, outside experimental error. The same features, with slightly different values, are found in the *meso* form. Among the

Table 3 Most characteristic NMR parameters of compound **2** in [^{2}H]chloroform (6 × 10^{-2} mol dm^{-3})[a]

		± form	*meso* form
$\delta_H(CH_3)$[b]		3.10 (3.10)	3.25
$^3J(CH_3, {}^{195}Pt)$		23.67 (23.31)	22.19
$^4J(CH_2, CH_3)$[c]		0.52 (0.52)	0.40
$\delta_H(CH_2)$[d]	H-1	5.09 (5.00)	4.88
	H-2	4.59 (4.58)	4.37
^3J(H-1, ^{195}Pt)		3.76 (3.76)	4.94
^3J(H-2, ^{195}Pt)		16.02 (16.12)	17.20
^2J(H-1, H-2)		(−)13.46 (−13.33)	(−)13.46
$\delta_C(CH_3)$[b]		41.43 (41.42)	41.35
$\delta_C(CH_2)$[b]		62.46 (62.47)	62.20
δ_C(C-1)[b]		126.72 (126.72)	126.65
δ_C(C-2, C-2′)[b,e]		129.13 (129.13)	129.16
δ_C(C-3, C-3′)[b,c]		131.93 (131.93)	131.90
δ_C(C-4)[b]		129.78 (129.77)	129.81
$^2J(CH_3, {}^{195}Pt)$		53.70	53.84
$^2J(CH_2, {}^{195}Pt)$		49.02	48.15
^3J(C-1, ^{195}Pt)		15.10	15.38
δ_{Pt}[f]		−1913.9 (−1914.0)	−1916.8

[a] Equilibrium mixture of ±:*meso* forms in the ratio 0.76:1. Chemical shifts in ppm and coupling constants *J* in Hz. In parentheses are reported the NMR parameters for compound **3**. The numbering of the carbon atoms refers to the position of the substituent in the ring. [b] From internal SiMe$_4$. [c] Only with the proton of the CH$_2$ group labelled H-1. [d] Diastereotopic protons with different coupling with the ^{195}Pt nucleus. [e] Assignment of chemical shifts of *ortho* and *meta* carbons could probably be reversed. [f] Referenced to external Na$_2$PtCl$_4$ in D$_2$O.

three conformers which should describe the minima for the internal rotation process around the S–CH$_2$ bond, depicted in Fig. 3, (*b*) should be disfavoured for steric reasons, as has also been pointed out previously.[9] In the solid-state structure of compound **3** the two ligands assume conformations (*a*) and (*c*), but not (*b*). Nevertheless, conformation (*a*), which is reported to be the more probable,[9] for the complex *cis*-PtCl$_2$-[(CH$_3$CH$_2$)$_2$SO]$_2$ does not seem to be the only one present in the case of compound **2**. Indeed, the higher value of the ^3J(Pt, H) coupling constant of the ethyl derivative is almost twice that of the benzyl derivative (32 against 16 Hz). Thus a mixture of the conformations (*a*) and (*c*) most probably represents the equilibrium composition of compound **2**. In the solid state, the two sulphoxides present in the complex adopt these two different conformations.

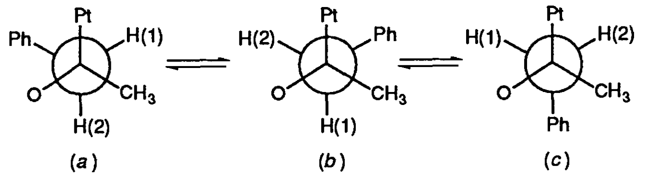

Fig. 3 Newman projections of the three conformers of compound **2**

From ^4J(H,H) in the saturated and unsaturated (*i.e.* propyl and propenyl) fragments the coupling pattern averaged over the three protons of the methyl group is found to be[20] slightly larger for a *transoid* than for a *gauche* orientation of the coupled proton. In free benzyl methyl sulphoxide these ^4J(H,H) coupling constants measured in benzene solution[21] are very small (<0.1 Hz). The predominant conformations reported,[22] in non-polar solvents, for this molecule, are those having the methyl and phenyl groups *gauche* to each other, mainly (*b*) followed by (*c*), according to Fig. 3 (the lone-pair should replace the Pt atom in the case of the free ligand). Assuming that complexation does not greatly perturb the mechanism of ^4J(H,H) coupling in this molecule, it seems reasonable to conclude that the conformational equilibrium in the free ligand differs from that found in compound **2**. In the latter, the contribution of conformation (*b*) should be rather small.

Discussion and Conclusions

The comparison of the results obtained from the solid state X-ray analysis and from NMR spectroscopy in solution enables us to advance a number of conclusions regarding the effect of complexation on the conformational properties of the sulphoxides examined.

From the NMR spectra differences in the parameters between the ± and *meso* forms have become evident; these differences have been observed in both compounds **1** and **2**. As regards the Me group, the ^{1}H and ^{13}C chemical shifts are at lower and higher field, respectively, in the *meso* form. The ^{195}Pt chemical shift is at higher field and the long-range ^3J(Pt,H) is greater in the ± form. More experimental data are nevertheless necessary to establish whether this is a general phenomenon, a conclusion that would be particularly useful in the case of the ^{195}Pt chemical shift.

As regards compound **1**, the crystal structure provided evidence that the torsional angle between the phenyl ring and the S–O bond is slightly increased in the complex (21.1–26.9°) relative to the free ligand[4,5] (*ca.* 10°), and the S–C bond of the methyl group is in a plane almost perpendicular to that of the ring. These quantitative differences apart, the conformation of the molecule is not substantially changed as a result of complexation. The short axial Pt ··· H contacts involving the *ortho* protons of the phenyl rings are likely to have a stabilizing effect on the ± form, and these interactions seem not to occur to the same extent in the *meso* form for steric reasons, at least on the evidence based on Dreiding models. The ^{1}H NMR spectrum of the solution of the ± and *meso* mixture shows that the *ortho* protons in the former diastereoisomer resonate at lower field (8.05 ppm) than in the latter (7.65 ppm).

In the complex obtained from (*S*)-benzyl methyl sulphoxide, compound **3**, the conformations relative to the S–CH$_2$ bond found in the crystal structure are different in the two ligand molecules and correspond to the two most populous conformations in solution. In the crystal structure the hydrogen atoms of one of the CH$_2$ groups, C(2) in Fig. 2, occupy two spatial positions: H(1) is nearly *trans* and H(2) nearly *gauche* with the C(1)–S(1) bond, while the two protons at C(10) are both nearly *gauche* to this bond. Even though these situations are continuously and rapidly interchanged in solution, one of the methylene protons should contain a higher *trans* character than the other and thus have a different stereochemical relationship and coupling constant with the ^{195} Pt nucleus. For the two protons at C(2), the one labelled H(1) is more distant from the square-plane of the complex than the other and, according to previous studies,[9,23] H(1) should be deshielded with respect to H(2). This is found experimentally and, since H(1) has the smaller ^3J(Pt,H) value, this proton should preferentially be *gauche* to the platinum atom, which means that conformers (*a*) and (*c*) should be present in higher proportions. For ^3J(Pt,H) relative to H(2), the value found experimentally should thus be an average of those relative to the *trans* and *gauche* forms. For H(1) a *transoid* relationship with the protons of the methyl group [from conformer (*c*)] should make a significant contribution, and this could explain the greater value of the $^4J(H,CH_3)$ coupling constant with respect to H(2).

In the present study we also clearly define the diastereoisomeric nature of platinum complexes **1** and **2**, previously recognized only as the latter,[9] and a slow interconversion between diastereomers in solution, by exchange of sulphoxide ligands at platinum, is observed for the first time.

Finally it is noteworthy that the solid-state X-ray structure defines unequivocally the absolute configuration of chiral benzyl methyl sulphoxide, otherwise based on the successful synthetic route proposed more than twenty years ago by Mislow and co-workers.[24]

Experimental

cis-Dichlorobis(methyl phenyl sulphoxide)platinum(II) (**1**).—To a sample of K_2PtCl_4 (0.41 g, 1 mmol) dissolved in water (4 cm^3) was added (*R,S*)-methyl phenyl sulphoxide (0.42 g, 3 mmol) and the mixture was stirred at room temperature overnight. The slightly yellow precipitate formed was collected by filtration, washed with water and then with carbon tetrachloride, and dried over P_2O_5. The product (0.51 g, 94%) had m.p. 175–184 °C and was shown by NMR analysis in [^{2}H]chloroform solution to be a mixture of *meso*- and ±-diastereoisomers of *cis*-[$PtCl_2(CH_3SOC_6H_5)_2$] in the ratio 0.13:1, which slowly changed to *ca.* 0.34:1 when the solution was allowed to stand in the NMR tube (*ca.* 48 h).

The 0.13:1 diastereomeric mixture was dissolved in boiling nitromethane and the hot solution filtered from charcoal. The solution was allowed to stand overnight whereupon a crystalline product was obtained, m.p. 192–194 °C, consisting of a single diastereoisomer by NMR analysis, which was subsequently identified as the ± diastereoisomer (same configuration at the two sulphur atoms) by X-ray crystallography (Found: C, 30.65; H, 2.95; S, 11.95. $C_{14}H_{16}Cl_2O_2PtS_2$ requires C, 30.77; H, 2.95; S, 11.74%).

cis-Bis(benzyl methyl sulphoxide)dichloroplatinum(II) (**2**).—(*i*) *From* (R,S)-*benzyl methyl sulphoxide.* The racemic sulphoxide was allowed to react for *ca.* 72 h with aqueous K_2PtCl_4 as described above. The yellowish solid obtained (100%) had m.p. 154–157 °C (lit.,[9] m.p. 141–143 °C; lit.,[25] m.p. 140 °C) (for a sample crystallized from butan-1-ol (Found: C, 33.5; H, 3.55; S, 11.85. $C_{16}H_{20}Cl_2O_2S_2Pt$ requires C, 33.45; H, 3.51; S, 11.16%). The NMR analysis ([^{2}H]chloroform) showed the presence of (*meso*)- and (±)-*cis*-[$PtCl_2(CH_3SOCH_2C_6H_5)_2$] in the ratio *ca.* 0.25:1 which changed after a few days to *ca.* 1:0.76. Attempts to isolate a single diastereoisomer by crystallization of the mixture from solvent were in this case unsuccessful. This could be achieved, however, by employing a chiral sulphoxide in the synthesis of the complex.

(*ii*) *From* (S)-*benzyl methyl sulphoxide.* Optically pure (*S*)-benzyl methyl sulphoxide,[24] $[\alpha]_D = +96$ ($c = 1.25$, ethanol 95%), was allowed to react with K_2PtCl_4 as above. A pale yellow solid was obtained, m.p. 133–135 °C, $[\alpha]_D = +24.0$ ($c = 0.894$, nitromethane). The NMR analysis showed the presence of a single compound. X-Ray crystallography on a sample obtained by slow crystallization from CH_3OH confirmed that the two sulphoxide ligands of the complex had the *S*-configuration at the sulphur atom. However, the presence in the lattice of $\frac{1}{2}$ CH_3OH per mole of complex was shown (Found: C, 33.65; H, 3.80; S, 10.95; $C_{16}H_{20}Cl_2O_2S_2Pt{\cdot}\frac{1}{2}CH_3OH$ requires C, 33.68; H, 3.99; S, 10.57%).

Crystal Data and X-Ray Structure Analysis.—Intensity data were collected on a CAD4 diffractometer, using the graphite monochromated Mo-Kα radiation and the $\omega/2\theta$ scan mode.

Compound **1**. $C_{14}H_{16}Cl_2O_2PtS_2$, $M = 546.39$. Monoclinic, $a = 9.186(1)$, $b = 15.709(2)$, $c = 12.417(2)$ Å, $\beta = 106.80(1)°$, $V = 1715.3$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\ 69$ Å), space group $P2_1/c$ (no. 14), $Z = 4$, $D_x = 2.12$ g cm^{-3}. Colourless, air-stable tablets. Crystal dimensions 0.33 × 0.28 × 0.20 mm, μ(Mo-Kα) = 83.77 cm^{-1}.

Table 4 Fractional atomic co-ordinates for the non-hydrogen atoms in compound **1**

Atom	*x*	*y*	*z*
Pt	0.043 46(2)	0.121 34(1)	0.152 01(2)
Cl(1)	−0.207 6(2)	0.095 6(1)	0.143 7(2)
Cl(2)	−0.036 5(2)	0.148 2(1)	−0.037 8(1)
S(1)	0.287 8(2)	0.138 35(8)	0.157 6(1)
O(1)	0.391 4(4)	0.077 0(3)	0.230 2(3)
C(1)	0.322 0(8)	0.134 5(4)	0.023 4(5)
C(2)	0.349 0(6)	0. 242 4(4)	0.204 1(4)
C(3)	0.244 8(7)	0.308 3(4)	0.189 4(5)
C(4)	0.292(1)	0.387 8(4)	0.229 2(7)
C(5)	0.441(1)	0.402 6(5)	0.283 4(7)
C(6)	0.546 7(9)	0.337 3(6)	0.298 7(7)
C(7)	0.500 3(7)	0.256 6(4)	0.259 1(6)
S(2)	0.123 1(2)	0.105 18(8)	0.339 6(1)
O(2)	0.243 2(5)	0.163 6(3)	0.398 6(3)
C(8)	−0.025 8(8)	0.113 7(4)	0.402 9(7)
C(9)	0.186 3(6)	−0.001 2(3)	0.376 4(4)
C(10)	0.301 4(6)	−0.012 4(4)	0.474 0(5)
C(11)	0.348 9(7)	−0.095 9(5)	0.503 5(6)
C(12)	0.282 9(8)	−0.163 4(4)	0.440 6(6)
C(13)	0.169 8(8)	−0.149 5(4)	0.344 2(6)
C(14)	0.118 5(7)	−0.067 4(4)	0.308 6(5)

For data collection the ω scan width was 0.65 + 0.35 tan θ, the scan speed being 1.2–3.3 ° min^{-1}; 4316 reflections were measured ($1.5 \leqslant \theta \leqslant 28°$, $\pm h$, $+k$, $+l$), 4126 unique [merging $R = 0.021$ after absorption correction based on the ψ scan[26] (max., min. correction factors 1.00, 0.71)], giving 3016 with $I > 3\sigma(I)$, used in the structure analysis. No crystal decay during data collection.

The structure was solved by conventional Patterson and Fourier methods and refined by means of full-matrix least-squares calculations with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were firstly located in ΔF Fourier maps and then constrained to ride in ideal positions on their bonded atoms, at a bond distance of 1.05 Å. Their isotropic thermal parameters were set 1.0 Å^2 higher than the last isotropic temperature factors of the bonded atoms. Final R and R_w values are 0.0269 and 0.0306, respectively. The weighting scheme $w = 0.96/[\sigma^2(F_o) + 0.0010\ F_o^{\ 2}]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analysis. During refinements, zero weight was assigned to seven strong low-order reflections, which may be affected by secondary extinction.

Compound **3**. $C_{33}H_{44}Cl_4O_5Pt_2S_4$, $M = 1180.92$. Monoclinic, $a = 13.499(1)$, $b = 8.659(1)$, $c = 17.278(2)$ Å, $\beta = 93.67(1)°$, $V = 2008.0$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\ 69$ Å), space group $P2_1$ (no. 4), $Z = 2$, $D_x = 1.95$ g cm^{-3}. Pale-yellow, air-stable prisms. Crystal dimensions 0.30 × 0.25 × 0.23 mm, μ(Mo-Kα) = 72.08 cm^{-1}.

The scan width employed was 0.75 + 0.35 tan θ, scan speed 1.2–4.1° min^{-1}; 5312 reflections were measured ($1.5 \leqslant \theta \leqslant 28°$, $\pm h$, $+k$, $+l$; no Friedel pairs), 5161 unique [merging $R = 0.010$ after absorption correction based on the ψ scan[26] (max., min. correction factors 1.00, 0.92)], giving 4218 with $I > 3\sigma(I)$, used in the structure analysis. Linear crystal decay with total loss in intensity of −2.3% corrected during processing.

The structure was solved and refined in the same way as the previous compound, including the treatment of hydrogen atoms. The protons belonging to the methanol solvate molecule, the atoms of which exhibit very large thermal motions (the loss of which may perhaps be the cause of the crystal decay observed during data collection), could not be located. Least-squares refinement of this model (432 variable parameters) led

Table 5 Fractional atomic co-ordinates[a] for the non-hydrogen atoms in compound **3**

Atom	*x*	*y*	*z*
Pt(1)	0.889 62(2)	0.75	0.886 44(1)
Cl(1)	0.907 6(1)	0.738 1(6)	1.019 7(1)
Cl(2)	0.719 5(1)	0.751 9(7)	0.898 6(1)
S(1)	1.055 77(9)	0.751 3(4)	0.875 97(8)
O(1)	1.093 8(3)	0.870 3(7)	0.826 1(3)
C(1)	1.089 3(5)	0.567(1)	0.841 5(4)
C(2)	1.124 6(4)	0.763(1)	0.969 4(4)
C(3)	1.235 7(4)	0.755(1)	0.961 5(4)
C(4)	1.286 4(6)	0.617(1)	0.972 9(5)
C(5)	1.388 1(7)	0.614(2)	0.965 2(6)
C(6)	1.438 2(6)	0.743(2)	0.943 7(6)
C(7)	1.388 9(7)	0.877(2)	0.931 7(5)
C(8)	1.284 6(6)	0.884(1)	0.941 2(5)
S(2)	0.858 3(1)	0.747 6(4)	0.757 45(8)
O(2)	0.943 0(3)	0.756 0(7)	0.708 0(2)
C(9)	0.771 8(6)	0.895(1)	0.727 6(5)
C(10)	0.787 0(5)	0.579 5(9)	0.731 7(4)
C(11)	0.849 2(5)	0.438 1(8)	0.740 6(4)
C(12)	0.911 7(5)	0.396 8(9)	0.681 4(4)
C(13)	0.972 8(6)	0.271(1)	0.690 9(5)
C(14)	0.975 3(7)	0.184(1)	0.757 9(5)
C(15)	0.913 5(6)	0.223(1)	0.816 0(4)
C(16)	0.852 5(6)	0.349(1)	0.807 9(4)
Pt(2)	0.622 95(2)	0.317 01(4)	0.411 14(1)
Cl(3)	0.451 7(1)	0.315 6(5)	0.414 21(9)
Cl(4)	0.602 5(2)	0.302 5(5)	0.277 99(9)
S(3)	0.787 5(1)	0.328 9(4)	0.399 16(9)
O(3)	0.851 2(3)	0.357 0(7)	0.469 5(3)
C(17)	0.818 8(7)	0.472(1)	0.331 0(5)
C(18)	0.829 7(6)	0.155(1)	0.353 2(4)
C(19)	0.827 3(5)	0.019 6(9)	0.406 0(4)
C(20)	0.904 9(5)	−0.004(1)	0.462 4(5)
C(21)	0.901 1(6)	−0.130(1)	0.513 5(5)
C(22)	0.821 5(6)	−0.226(1)	0.507 6(5)
C(23)	0.744 3(5)	−0.205(1)	0.453 4(5)
C(24)	0.745 9(5)	−0.080 0(9)	0.403 1(4)
S(4)	0.642 82(9)	0.330 3(4)	0.541 44(7)
O(4)	0.684 9(3)	0.476 8(6)	0.570 7(3)
C(25)	0.717 1(5)	0.174 3(9)	0.578 4(4)
C(26)	0.527 1(4)	0.293 0(9)	0.588 4(3)
C(27)	0.541 7(4)	0.300 9(8)	0.675 1(3)
C(28)	0.540 3(5)	0.443(1)	0.712 0(4)
C(29)	0.551 2(6)	0.448(1)	0.791 8(5)
C(30)	0.566 3(6)	0.316(2)	0.835 7(4)
C(31)	0.570 2(7)	0.176(1)	0.799 1(5)
C(32)	0.555 6(6)	0.167(1)	0.718 0(4)
Ome	0.700 4(6)	0.912(3)	0.206 9(6)
Cme	0.715(2)	0.757(3)	0.173(1)

[a] The origin of the unit cell was arbitrarily defined by assigning the value 0.75 to the *y* co-ordinate of the Pt(1) atom

to final convergence at *R* and R_w values of 0.0191 and 0.0208, respectively. The weighting scheme $0.804/[\sigma^2(F_o) + 0.000\,54\,F_o^2]$ gave satisfactory agreement analysis. During refinement, zero weight was assigned to one strong low-order reflection, which may be affected by secondary extinction. Least-squares refinement of the enantiomeric model (by inversion of all atomic co-ordinates) led to *R* and R_w values of 0.0242 and 0.0269, respectively. Our *R*-factor ratio of 1.267, largely exceeding the $\mathcal{R}$ (1.3786, 0.005) value (1.0011) of Hamilton's test,[27] confirms the reliability of our assignment of absolute configuration.

Complex, neutral-atom scattering factors, including anomalous dispersion terms, were taken from ref. 28. Major calculations were carried out on a VAX 6310 computer by using the SHELX76 program package[29] and the ORTEP plotting program.[30] Final atomic co-ordinates for non-hydrogen atoms are given in Tables 4 and 5. Full lists of bond lengths and angles, thermal parameters, least-squares planes and non-hydrogen atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.*

NMR Spectra.—The ^1H spectra at 80.13 MHz were recorded on a Bruker WP80-SY Spectrometer. The ^1H spectra at 200.058 MHz, ^{13}C at 50.308 MHz and ^{195}Pt spectra at 42.935 MHz were recorded on a Varian XL-200 spectrometer at a probe temperature of 296 K. A spectral width of 1000–2000 Hz was adopted for broad-band proton-decoupled ^{13}C spectra, with 32K data points. The pulse width was 11 μs corresponding to a pulse width of nearly 45°, the relaxation delay 5 s and 5000–6000 scans. For the broad-band proton-decoupled ^{195}Pt spectra, 100–500 scans were acquired, the spectral window was 4000 Hz and 32K data points. A pulse width of 25 μs was employed corresponding to a pulse angle of nearly 90° and the relaxation delay was 1 s. Solutions 6×10^{-2} mol dm^{-3} in [^2H]chloroform were employed. For ^1H and ^{13}C chemical shifts, $SiMe_4$ was employed as an internal standard, for ^{195}Pt a solution of Na_2PtCl_4 in D_2O was used as external standard.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors' (1991), *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

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