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Spectroscopic and structural properties of dimethyl-, diphenyl- and methylphenylsulfoxide platinum complexes. The crystal and molecular structures of *cis*-dichlorobis(methylphenylsulfoxide)-platinum(II) and potassiumtrichloro(phenylsulfoxide)platinum(II)-acetone solvate

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Abstract

The preparation and properties of platinum complexes with bulky sulfoxide ligands have been examined. The reaction of methylphenylsulfoxide (MePhSO) with K_2PtCl_4 gives as expected *cis*-[$PtCl_2(MePhSO)_2$] whereas the product with the more sterically demanding diphenylsulfoxide Ph_2SO is K[$PtCl_3(Ph_2SO)$]. This monosulfoxide anion is also formed with methyltert-butylsulfoxide, Met-BuSO. The molecular structures of *cis*-[$PtCl_2(MePhSO)_2$] (IIA) and K[$PtCl_3(Ph_2SO)$]·acetone (V) were resolved by X-ray diffraction. The crystals of *cis*-[$PtCl_2(MePhSO)_2$] are monoclinic $P2_1/c$ with cell dimensions $a=9.1834(2)$, $b=15.7256(4)$, $c=12.4279(3)$ Å, $\beta=106.78(2)°$ and $Z=4$. The structure was refined to $R_w=4.86\%$. The sulfoxides are S-bound as expected and the *meso (S,S* configuration around the chiral sulfur atom) diastereomer was solved. All bond lengths and bond angles around the square planar platinum are normal with Pt–S distances of 2.244(3) and 2.238(3) Å. The Pt–Cl distances of 2.315(3) and 2.303(3) Å are within the range expected for Cl *trans* S. The phenyl groups of the MePhSO lie essentially perpendicular to the coordination plane with dihedral angles of 92.1 and 84.2°. The crystals of K[$PtCl_3(Ph_2SO)$]·acetone are also monoclinic $P2_1/c$ with $a=9.775(3)$, $b=8.239(2)$ and $c=24.974(6)$ Å, $\beta=95.78(2)°$ and $Z=4$. Bond lengths and angles around the coordination plane are normal. The Pt–S distance is 2.214(3) Å and the Pt–Cl bond *trans* S is 2.327(3) Å, longer than the mutually *trans* Pt–Cl bonds 2.302(3) Å. The phenyl groups make dihedral angles of 81.8 and 100.9° with the coordination plane and are essentially mutually perpendicular with a Ph–Ph dihedral angle of 92.9°. The K cation has non-bonding contacts to both the sulfoxide and acetone oxygen atoms of 2.673(9) and 2.728(13)°, respectively. The structural parameters are discussed with respect to data from Me_2SO and sterically hindered sulfoxides. There are no major differences found in the structural parameters to explain the trends in reactivity of the various sulfoxides. Complementary studies using ^{195}Pt NMR spectroscopy show that the order of shielding in the series K[$PtCl_3(R'R''SO)$] is $Ph_2SO > MePhSO > Me_2SO$. The values of the ^{195}Pt chemical shifts are discussed with respect to models of sulfoxide bonding to platinum.

Introduction

We are presently examining the antitumor properties of the complexes [$PtCl(R'R''SO)(diam)$]NO_3, whose activity depends on both the structure and chirality of the sulfoxide ligand [1]. As part of this work it became necessary to study in detail the properties of non-amine-containing platinum–sulfoxide species formed from a simple starting material such as K_2PtCl_4. Although the Me_2SO complex has been extensively studied from a range of aspects and a large number of complexes with one Me_2SO ligand are also known, studies with sterically hindered sulfoxides are not as numerous [2–4] especially with phenyl groups directly bound to the sulfur. In this paper we report on spectroscopic studies of Me_2SO derivatives, properties of platinum complexes with sterically hindered sulfoxides and the crystal and molecular structures of *cis*-[$PtCl_2(MePhSO)_2$] and K[$PtCl_3$-(Ph_2SO)].

Experimental

Starting materials and physical methods

IR spectra were obtained as KBr discs on Nicolet FT6000 series and Perkin-Elmer 1430 spectrophotometers. Raman spectra were run as powdered solids on a SPEX model 1403 0.85m double monochromator

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using the 514 nm line of an Innova 100 argon ion laser. NMR spectra were run on Bruker 250 and 270 MHz spectrometers. ^{195}Pt NMR spectra (250MHz) were run in either d_7-DMF (for $[PtCl_2(R'R''SO)_2]$) or 50% acetone/D_2O (for $K[PtCl_3(R'R''SO)]$) with reference to a Na_2PtCl_6 solution in D_2O as external reference. Samples were run at a pulse width of 10 μs with a relaxation delay of 0.5 s. Usually a sweep width of 30 KHz was used and 5000–10000 scans were adequate. All shifts are positive to lower shielding. Elemental analyses were by Robertson Laboratories, Madison, NJ.

The known complexes *cis*- and *trans*-$[PtCl_2(Me_2SO)_2]$ and the monoanion $K[PtCl_3(Me_2SO)]$ were prepared by the literature procedures [4–6]. The deuterated complexes were prepared in an identical manner.

Preparation and separation of the diastereomers of cis-dichlorobis(methylphenylsulfoxide)platinum(II), complex IIA

The ligand MePhSO (0.56 g, 4 mmol) in EtOH (15 ml) was added to an aqueous solution of K_2PtCl_4 (0.93 g, 2 mmol in 20 ml). The solution was heated to 45 °C for 1 h and then stirred overnight. The solution acquired a bright yellow color and some white precipitate was observed. Evaporation to half-volume precipitated the mixture as light yellow needles, complex **II**. This product analysed as $C_{14}H_{16}Cl_2O_2S_2Pt$ but NMR spectra confirmed the presence of diastereomers. The mixture was then dissolved in hot acetone, filtered to remove KCl and evaporated to half volume. Upon cooling the product *cis*-$[PtCl_2(MePhSO)_2]$, complex **IIA**, precipitated from solution as colorless needles. Yield 35%. *Anal.* Calc. for $C_{14}H_{16}Cl_2O_2S_2Pt$: C, 30.77; H, 2.93. Found: C, 30.56; H, 3.02%. Slow cooling at room temperature gave crystals suitable for X-ray diffraction.

Preparation of potassiumtrichloro(methylphenylsulfoxide)platinum(II), complex IV

To the diastereomeric mixture of *cis*-$[PtCl_2(MePhSO)_2]$, (0.546 g, 1 mmol) in EtOH (25 ml) was added a stoichiometric amount of $K_2Pt_2Cl_4$ dissolved in 40 ml H_2O. The solution was left at room temperature for 2 days, during which the color darkens noticeably. After this time, the solution was evaporated to dryness, dissolved in ethanol and filtered through charcoal. This solution was further evaporated to dryness, the solid dissolved in hot acetone and again treated with activated charcoal. The resultant bright yellow solution was evaporated to small volume and cooled at 3 °C. Upon standing, bright yellow crystals of the product precipitated. Yield 42%. *Anal.* Calc. for $C_7H_8Cl_3KOSPt$: C, 17.45; H, 1.66; Cl, 22.08. Found: C, 17.83; H, 1.8, Cl, 22.45%.

Preparation of potassiumtrichloro(diphenylsulfoxide)platinum(II), complex V

The salt was prepared in a similar manner to the above by addition of Ph_2SO (0.808 g, 4 mmol) dissolved in EtOH (10 ml) to a solution of K_2PtCl_4 (0.415 g, 1 mmol) dissolved in H_2O (20 ml). Upon stirring overnight at r.t. evaporation to dryness yielded a bright yellow oil which was redissolved in acetone and filtered through celite. Upon further evaporation to a minimum volume and cooling to 5 °C yellow crystals of the product form. Yield 62%. Elemental analysis and ^{1}H NMR spectroscopy indicated the compound contained one molecule of acetone solvate. *Anal* Calc. for $C_{15}H_{16}Cl_3KO_2SPt$: C, 25.94; H, 2.66; Cl, 17.68. Found: C, 26.23; H, 2.80, Cl, 18.01%. Slow cooling at room temperature gave crystals suitable for X-ray diffraction.

Preparation of potassiumtrichloro(methyltert-butylsulfoxide) platinum(II), complex VI

The complex was prepared in an identical manner to the above. Yield 73%. *Anal.* Calc. for $C_5H_{12}Cl_3KOSPt$: C, 13.00; H, 2.60; Cl, 23.05. Found: C, 12.92; H, 2.75, Cl, 13.15%.

Crystal structure determination

Cell determination and data collection were performed on a Nicolet R3m/v single crystal diffractometer. The details are given in Table 1. The data were corrected for the effects of Lorentz and polarization. The space group $P2_1/c$ was determined in both cases by its systematic absences. An empirical absorption correction which models the crystal as a pseudo-ellipsoid was applied. The Pt atoms were located by direct methods (SHELX). The remaining non-hydrogen atoms were located in subsequent *F* maps. Hydrogen atoms were generated in idealized positions and assigned fixed isotropic temperature factors. They were repositioned after each refinement cycle. All non-hydrogen atoms were refined anisotropically using weights based on counting statistics.

Results and discussion

The ligands studied were dimethyl- (Me_2SO), methylphenyl- (MePhSO) and diphenylsulfoxide (Ph_2SO) and the characterization and spectroscopic data for all new complexes are given in Table 2. For completeness the known complexes with Me_2SO are included.

Complexes with Me_2SO

IR and Raman spectra

The crystal structure of *cis*-$[PtCl_2(Me_2SO)_2]$ is known [7, 8] and synthetic routes to the *trans* isomer have been reported [5, 9]. The monoanion $K[PtCl_3(Me_2SO)]$

TABLE 1. Crystal structure data collection for *cis*-$[PtCl_2(MePhSO)_2]$ and $K[PtCl_3(Ph_2SO)]\cdot$acetone

	cis-$[PtCl_2(MePhSO)_2]$	$K[PtCl_3(Ph_2SO)]\cdot$acetone
Formula	$C_{14}H_{16}O_2S_2Cl_2Pt$	$C_{15}H_{16}O_2SCl_3KPt$
Formula weight	546.4	600.9
Crystal size (mm)	$0.15\times0.20\times0.25$	$0.2\times0.2\times0.2$
Space group	monoclinic $P2_1/c$	monoclinic $P2_1/c$
a (Å)	9.1834(2)	9.775(3)
b (Å)	15.7256(4)	8.239(2)
c (Å)	12.4279(3)	24.974(6)
α (°)	90.0	90.0
β (°)	106.78(2)	95.78(2)
γ (°)	90.00	90.00
V (Å^3)	1718.3(7)	2001.1(9)
T (K)	295	295
Z	4	4
Diffractometer	Nicolet R3m/V	Nicolet R3m/V
Radiation	graphite monochromatized Mo Kα 0.71073 Å	graphite monochromatized Mo Kα 0.71073 Å
Scan mode limits (°)	$3<2\theta<50$	$3<2\theta<50$
Total reflections	3294(3029 independent)	3788(3490 independent)
Observed reflections ($I>3\sigma(I)$)	2436	2405
R (%)	4.59	4.9
R_w (%)	4.86	3.9

TABLE 2. Spectral data for platinum–sulfoxide complexes

Complex	IR (cm^{-1})		NMR[a] (ppm)	
	ν(SO)	ν(Pt–Cl)/ν(Pt–S)[b]	$\delta(^1H)$	$\delta(^{195}Pt)$
cis-$[PtCl_2(Me_2SO)_2]$ (**I**)	1160, 1140	334, 322, 315	3.45(24)	−3475
cis-$[PtCl_2(MePhSO)_2]$ (**IIA**)	1150(br) 1140	340, 319	3.55(21) 7.74, 8.08	−3471
$K[PtCl_3(Me_2SO)]$ (**III**)	1100	325	3.40(23)	−2951
$K[PtCl_3(MePhSO)]$ (**IV**)	1120	325, 305	3.57, 7.71, 8.08	−3004
$K[PtCl_3(Ph_2SO)]$ (**V**)	1145(br)	340, 320(sh) 300	7.53 7.93	−3064
$K[PtCl_3$(Met-BuSO] (**VI**)	1155	330, 320	3.10(24), 1.48	−2955

[a] Complexes **I** and **IIA** in DMF. Complexes **III–VI** in 1:1 acetone/H_2O. [b] See also Table 3.

is also structurally characterized [10]. There is little agreement in the literature on the correct values of ν(Pt–S) in the complexes of dimethyl sulfoxide and substituted sulfoxides and the assignment is complicated by possible coupling not only of ν(Pt–Cl) and ν(Pt–S) but also the presence of bands due to skeletal vibrations of the ligand itself. To assist in our structural comparison of a wider range of sulfoxide complexes we examined the IR and Raman spectra of *cis*- and *trans*-$[PtCl_2(Me_2SO)_2]$ and $K[PtCl_3(Me_2SO)]$ and their deuterated analogues. A similar study has been carried out for *trans*-$[PdCl_2(Me_2SO)_2]$, the crystal structure of which confirmed the geometry [11]. Our results on the platinum complexes agree in general with those for the palladium complex and our interpretation therefore follows that of Forel and Tranquille [12]. The results are summarized in Table 3 and below.

S-bonding results in an increase in frequency of ν(SO) from that of free Me_2SO [13, 14]. In platinum complexes ν(SO) usually appears at 1100–1150 cm^{-1}. In the low frequency region below 500 cm^{-1} the three bands in free Me_2SO at 382, 332 and 309 cm^{-1} have been assigned as δ(SO), γ(SO) and δ(CSC), respectively [15]. These assignments agree with independent studies [16]. These bands should be more susceptible to an isotope effect than Pt–S or Pt–Cl stretches and comparison of the shifts can help confirm the assignments. In all Pt–Me_2SO complexes the two bands related to SO

TABLE 3. Selected IR and Raman frequencies for *cis*- and *trans*-$[PtCl_2(Me_2SO)_2]$ and $K[PtCl_3(Me_2SO)]$ and their deuterated analogues[a]

	cis$[Pt\text{-}Cl_2(Me_2SO)_2]$		*trans*-$[PtCl_2(Me_2SO)_2]$		$K[PtCl_3(Me_2SO)]$		Free Me_2SO[b]		Assignment
	Me_2SO	d_6-Me_2SO	Me_2SO	d_6-Me_2SO	Me_2SO	d_6-Me_2SO	Me_2SO	d_6-Me_2SO	
IR	1160	1155	1120(br)	1120(br)	1100	1105	1058	1059	ν(SO)
	1140	1125							
	430	397(1.08)	419	384(1.09)	447	413(1.08)	382	339(1.12)	δ(SO)
	379	353(1.07)	376	350(sh)(1.09)	381	354(1.08)	332	306(1.08)	γ(SO)
							309	264(1.17)	δ(CSC)
	334	333	351	344	325(sh)	325(sh)			ν(Pt–Cl)
	322	318							ν(Pt–Cl)
	315(sh)	309	329	324(sh)					ν(Pt–S)
Raman	451	412(1.09)	442	400(1.1)	[c]	–	384	340(1.12)	
	382	356(1.09)	366	332(1.1)		–	333	307(1.08)	
	334		336	338		–	308	265(1.16)	
	318		308						
	312								

[a]Values in parentheses are ratios of isotopic shifts. [b]From ref. 15. [c]Decomposed in beam.

deformations undergo an increase in frequency of 40–50 cm^{-1}, Table 3. Assignment of these bands as related to skeletal ligand vibrations is supported by the facts that: (i) the relatively large isotopic ratios of these bands are similar to the free ligand; (ii) the bands are present in all complexes independent of symmetry; (iii) they are not observed in complexes *cis*-$[PtCl_2(R'R''SO)_2]$, where $R'R''SO = MePhSO$ or the chelating tetramethylenesulfoxide $(O)S(CH_2)_2S(O)$* and (iv) they are not observed in analogous Me_2S complexes [18, 19]. The values of ν(Pd–Cl) and ν(Pd–S) in *trans*-$[MCl_2(Me_2S)_2]$ have been assigned respectively as 361 and 310 cm^{-1}, M = Pd and 344 and 311 cm^{-1}, M = Pt [18].

The value of ν(Pt–Cl) in *trans*-$[PtCl_2L_2]$ is essentially invariant [20] and this geometry is easiest to analyse because the D_{2h} symmetry only allows one active IR band for both the Pt–Cl and Pt–S vibrations [21]. In *trans*-$[PtCl_2(Me_2SO)_2]$ the intense band at 351 cm^{-1} (shifted to 344 cm^{-1} in the d_6-Me_2SO derivative) is easily assigned therefore to ν(Pt–Cl). The expected one band due to ν(Pt–S) is therefore most likely assigned as 329 cm^{-1} (324 cm^{-1} in the d_6-Me_2SO derivative). Analysis of other Me_2SO complexes is more complicated because we expect to see both symmetric and asymmetric vibrations and deuteration results in some overlap of these bands. However, using the assignments above, we can attribute the three principal bands of *cis*-$[PtCl_2(Me_2SO)_2]$ at 334, 322 and 315 (sh) as due to ν_{asym}(Pt–Cl), ν_{sym}(Pt–Cl) and ν_{asym}(Pt–S), respectively. The observed Raman bands are also given in Table 3.

In summary, then, the high-frequency bands above 350 cm^{-1} are most likely due to ligand vibrations and should not be assigned (as has occurred in examples in the literature) to ν(Pt–S). This stretching vibration is most likely to occur in the region of 300–330 cm^{-1}. Possible overlap and coupling with ν(Pt–Cl) and ligand vibrations make ν(Pt–S) difficult to unequivocally assign in *cis*-$[PtCl_2(R'R''SO)_2]$ complexes and thus no further attempts were made for the MePhSO and Ph_2SO complexes. This difficulty in distinguishing ν(Pt–Cl) and ν(Pt–S) in routine spectra on standard spectrophotometers probably also extends to the many complexes of type $[PtCl_2(Me_2SO)L]$ described in the literature.

Complexes with MePhSO

Unsymmetrical sulfoxides R'R''SO are *racemic* and therefore $[PtCl_2(R'R''SO)_2]$ exists as a pair of diastereomers. The product from the reaction of MePhSO with K_2PtCl_4 in $H_2O/EtOH$ gives a pale yellow solid (complex **II**) whose ^1H NMR spectrum shows two peaks corresponding to the S-CH_3 protons of the diastereomeric pairs (*RS*/*SR* and *RR*/*SS*) at 3.55 and 3.63 ppm. The ^{195}Pt NMR spectrum also shows two peaks at −3471 and −3432 ppm. Soxhlet extraction of the pale yellow solid with acetone gives a colorless solution which upon cooling affords a white solid (complex **IIA**). This species now shows only one peak in both the ^1H (3.55 ppm) and ^{195}Pt (−3471 ppm) NMR spectra. Evaporation of the original mother liquor and dissolution of the oil in acetone gave a ^{195}Pt NMR spectrum with a small peak corresponding to **IIB** (−3432 ppm) and a main peak, for **IIC**, at −3090 ppm. This species could arise from decomposition or disproportionation

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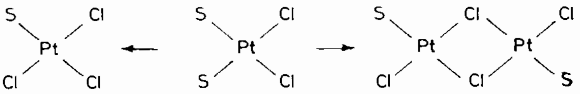
*In this complex there is only one band apparent at 370 cm^{-1} which should correspond to deformations involving S, O and the C atoms of the chelate ring. The (Pt–Cl) stretches are apparent at 338 and 322 cm^{-1} with v(Pt–S) probably appearing as a shoulder on the latter peak at 316 cm^{-1} [17].

of *cis*-[$PtCl_2(MePhSO)_2$] to either the [$PtCl_3(MePhSO)$] monoanion or by loss of sulfoxide to give the chloro-bridged dimer [$Pt_2Cl_4(MePhSO)_2$] (S is sulfoxide ligand):



The chloro-bridged dimer has been described for Me_2SO and the X-ray crystal structure for Et_2SO has been resolved [5]. Independent synthesis of the [$PtCl_3(MePhSO)$] anion (complex **IV**, see below) gave a ^{195}Pt chemical shift of −3004 ppm and therefore it is possible that the peak at −3090 ppm should be attributed to the species [$Pt_2Cl_4(MePhSO)_2$], **IIC**. The value of the chemical shift is still consistent with a $PtSCl_3$ coordination sphere [22]. Recrystallization of complex **IIA** from acetone gave crystals suitable for X-ray diffraction.

Description of structure (Fig. 1)

The structure determination confirmed the structure as *cis*-[$PtCl_2(MePhSO)_2$]. Crystal summary data are given in Table 1 and relevant bond lengths and bond angles are summarized in Table 4. The complex consists of discrete units of *cis*-[$PtCl_2(MePhSO)_2$]. The sulfoxide ligands are S-bonded as expected. The diastereomer is the *meso* form. A previous structure determination of a complex with an asymmetric sulfoxide, *cis*-[$PtCl_2(MeEtSO)_2$], resolved the *racemic R, S* form [23]. All bond lengths and angles around the Pt atom are normal, as are the parameters for the ligand. The phenyl rings make dihedral angles of 92.1 and 84.2° with respect to the coordination plane. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 5.

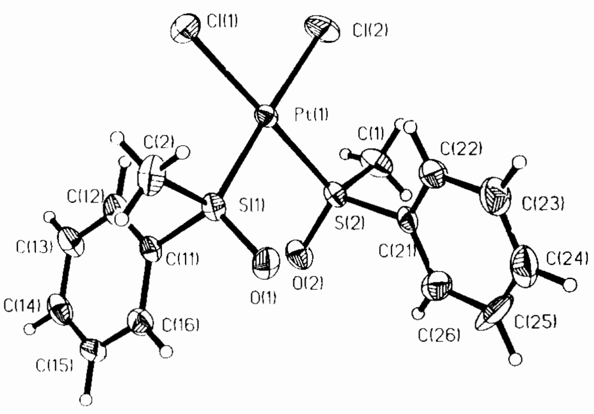


Fig. 1. The molecular structure of *cis*-[$PtCl_2(MePhSO)_2$].

Preparation of K[$PtCl_3(R'R''SO)$], R' = Me, R'' = Ph; R' = R'' = Ph

Upon separation of the diastereomers of *cis*-[$PtCl_2(MePhSO)_2$] and isolation of complex **IIA** we noted that the ^{195}Pt NMR spectrum of the mother liquor showed only a small amount of the other diastereomeric pair with disproportionation to another species, which is probably the chloro-bridged dimer (see above). To characterize the other possible disproportionation product, the [$PtCl_3(MePhSO)$] anion, and for comparison of NMR shifts with sulfoxide structure we prepared independently the monoanion K[$PtCl_3(MePhSO)$]. The corresponding Me_2SO anion is best prepared in an exchange reaction by heating *cis*-[$PtCl_2(Me_2SO)_2$] as a suspension in H_2O with a stoichiometric amount of K_2PtCl_4 [6]. The greater lability of MePhSO as ligand in comparison to Me_2SO is reflected in the fact that under these conditions extensive decomposition and production of platinum metal takes place. Much milder conditions are necessary in order to prepare K[$PtCl_3(MePhSO)$]. Even so, the exchange reaction is much slower than for Me_2SO, presumably due to the lower reactivity of the MePhSO ligand [24].

Preparation of K[$PtCl_3(Ph_2SO)$]

The reaction of Ph_2SO with K_2PtCl_4 gives bright yellow crystals from H_2O which analyse for K[$PtCl_3(Ph_2SO)$]. No evidence for a bis(sulfoxide) species was ever observed. The ^{195}Pt resonance at −3064 ppm also indicated this coordination sphere. The complex is soluble in various organic solvents despite its ionic nature and crystals from acetone were of sufficient quality for an X-ray crystal structure determination, which confirmed the product identity. Crystal data are collected in Table 1 and principal bond lengths and bond angles are also summarized in Table 4.

Description of structure (Fig. 2)

The complex consists of discrete K cations and [$PtCl_3(Ph_2SO)$] anions. The sulfoxide is S-bonded and the parameters around the coordination sphere are normal. The Ph groups make dihedral angles of 81.8 and 100.9° with the Pt coordination plane and lie essentially perpendicular to each other with a mutual Ph–Ph dihedral angle of 92.9°. There is one molecule of acetone of recrystallization whose parameters are normal. The structure is the first reported for a diarylsulfoxide complex of platinum. The analogous Et_4N^+ salt has also been recently independently characterized and its X-ray structure resolved [25]. Interestingly, the K cations are placed at non-bonding distances of 2.728(13) and 2.673(9) Å to the oxygen atoms of the acetone solvate and sulfoxide ligand respectively. The O(1)–K–O(2) angle is 79.3(4)°. Atomic coordinates and equivalent isotropic parameters are given in Table 6.

TABLE 4. Bond distances and angles for *cis*-$[PtCl_2(MePhSO)_2]$ and $K[PtCl_3(Ph_2SO)]\cdot$acetone

cis-$[PtCl_2(MePhSO)_2]$				$K[PtCl_3(Ph_2SO)]\cdot$acetone			
Pt(1)–S(1)	2.244(3)	Cl(1)–Pt–Cl(2)	88.0(1)	Pt–Cl(1)	2.327(3)	Cl(2)–Pt–Cl(1)	88.6(1)
Pt(1)–S(2)	2.238(3)	S(1)–Pt–S(2)	87.5(1)	Pt–Cl(2)	2.302(3)	Cl(3)–Pt–Cl(1)	88.7(1)
Pt(1)–Cl(1)	2.315(3)	Cl(1)–Pt–S(2)	176.6(1)	Pt–Cl(3)	2.302(3)	Cl(3)–Pt–Cl(2)	177.2(1)
Pt(1)–Cl(2)	2.303(3)	Cl(2)–Pt–S(1)	176.2(1)	Pt–S(1)	2.214(3)	S(1)–Pt–Cl(1)	177.4(1)
S(1)–O(1)	1.464(8)	Cl(1)–Pt–S(1)	92.9(1)	S(1)–O(1)	1.469(8)	S(1)–Pt–Cl(2)	92.6(1)
S(2)–O(2)	1.462(8)	Cl(2)–Pt–S(2)	91.7(1)	S(1)–C(11)	1.768(9)	S(1)–Pt–Cl(3)	90.0(1)
S(1)–C(2)	1.803(13)	O(1)–S(1)–Pt	114.9(3)	S(1)–C(21)	1.763(9)	O(1)–S(1)–Pt	116.9(4)
S(1)–C(11)	1.782(11)	O(2)–S(2)–Pt	113.7(4)			C(11)–S(1)–O(1)	105.9(5)
S(2)–C(1)	1.781(11)	C(2)–S(1)–O(1)	107.1(6)			C(21)–S(1)–O(1)	108.5(4)
S(2)–C(21)	1.781(10)	C(11)–S(1)–O(1)	109.1(5)			C(11)–S(1)–C(21)	103.7(4)
		C(1)–S(2)–O(2)	106.4(5)				
		C(21)–S(2)–O(2)	109.6(5)				
		C(1)–S(2)–C(21)	102.1(6)				
		C(2)–S(1)–C(11)	101.3(5)				

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *cis*-$[PtCl_2(MePhSO)_2]$[a]

	x	*y*	*z*	U_{eq}
Pt(1)	433(1)	1212(1)	1520(1)	37(1)
S(1)	1230(3)	1050(2)	3393(2)	40(1)
S(2)	2874(3)	1383(2)	1577(2)	39(1)
Cl(1)	−2080(4)	953(2)	1431(3)	68(1)
Cl(2)	−365(4)	1475(3)	−384(3)	73(1)
O(1)	2413(9)	1647(5)	3986(6)	56(3)
O(2)	3897(10)	765(5)	2294(7)	57(3)
C(11)	1864(12)	−8(6)	3777(8)	40(3)
C(12)	1198(15)	−684(7)	3089(10)	57(5)
C(13)	1649(17)	−1488(8)	3432(11)	64(5)
C(14)	2815(15)	−1643(8)	4386(11)	60(5)
C(15)	3492(14)	−962(9)	5037(11)	59(9)
C(16)	3028(13)	−136(8)	4735(9)	53(4)
C(21)	3486(12)	2428(7)	2025(9)	46(4)
C(22)	2441(14)	3065(7)	1877(11)	59(5)
C(23)	2961(20)	3872(8)	2301(13)	75(6)
C(24)	4401(21)	4001(10)	2836(13)	80(7)
C(25)	5484(19)	3366(13)	3003(14)	96(8)
C(26)	5017(14)	2562(10)	2577(11)	66(5)
C(1)	3218(17)	1330(9)	239(10)	64(5)
C(2)	−312(16)	1141(8)	4013(13)	65(6)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

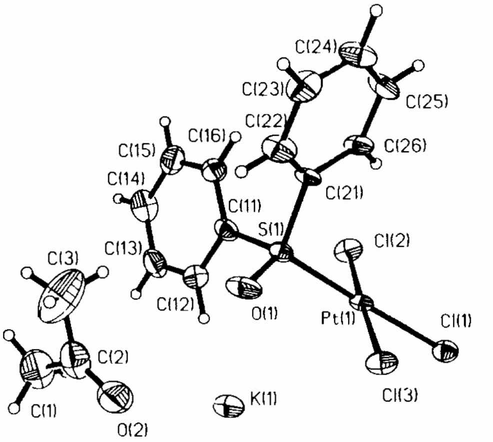


Fig. 2. The molecular structure of $K[PtCl_3(Ph_2SO)]\cdot$acetone.

Comparison of structures of platinum–sulfoxide complexes

Pertinent data on the complexes reported here and related literature values are collected in Table 7. The Pt–S bond lengths of the MePhSO derivative (2.244(3) and 2.238(3) Å) are essentially equivalent to those of Me_2SO (2.244(2) and 2.229(2) Å), whereas those in the chelating disulfoxide $PhSO–CH_2CH_2–SOPh$ complex are somewhat shorter (2.188(4) and 2.192(4) Å for the *meso* form; 2.209(3) and 2.217(2) Å for the *rac* form) [26]. The bond angles are also similar and the S–Pt–S angle of the MePhSO complex is actually smaller (87.5°) than for either Me_2SO (91.0°) or the chelates (89.7(2)°, *meso*, and 89.4(1)°, *rac*). This is in contrast to published reports on other *cis*-bis(sulfoxide) complexes with MeEtSO and $n-Pr_2SO$ where the S–Pt–S bond angles are enlarged (95.0 and 95.9°, respectively) presumably to compensate for the greater steric bulk around the S atom [23]. In the present case the relatively fixed nature of the phenyl group allows for the orientation of the two ligands such that steric repulsion between the two sulfoxide ligands is minimized readily with the $S-CH_3$ and SO groups lying away from each other and O(1)–O(2) repulsions minimized. The slightly greater S–Pt–S angles in the chelating disulfoxide may then be attributed to the steric constraints of the five-membered chelate ring.

In the case of the monoanions $K[PtCl_3(R'R''SO)]$, $R' = R'' = Me$ or Ph, there are no major differences in either bond lengths or bond angles around the platinum coordination sphere. The Pt–S bond in the diphenylsulfoxide derivative is slightly longer than in the Me_2SO

TABLE 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K[PtCl_3(Ph_2SO)] \cdot$ acetone[a]

	x	y	z	U_{eq}
Pt(1)	4127(1)	1221(1)	1432(1)	31(1)
Cl(1)	5695(4)	−612(3)	1855(1)	45(1)
Cl(2)	2813(4)	−949(4)	1106(1)	49(1)
Cl(3)	5526(4)	3305(3)	1770(1)	46(1)
S(1)	2708(4)	3004(4)	1009(1)	36(1)
K(1)	3577(3)	6500(3)	2084(1)	44(1)
O(1)	2652(11)	4623(10)	1252(3)	56(4)
C(12)	342(9)	2124(11)	1393(3)	58(5)
C(13)	−1022	1605	1363	73(6)
C(14)	−1735	1260	864	64(5)
C(15)	−1085	1433	395	69(6)
C(16)	279	1952	425	50(5)
C(11)	992	2298	924	42(4)
C(22)	2980(10)	4743(8)	98(3)	59(6)
C(23)	3377	4975	−417	64(6)
C(24)	3935	3689	−687	57(5)
C(25)	4097	2172	−440	58(5)
C(26)	3700	1940	75	51(5)
C(21)	3141	3226	345	38(4)
C(1)	−1495(20)	−4267(23)	2181(8)	120(10)
C(2)	−240(19)	−3633(23)	1973(9)	82(7)
O(2)	850(13)	−3664(20)	2227(5)	108(6)
C(3)	−405(22)	−3046(29)	1427(10)	158(14)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

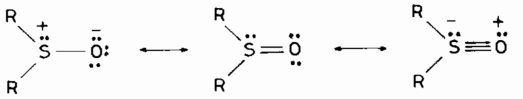
anion (2.214(3) and 2.193(5) Å, respectively). The discrete Pt–Cl bond *trans* to Ph_2SO at 2.327(3) Å is in the range for Cl *trans* S in these complexes and is longer than the l(Pt–Cl) of the mutually *trans* chlorides at 2.302(3) Å. The S–Pt–Cl angles are now 92.6 and 90.0° and within the range expected. The corresponding Me_2SO anion gives S–Pt–Cl angles of 93.8(1) and 88.4(1)°.

A major impetus for the development of this work is to examine the structural and electronic factors which contribute to sulfoxide lability. The chemical behavior of sterically hindered sulfoxides such as MePhSO and Ph_2SO is marked by a much greater lability (i.e. susceptibility to substitution by incoming ligands such as Cl^- or H_2O) [1] and a diminished reactivity (ability to displace a ligand such as Cl^- from Pt) [24]. The structural data given here, combined with those obtained for the amine–sulfoxide complexes $[PtCl(R'R''SO)(en)]^+$ cations ($R'R''SO = MePh$ or Me_2, en = ethylenediamine) [27] and $[PtCl(R'R''SO)(damch)]^+$ ($R' = R'' = Me$; $R' = Me$, $R'' = (+)p\text{-}CH_3C_6H_4$, *p*-tolyl; damch = 1,1-bisdiaminomethylcyclohexane) [28] confirm that there is really little difference in ground-state properties between the various sulfoxides and these are unlikely to be the major source of the differences in lability. It is likely that differences in reactivity are thus manifested in the five-coordinate transition state where steric crowding will be more critical. Similar conclusions were made with respect to the explanation of the unusual mutual labilization of two *cis*-Me_2SO groups [29]. With respect to the well documented mutual labilization of two *cis*-Me_2SO ligands we note that in our previous study of the properties of platinum–diaminesulfoxide complexes we were only able to prepare the $[Pt(R'R''SO)_2(R,R\text{-dach})]^{2+}$ species for Me_2SO [30]. Neither MePhSO nor MeBzSO afforded bis(sulfoxide) complexes, presumably due to the combined effects of steric hindrance and labilization of the one sulfoxide.

NMR spectroscopy

To examine differences in the electronic factors of sulfoxide binding we compared the ^{195}Pt chemical shifts in all the sulfoxide complexes prepared, Table 3. There is little substantial difference in the chemical shifts of *cis*-$[PtCl_2(R'R''SO)_2]$, given the wide range of ^{195}Pt chemical shifts [22]. In the monoanion series $K[PtCl_3(R'R''SO)]$ phenyl substitution confers on the sulfoxides better donor ability since the most shielded complex is that of Ph_2SO at −3064 ppm. The range of chemical shift from Me_2SO to Ph_2SO is 113 ppm. That this shift is due to phenyl substitution is supported by the fact that the complex with the sterically hindered but aliphatic sulfoxide (methyl)tert-butylsulfoxide, $K[PtCl_3\{(Me)t\text{-}BuSO\}]$, displays an almost identical chemical shift to the Me_2SO derivative, Table 3.

There are extensive correlations of alteration of platinum chemical shift with donor atom. Detailed analysis of a series of platinum–amine complexes using both ^{195}Pt and ^{15}N NMR indicated that, in general, changes in δ(Pt) upon systematic variation of one ligand X by ligand Y, are mainly influenced by the effect of the Pt–Y σ bond on the Pt 5d orbitals [31]. The canonical forms of sulfoxide are generally represented as:



1 2 3

Forms 1 and 2 are considered to contribute most to metal binding [32]. The net positive charge on free sulfoxides is decreased upon aryl substitution [32]. This diminution of positive charge would favor form 2 over form 1 in metal–sulfoxide binding upon replacement of alkyl by aryl substitutents. In simple terms this will strengthen the S-bonding through form 2 which may be reflected in a more shielded environment of the Pt nucleus. Similarly, reduced π-bonding from Pt to the less positively charged Ph_2SO ligand will also result in greater shielding of the Pt atom.

TABLE 7. Comparison of structural data for some platinum–sulfoxide complexes

Complex	*l*(Pt–S)	*l*(Pt–Cl)	*l*(SO)	∠(S–Pt–S)	∠(S–Pt–Cl)	Reference
cis-$[PtCl_2(MePhSO)_2]$	2.244(3) 2.239(3)	2.315(3) 2.303(3)	1.464(8) 1.462(8)	87.5(1)	92.9(1) 91.7(1)	this work
cis-$[PtCl_2(Me_2SO)_2]$	2.244(2) 2.229(2)	2.306(3) 2.312(2)	1.469(1) 1.454(9)	91.0(1)	92.6(1) 88.8(9)	8
$[PtCl_2[$*rac*-$\{PhSOCH_2\}_2]$	2.188(4) 2.192(4)	2.305(5) 2.295(4)	1.46(1) 1.40(2)	89.7(2)	90.4(2) 88.7(2)	26
$[PtCl_2($*meso*-$\{PhSOCH_2\}_2]$	2.209(3) 2.217(2)	2.318(3) 2.313(3)	1.47(8) 1.46(8)	89.4(1)	89.4(1) 89.2(1)	26
cis-$[PtCl_2(MeEtSO)_2]$	2.257(5) 2.272(5)	2.312(5) 2.317(5)	1.47(1) 1.46(1)	95.0(2)	87.4(1) 89.9(2)	23
cis-$[PtCl_2(n\text{-}Pr_2SO)_2]$	2.247(3) 2.272(5)	2.289(3) 2.302(3)	1.458(7) 1.471(7)	95.9(1)	87.8(1) 88.3(1)	23
$K(PtCl_3(Me_2SO)]$	2.193(5)	2.318(5) *trans* S 2.302(6) *trans* Cl 2.296(6) *trans* Cl	1.484(8)		93.8(1) 88.4(1)	10
$K[PtCl_3(Ph_2SO)]\cdot$acetone	2.214(3)	2.327(3) *trans* S 2.302(3) *trans* Cl 2.302(3) *trans* Cl	1.469(8)		92.6(1) 90.0(1)	this work
$NEt_4[PtCl_3(Ph_2SO)]$	2.207(2)	2.314(2) *trans* S 2.306(2) *trans* Cl 2.299(2) *trans* Cl	1.462(6)		94.6(1) 87.3(1)	25

Our studies on the lability of sulfoxide in the complexes $[PtCl(R'R''SO)\,(diam)]^+$ showed that the lability of the set of sulfoxides studied here is $Me_2SO <$ $MePhSO < Ph_2SO$, with the differences in kinetics ranging over an order of magnitude [1]. Likewise the formation of $[PtCl_3(R'R''SO)]^-$ from K_2PtCl_4 follows the inverse order $MePhSO < Me_2SO$ [24]. The structural parameters for complexes with bulky sulfoxides do not explain the increased lability of these ligands in comparison to the 'parent' Me_2SO with no significant differences in properties found. The spectroscopic studies indicate that, if anything, the donor strength of the ligand is $Ph_2SO > MePhSO > Me_2SO$.

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