Novel mixed-ligand Pt(II) complexes: Synthesis, multinuclear magnetic resonance, and crystal structures of *cis*- and *trans*-Pt(R_2SO)(pyrazine)Cl_2

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Abstract: A new type of mixed-ligand Pt(II) complexes, Pt(R_2SO)(pyrazine)Cl_2, was synthesized from the aqueous reaction of K[Pt(R_2SO)Cl_3] with pyrazine. The compounds were characterized mainly by IR and multinuclear magnetic resonance spectroscopies (^{1}H, ^{13}C, and ^{195}Pt) and crystallography. Compounds with dimethylsulfoxide, tetramethylenesulfoxide, di-*n*-propylsulfoxide, di-*n*-butylsulfoxide, dibenzylsulfoxide, and diphenylsulfoxide were studied. IR spectroscopy suggested a cis geometry for the di-*n*-propylsulfoxide complex and trans geometry for the other compounds. The ^{195}Pt NMR resonances of the complexes were observed between –3042 and –3121 ppm, with that of the diphenylsulfoxide complex being at higher field than those of the others. The pyrazine $^3J(^{195}Pt\text{-}^1H)$ coupling constant was observed for the DMSO compound (33 Hz), suggesting a trans geometry. No $J(^{195}Pt\text{-}^{13}C)$ coupling could be detected. The crystal structures of *trans*-Pt(tetramethylenesulfoxide)(pyrazine)Cl_2 and of *cis*-Pt(di-*n*-propylsulfoxide)(pyrazine)Cl_2 were determined and confirmed the geometry suggested by IR and NMR spectroscopies. The compound with di-*n*-butylsulfoxide could not be isolated, because it rapidly formed the pyrazine-bridged dimer.

Key words: platinum, sulfoxide, pyrazine, crystal structure, NMR, IR.

Résumé : Un nouveau type de complexes du platine(II) contenant des ligands mixtes a été synthétisé lors de la réaction en milieu aqueux de K[Pt(R_2SO)Cl_3] avec la pyrazine. Les composés Pt(R_2SO)(pyrazine)Cl_2 ont été caractérisés par spectroscopie infrarouge, par résonance magnétique multinucléaire (^{1}H, ^{13}C et ^{195}Pt) et par cristallographie. Des complexes avec les ligands diméthylsulfoxyde, tétraméthylènesulfoxyde, di-*n*-propylsulfoxyde, di-*n*-butylsulfoxyde, dibenzylsulfoxyde et diphénylsulfoxyde ont été étudiés. La spectroscopie IR a suggéré une géométrie cis pour le composé contenant le ligand di-*n*-propylsulfoxyde et une isomérie trans pour les autres complexes. Les résonances en RMN du ^{195}Pt ont été observées entre –3042 et –3121 ppm. Le composé contenant diphénylsulfoxyde a été observé à plus haut champ que les autres. La constante de couplage de la pyrazine $^3J(^{195}Pt\text{-}^1H)$ a été observé pour le composé contenant le DMSO (33 Hz) suggérant une géométrie trans. Aucun couplage de type $J(^{195}Pt\text{-}^{13}C)$ n'a été détecté. Les structures cristallines des deux composés *trans*-Pt(tétraméthylènesulfoxyde)(pyrazine)Cl_2 et *cis*-Pt(di-*n*-propylsulfoxyde)-(pyrazine)Cl_2 ont été déterminées par diffraction des rayons-X et les résultats ont confirmé les géométries suggérées par les spectroscopies IR et RMN. Le composé avec le ligand di-*n*-butylsulfoxyde n'a pas été isolé, car le dimère à pont pyrazine se forme trop rapidement.

Mots clés : platine, sulfoxyde, pyrazine, structures cristallines, RMN, IR.

Introduction

The antitumor activity of Pt(II) complexes of the type *cis*-Pt(amine)$_2Cl_2$ is well known. Cisplatin (*cis*-Pt(NH_3)$_2Cl_2$) remains the most commonly used anticancer agent in chemotherapy (1, 2), even though it exhibits numerous and significant side effects, but the search for more specific and less toxic drugs is still continuing.

A few *trans* Pt(II) complexes with amine ligands have shown anticancer activity in specific organs (3). Compounds with neutral ligands containing other donor atoms such as S have also shown some antitumor properties (4). Several Pt(II) complexes of the types [Pt(R_2SO)(diamine)Cl]NO_3 (5) and *cis*- and *trans*-Pt(R_2SO)(quinoline)Cl_2 (6) have shown biological activity, depending on the sulfoxide chain. Recently, it was reported that the pyrazine–Pt(II) complex [*cis*-{Pt(NH_3)$_2$Cl}$_2$(μ-pz)]Cl_2 and its derivatives showed good potential as anticancer compounds, especially because they largely seem to overcome the cross-resistance of cisplatin (7). The compounds possess an appropriate flexibility to provide the cross-links with a minimal distortion of the DNA.

Our group has been involved in research on Pt–sulfoxide complexes for many years. Sulfoxides are interesting ligands because they can accept π electron density from the metallic center. For these types of ligands, the cis complexes are usually more stable than the trans compounds (contrary to the amine systems). We have recently reported a study on mixed-ligand Pt(II) complexes containing pyrimidine (pm)

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and sulfoxide ligands (8, 9). Pyrimidine also has empty π antibonding orbitals that could accept electron density from Pt. The aqueous reaction of $K[Pt(R_2SO)Cl_3]$ with pyrimidine (1:1 ratio) produced first *trans*-$Pt(R_2SO)(pm)Cl_3$, which could then isomerize to the *cis* compound (8).

To determine the influence of the pyrimidine ligand in these reactions, we have started a new study with pyrazine (pz) instead of pyrimidine. Unlike the latter, pyrazine is a symmetric molecule, but it too has empty π* orbitals that could form π bonds with Pt. We have recently published the results of the first part of this study, on the pyrazine-bridged dinuclear compounds $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pz})$ (10), which were found to have the trans-trans geometry. Pyrazine can form bridges between two metallic centers quite easily, even when an excess of pyrazine is used. Most reported works in the literature involve pyrazine-bridged oligomers.

There is no reported research on Pt compounds containing both sulfoxides and pyrazine except our recent publication of the pyrazine-bridged dimers (10). Only four papers on Pt compounds with nonsubstituted pyrazine were found in the literature. Among them, only two papers involve Pt(II) monomeric compounds. Albinati et al. (11) synthesized and characterized *trans*-Pt(phosphine)$(pz)Cl_2$, while Siedle et al. (12) prepared *trans*-$Pt(C_2H_4)(pz)Cl_2$ and its derivatives and used them as catalysts in hydrosilation reactions. No cis mixed-ligand Pt monomeric compounds with pyrazine have been reported. The nature of the Pt–pyrazine bond has not been investigated yet.

In the present publication, we report the results of our study on the aqueous reactions of $K[Pt(R_2SO)Cl_3]$ with pyrazine. Six sulfoxides that differ in steric hindrance were studied: dimethylsulfoxide (DMSO), tetramethylenesulfoxide (TMSO), di-*n*-propylsulfoxide (DPrSO), di-*n*-butylsulfoxide (DBuSO), dibenzylsulfoxide (DBzSO), and diphenylsulfoxide (DPhSO). The products $Pt(R_2SO)(pz)Cl_2$ were characterized by IR and multinuclear magnetic resonance (^1H, ^{13}C, and ^{195}Pt) spectroscopies. The crystal structures of two compounds with different geometies were determined.

Experimental

$K_2[PtCl_4]$ was obtained from Johnson Matthey Inc. and was purified by recrystallization from water before use. $CDCl_3$ was purchased from CDN Isotopes. Pyrazine and the sulfoxide ligands were purchased from Aldrich except DMSO, which was bought from Anachemia Chemicals Ltd., and DPrSO, acquired from Phillips Petroleum Company. The latter was purified by distillation before use.

The decomposition points were measured on a Fischer-Johns instrument and were not corrected. The IR spectra were recorded in the solid state (KBr pellets) on a PerkinElmer 783 spectrometer between 4000 and 280 cm^{-1}. All NMR spectra were measured in $CDCl_3$ on a Varian Gemini 300BB spectrometer operating at 300.069, 75.460, and 64.326 MHz for ^1H, ^{13}C, and ^{195}Pt, respectively. The chloroform peaks were used as an internal standard for the ^1H (7.24 ppm) and ^{13}C (77.00 ppm) NMR spectra. For ^{195}Pt, the external reference was $K[Pt(DMSO)Cl_3]$ (in D_2O, adjusted to –2998 ppm from $K_2[PtCl_6]$). The ^{195}Pt NMR spectra were measured between –2500 and –4000 ppm.

The TMSO compound (crystal **I**) was crystallized from a dichloromethane–acetone (1:1) mixture, and the DPrSO crystal (crystal **II**) was obtained from a chloroform–acetone–methanol (3:1:1) solution. The crystallographic measurements were done on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα (λ = 0.71073 Å (1 Å = 0.1 nm) radiation. The crystals were selected after examination under a polarizing microscope for homogeneity. The cell dimensions were determined at room temperature, from a least-squares refinement of the angles 2θ, ω, and χ obtained for well-centered reflections. The data collections were made by the 2θ/ω scan technique using the XSCANS (13) program. The coordinates of the Pt atoms were determined from Patterson map calculations. All the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structures was done on F^2 by full matrix least-squares analysis. The hydrogen atoms were fixed in their calculated positions with U_{eq} = 1.2 x U_{eq} of the carbon to which they are bonded (or 1.5 x U_{eq} for methyl groups). Corrections were made for absorption (integration for *trans*-$Pt(TMSO)(pz)Cl_2$ and semiempirical for *cis*-$Pt(DPrSO)(pz)Cl_2$), Lorentz, and polarization effects. Crystal **II** did not diffract very well. It was also measured with Cu Kα radiation, but the results did not improve. Attempts to prepare crystals of better quality were not successful. The residual peaks were located in the close vicinity of the Pt atoms. The calculations were done using the Siemens SHELXTL (13) system. The pertinent crystal data and the experimental details are summarized in Table 1.

The $K[Pt(R_2SO)Cl_3]$ complexes were synthesized according to the method described by Kukushkin et al. (14). The DBzSO and DPhSO complexes were obtained in small quantities because of the aqueous insolubility of the ligands and the very favorable formation of the insoluble disubstituted compound $Pt(R_2SO)_2Cl_2$.

Preparation of *trans*-$Pt(R_2SO)(pz)Cl_2$

Pyrazine was dissolved in a minimum amount of water. The $K[Pt(R_2SO)Cl_3]$ compound, dissolved also in a minimum amount of water, was added gently to the pyrazine solution in a 1:1.1 proportion at room temperature. A pale yellow to yellow-orange precipitate appeared rapidly, but the stirring of the solution was continued until precipitation was complete. After filtration, the precipitate was dried, washed with ether, and dried in vacuum. For the DBzSO complex, the reaction was done in a 2:1 MeOH–H_2O mixture, while for the DPhSO complex, the reaction was done in a 3:1 EtOH–H_2O mixture.

trans-*Pt(DMSO)(pz)Cl₂*

Yield 89%; dec. 220–235 °C. IR (cm^{-1}): pz (vibration numbers assigned using the notation in ref. 15): 3117 m (ν_{13} (B_{1u})), 1417 s (ν_{19b} (B_{3u})), 1147 s (ν_{18a} (B_{1u})), 1112 w (ν_3 (B_{2g})), 1074 m (ν_{14} (B_{3u})), 1029 s (ν_1 (A_g)), 807 s (ν_{11} (B_{2u})); ν(S-O) 1122 w, ν(Pt-N) 517 m, ν(Pt-S) 444 s, ν(Pt-Cl) 350 s. ^1H NMR (ppm): H_{pz} 8.780 (d, 3.0), 8.770 (d, 3.0); H_α 3.48 (s+d, 23). ^{13}C NMR (ppm): C_{pz} 147.01, 145.33; C_α 44.46.

trans-*Pt(TMSO)(pz)Cl₂ (I)*

Yield 84%; dec. 156–195 °C. IR (cm^{-1}): pz (vibration

Table 1. Crystallographic data for the compounds $Pt(R_2SO)(pz)Cl_2$.

	I	II
Compound	*trans*-Pt(TMSO)(pz)Cl_2	*cis*-Pt(DPrSO)(pz)Cl_2
Chemical formula	$C_8H_{12}Cl_2N_2OPtS$	$C_{10}H_{18}Cl_2N_2OPtS$
MW	450.25	480.31
Space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
a (Å)	11.931(3)	8.911(7)
b (Å)	10.434(2)	17.534(12)
c (Å)	20.490(4)	9.843(9)
β (°)		90.69(7)
Volume (Å^3)	2550.8(9)	1538(2)
Z	8	4
ρ_{calcd} (g cm^{-3})	2.345	2.075
μ(Mo Kα) (cm^{-1})	11.560	9.594
F(000)	1680	912
Measured reflections	18 659	10 597
Independent reflections	2506	2715
Obs. reflections ($I > 2\sigma(I)$)	1398	1543
R_1 ($F > 2\sigma(I)$)[a]	0.0494	0.0791
wR_2 (all data)[b]	0.1009	0.1358
S	1.052	1.059

[a] $R_1 = \Sigma (|F_o - F_c|) / \Sigma |F_o|$.
[b] $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$.

numbers assigned using the notation in ref. 15): 3100 w (ν_{13} (B_{1u})), 1415 s (ν_{19b} (B_{3u})), 1394 w (ν_{19b} (B_{3u})), 1143 s (ν_{18a} (B_{1u})), 1119 s (ν_3 (B_{2g})), 1081 s (ν_{14} (B_{3u})), 1060 s (ν_1 (A_g)), 807 s (ν_{11} (B_{2u})); ν(S-O) 1160 m, ν(Pt-S) 479 m, ν(Pt-Cl) 348 s. ^{1}H NMR (ppm): H_{pz} 8.811 (dd, 3.0, 1.2), 8.764 (dd, 3.0, 1.2); H_α 4.00 (m), 3.65 (m); H_β 2.39 (m), 2.23 (m). ^{13}C NMR (ppm): C_{pz} 147.42, 145.70; C_α 57.05, C_β 24.67.

trans-*Pt(DBzSO)(pz)Cl$_2$*

Yield 89%; dec. 121–197 °C. IR (cm^{-1}): pz (vibration numbers assigned using the notation in ref. 15): 3123 w (ν_{13} (B_{1u})), 1495 m (ν_{19a} (B_{1u})), 1422 s (ν_{19b} (B_{3u})), 1381 m (ν_{19b} (B_{3u})), 1130 s (ν_{18a} (B_{1u})), 1114 s (ν_3 (B_{2g})), 1070 m (ν_{14} (B_{3u})), 1030 m (ν_1 (A_g)), 805 m (ν_{11} (B_{2u})); ν(S-O) 1167 s, ν(Pt-N) 516 vw, ν(Pt-S) 483 s, ν(Pt-Cl) 350 m.

trans-*Pt(DPhSO)(pz)Cl$_2$*:

Yield 85%; dec. 195–250 °C. IR (cm^{-1}): pz (vibration numbers assigned using the notation in ref. 15): 3094 w (ν_{13} (B_{1u})), 1470 w (ν_{19a} (B_{1u})), 1410 s (ν_{19b} (B_{3u})), 1381 w (ν_{19b} (B_{3u})), 1137 s (ν_{18a} (B_{1u})), 1112 m (ν_3 (B_{2g})), 1071 m (ν_{14} (B_{3u})), 1062 m (ν_1 (A_g)), 806 s (ν_{11} (B_{2u})); ν(S-O) 1153 m, ν(Pt-N) 507 vw, ν(Pt-S) 444 w, ν(Pt-Cl) 349 m. ^{1}H NMR (ppm): H_{pz} 8.896 (m); H_{ortho} 8.29 (t, 7.8), 7.93 (t, 7.4); $H_{meta,\ para}$ 7.58 (m). ^{13}C NMR (ppm): C_{pz} 147.32, 145.93; C_{phenyl} 138.42, 127.43, 128.76, 132.95.

Preparation of *cis*-Pt(DPrSO)(pz)Cl_2 (II)

Pyrazine was dissolved in a minimum amount of water. The K[Pt(R_2SO)Cl_3] compound, dissolved also in a minimum amount of water, was added gently to the pyrazine solution in a 1:1 proportion at room temperature. A yellow sticky paste formed immediately and stuck to the magnetic agitator. The paste was dissolved in chloroform and the solution evaporated to dryness. The residue was recrystallized in chloroform, filtered, washed with ether, and dried in vacuum.

Yield 68%; dec. 183–220 °C. IR (cm^{-1}): (vibration numbers assigned using the notation in ref. 15): 3086 w (ν_{13} (B_{1u})), 1457 m (ν_{19a} (B_{1u})), 1412 s (ν_{19b} (B_{3u})), 1379 m (ν_{19b} (B_{3u})), 1130 s (ν_{18a} (B_{1u})), 1111 w (ν_3 (B_{2g})), 1069 s (ν_{14} (B_{3u})), 807 m (ν_{11} (B_{2u})); ν(S-O) 1152 s, ν(Pt-N) 515 w, ν(Pt-S) 448 m, br, ν(Pt-Cl) 345 m, 341 m. ^{1}H NMR (ppm): H_{pz} 8.707 (d, 3.3), 8.685 (d, 3.3); H_α 3.76 (m), 3.12 (m); H_β 2.36 (m), 2.03 (m); H_γ 1.18 (t, 7.5). ^{13}C NMR (ppm): C_{pz} 147.59, 147.40; C_α 56.51, C_β 16.68, C_γ 12.75.

Results and discussion

Synthesis of the complexes

The aqueous reaction of K[Pt(R_2SO)Cl_3], where R_2SO = DMSO, TMSO, DBzSO, and DPhSO, with pyrazine in a 1:1.1 proportion produced the monomeric complexes *trans*-Pt(R_2SO)(pz)Cl_2 (eq. [1]). The K[Pt(R_2SO)Cl_3] solution must be added to the pyrazine solution to have an excess of pyrazine throughout the reaction because an excess of the Pt(II) salt will produce the pyrazine-bridged dimer recently reported (10), prepared by a similar reaction using a Pt:pz ratio of 2:1. For the DBzSO complex, the reaction was performed in a 1:2 water–methanol mixture, while a 1:3 water–ethanol solution was preferred for the DPhSO compound.

$$[1] \qquad K[Pt(R_2SO)Cl_3] + pz \rightarrow \textit{trans}\text{-}Pt(R_2SO)(pz)Cl_2 + KCl$$

A pale yellow to yellow-orange precipitate was formed. The time at which precipitation was observed varied with the bulkiness of the sulfoxide. The yields varied between 84% and 89%.

The characterization of the products has shown that these compounds have the trans configuration, as expected be-

cause of the large trans effect of sulfoxides. Sulfoxide complexes having the cis configuration are usually more stable than the trans compounds, because the π bonding is more effective in the cis configuration. For example, the aqueous reaction of $K[Pt(R_2SO)Cl_3]$ with R_2SO produces first the trans isomer, which rapidly isomerizes in water to the cis compound except in the case of very sterically demanding sulfoxides. Similarly, the reaction of $K[Pt(R_2SO)Cl_3]$ with pyrimidine produces first *trans*-$Pt(R_2SO)(pm)Cl_2$, which can isomerize to the cis compound (8). Since pyrazine is a very similar ligand to pyrimidine, both of them having empty π* orbitals that can accept electron density from Pt, the *trans*-$Pt(R_2SO)(pz)Cl_2$ compounds were expected to undergo isomerization, at least in organic solvents. However, several attempts in different solvents to isomerize the four *trans*-$Pt(R_2SO)(pz)Cl_2$ compounds were without success. Therefore, it appears that the reactivity of the R_2SO–pyrazine complexes is quite different from that of the R_2SO–pyrimidine compounds (8, 9). The pyrazine-bridged dimers recently published were identified as the trans-trans isomers (10), and various attempts to isomerize them were also not successful.

The aqueous reaction of $K[Pt(DPrSO)Cl_3]$ with pyrazine under the same conditions as for the other $K[Pt(R_2SO)Cl_3]$ complexes was quite different. With a Pt:pz ratio of 1:1 to 1:1.1, a bright yellow sticky paste formed immediately upon mixing. After the purification process in $CHCl_3$, the product was identified as the mononuclear complex *cis*-$Pt(DPrSO)(pz)Cl_2$.

[2] $K[Pt(DPrSO)Cl_3] + pz \rightarrow$ *cis*-$Pt(DPrSO)(pz)Cl_2 + KCl$

The lower yield of this reaction (68%) can be attributed to the oily nature of the product. When the Pt:pz ratio was greater than 1:1, the pyrazine-bridged dimeric species *trans*-$\{Pt(DPrSO)Cl_2\}_2(\mu\text{-pz})$ was formed as reported earlier. The fact that the final dinuclear product exhibits the trans-trans geometry (10) suggests that the mononuclear intermediate is *trans*-$Pt(DPrSO)(pz)Cl_2$. However, with a Pt:pz ratio of 1:1.1, the trans monomeric compound, which should first be produced, could not be isolated, suggesting that the compound *trans*-$Pt(DPrSO)(pz)Cl_2$ isomerized rapidly. This was quite surprising since all the complexes formed with the other ligands are believed to have the trans configuration and did not isomerize even upon heating in organic solvents.

The aqueous reaction of $K[Pt(DBuSO)Cl_3]$ with pyrazine under the same conditions (Pt:pz ratio of 1:1) produced the pyrazine-bridged dinuclear species *trans*-$\{Pt(DBuSO)Cl_2\}_2(\mu\text{-pz})$. No monomeric compound was obtained with the ligand DBuSO. The experimental conditions were varied (different solvents) and the Pt:pz ratio was varied from 1:1 to 1:15, but no monomeric mixed-ligand complex could be detected. It seems that in the case of $K[Pt(DBuSO)Cl_3]$, unlike the other $K[Pt(R_2SO)Cl_3]$ complexes, the binding of the first N atom of pyrazine to Pt activates the second N atom to react more rapidly than the first

All the mixed-ligand monomeric species were characterized by IR and multinuclear magnetic resonance spectroscopies. The low solubility of these complexes was a major problem in this project. The compound *trans*-$Pt(DBzSO)(pz)Cl_2$ could not be analyzed by NMR spectroscopy, being insoluble in all the solvents tested (H_2O, MeOH, EtOH, $CHCl_3$, CH_2Cl_2, CH_3COCH_3, and DMF).

The synthesized complexes were pure, since only one resonance was observed in their ^{195}Pt NMR spectra (confirmed by ^1H and ^{13}C NMR). The complexes *trans*-$Pt(TMSO)(pz)Cl_2$ and *cis*-$Pt(DPrSO)(pz)Cl_2$ were also studied by X-ray diffraction methods, which confirmed the geometry of the complexes.

IR spectroscopy

The IR spectrum of pyrazine has been reported (15), and our IR band assignments (Experimental section) are based on that study. The vibrations of coordinated pyrazine in the Pt complexes were observed at energies higher than or identical to those reported for the free ligand. The ν(S-O) vibrations absorb at higher energy than in the free sulfoxides (avg. +120 cm^{-1}), since the ligands are bonded to Pt by the S atom. The pπ–dπ bond is strengthened upon coordination in the complexes. The ν(S-O) energies (avg. 1151 cm^{-1}) are identical with those observed in the pyrazine-bridged dimeric compounds (avg. 1157 cm^{-1} (10)) and can be compared with the values reported for $Pt(DMSO)(NH_3)Cl_2$ and $Pt(DMSO)(2\text{-Me-py})Cl_2$ (1128 and 1138 cm^{-1}, respectively (16)).

For all the complexes except $Pt(DPrSO)(pz)Cl_2$, only one ν(Pt-Cl) vibration was observed, between 348 and 350 cm^{-1}. This suggests a trans geometry because, although two bands are predicted by group theory for both cis (C_s skeletal symmetry) and trans isomers (C_{2v}) of this type, two bands are usually observed for the cis compounds and only one band for the trans isomers (as reported, for example, for the complexes *cis*- and *trans*-$Pt(DMSO)(L)Cl_2$, where L = 2,6-lutidine and dimethylamine (17) and pyrimidine (8)). However, for $Pt(DPrSO)(pz)Cl_2$, two ν(Pt-Cl) bands located at 341 and 345 cm^{-1} were observed, suggesting a cis geometry.

An absorption band observed around 460 cm^{-1} was assigned to a ν(Pt-S) vibration as suggested in the literature (8–10, 16, 18–21), while a band around 515 cm^{-1} was assigned to the ν(Pt-N) vibration, based also on some published results (8–10, 22, 23).

^{195}Pt NMR spectroscopy

The ^{195}Pt NMR spectra of the monomeric compounds $Pt(R_2SO)(pz)Cl_2$ (except the DBzSO complex) were measured in $CDCl_3$, and the results were compared with those observed for the pyrimidine analogues $Pt(R_2SO)(pm)Cl_2$ (8) and for the pyrazine-bridged dimeric species *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pz})$ (10). The chemical shifts are summarized in Table 2. All the synthesized complexes were pure as shown by multinuclear (^{195}Pt, ^1H, and ^{13}C) magnetic resonance spectroscopy. The compound containing a DBzSO ligand was found to be insoluble in all the classical organic solvents.

Except for the DPhSO complex, the ^{195}Pt NMR chemical shifts vary between –3042 and –3046 ppm. The $\delta(^{195}Pt)$ values of these monomers are very close to those determined for the pyrazine-bridged dimeric species (Table 2). In the pyrimidine series, the signals of the monomers were observed at slightly lower fields (avg. –3065 ppm) than those of the pyrimidine-bridged dimers (avg. –3075 ppm) (8, 9). Our re-

Table 2. ^{195}Pt chemical shifts (ppm) of the complexes $Pt(R_2SO)(pz)Cl_2$ (in $CDCl_3$) and related complexes in the literature.

R_2SO	Geometry	$Pt(R_2SO)(pz)Cl_2$	$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pz})$[a]	$Pt(R_2SO)(pm)Cl_2$[b]
DMSO	trans	–3045	–3049[c]	–3070
TMSO	trans	–3042	–3041	–3056
DPrSO	cis	–3046		–2951
	trans		–3048	–3059
DBuSO	trans	—[d]	–3051	–3060
DPhSO	trans	–3121	–3113	–3148

[a]Reference 10; in $CDCl_3$ except where otherwise indicated.
[b]Reference 8; in CD_2Cl_2.
[c]In DMF-d_7.
[d]Not prepared.

sults are also in agreement with the published work on analogues with phosphine ligands (11), where the ^{195}Pt NMR chemical shift of *trans*-$Pt(PR_3)(pz)Cl_2$ was reported at –3589 ppm, and that of the dinuclear coompound *trans*-$\{Pt(PR_3)Cl_2\}_2(\mu\text{-pz})$ at –3587 ppm. These results seem to indicate that the electron density on the Pt atom is the same in the monomers as in the pyrazine-bridged dimers.

The value of $\delta(^{195}Pt)$ for the *cis*-DPrSO complex was within the range observed for the trans monomers (except the DPhSO compound), which was not expected. In the pyrimidine series (8), the signals of the cis compounds were reported at much lower fields than those of the trans isomers (avg. $\Delta\delta$ ($\delta_{cis} - \delta_{trans}$) = 132 ppm). For sulfoxide Pt(II) complexes, the cis isomers are more stable than the trans compounds since the π(d-d) bonding is more efficient in the cis geometry, resulting in a lower electron density on the Pt center. The δ(Pt) are therefore observed at lower field for the cis isomers. For mixed-ligand complexes, the value of $\Delta\delta$ ($\delta_{cis} - \delta_{trans}$) will also depend on the second ligand. If the latter can form π bonds, the difference between the two isomers should increase, while an amine ligand should reduce the $\Delta\delta$ ($\delta_{cis} - \delta_{trans}$) values. In $Pt(DMSO)(NH_3)Cl_2$, the signal of the cis isomer was reported at –3045 ppm, whereas that of its trans analogue was observed at –3067 ppm (16, 24). In our R_2SO-pz compounds, only one cis compound (with DPrSO) was prepared, and its signal was observed at the same field as those of the trans isomers of the other R_2SO-pz compounds. We do not have enough data at the moment to reach a sound conclusion and will continue our attempts, which have not been successful up to now, to prepare other cis compounds and the trans DPrSO complex.

The ^{195}Pt NMR signal of the DPhSO complex was observed at much higher fields than those of the other compounds, as also reported for the other DPhSO complexes in Table 2 and for a series of compounds of the types $Pt(R_2SO)(R\text{-}CN)Cl_2$ (25) and $K[Pt(R_2SO)Cl_3]$ (25, 26). DPhSO is not only the most sterically hindered ligand, but also it is different from the other sulfoxides in that it contains aromatic groups directly attached to the sulfur atom. These groups are probably responsible for the different electronic effects observed for this compound. The electron density on the Pt atom is increased in the DPhSO complex compared to the complexes containing the other sulfoxide ligands. The shielded resonance is probably not caused by the bulkiness of the substituents on the sulfur, because the presence of bulky substituents on the atom bonded to Pt usually has a deshielding effect. For Pt–amine complexes, δ(Pt) was found at lower fields for amines having bulky substituents on the nitrogen atom (27, 28). For $K[Pt(R_2SO)Cl_3]$ (29) and the corresponding pyrazine-bridged dimeric complexes (10), we have suggested that the difference was caused by inverse polarization of the π electrons of the S=O bond, and this concept might be an interesting interpretation of our results in the present study as well. This phenomenon has been suggested in the literature to explain some ^{13}C NMR results for Pt–carbonyl (30) and Pt–carboxylato complexes (31). Such an effect would be present in all Pt–R_2SO complexes but would be more important for sulfoxide ligands containing electron-attracting aromatic groups attached directly to the S atom. This effect would increase the electron density on the atoms in close proximity to the S atom, especially the Pt atom, which would result in a higher field δ(Pt) signal.

^{1}H and ^{13}C NMR spectroscopies

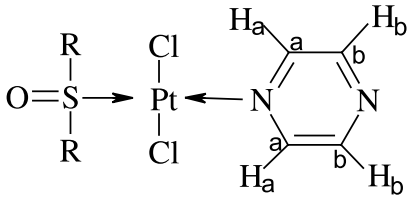
The pyrazine signals of the complexes will first be discussed. Pyrazine is a symmetric molecule, and only a single resonance is observed in the ^{1}H and ^{13}C spectra at 8.59 and 145.07 ppm, respectively, in $CDCl_3$. When pyrazine is bonded to a metal, the molecule is no longer symmetric, as shown in Scheme 1. Two signals should now be observed for the coordinated molecule in the ^{1}H NMR (H_a and H_b) and ^{13}C NMR (C_a and C_b) spectra. The atoms H_a and C_a should be more affected by coordination to the metal than H_b and C_b.

The chemical shifts and the coupling constants of the complexes are presented in the Experimental section, and the values $\Delta\delta$ ($\delta_{complex} - \delta_{pyrazine}$) are listed in Table 3. Coordination of pyrazine to the Pt atom causes a deshielding of all the pyrazine atoms. The chemical shifts of H_a and C_a are more deshielded than those of H_b and C_b as expected, resulting in larger $\Delta\delta$ values for H_a and C_a. For the DPhSO complex, the two multiplets were not separated. The reduction of electron density in bonded pyrazine is a consequence of the σ bond (N→Pt), which causes a deshielding effect in ^{1}H and ^{13}C NMR. In the literature, for a few complexes of the type *trans*-$Pt(PR_3)(pz)Cl_2$ (11), the reported $\Delta\delta_a$ values in ^{1}H NMR (avg. 0.38 ppm) were larger than ours, while their $\Delta\delta_b$ value was 0.15 ppm. The difference might be caused by the larger trans effect of phosphine ligands compared to that of sulfoxides (10). For the trans-trans pyrazine-bridged dimers $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pz})$ (in which the pyrazine is symmetric), the average $\Delta\delta$ value was around 0.52 ppm (10). It seems

Table 3. ^{1}H and ^{13}C NMR $\Delta\delta$ ($\delta_{complex} - \delta_{pyrazine}$) (ppm) of pyrazine resonances for the complexes $Pt(R_2SO)(pz)Cl_2$.

Compound	(^{1}H)$\Delta\delta_a$	(^{1}H)$\Delta\delta_b$	(^{13}C)$\Delta\delta_a$	(^{13}C)$\Delta\delta_b$
trans-Pt(DMSO)(pz)Cl_2	0.195	0.185	1.94	0.26
trans-Pt(TMSO)(pz)Cl_2	0.226	0.179	2.35	0.63
cis-Pt(DPrSO)(pz)Cl_2	0.122	0.100	2.52	2.33
trans-Pt(DPhSO)(pz)Cl_2	0.311	0.311	2.25	0.86

Scheme 1.



that the formation of two σ bonds (N→Pt) by pyrazine decreases further the electron density on pyrazine.

The ^{1}H $\Delta\delta$ values for *cis*-Pt(DPrSO)(pz)Cl_2 are smaller than those of the trans complexes (Table 3). These differences might be due to the different geometry, but more cis compounds are needed before a conclusion can be reached. Steric hindrance in the cis complex is an important factor that must be considered. In the trans compounds, the rotation around the Pt—N bond is not very restricted because the π component of the bond is probably not very important. For the cis isomers, the rotation of the pyrazine ring around the Pt—N bond is more hindered, and the planar ligand is probably close to being perpendicular to the Pt(II) coordination plane to reduce the steric hindrance. The rotation will be more restricted with more bulky sulfoxides.

The chemical shifts of the pyrazine protons in *trans*-Pt(DPhSO)(pz)Cl_2 were at lower fields ($\Delta\delta_{avg}$ = 0.311 ppm) than those of the other trans compounds ($\Delta\delta_{avg}$ = 0.20 ppm). This is in agreement with the observation of the ^{195}Pt NMR signal of this compound at higher field than those of the other complexes, since an increase of electron density on the Pt atom (upfield shift in ^{195}Pt NMR) corresponds to a reduction of electron density on the ligand (downfield shift in ^{1}H and ^{13}C NMR).

The coupling constants $^3J(^1H_a\text{-}^1H_b)$ are 3.0 Hz for *trans*-Pt(DMSO)(pz)Cl_2 and *trans*-Pt(TMSO)(pz)Cl_2 and 3.3 Hz for *cis*-Pt(DPrSO)(pz)Cl_2. A coupling constant with the Pt(II) nucleus, $^3J(^{195}\text{Pt-}^1\text{H})$ = 33 Hz, was also observed for the DMSO complex. This value is in agreement with the results in the literature reported for *trans*-Pt(DMSO)(Ypy)Cl_2 (Ypy = pyridine derivative) (32) and for *trans*-Pt(Ypy)$_2X_2$ (33). The coupling constants $^3J(^{195}\text{Pt-}^1\text{H})$ are usually smaller for trans isomers. For example, the values of $^3J(^{195}\text{Pt-}^1\text{H})$ for Pt(DMSO)(pm)Cl_2 are 31 and 44 Hz for the trans and cis compounds, respectively (8).

In ^{13}C NMR spectroscopy, similar results were observed. The two pyrazine signals in the spectra of the complexes were observed at lower fields than the single ^{13}C resonance of free pyrazine, with C_a being more affected ($\Delta\delta_a$ ~ 2 ppm) by coordination to the metal than C_b (Table 3). The formation of the N→Pt σ bond reduces the electron density on the pyrazine ligand. Surprisingly, $\Delta\delta$ for C_b is much larger for *cis*-Pt(DPrSO)(pz)Cl_2 ($\Delta\delta_b$ = 2.33 ppm) than for the other complexes ($\Delta\delta_b$ = 0.26–0.86 ppm). The difference is probably due to the cis geometry of the DPrSO compound. The latter ligand is very sterically demanding, and the rotation around the Pt—N bond is restricted. In solution, the pyrazine plane would probably be almost perpendicular to the Pt(II) coordination plane to reduce the steric hindrance to a minimum. The ^{13}C $\Delta\delta_{avg}$ of *cis*-Pt(DPrSO)(pz)Cl_2 is larger (2.44 ppm) than the corresponding values of the trans compounds (avg. 1.38 ppm). A similar observation was previously reported for $Pt(R_2SO)(pm)Cl_2$, where the value $\Delta\delta_{avg}$ was 2.13 ppm for the cis isomers and 1.51 ppm for the trans complexes (8). For *trans*-Pt(PR_3)(pz)Cl_2, the C_a and C_b signals were observed at 147.2 and 145.0 ppm, respectively (11). We have not observed any $J(^{195}\text{Pt-}^{13}\text{C})$ couplings for the pyrazine carbon atoms.

The chemical shifts and the coupling constants $J(^1\text{H-}^1\text{H})$ of the sulfoxide ligands are presented in the Experimental section, and the values of $\Delta\delta$ ($\delta_{complex} - \delta_{sulfoxide}$) are listed in Tables 4 (^{1}H NMR) and 5 (^{13}C NMR). In ^{1}H NMR, the $\Delta\delta$ values are positive, indicating that the sulfoxide protons are more deshielded in the ligands than in the free molecules. The protons located in positions α to the binding atom are the most affected by coordination to the metallic center. For the DMSO complex, only one signal at 3.48 ppm was observed; this chemical shift is close to that reported for *trans*-Pt(DMSO)(pm)Cl_2 (3.45 ppm (8)) and for *trans*-Pt(DMSO)(thiazole)Cl_2 (3.48 ppm (34)). For the other complexes, two series of signals were observed. For the TMSO complex, the two geminal protons of each CH_2 group are in different environments. Those closer to the O atom will be more deshielded than the others. For the other ligands, the two series of signals result from restricted rotation around the S—C bonds. The difference between the two series of resonances decreases as the distance from the S atom increases.

A coupling constant $^3J(^{195}\text{Pt-}^1\text{H})$ = 23 Hz was observed for *trans*-Pt(DMSO)(pz)Cl_2. This is in agreement with results reported for the similar trans complexes Pt(DMSO)(thiazole)Cl_2 (22 Hz) (34) and $Pt(R_2SO)(pm)Cl_2$ (22 Hz) (8). The other ligands gave low-intensity multiplets, and the coupling with ^{195}Pt could not be seen.

In ^{13}C NMR, the resonances of the C atoms in α positions were observed at lower fields than those of the corresponding atoms in the free sulfoxides ($\Delta_\alpha\delta$ = 2.31–3.76 ppm), except for the DPhSO complex (Table 5). These values are quite small compared to similar values for other types of ligands such as amines. Sulfoxides can accept electron density from the metal center, and the π (Pt→S) bond will increase the electron density on the sulfoxide ligand. Furthermore, the inverse polarization of the π electrons of the $^{\delta-}$S—O$^{\delta+}$

Table 4. ^{1}H NMR $\Delta\delta$ ($\delta_{complex} - \delta_{sulfoxide}$) (ppm) for the complexes $Pt(R_2SO)(pz)Cl_2$.

Complex	H_α	H_β	H_γ	H_δ
trans-$Pt(DMSO)(pz)Cl_2$	1.00			
	$J(^{195}Pt\text{-}^{1}H)$=23 Hz			
trans-$Pt(TMSO)(pz)Cl_2$	1.17, 0.82	0.25, –0.01		
cis-$Pt(DPrSO)(pz)Cl_2$	1.20, 0.56	0.62, 0.29	0.17	
trans-$Pt(DPhSO)(pz)Cl_2$		0.66, 0.30 (*ortho*)	0.14 (*meta*)	0.14 (*para*)

Note: H_α is located on the C atom closest to the S atom, H_β is on the second C from S, etc.

Table 5. ^{13}C NMR $\Delta\delta$ ($\delta_{complex} - \delta_{sulfoxide}$) (ppm) for the complexes $Pt(R_2SO)(pz)Cl_2$.

Complex	C_α	C_β	C_γ	C_δ
trans-$Pt(DMSO)(pz)Cl_2$	3.76			
trans-$Pt(TMSO)(pz)Cl_2$	2.66	–0.75		
cis-$Pt(DPrSO)(pz)Cl_2$	2.31	0.54	–0.52	
trans-$Pt(DPhSO)(pz)Cl_2$	–6.99	2.86 (*ortho*)	–0.34 (*meta*)	2.12 (*para*)

Note: C_α is the C atom closest to the S atom, C_β is the second C from S, etc.

bond would increase the electron density on the S atom and its neighbouring atoms, especially the α carbon atoms. This inverse polarization of the S—O π bond was first suggested by Cooper and Powell (30) to explain the ^{13}C NMR spectra of some Pt–carbonyl complexes and was later put forward in the interpretation of the ^{13}C NMR spectra of some Pt–carboxylate complexes (31). The chemical shifts in ^{13}C NMR spectroscopy are particularly dependent on such mesomeric effects.

For *trans*-$Pt(DPhSO)(pz)Cl_2$, the signals of the α carbon atoms were observed at much higher field than those of the free ligand ($\Delta_\alpha\delta$ = –6.99 ppm). Similar behavior was reported for the pyrazine-bridged dimer *trans*-$\{Pt(DPhSO)Cl_2\}_2(\mu\text{-pz})$, with $\Delta_\alpha\delta$ = –6.61 ppm (10). We suggest that the inverse polarization of the π electrons in the S=O bond would be greater in this ligand because of the presence of two strongly electron-attracting phenyl groups located directly on the S atom. This phenomenon would increase the electron density on the C atoms located in positions α to the S atom. The π component of the Pt—S bond (back-donation) might also be more important for this ligand because of the presence of the two electron-attracting groups on the ligand.

The NMR results for these complexes are very similar in general to those reported for the pyrazine-bridged dimers (10). This behavior is different from that reported for the R_2SO-pm complexes (8, 9). Since the two bridging atoms in pyrazine are far from each other, the presence of a second Pt atom does not influence the chemical shifts of the sulfoxides. There are seven bonds between C_α and the second Pt atom in the dinuclear species. In the pyrimidine series, the distances are shorter, and the influence of the second metal center is more important.

The results of this study seem to indicate that the Pt–pyrazine bond is more complicated than expected. Pyrazine has π^* orbitals that could form π bonds with Pt, but to a much reduced extent as compared to sulfoxides. Some published work on pyridine (33) and pyrimidine (8, 9) complexes seems to indicate the presence of some π bonding in the Pt—N bonds, although this is not easy to study.

Crystal structures

The crystal structures of one trans complex, $Pt(TMSO)(pz)Cl_2$ (**I**), and the one cis compound produced, $Pt(DPrSO)(pz)Cl_2$ (**II**), were studied by X-ray diffraction methods. The results confirmed the geometry of the complexes suggested by IR and NMR spectroscopies. Figures 1 and 2 show the labeled diagrams of the two complexes. The bond distances and angles are listed in Table 6. The CIF tables of the two crystal structure determinations have been deposited as supplementary material.[2]

The coordination around the Pt atoms is square planar as expected. The bond angles around the Pt atom are close to the ideal values. The largest deviation can be seen in the cis compound (**II**), where the N-Pt-Cl angle is reduced to 87.7(4)° while the N-Pt-S angle is increased to 92.0(4)°, to reduce the steric hindrance caused by the bulky sulfoxide ligand. In Pt–sulfoxide complexes, the O atom of the sulfoxide is often in the Pt coordination plane, which reduces the steric hindrance caused by the presence of the sulfoxide. In the cis compound (**II**), where this factor is very important, the O is almost in the coordination plane, with a deviation of 0.12(3) Å, while in the trans compound (**I**), the deviation is 1.41(1) Å.

The pyrazine ring is planar in both **I** and **II**. The dihedral angle between the pyrazine plane and the Pt coordination plane is 54.6(4)° and 60.3(5)° for the trans (**I**) and cis (**II**) complexes, respectively. This angle is usually larger in cis

[2] Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 216747 and 216748 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 1. Labeled diagram of *trans*-Pt(TMSO)(pz)Cl_2 (**I**). The ellipsoids correspond to 30% probability.

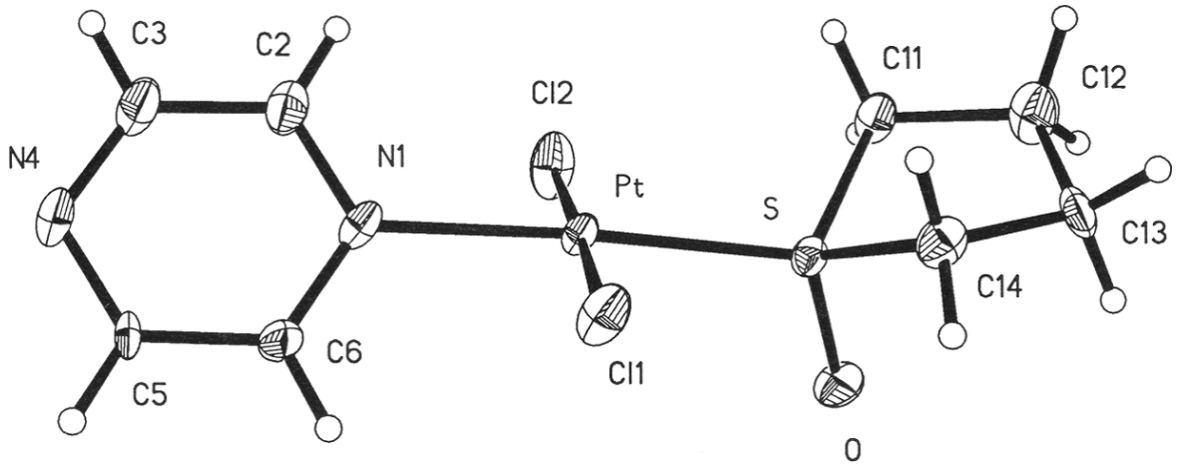
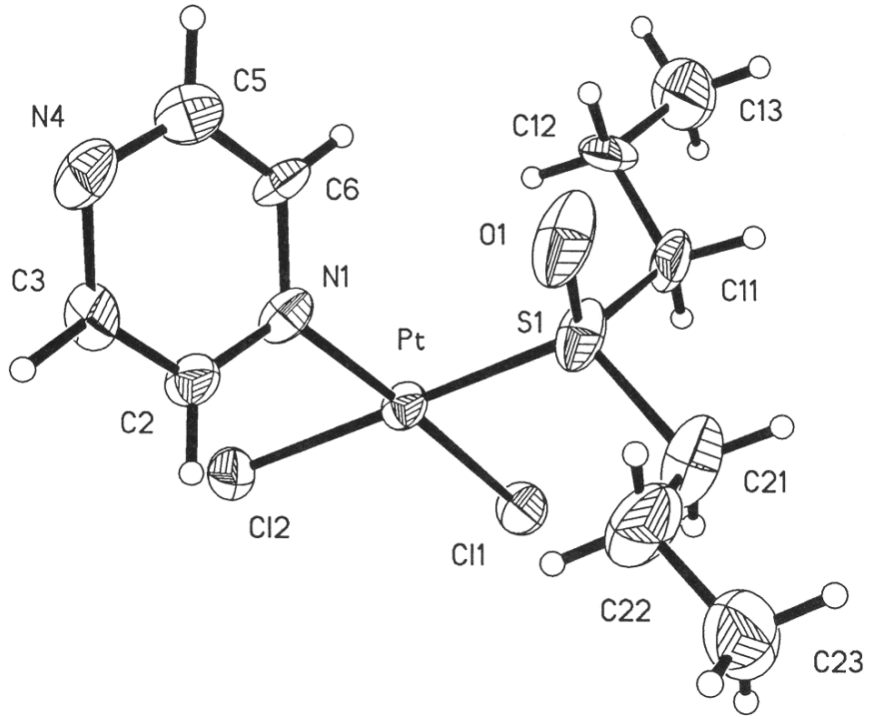


Fig. 2. Labeled diagram of *cis*-Pt(DPrSO)(pz)Cl_2 (**II**). The ellipsoids correspond to 25% probability.



compounds, where the bulkiness of the ligands is a more important factor.

The Pt—S bond lengths in the two structures are within the range reported for other Pt–sulfoxide complexes (8–10, 16, 34–36). In terms of trans influence, pyrazine and chloride are not very different, and the lengths of the Pt—S bonds do not seem to be very sensitive to the trans ligand. In *cis*-Pt(DPrSO)(pz)Cl_2, the Pt—Cl bond trans to the sulfoxide ligand is longer (2.316(5) Å) than the one trans to pyrazine (2.292(5) Å). The large trans influence of sulfoxides is well known. In crystal **I**, the Pt—Cl bonds are trans to each other, and their lengths (avg. 2.293(3) Å) are within the normal range. The lengths of Pt—N bonds are usually more sensitive to the trans ligands. In crystal **II**, where the trans ligand is a chloro ligand, the length of the Pt—N bond is 2.004(14) Å. In **I**, the Pt—N bond is trans to the sulfoxide and is significantly longer (2.053(11) Å). These results are close to those reported for similar compounds (8–10, 33, 34, 37, 38). All these data confirm that the trans influence of the sulfoxide ligand is clearly larger than that of the chloro ligand or pyrazine.

The bond distances and bond angles in the sulfoxide ligands are as expected and agree with published data on Pt–R_2SO complexes (8–10, 16, 39). As observed in other TMSO compounds, the C-S-C angle in *trans*-Pt(TMSO)(pz)Cl_2 is small (94.0(7)°) since the S atom is in a five-membered ring. The conformation of the TMSO ligand is of the envelope type, as seen in Fig. 1. The four C atoms are planar, and the S atom is 0.75(2) Å out of the plane. The dihedral angle between this plane and the Pt coordination plane is

Table 6. Bond distances and angles in crystals **I** and **II**.

	I, *trans*-Pt(TMSO)(pz)Cl_2	**II**, *cis*-Pt(DPrSO)(pz)Cl_2
Bond lengths (Å)		
Pt—Cl	2.290(3)	2.292(5)
	2.296(3)	2.316(5)[a]
Pt—S	2.217(3)	2.209(6)
Pt—N	2.053(11)	2.004(14)
S—O	1.488(10)	1.45(2)
S—C (avg.)	1.779(14)	1.78(2)
N—C (pz) (avg.)	1.34(2)	1.36(3)
C—C (pz) (avg.)	1.38(2)	1.36(3)
C—C (R_2SO) (avg.)	1.54(2)	1.47(3)
Bond angles (°)		
Cl-Pt-Cl	177.98(14)	90.3(2)
S-Pt-Cl	92.13(11)	90.0(2)
	89.89(12)	179.3(3)
N-Pt-Cl	89.0(3)	87.7(4)
	88.9(3)	177.2(5)
N-Pt-S	175.8(4)	92.0(4)
Pt-S-O	112.9(5)	115.5(7)
Pt-S-C (avg.)	115.7(5)	111.5(10)
Pt-N-C (avg.)	121.5(10)	122.3(13)
O-S-C (avg.)	108.5(7)	108.1(13)
C-S-C	94.0(7)	100.9(12)
C-N-C (pz) (avg.)	116.4(13)	115(2)
C-C-N (pz) (avg.)	122(2)	123(2)
S-C-C (R_2SO) (avg.)	104.1(11)	109(2)
C-C-C (R_2SO) (avg.)	109.1(12)	111(3)

[a]trans to DPrSO.

17.1(10)°. In *cis*-Pt(DPrSO)(pz)Cl_2, the C-S-C angle is smaller (100.9(12)°) than the other angles around the S atom, since the multiple S—O bond occupies more space than the single S—C bonds.

The average pyrazine C-N-C and C-C-N internal angles are 116.4(13)° and 122(2)°, respectively, for **I** and 115(2)° and 123(2)°, respectively, for **II**. For the free molecule, these angles were reported to be 115.1° and 122.4°, respectively (40). Therefore, the structure of pyrazine does not change upon coordination to Pt(II).

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