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Novel Pyrimidine-Bridged Platinum(II) Complexes: Multinuclear Magnetic Resonance Spectroscopy and Crystal Structures of $(NR_4)_2[(PtCl_3)_2(\mu\text{-pyrimidine})]$ and *cis*- and *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pyrimidine})$

Nicolas Nédélec and Fernande D. Rochon*

Département de Chimie, Université du Québec à Montréal, C. P. 8888,
Succ. Centre-ville, Montréal, Canada, H3C 3P8

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Two new types of pyrimidine-bridged Pt(II) complexes, $(NR_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ and *cis*- and *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ where pm = pyrimidine, were synthesized and characterized by IR and multinuclear magnetic resonance spectroscopies and by crystallographic methods. Compounds with dimethylsulfoxide, tetramethylenesulfoxide, di-*n*-propylsulfoxide (DPrSO), di-*n*-butylsulfoxide (DBuSO), dibenzylsulfoxide (DBzSO), and diphenylsulfoxide were studied. The aqueous reaction of K_2PtCl_4 with pyrimidine produced the $[(PtCl_3)_2(\mu\text{-pm})]^{2-}$ ions, which can be precipitated with a NR_4^+ salt. The aqueous reaction of $K[Pt(R_2SO)Cl_3]$ with pyrimidine in a 2:1 ratio produced the dinuclear species *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$. With DBuSO and DBzSO, the analogous *cis* isomers were also obtained. The ^{195}Pt NMR resonances of the *trans* dimeric complexes were observed at higher field (av −3088 ppm) than the *cis* compounds (av −2948 ppm). The ^{195}Pt coupling constants with the atoms of pyrimidine $^3J(^{195}Pt-^1H)$ and $^3J(^{195}Pt-^{13}C)$ are larger in the *cis* configuration than in the *trans* analogues. The crystal structures of two ionic complexes, $(NR_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ (R = Me and *n*-Bu), and of three mixed-ligands dimers, *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ (R_2SO = DMSO, DPrSO) and *cis*-$\{Pt(DBuSO)Cl_2\}_2(\mu\text{-pm})$, were determined.

Introduction

Pyrimidine and its derivatives are of biological interest, since they play an important role in many biological processes. However, there are very few papers in the literature on platinum compounds with nonsubstituted pyrimidine (pm). Fazakerley and Koch[1] synthesized and characterized *cis*-$[Pt(NH_3)_2(pm)_2](ClO_4)_2$ by ^{13}C NMR spectroscopy, while Rochon and coworkers[2] prepared *cis*- and *trans*-$Pt(pm)_2X_2$ (X = Cl and Br) and determined the crystal structures of the two *trans* isomers. Kaufmann et al. characterized *trans*-$Pt(PEt_3)(pm)Cl_2$ by ^1H and ^{31}P NMR, although they were not able to isolate the compound.[3] These authors have also prepared the dimer $\{PtCl_2(PR_3)\}_2(\mu\text{-pm})$. The nature of the platinum−pyrimidine bond has not been investigated yet.

In an attempt to prepare the ionic complex $[Pt(pm)Cl_3]^-$, we have studied the reaction of $K_2[PtCl_4]$ with pyrimidine in water. The isolated crystals were identified by X-ray diffraction methods as the pyrimidine-bridged dinuclear species $[(PtCl_3)_2(\mu\text{-pm})]^{-2}$, which had not been reported yet. Only one paper has been published on a pyrimidine-bridged dimer, $\{PtCl_2(PR_3)\}_2(\mu\text{-pm})$, where R = Et and *n*-Bu.[3] Although the crystal structures of the compounds were not determined, the authors suggested a *trans* configuration, because of the large *trans* effect of phosphines. The complexes were synthesized from the reaction of $Pt_2Cl_4(PR_3)_2$ with pyrimidine in $CDCl_3$. The PEt_3 compound was isolated and characterized by IR and ^{13}C NMR, while the $P(n\text{-}Bu)_3$ complex was not isolated. It was only synthesized directly in the NMR tube and characterized by ^1H and ^{31}P NMR.

Our research group has been involved in Pt-sulfoxide complexes for many years. These molecules have interesting behaviors, since they can accept π electron density from the metallic center. Most of the studies on Pt-sulfoxide complexes were done with the most common ligand, DMSO. The aqueous reaction of $K_2[PtCl_4]$ with an excess of sulfoxide produces *trans*-$Pt(R_2SO)_2Cl_2$, which radiply isomerizes to the *cis* isomer, unless the ligand is very sterically demanding. The greater stability of the *cis*-disubstituted complexes has been explained by the enhanced $(d-d)\pi$ bonding, which is more effective in the *cis* configuration than in the *trans* geometry.[4] In the Pt-amine system, where π bonding is absent, the *trans* isomers are more stable than the *cis* compounds.

We have recently undertaken a study on a new type of mixed-ligand Pt(II) complexes with pyrimidine and sulfoxide ligands. It appeared interesting to determine if a *trans* mixed-ligand complex containing sulfoxide and pyrimidine would also isomerize to the *cis* compound. Pyrimidine contains empty π antibonding orbitals, which could accept electron density from Pt. The reactions of $K[Pt(R_2SO)Cl_3]$ with pyrimidine were studied with different types of sulfoxides and in different experimental conditions. In the first part of this project, we have recently reported the synthesis and characterization of complexes the types *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$.[5] These compounds were prepared from the reaction of $K[Pt(R_2SO)Cl_3]$ with

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* Corresponding author. Tel: (514) 987-3000, 4896#. Fax: (514) 987-4054. E-mail: rochon.fernande@uqam.ca.

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Table 1. Experimental Details of the Crystallographic Studies of $(NR_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ (R = CH_3 (**I**) and C_4H_9 (**II**)), *trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ (R_2SO = DMSO (**III**) and DPrSO (**IV**)), and *cis*-$\{Pt(DBuSO)Cl_2\}_2(\mu\text{-pm})$ (**V**)

	I	**II**	**III**	**IV**	**V**
formula	$C_{12}H_{28}N_4Cl_6Pt_2$	$C_{36}H_{76}N_4Cl_6Pt_2$	$C_{8.5}H_{17}N_2O_2S_2Cl_5Pt_2$	$C_{16}H_{32}N_2O_2S_2Cl_4Pt_2$	$C_{20}H_{40}N_2O_2S_2Cl_4Pt_2$
fw	831.28	1167.89	810.79	880.54	936.64
space group	$P\bar{1}$	$P2_1/c$	*Pccn*	$C2/c$	I_1/a
a (Å)	8.406(4)	14.511(3)	14.474(2)	22.965(2)	15.059(3)
b (Å)	11.728(10)	16.316(3)	30.108(4)	7.3390(10)	15.059(3)
c (Å)	12.890(10)	20.571(9)	9.1560(10)	32.585(3)	28.372(10)
α (deg)	102.49(7)				
β (deg)	101.02(6)	99.62(3)		108.37(1)	
γ (deg)	93.13(6)				
volume (Å^3)	1211.7(14)	4802(3)	3990.0(9)	5212(1)	6434(3)
Z	2	4	8	8	8
F(000)	772	2312	2968	3312	3568
ρ_{calc} (Mg/m^3)	2.278	1.615	2.699	2.244	1.934
μ(Mo Kα) (mm^{-1})	12.324	6.181	14.890	11.310	9.168
ind reflns	5559	8460	3883	4594	2824
obs reflns ($I > 2\sigma(I)$)	3975 ($F > 4\sigma(F)$)	4447	1338	2894	855
R_1 ($I > 2\sigma(I)$)[a]	0.037 (F > 4σ(F))	0.0613	0.0638	0.0576	0.0661
wR_2 (all data)[b]	0.047	0.0975	0.1182	0.1079	0.1184
S	1.29	0.971	0.992	1.090	0.991

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

pyrimidine in water for the *trans* isomer and in methanol for the *cis* compound. The first product is the *trans* complex, which then isomerizes to the *cis* isomer. The isomerization is quite slow in water especially with more bulky ligands, but much faster in an organic solvent.

In the second part of the research project, we have isolated and characterized a new type of pyrimidine-bridged dinuclear complexes with sulfoxide ligands. Six sulfoxides with different steric hindrance were studied: dimethylsulfoxide (DMSO), tetramethylenesulfoxide (TMSO), di-*n*-propylsulfoxide (DPrSO), di-*n*-butylsulfoxide (DBuSO), dibenzylsulfoxide (DBzSO), and diphenylsulfoxide (DPhSO). We have now developed methods to synthesize *cis*- and *trans*-$Pt(R_2SO)Cl_2(\mu\text{-pm})Pt(R_2SO)Cl_2$, which were characterized by infrared and multinuclear magnetic resonance (^1H, ^{13}C, and ^{195}Pt) spectroscopies. The crystal structures of two *trans* compounds and one *cis* isomer were determined.

We also report in this paper the crystal structures of two ionic complexes of the type $(NR_4)_2[PtCl_3(\mu\text{-pm})PtCl_3]$ (R = Me and *n*-Bu).

Experimental Section

$K_2[PtCl_4]$ was obtained from Johnson Matthey Inc., and it was purified by recrystallization in water before use. The NR_4Cl salts, CD_2Cl_2, pyrimidine, and the sulfoxide ligands were purchased from Aldrich except dipropylsulfoxide, which was bought from Phillips Petroleum.

The melting and 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 Perkin-Elmer 783 spectrometer between 4000 and 270 cm^{-1}. All the NMR spectra were measured in CD_2Cl_2 on a Varian Gemini 300BB spectrometer operating at 300.075, 75.462, 64.400, or 64.335 MHz for ^1H, ^{13}C, and ^{195}Pt, respectively. The dichloromethane peaks were used as an internal standard for the ^1H (5.32 ppm) and ^{13}C (53.80 ppm) NMR spectra. For ^{195}Pt, the external references were $K_2[PtCl_4]$ (−1628 ppm in D_2O with KCl) or $K[Pt(DMSO)Cl_3]$ (in D_2O, adjusted at −2998 ppm from $Na_2[PtCl_6]$). The ^{195}Pt NMR spectra were measured between −1000 and −2500 ppm for $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ or between −2500 and −4000 ppm for the sulfoxide complexes.

The crystallographic measurements were done on a Siemens P4 (except crystal **I**, which was measured on a P-1) diffractometer using graphite-monochromatized Mo Kα (λ = 0.71073 Å) radiation. All 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 $2\theta/\omega$ scan technique using the XSCANS[6] program (except for crystal **I**). 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 (F for **I**) by full matrix least-squares analysis. The hydrogen atom positions were fixed in their calculated position with $U_{eq} = 1.2U_{eq}$ (or 1.5 for methyl groups) of the carbon to which they are bonded (for **I**, U_{eq} = 0.076 Å^2). Corrections were made for absorption (Gaussian integration except for **V** (empirical)), Lorentz, and polarization effects. In crystal **II**, three C atoms of one butyl chain of the cation were found disordered. Crystal **III** 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. It contained 0.5 molecule of CH_2Cl_2 per dinuclear species (the C atom is located on a 2-fold axis). In crystal **V** the two butyl chains of the DBuSO ligands were found very disordered and the different components intermingle. The H atoms of the disordered C atoms were neglected. The residual peaks were located in the close environment of the platinum atoms. The calculations were done using the Siemens SHELXTL[6] system (except for crystal **I**[7]). The pertinent data are summarized in Table 1.

The $K[Pt(R_2SO)Cl_3]$ complexes were synthesized according to the method described by Kukushkin et al.[8] The DBzSO complex was obtained in small quantities due to the great insolubility of the ligand and the very favorable formation of the *cis*-disubstituted compound.

***trans*-$\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$.** The $K[Pt(R_2SO)Cl_3]$ compounds and pyrimidine were dissolved in water in 2:1 proportions at room temperature. A yellow precipitate appeared rapidly, but the stirring of the solution was pursued until it became colorless. After filtration, the precipitate was dried, washed with ether, and dried in a vacuum. For the DPrSO and DBuSO complexes, the reactions were done in a 2:1 H_2O-CH_3OH mixture, while for the DBzSO, the reaction was done only in CH_3OH. *trans*-$\{Pt(DMSO)Cl_2\}_2(\mu\text{-pm})$ (**III**): yield 93%, mp 171 °C. IR (cm^{-1}): pm (vibration number[9,10]) 1614s (9,10), 1469m (22), 1416s (23), 1234w (3), 1198w (17), 1040s (1), 987w (5), 819m (12), 742w (13), 704m (4); ν(S−O) 1156s, ν(Pt−S) 445m, ν(Pt−Cl)

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353m. ^{1}H NMR (ppm): H_2 9.986s, $H_{4,6}$ 9.329dd, H_5 7.708dt, H_α 3.487s. ^{13}C NMR (ppm): C_2 162.58, $C_{4,6}$ 161.43, C_5 123.34, C_α 45.09. *trans*-{Pt(TMSO)Cl_2}$_2$(μ-pm): yield 89%, mp 167 °C. IR (cm^{-1}): pm 1608s (9,10), 1467m (22), 1409s (23), 1225w (3), 1190m (17), 1079s (14), 1046w (1), 990w (5), 820m (12), 698sh (4), 665sh (6); ν(S−O) 1149s, ν(Pt−Cl) 347s. ^{1}H NMR (ppm): H_2 10.003s, $H_{4,6}$ 9.349dd, H_5 7.714dt, H_α 4.016ddd, 3.627ddd, H_β 2.387m, 2.221m. ^{13}C NMR (ppm): C_2 162.44, $C_{4,6}$ 161.33, C_5 123.26, C_α 57.66, C_β 24.83. *trans*-{Pt(DPrSO)Cl_2}$_2$(μ-pm) (**IV**): yield 74%, mp 164 °C. IR (cm^{-1}): pm 1604s (9,10), 1466m (22), 1413m (23), 1228sh (3), 1187w (17), 1077w (14), 1041w (1), 830m (12), 738w (13), 688sh (4), 662w (6); ν(S−O) 1146s, ν(Pt−S) 450w, ν(Pt−N) 503m, ν(Pt−Cl) 352m. ^{1}H NMR (ppm): H_2 10.011s, $H_{4,6}$ 9.331dd, H_5 7.678dt, H_α 3.680ddd, 3.270ddd, H_β 2.240dddq, 2.117dddq, H_γ 1.211t. ^{13}C NMR (ppm): C_2 162.45, $C_{4,6}$ 161.28, C_5 122.95, C_α 57.21, C_β 17.00, C_γ 12.99. *trans*-{Pt(DBuSO)Cl_2}$_2$(μ-pm): yield 79%, mp 108 °C. IR (cm^{-1}): pm 1607s (9,10), 1467m (22), 1412m (23), 1230w (3), 1192w (17), 1044w (1), 970w (5), 814w (12), 727w (13), 698w (4), 661w (6); ν(S−O) 1149s, ν(Pt−S) 457w, ν(Pt−N) 510 w, ν(Pt−Cl) 348m. ^{1}H NMR (ppm): H_2 10.026s, $H_{4,6}$ 9.336dd, H_5 7.683dt, H_α 3.707ddd, 3.293ddd, H_β 2.195m, 2.067m, H_γ 1.629sextuplet, H_δ 1.037t. ^{13}C NMR (ppm): C_2 162.47, $C_{4,6}$ 161.28, C_5 122.94, C_α 55.35, C_β 25.03, C_γ 21.89, C_δ 13.82. *trans*-{Pt(DBzSO)Cl_2}$_2$(μ-pm): yield 64%, mp 134 °C. IR (cm^{-1}): pm 1606s (9,10), 1457s (22), 1410s (23), 1180 m (17), 1070w (14), 1027w (1), 813w (12), 760m (13), 694s (4); ν(S−O) 1122, ν(Pt−Cl) 345m. ^{1}H NMR (ppm): H_2 9.869s, $H_{4,6}$ 9.181dd, H_5 7.618dt, H_α 5.120d, 4.579d, H_{ortho} 7.657m, $H_{meta,para}$ 7.496m. ^{13}C NMR (ppm): C_2 161.86, $C_{4,6}$ 160.92, C_5 122.53, C_α 60.97, C_{phenyl} 129.21, 129.67, 130.11, 132.00. *trans*-{Pt(DPhSO)Cl_2}$_2$(μ-pm): yield 87%, mp dec 121−246 °C. IR (cm^{-1}): pm 1606s (9,10), 1474s (22), 1413s (23), 1230w (3), 1181sh (17), 1067s (14), 1044w (1), 997m (5), 811w (12), 744s (13), 693s (4), 640w (6); ν(S−O) 1147s, ν(Pt−S) 446w, ν(Pt−Cl) 348s. ^{1}H NMR (ppm): H_2 10.132s, $H_{4,6}$ 9.383dd, H_5 7.693dt, H_{ortho} 7.942m, $H_{meta,para}$ 7.553m. ^{13}C NMR (ppm): C_2 162.76, $C_{4,6}$ 161.55, C_5 123.07, C_{phenyl} 142.28, 127.56, 129.18, 133.40.

***cis*-{Pt(R_2SO)Cl_2}$_2$(μ-pm) (R_2SO = DBuSO and DBzSO).** The K[Pt(R_2SO)Cl_3] complex and pyrimidine (2:1 ratio) were dissolved in a minimum quantity of methanol at room temperature. After 3 days, a white precipitate was observed and the solvent was evaporated. The residue was mixed with water, and the solution was filtered to remove the soluble K[Pt(R_2SO)Cl_3] and KCl. The *cis* dimer was then dried, washed with ether, and finally dried in a vacuum. *cis*-{Pt(DBuSO)Cl_2}$_2$(μ-pm) (**V**): yield 33%, mp 165 °C. IR (cm^{-1}): pm 1613s (9,10), 1467m (22), 1415m (23), 1233w (3), 1189w (17), 1087sh (14), 1053w (1), 820m (12), 732w (13), 681m (4), 663w (6); ν(S−O) 1137s, ν(Pt−S) 460w, ν(Pt−N) 505w, ν(Pt−Cl) 353m, 322m. ^{1}H NMR (ppm): H_2 9.851s, $H_{4,6}$ 9.089dd, H_5 7.565dt, H_α 3.766ddd, 3.198ddd, H_β 2.299m, 1.950m, H_γ 1.609dtq, 1.602dtq, H_δ 1.028t. ^{13}C NMR (ppm): C_2 165.06, $C_{4,6}$ 162.14, C_5 123.19, C_α 54.77, C_β 25.05, C_γ 21.84, C_δ 13.78. *cis*-{Pt(DBzSO)Cl_2}$_2$(μ-pm): yield 53%, dec 193−230 °C. IR (cm^{-1}): pm 1609s (9,10), 1454s (22), 1418s (23), 1227w (3), 1185m (17), 1072w (14), 1030m (1), 818m (12), 759m (13), 697s (4), 674m (6); ν(S−O) 1120s, ν(Pt−S) 477s, ν(Pt−N) 485m, ν(Pt−Cl) 352m, 320m. ^{1}H NMR (ppm): H_2 8.273s, $H_{4,6}$ 7.381dd, H_5 6.733dt, $J = 5.9$ Hz, H_α 5.058d, 4.466d, H_{ortho} 7.590m, $H_{meta,para}$ 7.498m. ^{13}C NMR (ppm): C_2 163.58, $C_{4,6}$ 161.05, C_5 122.54, C_α 59.66, C_{phenyl} 127.73, 129.63, 130.24, 132.42.

$(NR_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ (R = CH_3 and C_4H_9). One millimole of $K_2[PtCl_4]$ was dissolved in water (~8 mL), and 0.5 mmol of pyrimidine (in 1 mL of H_2O) was added to the solution at room temperature. After 1 day, the solution was filtered to remove $Pt(pm)_2Cl_2$ and evaporated to dryness. The residue was then dissolved in acetone and filtered to remove KCl and unreacted $K_2[PtCl_4]$. After evaporating the acetone, the $K_2[(PtCl_3)_2(\mu\text{-pm})]$ compound was dried, washed with ether, and dried in a vacuum. The potassium dimeric salt and NR_4Cl were dissolved in water (1:1 ratio), and a yellow precipitate appeared immediately. The mixture was stirred until the solution became colorless, and the $(NR_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ compound was filtered out, dried, washed with ether, and dried in a vacuum. Yield: 5−10%. $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ (**II**): mp 157 °C. IR (cm^{-1}): pm (vibration no.[9,10]): 1597s (9,10), 1460s (22), 1407s (23), 1218w (3), 1176w (17), 1066w (14), 1025w (1), 818m (12), 736m (13), 681s (4); ν(Pt−Cl) 332s. ^{1}H NMR (ppm): H_2 10.239s, $H_{4,6}$ 9.384dd, H_5 7.167dt. ^{13}C NMR (ppm): C_2 164.77, $C_{4,6}$ 160.16, C_5 121.66. ^{195}Pt NMR: −1820 ppm.

Results and Discussion

Synthesis of the Complexes. The aqueous reaction of K[Pt(R_2SO)Cl_3] with pyrimidine in a 2:1 ratio produced the dimeric complexes *trans*-{Pt(R_2SO)Cl_2}$_2$(μ-pm). Compounds with R_2SO = DMSO, TMSO, DPrSO, DBuSO, DBzSO, and DPhSO were prepared. The quantities must be exact to avoid the formation of *trans*-Pt(R_2SO)(pm)Cl_2, which was prepared by a similar reaction using a 1:1 ratio. For the preparation of the DPrSO and DBuSO complexes, the reactions were done in a 2:1 water−methanol mixture, while the DBzSO compound was synthesized in methanol only.

$$\begin{array}{l} 2K[Pt(R_2SO)Cl_3] + pm \rightarrow \\ \qquad \qquad \textit{trans}\text{-}(R_2SO)Cl_2Pt(\mu\text{-pm})Pt(R_2SO)Cl_2 + 2KCl \end{array}$$

As expected, the *trans* compound is first formed, since the *trans* effect of the sulfoxide ligands is much larger than that of chlorides. The reaction time depends on the steric hindrance of the sulfoxide ligand. The yields varied between 64 and 93%.

The same reactions in methanol produce the yellow *trans* dimers. In the case of DBuSO and DBzSO, the *trans* compounds isomerize completely in about 3 days to the almost white *cis* dinuclear species. The *trans* dimers can be isolated at the beginning of the reaction if desired. With sulfoxides other than DBuSO and DBzSO, the *trans* dimers did not isomerize even with prolonged time. The isomerization of the *trans* dimers (other that DBuSO and DBzSO) was also studied in dichloromethane and chloroform, but without success.

These dinuclear species were characterized by IR and multinuclear magnetic resonance spectroscopies. The synthesized complexes were pure, since only one resonance was observed in ^{195}Pt NMR spectroscopy (confirmed also by ^{1}H and ^{13}C NMR). Two *trans* and one *cis* dinuclear compound, {Pt(R_2SO)Cl_2}$_2$(μ-pm), were also studied by X-ray diffraction methods.

The aqueous reaction of $K_2[PtCl_4]$ with pm in a 2:1 ratio produced the ionic potassium dinuclear species. The yield of this reaction is limited by the important precipitation of *cis*-Pt(pm)$_2$Cl$_2$, which has already been reported.[2] The product $K_2[(PtCl_3)_2(\mu\text{-pm})]$ was transformed into the tetraalkylammonium salt by its aqueous reaction with NR_4Cl, which instantaneously produced the insoluble salt $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$. The latter was prepared in order to compare its NMR spectra with those of the mixed-ligand dimers in the same solvent, since $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ is more soluble in organic solvents than the potassium analogue. It also produced crystals of better quality. Crystals of $K_2[(PtCl_3)_2(\mu\text{-pm})]$ could not be obtained.

$$\begin{array}{l} K_2[PtCl_4] + pm \rightarrow \\ \qquad \qquad K_2[(PtCl_3)_2(\mu\text{-pm})] \quad + KCl + Pt(pm)_2Cl_2\downarrow \\ \qquad \qquad \qquad \downarrow NR_4Cl \\ \qquad \qquad (NR_4)_2[(PtCl_3)_2(\mu\text{-pm})] \end{array}$$

The crystal structures of two ionic dimers (R = *n*-Bu and Me) were determined.

IR Spectroscopy. The IR spectrum of pyrimidine has been reported, and our assignments (Experimental Section) are based on these studies.[9,10] The vibrations of coordinated pyrimidine were observed at higher or energies similar to those of the free ligand. The ν(S−O) vibrations absorb at higher energy than in

Table 2. ^{195}Pt Chemical Shifts (ppm) of the Complexes $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ (in CD_2Cl_2) and $\Delta\delta$ ($\delta_{dimer} - \delta_{monomer}$ [5])

R_2SO	*trans*	$\Delta\delta$	*cis*	$\Delta\delta$	$\Delta\delta_{trans-cis}$
DMSO	−3081	−11			
TMSO	−3066	−10			
DPrSO	−3067	−8			
DBuSO	−3069	−9	−2941	13	128
DBzSO	−3090	−12	−2955	19	135
DPhSO	−3155	−7			

the free sulfoxides, since the ligands are bonded to Pt by the S atom. The ν(S−O) energies are identical in the *cis* and *trans* compounds. The IR spectra of the *cis* isomers showed two ν(Pt−Cl) bands at average values of 353 and 321 cm^{-1}, while only one vibration mode was observed for the *trans* complexes at about 349 cm^{-1}. Similar results have been reported for the monomers $Pt(R_2SO)(pm)Cl_2$.[5] One absorption band observed around 450 cm^{-1} was assigned to a ν(Pt−S) vibration, as suggested in the literature,[4,11−14] while a band at 520 cm^{-1} was assigned to the ν(Pt−N) vibration, based also on the published results.[15,16]

^{195}Pt NMR Spectroscopy. The ^{195}Pt NMR spectra of all the pyrimidine-bridged dinuclear complexes were measured in CD_2Cl_2, and the results were compared with those observed for the monomeric species $Pt(R_2SO)(pm)Cl_2$. The chemical shifts are summarized in Table 2. All the complexes are pure, as shown by ^{195}Pt, ^{1}H, and ^{13}C NMR spectroscopy. The ^{195}Pt NMR signals of the *trans* dinuclear species were observed at higher fields (between −3066 and −3155 ppm) than the *cis* analogues (av −2948 ppm), as reported for the monomeric species $Pt(R_2SO)(pm)Cl_2$.[5] They are also in agreement with the published values for $Pt(DMSO)(NH_3)Cl_2$ (−3045 for *cis* and −3067 ppm for *trans*[11,17]) and $Pt(DMSO)(L)Cl_2$ (L = pyridine derivative, −2856 to −3043 ppm[11,18]) and those published for $Pt(R_2SO)(R{-}CN)Cl_2$ (−3041 to −3186 ppm).[19]

The $\Delta\delta_{trans-cis}$ values are 128 and 134 ppm. The corresponding values were between 102 and 192 ppm for the monomers $Pt(R_2SO)(pm)Cl_2$.[5] The *cis* dimers are observed at lower fields, since the (d−d)π bonds are more effective in the *cis* configuration. The π bonds decrease the electron density on the Pt atom, causing a deshielding effect on the Pt atom in the *cis* compound. The group of Marzilli[18] has observed for $Pt(DMSO)(pyridine)Cl_2$ a $\Delta\delta_{trans-cis}$ value of 162 ppm. This $\Delta\delta_{trans-cis}$ value was found to vary with the bulkiness of the sulfoxide in the monomeric compounds $Pt(R_2SO)(pm)Cl_2$.[5] For the dinuclear species, there are not enough data to reach a similar conclusion, since the *cis* compounds could be synthesized with only two ligands. Our values of 128 and 134 ppm on the dimers are slightly larger than those reported for the corresponding monomers (106 and 102 ppm, respectively[5]). In a series of *cis*- and *trans*-$Pt(DPhSO)(R{-}CN)Cl_2$ complexes,[19] the $\Delta\delta_{trans-cis}$ values were between 134 and 138 ppm. As shown in Table 2, the δ(^{195}Pt) of these dimers are close to those determined for the *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$ compounds since the $\Delta\delta$ ($\delta_{dimer} - \delta_{monomer}$) values are very small. The *cis* dimers were observed at slightly lower fields than the *cis* monomers ($\Delta\delta$ = 13 and 19 ppm), while surprisingly, the *trans* dimers were found at slightly higher fields than the corresponding *trans* monomers ($\Delta\delta$ = −7 to −14 ppm). This difference might be due to the greater bulkiness around the Pt atom in the *cis* configuration compared to the one in the *trans* isomers. Rotation around the Pt−N bond might be more limited in the *cis* configuration than in the *trans* isomers.

The ^{195}Pt NMR chemical shifts seem to be dependent on the substituents on the sulfoxide ligands. The DPhSO complex is observed at much higher field than the others. The difference does not seem to depend on the presence of an aromatic group, since the DBzSO complex is observed in the same region as the other alkyl sulfoxides. But it contains a methylene group between the sulfoxide group and the phenyl ring, which reduces the steric hindrance around the binding atom. The shielded resonance observed for the DPhSO compound might then be due to the greater bulkiness around the S atom in this ligand. But for Pt-amine complexes, the δ(Pt) were found at lower fields for amines containing bulky substituents on the binding atom.[20,21] Another explanation was examined, namely, inverse polarization of the π electrons of the S=O bond. This phenomenon has been suggested in the literature to explain some ^{13}C NMR results on Pt−C≡O[22] and Pt-carboxylato complexes.[23] This effect would be present in all $Pt{-}R_2SO$ complexes, but it is more important for a ligand containing electroattracting aromatic groups directly on the binding atom. This effect, which will be discussed further in the ^{13}C NMR spectroscopic section, would increase the electron density on the Pt atom and therefore shift its NMR signal to higher field.

^{1}H and ^{13}C NMR Spectroscopies. The pyrimidine signals of the complexes will first be discussed. The chemical shifts are shown in the Experimental Section, and the values $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) and the coupling constants with ^{195}Pt are listed in Tables 3 and 4. Three signals are observed in the ^{1}H and ^{13}C spectra of free pyrimidine (C_{2v} symmetry).

In the pyrimidine-bridged Pt(II) dimers, the symmetry of the aromatic ligand is the same (Scheme 1). The signal of H_2 which is close to two nitrogen atoms is a singlet, since the ^{14}N isotope has a large quadrupolar moment, which leads to a broadening of the signal. The resonance of H_4 and H_6 consists of a doublet of doublets, whereas the one of H_5 is a doublet of triplets. All the $J(^{1}H{-}^{1}H)$ coupling constants are identical in the *cis* and *trans* configurations of the dimers and are normal.[24,25] However, as observed in the $Pt(R_2SO)(pm)Cl_2$ series,[5] the coupling constants $^{4}J(^{1}H_{4,6}{-}^{1}H_2)$ (0.7 Hz) are quite small. Kaufmann et al. have also observed similar coupling constants in *trans*-$\{Pt(PEt_3)Cl_2\}_2(\mu\text{-pm})$ and *trans*-$Pt(PEt_3)(pm)Cl_2$.[3]

The pyrimidine proton signals are shifted toward lower field upon coordination. The average chemical shift variations of the

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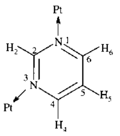
Table 3. ^{1}H NMR $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) (ppm) and $^3J(^{195}Pt-^1H)$ (Hz) of Pyrimidine in $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ and the Complexes $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$

ligand		H_2	$H_{4,6}$	H_5	$\Delta\delta_{av}$	$^3J(^{195}Pt-^1H_2)$	$^3J(^{195}Pt-^1H_6)$
Cl		1.062	0.666	−0.160	0.559		
DMSO	*trans*	0.809	0.611	0.381	0.603	24	28
TMSO	*trans*	0.826	0.630	0.387	0.618	23	32
DPrSO	*trans*	0.834	0.614	0.351	0.603	20	31
DBuSO	*cis*	0.674	0.371	0.237	0.413	25	42
	trans	0.850	0.619	0.356	0.611	20	29
DBzSO	*cis*	−0.904	−1.337	−0.594	−1.043	26	40
	trans	0.692	0.463	0.291	0.477	20	30
DPhSO	*trans*	0.955	0.665	0.366	0.663	20	31

Table 4. ^{13}C NMR $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) (ppm) and $^3J(^{195}Pt-^{13}C)$ (Hz) of Pyrimidine in $(NBu_4)_2[(PtCl_3)_2(\mu\text{-pm})]$ and the Complexes $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$

ligand		C_2	$C_{4,6}$	C_5	$\Delta\delta_{av}$	$^3J(^{195}Pt-^{13}C_5)$
Cl		5.45	2.94	−0.28	2.76	
DMSO	*trans*	3.24	4.21	1.41	3.27	
TMSO	*trans*	3.10	4.11	1.33	3.16	28
DPrSO	*trans*	3.11	4.06	1.02	3.06	25
DBuSO	*cis*	5.72	4.92	1.26	4.21	35
	trans	3.13	4.05	1.01	3.06	25
DBzSO	*cis*	4.24	3.82	0.61	3.12	35
	trans	2.52	3.70	0.60	2.63	
DPhSO	*trans*	3.42	4.33	1.14	3.31	

Scheme 1



pyrimidine protons $\Delta\delta_{av}$ (Table 3) are higher for the *trans* isomers, in agreement with the ^{195}Pt chemical shifts, which were observed at higher fields for the *trans* compounds. These results seem to suggest a potential π-back-bonding with pyrimidine, but to a much smaller extent than with sulfoxides, as discussed for the complexes $Pt(R_2SO)(pm)Cl_2$.[5] Again, π-bonding seems much more important in the *cis* complexes than in the *trans* isomers. The $\Delta\delta_{av}$ value is larger for the DPhSO complex compared to the other *trans* analogues, in agreement with the ^{195}Pt NMR results. The proton H_2 is the most affected by coordination and seems to be the most dependent on the nature of the sulfoxide ligand.

Kaufmann and co-workers have characterized *trans*-$\{Pt(PR_3)Cl_2\}(\mu\text{-pm})$ (R = Et and *n*-Bu) by ^{1}H NMR in the same solvent (CD_2Cl_2).[3] For these phosphine ligands the average $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) values were 0.948, 0.651, and 0.243 ppm for H_2, $H_{4,6}$, and H_5, respectively, compared with our values 0.827, 0.600, and 0.355 ppm for the *trans* R_2SO dinuclear complexes, and 1.062, 0.666, and −0.160 ppm for the ion $[(PtCl_3)_2(\mu\text{-pm})]^-$. Thus, H_2 and H_5 of pyrimidine are the most affected by the presence of the second ligand. The deshielding order for H_2 is $Cl^- > PR_3 > R_2SO$, whereas the opposite order was found for H_5. However, the $\Delta\delta_{av}$ study shows similar values for all the three types of compounds (0.559 ppm for Cl^-, 0.596 ppm for R_2SO, and 0.623 ppm for PR_3). It is difficult to discuss the results observed for the *cis* dimers, since only two compounds could be synthesized. The $\Delta\delta_{av}$ value for the *cis* DBuSO complex is slightly lower than the corresponding value for the *trans* isomer. The *cis* DBzSO complex is totally different, since all the signals are shifted to higher fields. The study on this complex was repeated a few times in order to confirm the results. The same spectra were always obtained. We have made some efforts to crystallize this compound in order to study its crystal structure, but we were not successful.

In ^{13}C NMR spectroscopy, the variation on the chemical shift ($\Delta\delta$) of C_2 for the *trans* complexes follows the order of the $\delta(^{195}Pt)$. In contrast to the proton signals, the ^{13}C NMR resonances showed greater $\Delta\delta$ values for the *cis* dimers compared to the *trans* compounds, especially for C_2. This study seems to indicate that the platinum−pyrimidine bond is more complicated than expected, especially with mixed-ligands capable of forming π bonds.

The chemical shifts of the sulfoxide ligands are presented in the Experimental Section, and the values $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) are listed in Tables 5 and 6. The multiplicity of the signals and the coupling constants $J(^1H-^1H)$ are identical to those determined in the complexes *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$.[5] The ^{1}H spectrum of the DMSO dimer showed only one peak for the methyl groups, but two large multiplets were observed for the hydrogen atoms located in *ortho*, *meta*, and *para* position of the DPhSO ligand. For TMSO, all the geminal methylene protons possess different chemical environments. Each α proton consists of a doublet of doublets of doublets with coupling constants $^2J = 14.2$, $^3J = 7.0$, and $^3J = 7.0$ Hz. For the DPrSO and DBuSO complexes, the geminal methylene protons also have different chemical environments due to limited rotation. The signals of the α protons are again a ddd, with $^2J = 13.0$, $^3J = 11.2$, and $^4J = 5.1$ Hz. The separation between the signals of the geminal protons decreases as the distance from the coordination site increases (Table 5). For DBuSO, this difference is smaller in the *trans* complexes (0.415, 0.128, and 0.00 ppm) than in the *cis* isomers (0.568, 0.349, and 0.007 ppm). The signals of the H_γ protons in the *cis* DBuSO complex consist of a doublet of triplets of quadruplets (dtq), while a sextuplet was observed in *trans*-$\{Pt(DBuSO)Cl_2\}_2(\mu\text{-pm})$ (the two H_β are felt as equivalent).

The ^{13}C NMR chemical shift variations ($\Delta\delta$) are in agreement with those reported for $K[Pt(R_2SO)Cl_3]$[26] and $Pt(R_2SO)(pm)Cl_2$[5] complexes. The signal of the α DPhSO carbon atoms is very shielded ($\Delta\delta = -4.22$ ppm) upon coordination. All the sulfoxide signals are less deshielded upon coordination than other types of ligands. We have suggested that the presence of inverse polarization of the π electrons in the S═O bond might be responsible for this phenomenon observed in complexes of the type $K[Pt(R_2SO)Cl_3]$.[26] Bonding of the sulfoxide ligand to the metal atom would reduce the π-electronic density on the O atom and increase it on the S atom and its neighboring atoms, including the Pt atom. This explanation has been suggested in the literature to explain the ^{13}C NMR spectra of Pt-CO[22] and Pt-carboxylate complexes.[23] The chemical shifts in ^{13}C NMR spectroscopy are particularly dependent on such mesomeric effects. The inverse polarization of the π electrons in the S═O

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Table 5. ^{1}H NMR $\Delta\delta$ ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) (ppm) and $^3J(^{195}\text{Pt}-^1\text{H})$ (Hz) of the Sulfoxides in the Complexes $\{\text{Pt}(\text{R}_2\text{SO})\text{Cl}_2\}_2(\mu\text{-pm})$

R_2SO		H_α	H_β	H_γ	H_δ	$^3J(^{195}\text{Pt}-^1\text{H}_\alpha)$
DMSO	*trans*	0.946				23
TMSO	*trans*	1.234, 0.845	0.252, 0.022			
DPrSO	*trans*	1.083, 0.672	0.476, 0.353	0.147		
DBuSO	*cis*	1.148, 0.580	0.599, 0.250	0.141, 0.134	0.073	
	trans	1.090, 0.675	0.495, 0.367	0.161	0.082	
DBzSO	*cis*	1.160, 0.568	0.229 (*ortho*)	0.137 (*meta*+*para*)		26
	trans	1.222, 0.681	0.296 (*ortho*)	0.135 (*meta*+*para*)		
DPhSO	*trans*	0.303	0.086	0.086		

Table 6. ^{13}C NMR $\Delta\delta$ ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) (ppm) and $J(^{195}\text{Pt}-^{13}\text{C})$ (Hz) of the Sulfoxides in the Complexes $\{\text{Pt}(\text{R}_2\text{SO})\text{Cl}_2\}_2(\mu\text{-pm})$

R_2SO		C_α	C_β	C_γ	C_δ	C_ϵ	$^2J(^{195}\text{Pt}-^{13}\text{C}_\alpha)$	$^3J(^{195}\text{Pt}-^{13}\text{C}_\beta)$
DMSO	*trans*	3.66					64	
TMSO	*trans*	2.66	−0.93				62	23
DPrSO	*trans*	2.44	0.32	−0.58			52	
DBuSO	*cis*	2.19	0.02	−0.63	−0.07		53	
	trans	2.76	0.00	−0.58	−0.03		49	25
DBzSO	*cis*	1.64	−0.79	1.321	0.176	−0.27	49	
	trans	2.95	−0.52	1.06	0.27	−0.64	55	
DPhSO	*trans*	−4.22	2.75	−0.47	2.10			

bond would be more important in the DPhSO complex, since the two electroattracting phenyl groups are attached directly on the S atom.

Coupling Constants with ^{195}Pt. In ^{1}H and ^{13}C NMR, satellites arising from the coupling with the ^{195}Pt nucleus are observed for H_2, H_6, and C_5 (^3J) of the pyrimidine ligand (Tables 3 and 4). The $^3J(^{195}\text{Pt}-^1\text{H}_6)$ values are geometry-dependent. They vary between 28 and 32 Hz for the *trans* dimers, while a higher value (40−42 Hz) was observed for the *cis* compounds, as reported for $\text{Pt(py)}_2\text{X}_2$[27−29] (py = pyridine derivative), for *cis*-$[\text{Pt}(\text{NH}_3)_2(\text{pm})_2](\text{ClO}_4)_2$,[1] and for *cis*- and *trans*-$\text{Pt}(\text{R}_2\text{SO})(\text{pm})\text{Cl}_2$.[5] However, lower values were reported for *trans*-$\{\text{Pt}(\text{PR}_3)\text{Cl}_2\}_2(\mu\text{-pm})$ (21 Hz).[3] Similarly, the $^3J(\text{Pt}-\text{C}_5)$ coupling constants for the pyrimidine-bridged dimers seem also geometry-dependent. The average values are 35 and 26 Hz for the *cis* and *trans* complexes, respectively (Table 4). These values are identical to those reported for *cis*- and *trans*-$\text{Pt}(\text{R}_2\text{SO})(\text{pm})\text{Cl}_2$.[5] The $^3J(^{195}\text{Pt}-\text{H}_2)$ coupling constants seem also to depend on the geometry of the complexes, although the differences are smaller. Values of ~25 Hz were found in the *cis* compounds, while these values are ~20 Hz for the corresponding *trans* isomers (Table 3). We have already reported similar results for $\text{Pt}(\text{R}_2\text{SO})(\text{pm})\text{Cl}_2$ (~23 Hz for *cis* and ~20 Hz for *trans*).[5] A value of 16 Hz was published for *trans*-$\{\text{Pt}(\text{PR}_3)\text{Cl}_2\}_2(\mu\text{-pm})$.[3] These results indicate that NMR is an excellent and easy method to determine unambiguously the geometry of these complexes.

The sulfoxide proton signals are often broad, and consequently, the ^{195}Pt satellites overlap with the other signals, except for DMSO and DBzSO. $^3J(^{195}\text{Pt}-^1\text{H}_\alpha)$ values of 23−26 Hz were measured. In ^{13}C NMR, the coupling constants $^2J(^{195}\text{Pt}-^{13}\text{C}_\alpha)$ are between 49 and 64 Hz (Table 6). These constants seem to vary with the nature of the sulfoxide. A few coupling constants $^3J(^{195}\text{Pt}-^{13}\text{C}_\beta)$ were observed between 23 and 25 Hz, in agreement with the values reported for the $\text{K}[\text{Pt}(\text{R}_2\text{SO})\text{Cl}_3]$ complexes.[26]

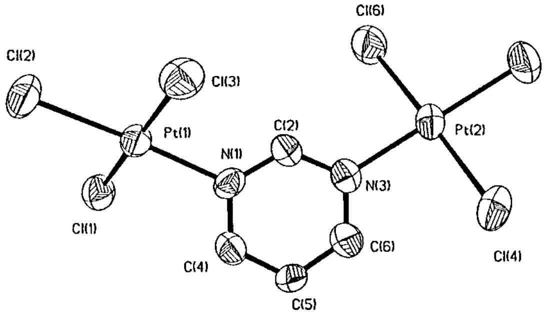

Figure 1. Labeled diagram of the complexed anion in the crystal $(\text{NBu}_4)_2[(\text{PtCl}_3)_2(\mu\text{-pm})]$ (**II**). The ellipsoids correspond to 40% probability.

Crystal Structures. The crystal structures of $(\text{NMe}_4)_2[(\text{PtCl}_3)_2(\mu\text{-pyrimidine})]$ (**I**) and $(\text{NBu}_4)_2[(\text{PtCl}_3)_2(\mu\text{-pyrimidine})]$ (**II**) were determined. Figure 1 shows the dinuclear anion in crystal **II**. Selected bond distances and angles for the two structures are shown in Table 7. The average (of the two structures) Pt−Cl bond in *trans* position to a Cl^- ligand (2.299(3) Å) is slightly longer than the one in *trans* position to pyrimidine (2.288(3) Å). The average Pt−N bonds located in *trans* position to a Cl^- ligand are 2.032(7) for **I** and 2.025(8) Å for **II**, slightly longer than the values reported for *trans*-$\text{Pt}(\text{pm})_2\text{X}_2$ (av 2.011(6) Å),[2] where the Pt−N bonds are in *trans* position to pyrimidine. These results suggest that the *trans* influence of the Cl^- ligand is slightly larger than that of pyrimidine. The angles around the Pt atoms are close to the values expected for square-planar coordination. The best planes were calculated through the two Pt planes and through the pyrimidine ligand. The dihedral angles between the Pt and the pyrimidine planes are 47.9(2)° and 42.3(2)° for **I** and 46.8(2)° and 40.5(2)° for **II**. The dihedral angle between the two platinum planes is 74.9(1)° (**I**) and 75.3(1)° (**II**).

The pyrimidine bonds and angles agree well with the values reported for the free ligand,[30] for the complexes *trans*-$\text{Pt}(\text{pm})_2\text{X}_2$,[2] and for *cis*- and *trans*-$\text{Pt}(\text{R}_2\text{SO})(\text{pm})\text{Cl}_2$.[5] The angle N−C−N is larger (av 124.9(9)°) than the other internal angles. No H-bonding is expected in this type of structure. The ions are held together by electrostatic and van der Waals forces.

The crystal structures of the two complexes *trans*-$(\text{R}_2\text{SO})\text{Cl}_2\text{Pt}(\mu\text{-pm})\text{Pt}(\text{R}_2\text{SO})\text{Cl}_2$ (R_2SO = DMSO (**III**), DPrSO (**IV**)) and of *cis*-$(\text{DBuSO})\text{Cl}_2\text{Pt}(\mu\text{-pm})\text{Pt}(\text{DBuSO})\text{Cl}_2$ (**V**) were studied by X-ray diffraction methods. Crystal **III** contained 0.5 molecule of CH_2Cl_2 per dinuclear species (the C atom is located on a 2-fold axis). The butyl chains in crystal **V** are very disordered, and the different components intermingle. Crystal **V** did not

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Table 7. Selected Bond Distances (Å) and Angles (deg) in Crystals **I** and **II**

	I	II
Pt−Cl (*trans* to Cl$^-$)	2.309(3)	2.306(3)
	2.310(3)	2.290(3)
	2.294(3)	2.301(3)
	2.298(3)	2.282(3)
Pt−Cl (*trans* to pm)	2.300(3)	2.283(3)
	2.296(3)	2.274(3)
Pt−N	2.021(7)	2.028(8)
	2.042(7)	2.022(8)
N−C (pm) av	1.343(11)	1.332(12)
C−C (pm) av	1.373(13)	1.372(14)
Cl−Pt−Cl	179.3(1)	177.4(1)
	90.5(1)	90.7(1)
	90.2(1)	90.4(1)
	177.9(1)	178.6(1)
	91.7(1)	90.5(1)
	90.1(1)	90.7(1)
N−Pt−Cl	179.4(2)	176.8(3)
	89.0(2)	89.8(3)
	90.4(2)	89.2(3)
	178.3(2)	179.4(2)
	89.5(2)	89.6(3)
	88.7(2)	89.1(3)
Pt−N−C (av)	121.0(6)	121.3(8)
N−C−N	124.5(8)	125.3(10)
C−N−C (pm) (av)	117.9(7)	117.4(9)
N−C−C (pm) (av)	120.6(8)	121.0(11)
C−C−C (pm)	118.4(9)	118.0(11)

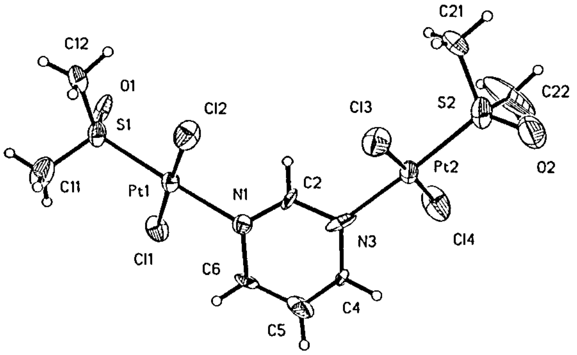

Figure 2. Labeled diagram of *trans*-(DMSO)Cl_2Pt(μ-pm)Pt(DMSO)-Cl_2 in crystal **III**. The ellipsoids correspond to 30% probability.

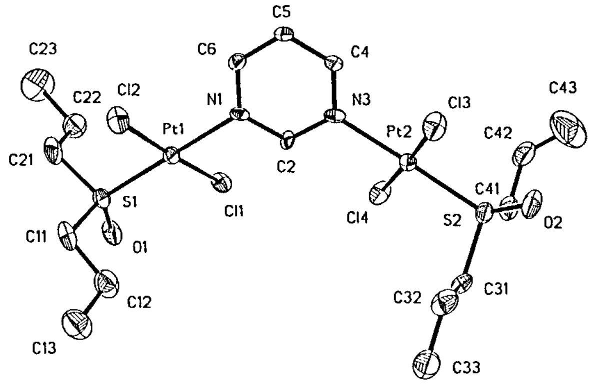

Figure 3. Labeled diagram of *trans*-(DPrSO)Cl_2Pt(μ-pm)Pt(DPrSO)-Cl_2 (**IV**). The ellipsoids correspond to 30% probability.

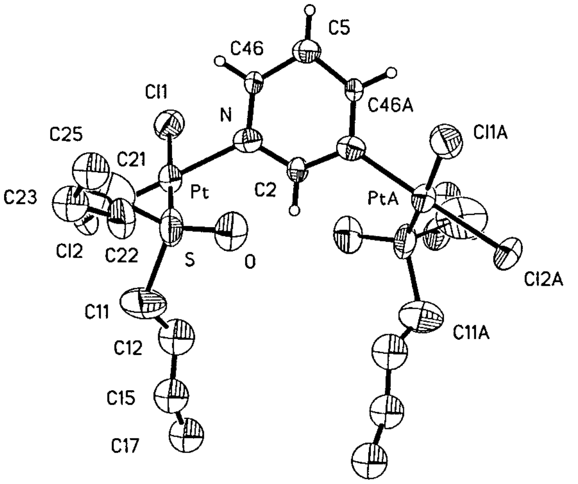

Figure 4. Labeled diagram of *cis*-(DBuSO)Cl_2Pt(μ-pm)Pt(DBuSO)-Cl_2 (**V**). The ellipsoids correspond to 30% probability. Only one component is shown for each butyl chain.

diffract very well, and the thermal factors of the atoms are high. Attempts to prepare crystals of better quality failed. Furthermore, the crystals were not very stable. Although the bond distances and angles involving the sulfoxide ligand are not very good (high standard deviations because of the disorder), the data on this compound are reported in this paper in order to confirm that the compound has indeed the *cis* geometry. Bond distances and angles related to the DBuSO ligand in crystal **V** will not be further discussed. Labeled diagrams of crystals **III**, **IV**, and **V** are shown in Figures 2, 3, and 4. Selected bond distances and angles are listed in Table 8.

The *cis* dimeric compound (**V**) contains a 2-fold axis. The atoms C2 and C5 of the bridged pyrimidine are located on the axis. The two *trans* compounds (**III** and **IV**) do not contain any element of symmetry. The coordination around the Pt atoms is square planar as expected. The best planes were calculated, and the dihedral angles between the Pt coordination planes and the pyrimidine ligand are 47.7(7)° and 62.0(6)° for **III**, 44.4(4)° and 46.0(4)° for **IV**, and 55.6(5)° for **V**. These angles are smaller than those reported in the monomers Pt(R_2SO)(pm)-Cl_2,[5] where these values vary between 62.6(2)° and 79.5(3)°. The dihedral angles between the two Pt coordination planes are 60.8(3)° (*trans*-DMSO, **III**), 48.7(2)° (*trans*-DPrSO, **IV**), and 90.8(4)° (*cis*-DBuSO, **V**). In the *trans* complexes, this angle seems to depend on the bulkiness of the sulfoxide. When R_2SO is replaced by Cl, the steric hindrance is reduced and the angle is larger (74.9(1)° for **I** and 75.3(1)° (**II**)). For the *cis*-DBuSO complex, the conformation of the molecule is quite different. The two coordination Pt planes are perpendicular to each other in order to reduce the steric hindrance caused by the presence of the bulky sulfoxides located in *cis* position to the pyrimidine ligand.

Packing forces are important factors in the orientation of the pyrimidine ring, when there is no steric hindrance. No π-stacking is possible in the *cis* compound, since the bulky sulfoxide ligands prevent the close contact of the pyrimidine ligands. In the *trans* crystals, the packing of the molecules is more efficient. In the DPrSO complex (**IV**), $\pi-\pi$ stacking can be observed. The distance between the pyrimidine rings is 3.88 Å, but the aromatic rings are not perfectly stacked. An angle of 15.5° is observed between the planes.

In the DMSO complex, the oxygen atom of the sulfoxide ligands are far from the coordination plane (deviations = −1.19(2) and 1.29(2) Å), while they are much closer in the DPrSO crystal (deviations = 0.259(16) and 0.208(11) Å). In the *cis* dinuclear complex, the deviation of the O atom is 0.31(2) Å from the coordination plane. The O atom of the sulfoxide ligand is often in the Pt plane, especially for bulky ligands in order to reduce the steric hindrance.

The angles around the Pt atoms are close to the expected square planar values. The average Pt−Cl bonds (*trans* to Cl$^-$)

Table 8. Selected Bond Distances (Å) and Angles (deg) in Crystals **III**−**V**

	III	IV	V
Pt−Cl (*trans* to Cl^-)	2.298(7)	2.295(4)	
	2.296(7)	2.296(4)	
	2.292(7)	2.278(4)	
	2.295(6)	2.309(4)	
Pt−Cl (*trans* to pm)			2.272(5)
Pt−Cl (*trans* to R_2SO)			2.311(6)
Pt−S	2.224(7)	2.218(3)	2.171(7)
	2.241(9)	2.221(4)	
Pt−N	2.04(2)	2.099(10)	2.01(2)
	2.02(2)	2.103(11)	
S−O (av)	1.46(2)	1.459(12)	1.457(14)
S−C (av)	1.77(3)	1.80(2)	1.83(2)
N−C (pm) (av)	1.35(3)	1.34(2)	1.32(2)
C−C (pm) (av)	1.36(3)	1.36(2)	1.41(2)
Cl−Pt−Cl (av)	176.7(3)	177.0(1)	90.4(5)
S−Pt−Cl (av)	91.3(3)	91.3(2)	91.3(2) 176.3(2)
N−Pt−Cl	88.8(6)	88.7(3)	87.5(5) 177.8(5)
N−Pt−S	176.8(6)	178.2(3)	90.9(5)
Pt−S−O (av)	113.2(9)	118.0(5)	115.2(6)
Pt−S−C (av)	111.4(11)	108.2(5)	107.9(9)
Pt−N−C (av)	123(2)	120.3(9)	123(2)
C−S−C (av)	99.6(15)	102.7(9)	
C−S−O (av)	110.4(16)	109.4(8)	
N−C−N	128(2)	120.7(12)	127(3)
C−N−C (pm) (av)	115(2)	119.3(11)	115(2)
N−C−C (pm) (av)	123(2)	121.1(13)	126(2)
C−C−C (pm)	119(3)	118.2(12)	111(2)

are 2.295(7) Å for **III** and 2.295(4) Å for **IV**. In crystal **V**, the Pt−Cl bond located in *trans* position to the sulfoxide is longer (2.311(6) Å) than the one *trans* to Cl^- (2.272(5) Å). The average Pt−S distance is 2.226(6) Å for **III** and **IV**. These values agree well with those reported in the literature for similar compounds.[7,31−40] The average Pt−N bond is 2.066(15) Å for **III** and **IV** and 2.01(2) Å for **V**. The Pt−N bonds located in *trans* position to the sulfoxide ligand are much longer than those located in *trans* position to Cl^- as observed in *trans*-Pt(TMSO)(pm)Cl_2 (2.063(5) Å).[5] In *trans*-Pt$(pm)_2Cl_2$, the Pt−N bond was 2.008(5) Å (*trans* to pm).[2] The Pt−N bond in *trans* position to PEt_3 is even much longer (av 2.14(1) Å in *trans*-$\{Pt(PEt_3)Cl_2\}_3$-(μ-triazine)[3]). The Pt−N bond seems to be more sensitive to the *trans* ligand than the Pt−Cl bond. All these results indicate that the *trans* influence vary in the order $PR_3 \gg R_2SO \gg Cl^- > pm$.

The S atom in the sulfoxide ligands is in an approximate tetrahedral environment. The C−S−C angles (av 99.6(15)° for DMSO and 102.7(9)° for DPrSO) are smaller than the angles observed in other Pt−R_2SO structures.[7,31−41] This angle often varies with the bulkiness of the sulfoxide ligand, as observed in this study. The bond distances and angles of the different sulfoxide ligands are normal and similar in all the compounds. The average S−O bond lengths are 1.46(2) (**III**) and 1.462(13) Å (**IV**). The S−C bond might depend on the lengths of the alkyl chains. The average values are 1.77(3) Å for the DMSO compound and 1.80(2) Å for the DPrSO complexes.

In the pyrimidine ligands, the average N−C distances are 1.35(3), 1.34(2), and 1.32(2) Å, while the average C−C bond lengths are 1.36(3), 1.36(2), and 1.41(2) Å for crystals **III** to **V**, respectively. These distances are in agreement with those determined in free pyrimidine (1.33(1) and 1.37(1) Å, respectively).[30] The average Pt−N−C angles are 123(2)° (**III**), 120.3(9)° (**IV**), and 123(2)° (**V**). The internal N−C−C (av 123(2)°) and N−C−N (av 125(2)°) angles are larger than the C−N−C (av 116(2)°) and C−C−C angles (av 116(2)°). All these angles are in agreement with those of the free ligand[30] and the values reported in Pt(R_2SO)(pm)Cl_2[5] and in *trans*-Pt$(pm)_2X_2$.[2] The binding of pyrimidine to the Pt atom does not change the internal angle at the N atom, as it does in the hydrochlorides of pyrimidine and pyrimidin-2-one.[42,43] The protonation at N1 in both these compounds increased the ring angle at the N atom by about 6°. This effect is not observed when Pt is the exocyclic bonded group. Therefore, contrary to protonation, coordination to the platinum atom does not affect the structure of the pyrimidine ligand.

Conclusion

The reaction of $K_2[PtCl_4]$ with pyrimidine produced a novel pyrimidine-bridged ionic dimeric anion $[Cl_3Pt(\mu\text{-pm})PtCl_3]^-$. The crystal structures of the NMe_4 and N(*n*-Bu)$_4$ complexed salts were determined by X-ray diffraction. Crystal structures of pyrimidine-bridged Pt complexes have not been reported yet in the literature.

Two methods were developed for the synthesis of new mixed-ligand dinuclear platinum(II) complexes of the types *cis*- and *trans*-$(R_2SO)Cl_2Pt(\mu\text{-pm})Pt(R_2SO)Cl_2$. The compounds were characterized by infrared and multi-NMR spectroscopies and a few by crystallographic methods. The *trans* compounds were prepared using K[Pt(R_2SO)Cl_3] and pm in water, whereas methanol was used for the preparation of the *cis* isomers. In an organic solvent like methanol, the *trans* compounds are first formed, and with R_2SO = DBuSO and DBzSO, they isomerize to the *cis* isomers. No isomerization was observed for the other sulfoxides. The *cis* complexes were observed at lower field in ^{195}Pt NMR spectroscopy than their *trans* analogues. These results can be explained by more effective (d−d)π bonds in the *cis* isomers.

Inversed polarization of the S═O bond was suggested to explain the ^{13}C NMR results. This effect would be more important in the DPhSO complex, which contains two electroattracting groups located directly on the binding atom, which would increase the electron density on the S atom and its neighbors. This phenomenon would also explain partially the high-field ^{195}Pt NMR chemical shift observed for this compound.

The configuration of the complexes can be determined by the study of the Pt−Cl stretching vibrations. Two ν(Pt−Cl) vibrations were observed for the *cis* compounds and only one for the *trans* isomers. The geometry of the compounds can also

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be determined unambiguously from the coupling constants between the pyrimidine atoms and ^{195}Pt. The coupling constants $^{3}J(^{195}Pt-^{1}H_2)$, $^{3}J(^{195}Pt-^{1}H_6)$, and $^{3}J(^{195}Pt-^{13}C_5)$ are larger in the *cis* isomers than in the *trans* complexes.

The crystal structure determinations of one *cis* complex and two *trans* compounds confirmed the IR and NMR results. The comparison of the Pt−ligand bond distances gave interesting information on the *trans* influence of the different ligands. Sulfoxides have clearly a larger *trans* influence than chlorides or pyrimidine. Our results on the Pt−N bonds seem to indicate that the *trans* influence of chlorides is slightly larger than that of pyrimidine.

The CIF tables of the five crystal structure determinations have been deposited at the Cambridge Data File Centre. The deposit numbers are CCDC 166032−166036.

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Supporting Information Available: Crystal data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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