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Novel mixed-ligands Pt(II) complexes: synthesis, multinuclear magnetic resonance and crystal structures of *cis*- and *trans*-Pt(sulfoxide)(pyrimidine)Cl_2

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Abstract

New types of mixed-ligands Pt(II) complexes, *cis*- and *trans*-Pt(R_2SO)(pyrimidine)Cl_2, were synthesized and characterized by IR and multinuclear magnetic resonance spectroscopies and by crystallographic methods. Compounds with R_2SO = dimethylsulfoxide (DMSO), tetramethylenesulfoxide (TMSO), di-n-propylsulfoxide (DPrSO), di-n-butylsulfoxide (DBuSO), dibenzylsulfoxide and diphenylsulfoxide were studied. The aqueous reaction of K[Pt(R_2SO)Cl_3] with pyrimidine (pm) in a 1:1 ratio produced *trans*-Pt(R_2SO)(pm)Cl_2, which can isomerize to the *cis* isomer in an organic solvent. The ^{195}Pt NMR resonances of the *trans* complexes were observed at higher field (ave. −3079 ppm) than the *cis* analogues (ave. −2932 ppm). The ^{195}Pt coupling constants with the pyrimidine atoms $^3J(^{195}Pt–^1H)$ and $^3J(^{195}Pt–^{13}C)$ are larger in the *cis* configuration ($\sim$40 Hz) than in the *trans* analogues ($\sim$30 Hz). One ν(Pt–Cl) vibration was observed for the *trans* compounds, while two such bands were observed for the *cis* isomers. The crystal structures of *cis*-Pt(R_2SO)(pm)Cl_2 (R_2SO = DMSO, TMSO, DPrSO and DBuSO) and of *trans*-Pt(TMSO)(pm)Cl_2 were determined. The *trans* influence of the three different ligands was compared.

Keywords: Platinum complexes; Sulfoxide complexes; Pyrimidine complexes; Crystal structures

1. Introduction

Platinum complexes with nitrogen-donor ligands have been the object of numerous reports for the last 40 years and several studies have shown that some of these complexes have an antitumor activity [1–3]. The disubstituted platinum(II) compounds with pyridine ligands were first prepared in the 1960s by Kauffman [4]. However, only three papers were published on platinum compounds with non-substituted pyrimidine (pm). Fazakerley and Koch [5] synthesized and characterized *cis*-[Pt(NH_3)$_2$(pm)$_2$](ClO_4)$_2$ by ^{13}C NMR spectroscopy while Rochon and coworkers [6] prepared *cis*- and *trans*-Pt(pm)$_2X_2$ (X = Cl and Br) and determined the structure of the two *trans* isomers. Kaufmann et al. characterized *trans*-Pt(PEt_3)(pm)Cl_2 by ^{31}P and ^{1}H NMR, although they were not able to isolate the compound [7].

Pyrimidine and its derivatives are of great interest, since they play an important role in many biological processes. The nature of the Pt–pyrimidine bond has not yet been studied in the literature. We have recently undertaken a study on a new type of mixed-ligands platinum(II) complexes containing pyrimidine and sulfoxide ligands. Our research group has been involved in Pt–sulfoxide complexes for several years. These ligands have interesting behaviors, especially because of their π-back electron accepting properties. Sulfoxides are bonded to Pt(II) (soft metal) through their S atom. Most of the studies on Pt–sulfoxides complexes were done with the most common ligand, DMSO. Marzilli and coworkers made a comparative study of the compounds *cis*- and *trans*-Pt(DMSO)(py)Cl_2 (py = pyridine and its derivatives) [8]. A few other mixed-ligands complexes with DMSO are known. Published results on other sulfoxides are much less common. Our laboratory

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recently published a study on *cis*- and *trans*-Pt(DPhSO)(R–CN)Cl_2 complexes [9].

The aqueous reaction of $K_2[PtCl_4]$ with an excess of sulfoxide produces the *trans* disubstituted isomer, which rapidly isomerizes to *cis*-Pt$(R_2SO)_2Cl_2$, unless the ligand is very sterically demanding. The greater stability of the *cis*-disulfoxide complexes has been explained by the enhanced (d–d) π-bonding, which is more effective in the *cis* configuration [10]. It appeared interesting to determine if a mixed-ligand complex containing sulfoxide and pyrimidine, which can theoretically form π-bonding with Pt, would also isomerize to the *cis* compound. We have therefore undertaken a systematic study of the reaction of K[Pt$(R_2SO)Cl_3$] with pyrimidine. Six sulfoxides with different steric hindrance were used: dimethylsulfoxide (DMSO), tetramethylenesulfoxide (TMSO), di-n-propylsulfoxide (DPrSO), di-n-butylsulfoxide (DBuSO), dibenzylsulfoxide (DBzSO) and diphenylsulfoxide (DPhSO). We have now developed methods to synthesize the *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 complexes, which were characterized by infrared and multinuclear magnetic resonance (^1H, ^{13}C and ^{195}Pt) spectroscopies. The structure of four *cis* complexes and one *trans* isomer are also reported.

2. Experimental

$K_2[PtCl_4]$ was obtained from Johnson Matthey Inc. and was recrystallized in water before use. Pyrimidine, CD_2Cl_2 and the sulfoxide ligands were purchased from Aldrich except dipropylsulfoxide, which was bought from Phillips Petroleum Company.

A Fisher–Johns instrument was used to determine the melting and decomposition points, which are not corrected. The IR spectra were measured in KBr pellets on a Perkin–Elmer 783 spectrometer between 4000 and 280 cm^{-1}. All the NMR spectra were measured in CD_2Cl_2 on a Varian Gemini 300BB spectrometer operating at 300.075, 75.462 and 64.335 or 64.270 MHz for ^1H, ^{13}C and ^{195}Pt, respectively. The dichloromethane peaks (5.32 and 53.80 ppm) were used as references for the ^1H and ^{13}C NMR spectra. The external reference for ^{195}Pt was K[Pt(DMSO)Cl_3] (in D_2O adjusted at -2998 ppm from $Na_2[PtCl_6]$) and $K_2[PtCl_4]$ (in D_2O with KCl adjusted at -1628 ppm from $Na_2[PtCl_6]$).

The crystallographic studies were done on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å). 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 a minimum of 25-well-centered reflections. The data collections were made by the $2\theta/\omega$ scan technique using the XSCANS program [11]. Intensities of three standard reflections were monitored for every 97 reflections to check the stability of the crystals. The coordinates of the Pt atoms were determined from a Patterson map calculation using the Siemens SHELXTL system [11]. 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 using all reflections. Hydrogen atom positions were fixed in their calculated position with $U_{eq} = 1.2U_{eq}$ (or 1.5 for methyl group) of the carbon to which they are bonded. Corrections were made for absorption (Gaussian integration), Lorentz and polarization effects. The residual peaks were below 1.66 e $Å^{-3}$ and located in the close environment of the platinum atom. Disorder was observed on the C_β and C_γ of one alkyl chain of the DPrSO crystal (**III**) and on a terminal C atom of one butyl chain in the DBuSO crystal (**IV**). Two positions were refined for each disordered C atom with occupancy factors of 0.5. The final refinement converged to the R_1 and wR_2 values shown in Table 1.

The K[Pt$(R_2SO)Cl_3$] complexes were synthesized according to the method described by Kukushkin et al. [12]. The *cis*-Pt$(R_2SO)_2Cl_2$ compounds were prepared according to published methods [10,13].

2.1. *cis*-Pt(R_2SO)(pm)Cl_2 (R_2SO = DMSO, TMSO, DPrSO, DBuSO and DBzSO)

The K[Pt$(R_2SO)Cl_3$] compound (~ 100 mg) was dissolved in methanol (~ 5 ml) and pyrimidine in a 1:1 ratio (dissolved in 1 ml of CH_3OH) was added slowly with stirring at room temperature (r.t.). After several days, a white precipitate was formed. The solution was evaporated to dryness and the residue washed with water and dried under vacuum. It was then washed with ether and dried again. *cis*-Pt(DMSO)(pm)Cl_2 (**I**): Yield 89%, m.p. (dec.) 162 to >300°C. IR (cm^{-1}): pm (vibration no. [14,15]): 1596s and 1561m (9, 10), 1472m (22), 1407s (23), 1229m (3), 1183sh (17), 1072w and 1058w (14), 1028s (1), 980m (5), 830s (12), 736m (13), 697s (4), 642s (6); ν(S–O) 1136s; ν(Pt–S) 440s; ν(Pt–Cl) 343s, 317s. ^1H NMR (ppm): $\delta = 9.418$ (s, H_2), 8.857 (dd, H_4), 7.487 (ddd, H_5), 8.996 (ddd, H_6), 3.502 (s, H_α). ^{13}C NMR (ppm): $\delta = 161.64$ (C_2), 159.39 (C_4), 122.88 (C_5), 160.42 (C_6), 45.13 (C_α). *cis*-Pt(TMSO)(pm)Cl_2 (**II**): Yield 66%, m.p. (dec.) 150–250°C. IR (cm^{-1}): pm: 1595s and 1559m (9, 10), 1472m (22), 1410s (23), 1228w (3), 1175w (17), 1076s and 1059sh (14), 1028m (1), 978w (5), 821m (12), 698s (4), 640m (6); ν(S–O) 1151s, 1134sh; ν(Pt–S) 448w; ν(Pt–N) 523w; ν(Pt–Cl) 343m, 321m. ^1H NMR (ppm): $\delta = 9.443$ (s, H_2), 8.849 (dd, H_4), 7.477 (ddd, H_5), 9.021 (ddd, H_6), 4.180, 3.428 (ddd, H_α), 2.376, 2.221 (m, H_β). ^{13}C NMR (ppm): 161.80 (C_2), 159.29 (C_4), 122.81 (C_5), 160.52 (C_6), 59.24 (C_α), 26.44 (C_β). *cis*-Pt(DPrSO)(pm)Cl_2 (**III**): Yield 74%, m.p. (dec.) 130 to >300°C. IR (cm^{-1}): pm: 1594s and

1560m (9, 10), 1467sh (22), 1410s (23), 1224w (3), 1173w (17), 1084sh and 1061m (14), 1032w (1), 826m (12), 733w (13), 704s (4), 640m (6); ν(S–O) 1130s; ν(Pt–S) 450w; ν(Pt–N) 527m; ν(Pt–Cl) 349m; 321m. ^{1}H NMR (ppm): $\delta = 9.358$ (s, H_2), 8.851 (dd, H_4), 7.476 (ddd, H_5), 8.931 (ddd, H_6), 3.757, 3.153 (ddd, H_α), 2.368, 2.041 (dddq, H_β), 1.201 (t, H_γ). ^{13}C NMR (ppm): $\delta = 161.65$ (C_2), 159.28 (C_4), 122.86 (C_5), 160.31 (C_6), 56.78 (C_α), 17.09 (C_β), 12.93 (C_γ). *cis*-Pt(DBuSO)(pm)Cl_2 (**IV**): Yield 56%, m.p. 110°C. IR (cm^{-1}): pm: 1597s and 1563m (9, 10), 1469m (22), 1420s (23), 1233m (3), 1182m (17), 1082w and 1057w (14), 1034w (1), 831m (12), 745w (13), 702m (4), 644m (6); ν(S–O) 1136s; ν(Pt–S) 459w; ν(Pt–N) 502w, ν(Pt–Cl) 344m, 321m. ^{1}H NMR (ppm): $\delta = 9.362$ (s, H_2), 8.854 (dd, H_4), 7.478 (ddd, H_5), 8.933 (ddd, H_6), 3.783, 3.166 (ddd, H_α), 2.324, 1.961 (m, H_β), 1.620, 1.597 (dtq, H_γ), 1.030 (t, H_δ). ^{13}C NMR (ppm): 161.63 (C_2), 159.26 (C_4), 122.83 (C_5), 160.28 (C_6), 54.95 (C_α), 25.14 (C_β), 21.83 (C_γ), 13.80 (C_δ). *cis*-Pt(DBzSO)(pm)Cl_2: Yield 50%, m.p. (dec.) 200–290°C. IR (cm^{-1}): pm: 1596s and 1559m (9,10), 1456m (22), 1411s (23), 1230w (3), 1172m (17), 1082w and 1071m (14), 1030w (1), 812w (12), 763m (13), 697s (4), 640w (6); ν(S–O) 1117s; ν(Pt–S) 459w; ν(Pt–N) 485w; ν(Pt–Cl) 343m, 323m. ^{1}H NMR (ppm): $\delta = 8.091$ (s, H_2), 8.572 (dd, H_4), 7.066 (ddd, H_5), 7.659 (ddd, H_6), 5.189, 4.446 (d, H_α), 7.683 (m, H_{ortho}), 7.500 (m, $H_{meta,para}$). ^{13}C NMR (ppm): $\delta = 160.88$ (C_2), 158.72 (C_4), 122.40 (C_5), 159.44 (C_6), 60.02 (C_α), others 128.28–132.51.

2.2. *trans*-Pt(R_2SO)(pm)Cl_2 (R_2SO = DMSO, TMSO, DBuSO and DPhSO)

The complex K[Pt(R_2SO)Cl_3] and pm were mixed in a 1:1 ratio in water at r.t. for TMSO, DBuSO and DPhSO and at about 3°C for DMSO. A pale yellow precipitate appeared rapidly depending on the steric hindrance of the sulfoxide ligand. The mixture was stirred until the solution became colorless except for the DMSO complex which was stopped after $\sim$2 min. The precipitate was then filtered, dried, washed with ether and dried in vacuum. The ^{195}Pt NMR spectrum of the product with DBuSO showed that it contained five species which will be discussed later in the text. *trans*-Pt(DMSO)(pm)Cl_2: Yield 27%, m.p. 96°C. IR (cm^{-1}): pm: 1594s and 1559m (9,10), 1472m (22), 1408s (23), 1224m (3), 1173sh (17), 1072w and 1062m (14), 1033s (1), 979w (5), 811m (12), 733m (13), 699s (4), 648m (6); ν(S–O) 1138s, ν(Pt–S) 444s; ν(Pt–Cl) 346s. ^{1}H NMR (ppm): 9.459 (s, H_2), 8.887 (dd, H_4), 7.526 (ddd, H_5), 9.007 (ddd, H_6), 3.448 (s, H_α). ^{13}C NMR (ppm): $\delta = 160.44$ (C_2), 158.93 (C_4), 122.60 (C_5), 159.99 (C_6), 44.65 (C_α). *trans*-Pt(TMSO)(pm)Cl_2 (**V**): Yield 84%, m.p. 121°C. IR (cm^{-1}): pm: 1595s and 1561m (9,10), 1471m (22), 1413s (23), 1233m (3), 1176sh (17), 1071s (14), 1028m (1), 817m (12), 696s (4), 641s (6); ν(S–O) 1150s; ν(Pt–S) 445w; ν(Pt–Cl) 348s. ^{1}H NMR (ppm): $\delta = 9.472$ (s, H_2), 8.885 (dd, H_4), 7.524 (ddd, H_5), 9.024 (ddd, H_6), 3.990, 3.573 (ddd, H_α), 2.358, 2.196 (m, H_β). ^{13}C NMR (ppm): $\delta = 160.40$ (C_2), 158.86 (C_4), 122.60 (C_5), 159.98 (C_6), 57.24 (C_α), 24.86 (C_β). *trans*-Pt-

Table 1
Crystallographic data for the complexes Pt(R_2SO)(pm)Cl_2

Sulfoxide	*cis*-DMSO (**I**)	*cis*-TMSO (**II**)	*cis*-DPrSO (**III**)	*cis*-DBuSO (**IV**)	*trans*-TMSO (**V**)
Chemical formula	$C_6H_{10}Cl_2N_2OSPt$	$C_8H_{12}Cl_2N_2OSPt$	$C_{10}H_{18}Cl_2N_2OSPt$	$C_{12}H_{22}Cl_2N_2OSPt$	$C_8H_{12}Cl_2N_2OSPt$
MW	424.21	450.25	480.31	508.37	450.25
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
Unit cell dimensions					
a (Å)	8.273(2)	9.898(2)	9.502(2)	7.4590(10)	11.9465(14)
b (Å)	16.193(4)	15.278(4)	16.237(4)	19.977(6)	8.5850(8)
c (Å)	9.288(2)	8.639(2)	10.042(2)	12.387(3)	13.466(2)
β (°)	112.040(10)	107.850(13)	92.640(10)	95.48(2)	113.897(11)
V (Å^3)	1153.3(5)	1243.6(5)	1547.7(6)	1837.3(8)	1262.7(2)
Z	4	4	4	4	4
ρ_{calcd} (g cm^{-3})	2.443	2.405	2.061	1.838	2.369
μ(Mo Kα) (mm^{-1})	12.775	11.856	9.533	8.036	11.677
F(000)	784	840	912	976	840
Independent reflections (R_{int})	2395 (0.0373)	3631 (0.0277)	4511 (0.0606)	3231 (0.0477)	3664 (0.0202)
Reflections observed [$I>2\sigma(I)$]	1769	2626	3459	1963	2900
R_1 [a] [$I>2\sigma(I)$]	0.0386	0.0395	0.0429	0.0555	0.0345
wR_2 [b] (all data)	0.0829	0.0895	0.0904	0.1050	0.0935
S [c]	1.040	1.038	1.054	1.046	1.021

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

(DBuSO)(pm)Cl_2: Yield $< 10\%$. ^1H NMR (ppm): $\delta = 9.477$ (s, H_2), 8.879 (dd, H_4), 7.515 (ddd, H_5), 9.029 (ddd, H_6). ^{13}C NMR (ppm): $\delta = 160.42$ (C_2), 158.90 (C_4), 122.47 (C_5), 159.83 (C_6). *trans*-Pt(DPhSO)(pm)Cl_2: Yield 82%, m.p. (dec.) 195– > 300°C. IR (cm^{-1}): pm: 1593s and 1556m (9,10), 1467m (22), 1408s (23), 1229m (3), 1180m (17), 1073s and 1061sh (14), 1028m (1), 994m (5), 811s (12), 739s (13), 698s (4), 640m (6); ν(S–O) 1147s; ν(Pt–S) 450w; ν(Pt–Cl) 349m. ^1H NMR (ppm): $\delta = 9.538$ (s, H_2), 8.884 (dd, H_4), 7.527 (ddd, H_5), 9.081 (ddd, H_6), 7.952 (m, H_{ortho}), 7.558 (m, $H_{meta,para}$). ^{13}C NMR (ppm): $\delta = 160.50$ (C_2), 159.06 (C_4), 122.56 (C_5), 160.00 (C_6), 141.66 (C_α), 127.53 (C_β), 129.06 (C_γ), 133.15 (C_δ).

2.3. *trans*-Pt(R_2SO)(pm)Cl_2 (R_2SO = DPrSO and DBzSO)

These two compounds were prepared exactly as the equivalent *cis* isomer, but the reactions were done in methanol at low temperature (3°C) for DPrSO and at r.t. for DBzSO. A yellow precipitate appeared after 1 h. It was filtered, washed with ether and dried in vacuum. *trans*-Pt(DPrSO)(pm)Cl_2: Yield 21%, m.p. 83°C. IR (cm^{-1}): pm: 1595s and 1562m (9, 10), 1465sh (22), 1415s (23), 1231m (3), 1176w (17), 1076m and 1060w (14), 1028w (1), 820m (12), 737m (13), 701m (4), 640m (6); ν(S–O) 1131s; ν(Pt–S) 454m; ν(Pt–N) 515m; ν(Pt–Cl) 348m. ^1H NMR (ppm): $\delta = 9.474$ (s, H_2), 8.877 (dd, H_4), 7.511 (ddd, H_5), 9.025 (ddd, H_6), 3.655, 3.241 (ddd, H_α), 2.241, 2.114 (dddq, H_β), 1.211 (t, H_γ). ^{13}C NMR (ppm): 160.43 (C_2), 158.91 (C_4), 122.47 (C_5), 159.84 (C_6), 56.80 (C_α), 16.96 (C_β), 13.04 (C_γ). *trans*-Pt(DBzSO)(pm)Cl_2: Yield 60%, m.p. 150°C. IR (cm^{-1}): pm: 1592s and 1556m (9, 10), 1467m (22), 1409s (23), 1223w (3), 1186m (17), 1072m and 1059m (14), 1028m (1), 820m (12), 694s (4), 637m (6); ν(S–O) 1132s; ν(Pt–Cl) 350m. ^1H NMR (ppm): $\delta = 9.370$ (s, H_2), 8.866 (dd, H_4), 7.445 (ddd, H_5), 8.900 (ddd, H_6), 5.088, 4.535 (d, H_α), 7.650 (m, H_{ortho}), 7.485 (m, $H_{meta,para}$). ^{13}C NMR (ppm): 160.24 (C_2), 158.79 (C_4), 122.56 (C_5), 159.86 (C_6), 60.57 (C_α), 128.41, 129.25, 129.67, 132.16 (C_{phenyl}).

3. Results and discussion

3.1. Preparation of the complexes

The aqueous reaction of K[Pt(R_2SO)Cl_3] with pyrimidine in a 1:1 proportion produced *trans*-Pt(R_2SO)(pm)Cl_2 as expected, since the *trans* effect of the sulfoxide ligands is much larger than the one of chlorides. The time of reaction depends on the steric hindrance of the sulfoxide ligand. Disubstituted Pt(R_2SO)$_2Cl_2$ compounds have been shown to be *cis* isomers except for very bulky ligands. In the preparation of the bis-sulfoxide complexes, the first product is the *trans* compound, which then isomerizes to the *cis* isomer. For DMSO, the *trans* compound cannot be isolated, but *trans*-Pt(DPrSO)$_2Cl_2$ has been isolated after a few minutes of reaction [16]. The rapid isomerization in water has been explained by the enhanced (d–d) π-bonding which is more effective in the *cis* configuration [10]. For the Pt(R_2SO)(pm)Cl_2 complexes, the isomerization seems to be slower in water, because pyrimidine cannot accept π-electrons as effectively as sulfoxides. The reaction with the least bulky sulfoxide (DMSO) was done at cooler temperature (about 3°C) and the pale yellow precipitate was filtered very rapidly (~ 2 min) in order to prevent its isomerization. No isomerization was observed with the other sulfoxides at room temperature in aqueous media.

A few methods were studied to prepare the *cis*-Pt(R_2SO)(pm)Cl_2 complexes. In the first method, *cis*-Pt(R_2SO)$_2Cl_2$ reacted with pyrimidine in a 1:1 ratio in dichloromethane. However, the products contained a small quantity of the initial disubstituted complexes, which could not be completely separated from *cis*-Pt(R_2SO)(pm)Cl_2. Thus, a second method was developed, where K[Pt(R_2SO)Cl_3] reacted with pyrimidine (1:1 ratio) in methanol. After evaporating the solvent, the separation of the mixed-ligand complex from the starting material (soluble in water) is then easy. Again, the *trans* compound is first formed. The reaction can be stopped rapidly if the *trans* analogue is desired (method used to synthesize the *trans* DPrSO and DBzSO complexes). If the reaction in methanol is stirred for a few days, the color of the mixture gradually changed from yellow (*trans* isomer) to almost white (*cis* analogue). If the sulfoxide has a large steric hindrance, the isomerization is much slower and might not be complete. With the most bulky ligand, DPhSO, there was no isomerization and only *trans*-Pt(DPhSO)(pm)Cl_2 was formed in all these reactions, although the ^1H NMR spectrum of an old solution of *trans*-Pt(DPhSO)(pm)Cl_2 in CD_2Cl_2 has shown (after a few weeks) the presence of a small quantity of a different compound which was assumed to be the *cis* isomer. The *trans* compounds can isomerize much faster in dichloromethane than in water. For example, the crystal *cis*-Pt(TMSO)(pm)Cl_2 (**II**) which was studied by crystallographic methods was isolated from a dichloromethane solution of the *trans* isomer.

All the synthesized compounds were characterized by IR and multinuclear (^{195}Pt, ^{13}C and ^1H) magnetic resonance spectroscopies. A few selected compounds which gave adequate crystals were studied by X-ray diffraction methods.

3.2. ^{195}Pt NMR spectroscopy

The complexes *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 were studied by ^{195}Pt NMR spectroscopy in dichloro-

Table 2
^{195}Pt chemical shifts (ppm) of the *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 complexes (in CD_2Cl_2)

R_2SO	*cis*	*trans*	$\Delta\delta$
DMSO	−2917	−3070	153
TMSO	−2864	−3056	192
DPrSO	−2951	−3059	108
DBuSO	−2954	−3060	106
DBzSO	−2975	−3078	103
DPhSO		−3148	

methane-d_2. The chemical shifts of the complexes are shown in Table 2. Except for *trans*-Pt(DBuSO)(pm)Cl_2, only one signal was observed in the ^{195}Pt NMR spectra. The *cis* compounds were observed between −2864 and −2975 ppm while the *trans* analogues were found at higher field, between −3056 and −3148 ppm. These values are in agreement with the values published for Pt(DMSO)(NH_3)Cl_2 (−3045 (*cis*) and −3067 (*trans*) ppm) [17,18], and Pt(DMSO)(L)Cl_2 (L = pyridine derivative, −2856 to −3043 ppm [8,17]), which were all measured in DMSO-d_6 or DMF-d_7 and those published for Pt(DPhSO)(R–CN)Cl_2 (−3041 to −3186 ppm in $CDCl_3$) [9].

The *cis* compounds were observed at lower fields than the *trans* analogues contrary to diamine compounds, where the *cis* complexes were found at slightly higher fields. For example, *cis*-Pt(1-adamantanamine)$_2Cl_2$ was reported at −2184 ppm, while the *trans* analogue was observed at −2141 ppm [19]. The difference could be explained by the presence of π-bonding in the sulfoxide complexes, while the amine ligands cannot accept π-backbonding from the metal. For Pt(amine)$_2X_2$ complexes, the *trans* isomers are usually more stable than the *cis* compounds because of steric effects, while for Pt(R_2SO)$_2X_2$, the *cis* compounds are the most stable (except for very bulky ligands), because of the more effective (d–d) π-bonding in the *cis* configuration [10]. The π-bond decreases the electron density on the Pt atom. Therefore in the *cis* compound, the electronic density on the Pt atom will be reduced compared to the one in the *trans* isomer, causing a deshielding of the *cis* compound. The group of Marzilli [8] has observed for Pt(DMSO)(pyridine)Cl_2 a $\Delta\delta$ ($\delta_{trans} - \delta_{cis}$) value of 162 ppm (in DMSO-d_6), which is close to our value for the DMSO–pm complexes (153 ppm in CD_2Cl_2). These results suggest that the Pt–N bonds in pyridine and pyrimidine complexes are not too different. For sulfoxides other than DMSO, the $\Delta\delta$ are slightly different (Table 2). The values are larger for TMSO (192 ppm) and smaller for DPrSO (108 ppm), DBuSO (106 ppm) and DBzSO (103 ppm). This $\Delta\delta$ value seems to vary with the bulkiness of the sulfoxide close to the binding site. TMSO is the least bulky around the S binding site (angle C–S–C reduced to ~94°) because of its rigid four-membered ring. It is interesting to note that in a series of *cis*- and *trans*-Pt(DPhSO)(R–CN)Cl_2 complexes [9], the chemical shift variations (*trans*–*cis*) are not affected by the R group on the nitrile ligand (the $\Delta\delta$ values varied from 134 to 138 ppm), probably because the nitrile ligand is linear and the R group is far from the binding N atom.

In order to obtain more information on the multiplicity of the Pt–pyrimidine bond, we have synthesized *cis*- and *trans*-Pt(pm)$_2Cl_2$ and measured the ^{195}Pt NMR spectra. The chemical shift of the *trans* isomer was observed at −2061 ppm in $CDCl_3$, while that of the *cis* compound appeared at −2043 ppm in deuterated DMF (the *cis* analogue is not soluble in chloroform or dichloromethane, but the δ(Pt) are usually very similar in these three solvents). Contrary to the diamine complexes, the resonance of *trans*-Pt(pm)$_2Cl_2$ is found at higher field ($\Delta\delta = 18$ ppm) as observed in our Pt(R_2SO)(pm)Cl_2 complexes, although the $\Delta\delta$ value is much smaller. The fact that *trans*-Pt(pm)$_2Cl_2$ is observed at higher field than the *cis* analogue, might be an indication of the presence of electronic back-donation (Pt → pm) in the Pt–pyrimidine bond. These results could be compared to those reported for Pt(py)$_2Cl_2$ (py = pyridine derivative) complexes, where the *trans* isomers were observed at lower fields than the *cis* compounds. The authors came to the conclusion that π-bonding in Pt–py complexes is not very important [20]. Our results seem to indicate that π-bonding is slightly more important in Pt–pm compounds.

The complex *trans*-Pt(DPhSO)(pm)Cl_2 is the most shielded compound of the series. Two explanations were examined. The observed shielding of the DPhSO complex could be caused by the presence of two aromatic phenyl groups on the S atom. The phenyl groups might account for a stronger σ-bond and/or a weaker π-bond. Inversed polarization of the π-electrons of the S=O bond has been suggested [21] to explain an increased electronic density on the sulfoxide ligand when bonded to Pt. This inverse polarization would be more important in sulfoxides containing aromatic groups and might change the strength of the Pt–S bond. The DBzSO complex, which also contains aromatic groups, although they are farther away from the S atom was observed in the same region as the complexes with sulfoxides containing only alkyl groups. The second explanation for the difference observed for the DPhSO complex is related to its much greater bulkiness around the binding atom. All the other sulfoxides contain $-CH_2$ or $-CH_3$ groups attached to the S atom. For Pt(amine)$_2Cl_2$ compounds, deshielding effects have been observed for Pt complexes containing secondary amines compared to primary amines [19]. For our complexes Pt(R_2SO)(pm)Cl_2, we have observed opposite effects. Again the presence of π-bonding in our compounds might lead to different results. We intend to continue

the work with more bulky alkyl sulfoxides, to determine if bulkiness can be partly responsible for the higher field chemical shift observed for the DPhSO complex.

We were not able to prepare the *cis* isomer with DPhSO, probably because of the bulkiness of the ligand. Furthermore, pyrimidine is a weaker π-back electron acceptor than sulfoxides, which would decrease the stability of the *cis* isomer (compared to the bis-sulfoxide complex) and partially account for the unsuccessful preparation of the *cis* DPhSO-pm isomer.

As mentioned above, the synthesized complexes were pure, since only one resonance was observed in ^{195}Pt NMR (also confirmed by ^{1}H NMR), except for *trans*-Pt(DBuSO)(pm)Cl_2, whose spectrum showed the presence of five different species. The *trans* compound (∼5%) was assigned to the signal at −3060 ppm, while the *cis* isomer (∼12%) was observed at −2954 ppm. Two other species observed at −2940 (∼41%) and −3069 ppm (∼8%) were assigned, respectively, to the pyrimidine-bridged dimers *cis*- and *trans*-{Pt(DBuSO)Cl_2}$_2$(μ-pm), which have been partially characterized and will be discussed in a subsequent publication. The fifth signal (∼34%) observed at −3079 ppm has not been assigned yet with certainty. The ^{1}H NMR spectrum has shown that it contains the pyrimidine ligand. The possibility of the presence of rotamers was examined. Since it was not observed in the spectrum of *cis*-Pt(DBuSO)(pm)Cl_2, where it should be mostly present, the hypothesis was rejected. The presence of K[Pt(DBuSO)Cl_3] was also rejected, since its resonance should be found at lower field. It might be caused by the presence of unsymmetric pyrimidine-bridged dimers, which would show two different signals. The resonance at −3079 ppm would account for one segment with the *trans* configuration, while the *cis* segment would be hidden under the *cis* dimers observed at −2940 ppm. This hypothesis will be further discussed in a subsequent publication on the synthesis and characterization of pyrimidine-bridged dimeric species.

3.3. ^{1}H and ^{13}C NMR spectroscopies

The signals of free pyrimidine and bonded pyrimidine in the complexes will be first discussed. The ^{1}H and ^{13}C chemical shifts of the complexes are presented in Section 2, while the $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) of the

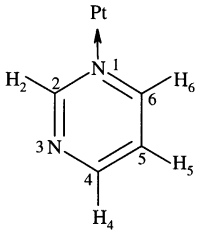
Table 3
^{1}H NMR $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) (ppm) and $^{3}J(^{195}Pt–^{1}H)$ (Hz) of the pyrimidine ligand in the *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 complexes

R_2SO		H_2	H_4	H_5	H_6	$\Delta\delta_{ave}$	$^{3}J(^{195}Pt–^{1}H_2)$	$^{3}J(^{195}Pt–^{1}H_6)$
DMSO	*cis*	0.241	0.138	0.160	0.277	0.204	24	44
	trans	0.282	0.169	0.199	0.288	0.235	20	31
TMSO	*cis*	0.267	0.131	0.150	0.302	0.213	23	42
	trans	0.295	0.167	0.197	0.306	0.241	20	31
DprSO	*cis*	0.181	0.132	0.149	0.212	0.169	22	39
	trans	0.298	0.159	0.184	0.308	0.237	19	32
DBuSO	*cis*	0.185	0.135	0.150	0.215	0.171	24	40
	trans	0.300	0.161	0.188	0.311	0.240		
DBzSO	*cis*	−1.086	−0.146	−0.261	−1.059	−0.638	22	[a]
	trans	0.193	0.148	0.118	0.182	0.160	20	23
DPhSO	*cis* [b]	0.229	0.113	0.150	0.276	0.192		
	trans	0.361	0.166	0.200	0.362	0.272	20	

[a] Hidden under the phenyl signals.
[b] Values obtained from an old solution of the *trans* isomer in CD_2Cl_2, which contained a small quantity of *cis* isomers.

Table 4
^{13}C NMR $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) (ppm) and $^{3}J(^{195}Pt–^{13}C)$ (Hz) of the pyrimidine ligand in the *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 complexes

R_2SO		C_2	C_4	C_5	C_6	$\Delta\delta_{ave}$	$^{3}J(^{195}Pt–^{13}C_5)$
DMSO	*cis*	2.30	2.17	0.95	3.20	2.16	39
	trans	1.10	1.71	0.67	2.77	1.56	30
TMSO	*cis*	2.46	2.06	0.87	3.30	2.17	37
	trans	1.06	1.64	0.67	2.76	1.53	29
DPrSO	*cis*	2.31	2.06	0.92	3.09	2.10	40
	trans	1.08	1.69	0.54	2.61	1.48	29
DBuSO	*cis*	2.29	2.03	0.90	3.06	2.07	39
	trans	1.08	1.68	0.54	2.61	1.48	
DBzSO	*cis*	1.52	1.52	0.47	2.22	1.43	
	trans	0.90	1.57	0.63	2.64	1.44	
DPhSO	*trans*	1.16	1.84	0.63	2.78	1.60	30



Scheme 1.

pyrimidine ligand and coupling constants with platinum-195 are summarized in Tables 3 and 4. Free pyrimidine is a symmetric molecule, which shows three signals in ^{1}H or ^{13}C NMR. The most deshielded signal is H_2 observed at 9.177 ppm (in CD_2Cl_2), then H_4 and H_6 (8.718 ppm, $^{3}J = 4.9$ Hz) while H_5 (7.327 ppm, $^{3}J = 4.9$ Hz, $^{5}J = 1.5$ Hz) is the most shielded. No coupling of H_2 can be observed because of its proximity to two N atoms. The shielding order is the same in ^{13}C NMR. These results are similar to those reported for pyrimidine in other solvents [22,23].

Pyrimidine bonded to Pt(II) is no longer symmetric (Scheme 1) and four different signals are expected. The proton H_6 is more influenced by Pt binding than H_4 and the deshielding order is H_2, H_6, H_4 and H_5. All protons should couple to each other, but the couplings on H_2 are not observed. The signals of H_5 and H_6 consist of a doublet of doublets of doublets (ddd) with normal aromatic coupling constants, except for $^{4}J(H_6–H_2)$ (1.1 Hz) which is slightly low, close to the coupling constant $^{5}J(H_5–H_2)$. Castellano et al. have also noted smaller coupling constants for protons in *meta* position close to the nitrogen atom in the pyridine ring [24]. No coupling of H_4 was observed with H_2, and the signal of H_4 appears as a doublet of doublets. The absence of couplings on H_2 can be explained by the presence of the two neighboring N atoms. The coupling of H_2 with the two ^{14}N nuclei, which possesses a large quadrupolar moment, leads to the broadening of the signal.

The binding of pyrimidine to platinum leads to a deshielding of the ligand signals in ^{1}H and ^{13}C NMR spectroscopies, as indicated by the positive $\Delta\delta$ values (Tables 3 and 4), except for the ^{1}H NMR signals of the *cis*-DBzSO compound. The protons close to the binding site are more affected by coordination to the metal as expected. An average value of $\Delta\delta$ has been calculated in order to compare the results shown in Table 3. All the complexes containing no aromatic groups have similar chemical shifts. The *trans* diphenylsulfoxide (DPhSO) compound is slightly different, with H_2 and H_6 at slightly lower field. This ligand is the most bulky, but it is also different from the other ligands, since it contains aromatic groups directly on the binding atom, which could produce different electronic effects. The $\Delta\delta_{ave}$ is slightly higher (0.272 ppm) for DPhSO than for the other *trans* isomers (~ 0.240 ppm, excluding DBzSO). In this configuration, the bulkiness is less important than in the *cis* analogues. Since the DPhSO compound was observed at higher field in ^{195}Pt NMR, the signals of its ligands should be more deshielded in ^{1}H or ^{13}C NMR. The *cis* complex with DBzSO is drastically different from the other complexes. The preparation of the compound was repeated several times in order to certify our results. For this compound, all the pyrimidine ^{1}H signals were observed at higher field than those of free pyrimidine.

The variation of $\Delta\delta_{ave}$ with the different sulfoxides should be more important in the *cis* isomers, where the bulkiness of the sulfoxide becomes an important factor. In the *trans* compounds, the rotation of the pyrimidine ligand around the Pt–N bond is less limited (π-bonding is not very strong), but not in the *cis* isomers, especially for more bulky sulfoxides. In the latter compounds, the rotation of the pyrimidine ligand will be more limited and the pyrimidine ring will be predominantly perpendicular to the platinum plane. The results on the *cis* compounds in Table 3 show that the $\Delta\delta_{ave}$ are slightly smaller for more bulky ligands, although it is difficult to compare these values. The rotation around the Pt–N bond will be more important in the TMSO complex (angle C–S–C is the smallest) and the observed value will be an average value of the different conformations of the molecule, while in the more bulky ligand like DBuSO, it might correspond to only one conformation. Therefore, the chemical shifts of H_4 and H_5, which are far from the *cis* sulfoxide ligand do not vary very much, but the ones of H_2 and H_6 depend on the sulfoxide. The $\Delta\delta_{ave}$ values decrease (0.213–0.169 ppm) with an increase in the bulkiness of the sulfoxide, TMSO > DMSO $\gg$ DPrSO $\sim$ DBuSO (omitting the ligands containing aromatic rings). It is interesting to note that the ^{195}Pt chemical shift variations $\Delta\delta$ (Table 2) follow the same order. The relation $\Delta\delta(H_2$ or $H_6)$ versus $\delta(^{195}Pt)$ is linear for these four *cis* compounds.

The ^{1}H signals of all the *cis* compounds were observed at higher field ($\Delta\delta_{ave} = -0.638$ to 0.213 ppm) than those of the corresponding *trans* isomers ($\Delta\delta_{ave} =$ 0.160–0.272 ppm), in agreement with the ^{195}Pt NMR spectroscopic results. Since the *trans* isomers were observed at higher fields in ^{195}Pt NMR, the pyrimidine signals will be observed at lower fields in ^{1}H NMR. Binding of pyrimidine to the Pt atom reduces the electronic density on pyrimidine (except for *cis*-Pt(DBzSO)(pm)Cl_2) but increases it on the Pt atom. The presence of π-bonding between the metal center and the ligand will produce the opposite effect. The results on ^{195}Pt NMR described above for *cis*- and *trans*-Pt$(pm)_2Cl_2$ seem to indicate that π-bonding is present to a small extent in Pt–pm complexes, contrary to Pt–amine compounds.

The ^{13}C NMR results on the pyrimidine ligand showed a deshielding of all the carbons atoms, but contrary to the protons signals, the $\Delta\delta$ are slightly greater for the *cis* isomers. Mesomeric effects on the pyrimidine ligand are affected to a large extent by bonding to the Pt atom and the results are more reflected on the electron density of the C atoms than on the protons. This study indicates that the Pt–pyrimidine bond is much more complicated than expected, especially when mixed-ligands capable of forming π-bonds and containing aromatic rings are coordinated to platinum. Inversed polarization of the π-electrons of the S=O bond [21] probably also influence the C spectrum of the other ligands as observed by Cooper and Powell, who have suggested an influence of the inversed polarization of the C≡O bond on the ligand located in *trans* position in the complexes *trans*-Pt(CO)(pyX)Cl_2 (where pyX is a *para*-substituted pyridine derivative) [25].

The R substituent on the sulfoxide ligand does not seem to have an important influence on the pyrimidine carbon atoms. The value for C_6 seems to depend slightly on the bulkiness of the sulfoxide in the *cis* isomers and vary in the order TMSO > DMSO > DPrSO ~ DBuSO (excluding the ligands containing aromatic groups). The difference of $\Delta\delta$ between the two isomers is the most important on C_2, with average values of 2.18 and 1.06 ppm for the *cis* and *trans* complexes, respectively.

The sulfoxide chemical shifts are shown in Section 2, except for *trans*-Pt(DBuSO)(pm)Cl_2 which contained other species and its precise assignment was not possible, because of the overlap of the signals. In the DMSO complexes, the six methyl H atoms are found to be equivalent and an intense single peak was observed. In the other R_2SO complexes, the H atoms close to the binding site are more deshielded than the others (Table 5). For TMSO, the two geminal hydrogens bonded to the α carbon (the same is true for C_β) have different chemical environments and two separated signals were noted in the ^1H NMR spectra. One proton of each methylene group is closer to the oxygen atom, because of the rigidity of the ring, and its resonance was found at lower field than the second proton. In the DPrSO, DBuSO and DBzSO complexes, the geminal H atoms are also non-equivalent, except for the terminal methyl groups. The non-equivalence is caused by limited rotation around the bonds, because of the presence of the two bulky groups. The separation between the signals of the geminal protons decreases as the distance from the coordination site increases. This difference is larger in the *cis* compounds than in the *trans* isomers. The aromatic protons of the DPhSO and DBzSO complexes appeared as two not well-resolved multiplets, one for the *ortho* and one for the *meta* and *para* protons (Table 5).

Some ^1H NMR signals were not well-resolved and some coupling constants could not be measured. In the complexes with TMSO, DPrSO and DBuSO, the coupling constants $^2J(^1H–^1H)$ between geminal H atoms vary from 12.5 to 15.0 Hz, whereas $^3J(^1H_\alpha–^1H_\beta)$ are 5.0 or 11.0 Hz. In the TMSO compounds, the average coupling constant ^3J is 7.0 Hz. The H_α signal is a doublet of doublets of doublets (eight peaks) but only five peaks were observed (relative intensity 1:2:2:2:1). For the DPrSO β hydrogens, an additional coupling with the protons of the methyl group led to a dddq signal. The DBuSO H_γ signals consisted of eight peaks because of the additional coupling between the two geminal protons.

The chemical shift variations of the sulfoxides in ^{13}C NMR spectroscopy are listed in Table 6. The $\Delta\delta$ values are in agreement with those of the K[Pt(R_2SO)Cl_3] compounds [21]. For the DMSO and TMSO complexes, the *cis* compounds are found at lower fields than the *trans* analogues, while for DPrSO, the chemical shift variations are identical. For *trans*-Pt(DPhSO)(pm)Cl_2, the signals of the α carbons were observed at much higher field ($\Delta\delta = -4.84$ ppm). The observed $\Delta\delta$ values are smaller than expected as observed for the ionic K[Pt(R_2SO)Cl_3] complexes [21]. ^{13}C NMR spectroscopy is very dependent on mesomeric effects and the smaller $\Delta\delta$ values have been assigned to

Table 5
^1H NMR $\Delta\delta$ ($\delta_{complex}-\delta_{ligand}$) (ppm) and $^3J(^{195}Pt–^1H)$ (Hz) of the sulfoxide ligands in the *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 complexes

R_2SO		H_α	H_β	H_γ	H_δ	$^3J(^{195}Pt–^1H_\alpha)$
DMSO	*cis*	0.961				25
	trans	0.908				22
TMSO	*cis*	1.399, 0.647	0.252, 0.010			
	trans	1.208, 0.791	0.227, −0.008			
DPrSO	*cis*	1.159, 0.556	0.604, 0.277	0.137		
	trans	1.057, 0.644	0.477, 0.350	0.147		
DBuSO	*cis*	1.166, 0.548	0.624, 0.261	0.152, 0.129	0.075	
DBzSO	*cis*	1.29, 0.55	0.32*ortho*	0.14*meta*+*para*		
	trans	1.19, 0.64	0.29*ortho*	0.12*meta*+*para*		
DPhSO	*trans*	0.313*ortho*	0.091*meta*+*para*			

Table 6
^{13}C NMR $\Delta\delta$ ($\delta_{complex}-\delta_{ligand}$) (ppm) and $^{3}J(^{195}Pt–^{13}C)$ (Hz) of the sulfoxide ligands in the *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$ complexes

R_2SO		C_α	C_β	C_γ	C_δ	$^{2}J(^{195}Pt–^{13}C_\alpha)$	$^{3}J(^{195}Pt–^{13}C_\beta)$
DMSO	*cis*	3.70				59	
	trans	3.22				59	
TMSO	*cis*	4.24	0.69			63	29
	trans	2.24	−0.90			63	
DPrSO	*cis*	2.00	0.41	−0.64		47	17
	trans	2.03	0.28	−0.53		47	
DBuSO	*cis*	2.36	0.11	−0.64	−0.04	48	
DBzSO	*cis*	2.00	−0.24	1.41	0.30 ($C_\varepsilon = -0.52$)	49	
	trans	2.55	−0.11	1.06	0.12 ($C_\varepsilon = -0.83$)	53	
DPhSO	*trans*	−4.84	2.72	−0.59	1.86		

an inversed polarization of the π-electrons in the S=O bond. This effect might be more important when the ligand contains an aromatic groups, which should increase the inversed polarization of the S=O π-bond.

3.4. Coupling constants with ^{195}Pt

Several couplings between ^{195}Pt and H_2, H_6 and C_5 of pyrimidine were observed and the constants are listed in Tables 3 and 4. These coupling constants are very important, since they can allow fast identification of the geometry of the Pt(II) complexes. Average values of 20 and 23 Hz were observed for $^{3}J(^{195}Pt–^{1}H_2)$ in *trans* and *cis* complexes, respectively. The study of the $^{3}J(^{195}Pt–^{1}H_6)$ couplings seems particularly important, since the difference between the two configurations is much more significant. Values of about 31 Hz were observed for the *trans* complexes, whereas much higher values (39–44 Hz) were calculated for the *cis* derivatives. Our results are slightly different from those reported for *trans*-$Pt(PEt_3)(pm)Cl_2$, where the $^{3}J(^{195}Pt–^{1}H_2)$ and the $^{3}J(^{195}Pt–^{1}H_6)$ coupling constants were found identical (22.3 Hz) [7]. Our $^{3}J(^{195}Pt–^{13}C_5)$ values are also geometry-dependent and are similar to those determined with H_6, 39 Hz for the *cis* complexes and 30 Hz for the *trans* isomers. Our results are in agreement with those published for complexes of the types $Pt(py)_2Cl_2$ [20] and $Pt(DMSO)(py)Cl_2$ [26] (py = pyridine and its derivatives).

Coupling constants between ^{195}Pt and the sulfoxide protons could be measured only with DMSO, since in the other complexes, the sulfoxide signals are multiplets of lower intensity and the satellites arising from ^{195}Pt couplings could not be observed in our instrument. The coupling constant in *cis*-$Pt(DMSO)(pm)Cl_2$ (25 Hz) appears to be slightly higher than the one measured in the *trans* analogue (22 Hz). Similar results were published for *cis*- and *trans*-$Pt(DMSO)(py)Cl_2$ complexes (average values of 24 and 21 Hz, respectively) [27]. In contrast to the $^{3}J(^{195}Pt–^{13}C)$ values observed for pyrimidine, the coupling constants between ^{195}Pt and the C_α of sulfoxides are identical in the two types of compounds (shown in Table 6). These constants vary with the sulfoxide with ^{2}J values between 47 and 63 Hz and ^{3}J between 17 and 29 Hz, in agreement with the values determined for the $K[Pt(R_2SO)Cl_3]$ complexes [21].

3.5. Infrared spectroscopy

The pyrimidine vibrations have been reported in the literature and our assignments (Section 2) are based on these studies [14,15]. Upon coordination, the pyrimidine vibrations in our complexes were observed at higher or identical energies than those of free pyrimidine. These values are similar in the two types of complexes for all the sulfoxides. The vibrations 9, 10, 22 and 23 [15] exhibit high intensities and involve C=C and C=N stretching vibrations. The vibrations 1, 6 and 14 involve ring deformations, whereas the bands 3 and 17 are β(C–H) plane deformation of the molecule. Finally, the vibrations 5, 12 and 13 are out of plane C–H deformations, while band 4 is an out of plane ring deformation mode.

The ν(S–O) absorption band of free sulfoxides were observed in the region 1020–1060 cm^{-1}. In Pt(II) complexes, sulfoxides are bonded to the metal by the S atom and the vibration is expected to absorb at higher energy [28]. An increase in frequency between 80 and 130 cm^{-1} were observed. The ν(S–O) values are similar for the two geometries, as already observed for $Pt(Et_2SO)LCl_2$ (L = NH_3 and py) [29]. For the corresponding DMSO compounds, the ν(S–O) vibration was reported at slightly higher energy in the *cis* complexes [12].

The $Pt(R_2SO)(pm)Cl_2$ complexes possess C_s point symmetries for both *cis* and *trans* configurations. From group theory, two ν(Pt–Cl) vibrations are expected for both geometries. Our IR spectra of the *cis* isomers showed two ν(Pt–Cl) bands but only one vibration mode was observed for the *trans* complexes (as expected for C_{2v} and D_{2h} symmetries). An average value of 348 cm^{-1} was obtained for the *trans* compounds,

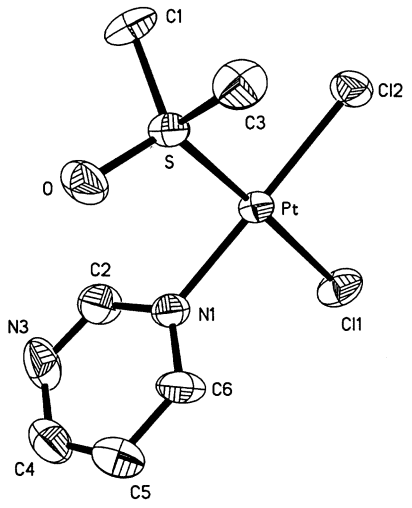


Fig. 1. Labeled diagram of *cis*-Pt(DMSO)(pm)Cl_2 (**I**). The ellipsoids correspond to 40% probability.

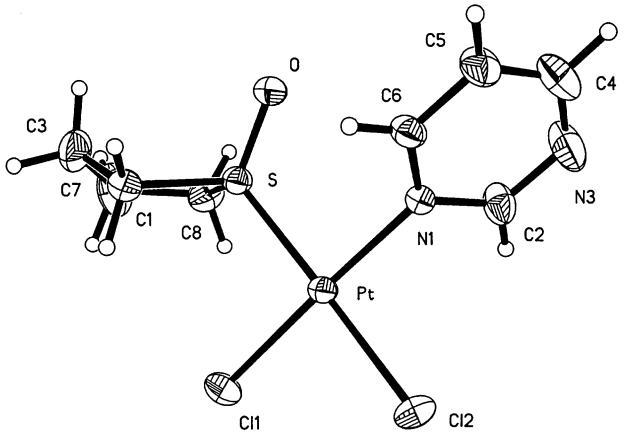


Fig. 2. Labeled diagram of *cis*-Pt(TMSO)(pm)Cl_2 (**II**). The ellipsoids correspond to 30% probability.

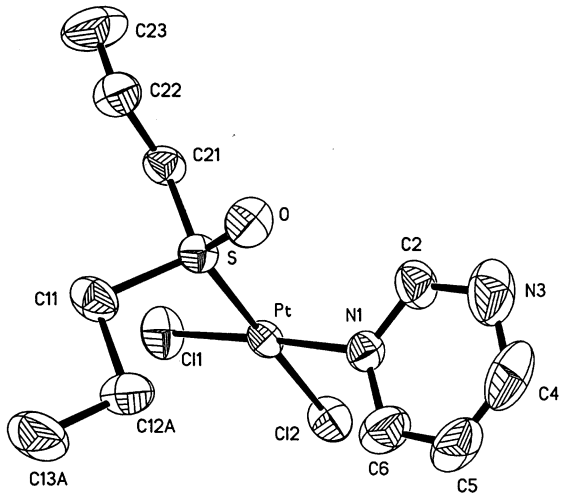


Fig. 3. Labeled diagram of *cis*-Pt(DPrSO)(pm)Cl_2 (**III**). The ellipsoids correspond to 40% probability. For clarity, only one conformation is shown for C12 and C13.

whereas values of about 345 and 320 cm^{-1} were measured for the *cis* complexes. Similar results have also been observed for a series of complexes Pt(DMSO)(L)Cl_2 [17,30].

One absorption band observed around 450 cm^{-1} was assigned to a ν(Pt–S) vibration, as suggested in the literature [10,17,31–33]. This band seems independent of the geometry of the complex. A plot of the frequency of the vibration versus the Pt–S bond distance was made for the five compounds (four *cis* complexes and one *trans* isomer) analyzed by X-ray diffraction methods and a linear relationship was obtained. The bond distance increases as the energy of the vibration decreases.

The ν(Pt–N) vibrations are usually difficult to identify, since these absorption bands are usually of low intensity. A few compounds showed a band between 502 and 527 cm^{-1}, which could be assigned to this vibration as suggested in the literature [34,35].

3.6. Crystal structures

The crystal structures of four complexes *cis*-Pt(R_2SO)(pm)Cl_2 (R_2SO = DMSO (**I**), TMSO (**II**), DPrSO (**III**) and DBuSO (**IV**)) and of *trans*-Pt(TMSO)(pm)Cl_2 (**V**) were studied by X-ray diffraction methods. Crystal **IV** is the first example in the literature of a Pt–DBuSO compound. Labeled diagrams of the five complexes are shown in Figs. 1–5. Selected bond distances and angles are listed in Table 7. Crystals of the *trans* complexes are difficult to obtain, since they isomerize to the *cis* compounds in organic solvents.

The coordination around the Pt atom is square planar as shown by the calculation of the best planes. In the *cis* compounds, the oxygen atom of the sulfoxide ligand is almost in the Pt(II) coordination plane and it is oriented towards the pyrimidine ligand. Therefore, the alkyl groups of the sulfoxide are far from pyrimidine, in order to reduce steric hindrance. The deviations of the O atom from the calculated best plane are −0.209(9) (**I**), 0.038(7) (**II**), −0.168(7) (**III**) and 0.006(11) Å (**IV**). In the *trans* TMSO isomer, the O atom of TMSO is clearly out of the coordination plane (deviation of −1.320(5) Å). The angles around the platinum atom are close to the expected 90 and 180°. These results are similar to those determined in *trans*-Pt(DMSO)LCl_2 complexes (L = 2-picoline, py, NH_3) [36–38].

The pyrimidine ring is planar in all the complexes. The dihedral angles between the coordination and the pyrimidine planes in the *cis* complexes are 79.5(3) for **I**, 62.6(2) for **II**, 65.7(2) for **III** and 74.0(4)° for **IV**. The angle in the *cis* DMSO compound is larger than the one determined in *cis*-Pt(DMSO)(py)Cl_2 (56.8°) [39] and not too far from the one found in *cis*-Pt-

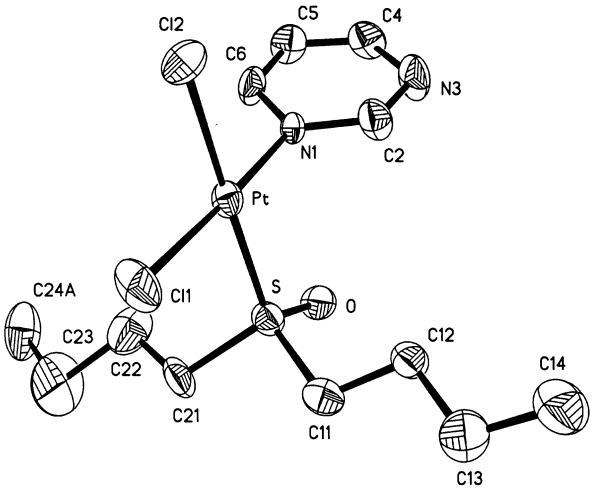


Fig. 4. Labeled diagram of *cis*-Pt(DBuSO)(pm)Cl_2 (**IV**). The ellipsoids correspond to 30% probability. For clarity, only one position for C24 is shown.

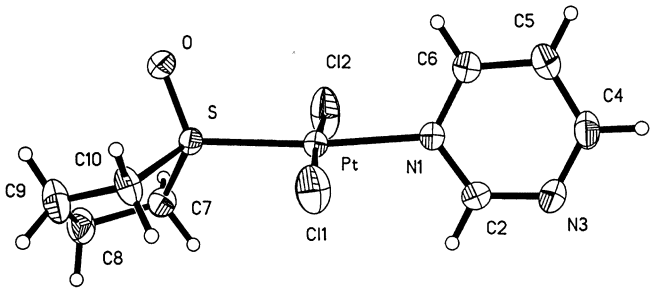


Fig. 5. Labeled diagram of *trans*-Pt(TMSO)(pm)Cl_2 (**V**). The ellipsoids correspond to 30% probability.

(DMSO)(thiazole)Cl_2 (72.8 and 65.6°) [40]. This angle is usually related to the bulkiness of the two *cis* ligands. Pyridine and pyrimidine have very similar steric requirements. In *cis*-Pt(DMSO)(2-picoline)Cl_2, the dihedral angle was found to be 87° [41]. The dihedral angle in *trans*-Pt(TMSO)(pm)Cl_2 (78.0(3)°) is larger than the one measured in the *cis* analogue. This angle can be compared to those reported for *trans*-Pt(DMSO)(2-picoline)Cl_2 ($\sim$73°) [36], *trans*-Pt(DMSO)(thiazole)Cl_2 (39.1°) [40], *trans*-Pt(pm)$_2X_2$ (X = Cl and Br) (52.5 and 54.3°) [6], *trans*-Pt(DMSO)(py)Cl_2 (59.4°) [37], and *trans*-Pt(DMSO)(piperidine)Cl_2 (96(1)°) [42]. Packing forces are important factors in the orientation of the pyrimidine ring, when there is less steric hindrance as in the *trans* compounds.

Sulfoxides have a higher *trans* influence than chloride and amine ligands. In the *cis* compounds, the Pt–Cl bonds located in *trans* position to R_2SO are longer (2.305(2)–2.318(2) Å) than the Pt–Cl distances located in *trans* position to pm (2.286(2)–2.300(2) Å). In *trans*-Pt(TMSO)(pm)Cl_2, the average Pt–Cl distance is 2.286(2) Å. The Pt–S bond length is identical in the five complexes (ave. 2.214(2) Å). This value is very close to those found in *cis*-Pt(DMSO)LCl_2 complexes where L is RCN [17,43,44], 2-picoline [41] or py [39] and in the *trans* analogues, where L = piperidine [42], 2-picoline [36], ammine [38], isopropylamine [45] or pyridine [37]. These values are much smaller than Pt–S bonds in *trans* position to another sulfoxide ligand as in *trans*-Pt(DPrSO)$_2Cl_2$ (2.292(2) Å) [16].

The Pt–N bonds in the *cis* isomers, which are located in *trans* position to a chloride ligand vary between 2.020(9) and 2.043(6) Å whereas the one in *trans*-Pt(TMSO)(pm)Cl_2 is longer, 2.063(5) Å. There is only one structure in the literature on chloro Pt–pm compounds. The Pt–N distance in *trans*-Pt(pm)$_2Cl_2$ is 2.008(5) Å [6] (*trans* to pm). Thus, it seems from these results, that the *trans* influence on the Pt–N bond vary in the order $R_2SO > Cl^- >$ pm. The Pt–N bond seems to be more sensitive to the *trans* ligand than the Pt–Cl bond.

Ligand *trans* to pm:	pm	<	Cl^-	<	R_2SO
Pt–N ave. bond (Å)	2.008(5)		2.028(7)		2.063(5)

The bond distances and angles of the different ligands are normal and similar in all the compounds. The average S–O and S–C bond lengths are 1.466(6) and 1.790(9) Å, respectively. The S–C bond does not seem to depend on the lengths of the alkyl chains. The S atom in the sulfoxide ligands is in an approximate tetrahedral environment. The Pt–S–O angles (ave. 115.2(3)°) are slightly larger than the Pt–S–C angles (ave. 112.0(4)°). The O–S–C bond angles are also slightly larger (ave. 108.8(4)°) than the C–S–C angles (ave. 93.8(4)° for TMSO, 102.0(5)° for others). Again, the C–S–C angles do not seem to vary with the lengths of the alkyl chains. It is 102.4(5)° for DMSO, 101.5(4)° for DPrSO and 102.1(7)° for DBuSO. All these values are similar to those observed in reported Pt–R_2SO complexes [46].

In the pyrimidine ligands, the ave. N–C distance is 1.330(13) Å while the ave. C–C bond length is 1.348(15) Å. These distances are in agreement with those determined in free pyrimidine (1.33(1) and 1.37(1) Å, respectively) [47]. The ave. Pt–N–C angle is 121.5(6)°. The internal N–C–C (ave. 122.0(9)°) and N–C–N angles (ave. 124.8(10)°) are larger than the C–N–C (ave. 116.7(9)°) and C–C–C angles (ave. 117.8(10)°). All these angles are in agreement with those of the free ligand [47] and the values reported in *trans*-Pt(pm)$_2X_2$ [6]. The binding of N1 to the Pt atom does not change the internal angle at the N1 atom as it does in the hydrochlorides of pyrimidine and pyrimidin-2-one [48,49]. 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, coordina-

tion to the platinum atom does not affect the structure of the pyrimidine ligand.

The conformation of the TMSO ligand in *cis*- and *trans*-Pt(TMSO)(pm)Cl_2 is of the envelope type, but they are different as seen by comparing Figs. 2 and 5. In the *cis* compound, four atoms including the S atom are almost in the same plane (deviations from 0.035 to 0.058 Å), while C3 is out of the plane by 0.584 Å. In the *trans* isomer, the deviations are slightly more important (deviations of C7 to C10 between 0.061 and 0.111 Å), while the S atom is out of the plane by 0.716 Å.

The possibility of π–π stacking was examined. It can be observed in the crystal of *trans*-Pt(TMSO)(pm)Cl_2 complex, but none could be found in the *cis* isomers. The packing of the *trans* molecules is more efficient and the distances between the pyrimidines rings is 3.67 Å.

4. Conclusions

A few methods were developed for the synthesis of new platinum(II) mixed-ligand complexes of the types *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2. The compounds were characterized by IR 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 1:1 proportion in water whereas methanol was used for the preparation of the *cis* isomers. The *trans* compounds can isomerize to the *cis* isomers, especially in organic solvents. The *cis* complexes were observed at lower field in ^{195}Pt NMR spectroscopy than their *trans* analogues. These results can be explained by a more effective (d–d) π-bond in the *cis* isomers. Moreover, the study of the chemical shift variations seems to indicate the presence of π-bonding between Pt and pyrimidine, but to a much smaller extent than in the Pt–R_2SO bonding. The δ(Pt) chemical shift of the DPhSO complex was observed at higher field than those of the other ligands, which might be explained by its greater bulkiness around the donor atom. In order to determine the importance of bulkiness on the δ(Pt) chemical shifts, we intend to continue the work with more bulky alkyl sulfoxides, but these molecules are not very easily available.

Inversed polarization of the π-electrons of the S=O bond in the sulfoxide complexes was suggested to explain some of the NMR results. This phenomenon has already been suggested by our group in the ^{13}C NMR spectroscopic interpretation of the complexes K[Pt(R_2SO)Cl_3] [21] and $PtL_2(RCOO)_2$ [50]. The concept was originally suggested in the literature by Cooper and Powell [25] to explain the ^{13}C NMR chemical shifts in Pt–C≡O complexes.

The configuration of these Pt(II) complexes can be determined by IR spectroscopy. Two ν(Pt–Cl) vibrations were observed for the *cis* compounds and only one for the *trans* complexes. The geometry can also be determined from the coupling constants between the

Table 7
Selected bond distances (Å) and angles (°) in the Pt(R_2SO)(pm)Cl_2 crystals **I**–**V**

Crystal	*Cis*-DMSO (**I**)	*cis*-TMSO (**II**)	*cis*-DPrSO (**III**)	*cis*-DBuSO (**IV**)	*trans*-TMSO (**V**)
Pt–Cl(1) (*trans* to pm)	2.300(2)	2.296(2)	2.286(2)	2.290(3)	2.285(2) (*trans* to Cl^-)
Pt–Cl(2)(*trans* to R_2SO)	2.318(2)	2.314(2)	2.305(2)	2.311(4)	2.287(2) (*trans* to Cl^-)
Pt–S	2.209(2)	2.214(2)	2.218(2)	2.219(3)	2.2114(14)
Pt–N	2.023(7)	2.043(6)	2.025(5)	2.020(9)	2.063(5)
S–O	1.475(7)	1.460(5)	1.471(5)	1.453(8)	1.473(5)
S–C	1.775(9), 1.771(9)	1.808(9), 1.822(9)	1.796(8), 1.795 (7)	1.793(13), 1.775(12)	1.784(6), 1.784(6)
N–C	1.344(12), 1.318(11)	1.342(10), 1.353(10)	1.332(9), 1.333(10)	1.33(2), 1.345(14)	1.293(9), 1.331(9)
	1.302(14), 1.339(14)	1.340(14), 1.315(12)	1.377(11), 1.334(14)	1.31(2), 1.34(2)	1.326(11), 1.299(11)
C–C (pm)	1.347(15), 1.380(14)	1.353(11), 1.36(2)	1.295(15), 1.328(12)	1.34(2), 1.34(2)	1.372(12), 1.367(11)
Cl(1)–Pt–Cl(2)	91.68(10)	90.44(9)	90.51(8)	90.99(14)	174.87(9)
S–Pt–Cl(1)	90.53(9)	89.76(8)	90.88(7)	90.02(13)	94.62(7)
S–Pt–Cl(2)	175.10(8)	177.59(8)	178.59(7)	178.78(13)	88.85(7)
N(1)–Pt–Cl(1)	176.6(2)	177.3(2)	177.2(2)	177.6(3)	87.6(2)
N(1)–Pt–Cl(2)	87.1(2)	88.5(2)	87.4(2)	87.6(3)	89.3(2)
N(1)–Pt–S	90.9(2)	91.4(2)	91.2(2)	91.4(3)	174.82(14)
O–S–Pt	115.6(3)	116.0(2)	115.1(2)	115.5(4)	113.9(2)
C–S–Pt	111.4(4), 109.6(4)	111.9(3), 114.5(3)	111.6(3), 109.8(2)	109.9(5), 110.8(5)	114.0(2), 116.5(2)
C–N–Pt	120.7(7), 122.7(6)	119.3(6), 122.8(5)	122.4(5), 119.3(6)	124.2(9), 120.2(8)	122.6(5), 120.8(5)
O–S–C	109.1(5), 107.9(5)	108.6(4), 109.2(4)	109.0(4), 109.0(3)	109.0(6), 108.6(6)	109.1(3), 108.3(3)
C–S–C	102.4(5)	94.4(4)	101.5(4)	102.1(7)	93.1(3)
N–C–N	125.8(10)	124.2(9)	121.1(9)	126.2(13)	126.5(8)
C–N–C	116.6(9), 116.8(10)	117.9(7), 116.6(9)	118.3(7), 116.6(9)	115.5(10), 115.1(12)	116.6(6), 117.0(8)
N–C–C	121.3(10), 121.8(10)	120.3(8), 122.9(9)	121.6(10), 122.9(8)	122.9(12), 124.1(12)	120.9(8), 121.1(7)
C–C–C (pm)	117.7(10)	117.9(9)	119.5(9)	116.1(13)	117.7(8)

pyrimidine atoms and platinum-195. In ^{1}H NMR, the coupling constants $^{3}J(^{195}Pt–^{1}H_{2})$ are slightly larger in the *cis* complexes than in the *trans* analogues, whereas the constants $^{3}J(^{195}Pt–^{1}H_{6})$ are very different in the two geometries. Values between 39 and 44 Hz were observed for *cis* complexes, while lower values (average 31 Hz) were measured for *trans* compounds. The $^{3}J(^{195}Pt–^{13}C_{5})$ coupling constants are also geometry-dependent and values around 40 (*cis*) and 30 Hz (*trans*) were measured.

The crystal structures of four *cis* complexes and one *trans* compound were determined. The study of these crystals confirmed the IR and NMR results. The comparison of the Pt-ligands bond distances gave interesting information on the *trans* influence of the different ligands. Sulfoxides have clearly a larger *trans* influence than the chloride ligand 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. Nevertheless, more crystal structure determinations on chloro Pt–pyrimidine compounds are needed to confirm our suggestion on the relative order of the three ligands in the *trans* influence series: sulfoxide $\gg Cl^{-} >$ pm.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 161930 to 161934 for compound X. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] N. Farrell, T.B.T. Ha, J.-P. Souchard, F.L. Wimmer, S. Cros, N.P. Johnson, J. Med. Chem. 32 (1989) 2240.
[2] M.V. Beusichem, N. Farrell, Inorg. Chem. 31 (1992) 634.
[3] Y. Zou, B. Van Houten, N. Farrell, Biochemistry 32 (1993) 9632.
[4] G.B. Kauffman, Inorg. Synth. 7 (1963) 249.
[5] G.V. Fazakerley, K.R. Koch, Inorg. Chim. Acta 36 (1979) 13.
[6] F.D. Rochon, P.-C. Kong, R. Melanson, Can. J. Chem. 59 (1981) 195.
[7] W. Kaufmann, L.M. Venanzi, A. Albinati, Inorg. Chem. 27 (1988) 1178.
[8] L.G. Marzilli, Y. Hayden, M.D. Reily, Inorg. Chem. 25 (1986) 974.
[9] F.D. Rochon, S. Boutin, P.-C. Kong, R. Melanson, Inorg. Chim. Acta 264 (1997) 89.
[10] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.
[11] XSCANS and SHELXTL (PC, version 5) programs, Bruker Analytical X-ray Systems, Madison, WI, 1995.
[12] Yu.N. Kukushkin, Yu.E. Vyaz'menskii, L.I. Zorina, Russ. J. Inorg. Chem. 13 (1968) 1573.
[13] F.D. Rochon, P.-C. Kong, L. Girard, Can. J. Chem. 64 (1986) 1897.
[14] R.C. Lord, A.L. Marston, F.A. Miller, Spectrochim. Acta 9 (1957) 113.
[15] D.J. Brown, The Chemistry of Heterocyclic Compounds. The Pyrimidines, vol. 16, Wiley, New York, 1962 (Ch. 13).
[16] R. Melanson, F.D. Rochon, Acta Crystallogr., Sect. C 44 (1988) 1893.
[17] V.Yu. Kukushkin, V.K. Belsky, V.E. Konovalov, G.A. Kirakosyan, L.V. Konovalov, A.I. Moiseev, V.M. Tkachuk, Inorg. Chim. Acta 185 (1991) 143.
[18] S.J.S. Kerrison, P.J. Sadler, J. Chem. Soc., Chem. Commun. (1977) 861.
[19] F.D. Rochon, M. Doyon, I.S. Butler, Inorg. Chem. 32 (1993) 2717.
[20] C. Tessier, F.D. Rochon, Inorg. Chim. Acta 295 (1999) 25.
[21] C. Bensimon, MSc Thesis, Université du Québec à Montréal, Montréal, Canada, 1986.
[22] D.J. Brown, R.F. Evans, T.J. Batterham, The Chemistry of Heterocyclic Compounds. The Pyrimidines, vol. 16, Wiley, New York, 1970 (Suppl. I, Ch. 13).
[23] G.S. Reddy, R.T. Hobgood Jr., J.H. Goldstein, J. Am. Chem. Soc. 84 (1962) 336.
[24] S. Castellano, C. Sun, R. Kostelnik, J. Chem. Phys. 46 (1967) 327.
[25] D.G. Cooper, J. Powell, Inorg. Chem. 16 (1977) 142.
[26] T.B.T. Ha, J.-P. Souchard, F.L. Wimmer, N.P. Johnson, Polyhedron 9 (1990) 2647.
[27] G. Annibale, M. Bonivento, L. Cattalini, M.L. Tobe, J. Chem. Soc., Dalton Trans. (1992) 3433.
[28] J.A. Davies, Adv. Inorg. Chem. Radiochem. 24 (1981) 115.
[29] Yu.N. Kukushkin, V.I. Spevak, Russ. J. Inorg. Chem. 16 (1971) 228.
[30] V.N. Spevak, V.I. Lobadyuk, D.M. Batueva, J. Gen. Chem. USSR 60 (1990) 1178.
[31] Yu.N. Kukushkin, V.N. Spevak, Russ. J. Inorg. Chem. 18 (1973) 240.
[32] Yu.N. Kukushkin, I.V. Pakhomova, Russ. J. Inorg. Chem. 16 (1971) 226.
[33] B.F.G. Johnson, R.A. Walton, Spectrochim. Acta 22 (1966) 1853.
[34] Yu.N. Kukushkin, N.V. Ivannikova, K.A. Khokhryakov, Russ. J. Inorg. Chem. 15 (1970) 1595.
[35] K. Nakamoto, P.J. McCarthy, J. Fujita, R.A. Condrate, G.T. Behnke, Inorg. Chem. 4 (1965) 36.
[36] R. Melanson, F.D. Rochon, Acta Crystallogr., Sect. B 34 (1978) 1125.
[37] F. Caruso, R. Spagna, L. Zambonelli, Acta Crystallogr., Sect. B 36 (1980) 713.
[38] B. Viossat, P. Khodadad, N. Rodier, Acta Crystallogr., Sect. C 47 (1991) 1316.
[39] V.K. Belsky, V.E. Konovalov, V.Yu. Kukushkin, Acta Crystallogr., Sect. C 47 (1991) 292.
[40] A. Cornia, A.C. Fabretti, M. Bonivento, L. Cattalini, Inorg. Chim. Acta 255 (1997) 405.
[41] R. Melanson, F.D. Rochon, Acta Crystallogr., Sect. B 33 (1977) 3571.

[42] K. Lövqvist, Å. Oskarsson, Acta Crystallogr., Sect. C 48 (1992) 2073.
[43] V.K. Belsky, V.E. Konovalov, V.Y. Kukushkin, A.I. Moiseev, Inorg. Chim. Acta 169 (1990) 101.
[44] F.D. Rochon, P.-C. Kong, R. Melanson, Inorg. Chim. Acta 216 (1994) 163.
[45] R. Melanson, F.D. Rochon, Acta Crystallogr., Sect. C 40 (1984) 793.
[46] (a) R. Melanson, F.D. Rochon, Can. J. Chem. 53 (1975) 2371;
(b) R. Melanson, C. de la Chevrotière, F.D. Rochon, Acta Crystallogr., Sect. C 41 (1985) 1428;
(c) R. Melanson, F.D. Rochon, Acta Crystallogr., Sect. C 43 (1987) 1869;
(d) L. Antolini, U. Folli, D. Iarossi, L. Schenetti, F. Taddei, J. Chem. Soc., Perkin Trans. 2 (1991) 955;
(e) J. Ebbighausen, N. Farrell, K. Lövqvist, Å. Oskarsson, Acta Crystallogr., Sect. C 52 (1996) 1091.
[47] P.J. Wheatley, Acta Crystallogr. 13 (1960) 80.
[48] S. Furberg, J.B. Aas, Acta Chem. Scand. A 29 (1975) 713.
[49] C. Singh, Acta Crystallogr. 19 (1965) 861.
[50] F.D. Rochon, L.M. Gruia, Inorg. Chim. Acta 306 (2000) 193.