Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 346 (2003) 197–206
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis and characterization of the iodo-bridged Pt(II) complexes $\{Pt(R_2SO)I\}_2(\mu\text{-}I)_2$ and of *trans*-$Pt(R_2SO)(pyrimidine)I_2$

Fernande D. Rochon *, Gassan Masserweh, Nicolas Nédélec

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

Received 20 August 2002; accepted 8 October 2002

Abstract

The reactions of $K_2[PtI_4]$ with sulfoxides produce the iodo-bridged dinuclear species $(R_2SO)IPt(\mu\text{-}I)_2Pt(R_2SO)I$, which have shown two resonances in ^{195}Pt NMR spectroscopy at average values of −4933 and −4827 ppm. The signals have been assigned to the presence of *cis* and *trans* dimeric isomers in solution. The compounds with di-*n*-propylsulfoxide and dibenzylsulfoxide were studied by X-ray diffraction methods and the results have shown that the two sulfoxide ligands are in *trans* positions. The reactions of these dimers with pyrimidine (pm) gave the compounds *trans*-$Pt(R_2SO)(pm)I_2$. The ^{195}Pt chemical shifts of these complexes vary between −4387 and −4438 ppm. The ^{195}Pt coupling constants with the atoms of pyrimidine $^3J(^{195}Pt-^1H_2)$, $^3J(^{195}Pt-^1H_6)$ and $^3J(^{195}Pt-^{13}C_5)$ are (ave.) 22, 32 and 28 Hz, respectively, suggesting a *trans* configuration. A few ^{195}Pt coupling constants with the sulfoxide atoms were observed. The ^2J vary between 56 and 71 Hz, while the ^3J are between 15 and 27 Hz. The crystal structures of the compounds with dimethylsulfoxide, di-*n*-propylsulfoxide and tetramethylenesulfoxide were determined, confirming the *trans* geometry.
© 2002 Published by Elsevier Science B.V.

Keywords: Platinum compounds; Sulfoxide; Pyrimidine; Crystal structures; NMR

1. Introduction

Although many studies have been reported on Pt(II) compounds with pyrimidine derivatives, there are only a few papers with non-substituted pyrimidine (pm). Rochon and coworkers [1] reported the synthesis of *cis*- and *trans*-$Pt(pm)_2X_2$ (X = Cl and Br) and determined the crystal structures of the two *trans* isomers. Fazakerley and Koch [2] synthesized and characterized *cis*-$[Pt(NH_3)_2(pm)_2](ClO_4)_2$ by ^{13}C NMR spectroscopy, while 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]. The latter authors have also prepared the pyrimidine-bridged dimer $\{PtCl_2(PR_3)\}_2(\mu\text{-pm})$.

We have recently started a study on mixed-ligands chloro Pt(II) complexes containing sulfoxides and pyrimidine. We have reported the synthesis and characterization of the compounds *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$ [4]. The reaction of $K[Pt(R_2SO)Cl_3]$ with pm in a 1:1 ratio produces *trans*-$Pt(R_2SO)(pm)Cl_2$, which isomerize to the *cis* complex, except for bulky ligands like diphenylsulfoxide. The isomerization is quite slow in water especially with more bulky ligands, but much faster in an organic solvent. When the Pt:pm ratio was 2:1, *trans*-pyrimidine-bridged dimers, $Pt(R_2SO)Cl_2(\mu\text{-pm})Pt(R_2SO)Cl_2$ were isolated [5]. With a few sulfoxides, the latter isomerized to the *cis* dimers. These compounds were characterized by multinuclear magnetic resonance spectroscopy and several by crystallographic methods. The geometry of the isomer can be determined by the coupling constants $J(^{195}Pt-^1H)$ and $J(^{195}Pt-^{13}C)$. The *cis* compounds have larger coupling constants than the *trans* complexes.

Sulfoxide molecules have interesting behaviors as ligands, since they can accept π electron density from the metallic center. Most of the published 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*-$Pt(R_2SO)_2Cl_2$,

* Corresponding author. Tel.: +1-514-987 3000/4896; fax: +1-514-987 4054.
E-mail address: rochon.fernande@uqam.ca (F.D. Rochon).

0020-1693/03/$ - see front matter © 2002 Published by Elsevier Science B.V.
doi:10.1016/S0020-1693(02)01394-4

which rapidly 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)π-bonding, which is more effective in the *cis* configuration than in the *trans* geometry [6]. In the Pt–amine system, where π bonding is absent, the *trans* isomers are more stable than the *cis* compounds. Pyrimidine also contains empty π antibonding orbitals, which could accept electron density from Pt. Our recent work [4,5] seem to indicate that π-bonding also exists in Pt–pyrimidine compounds, but to a much smaller extent that in Pt–sulfoxide complexes.

It appeared interesting to compare the results observed in the dichloro system with similar compounds containing iodo ligands. The aqueous reaction of $K_2[PtI_4]$ with sulfoxides does not produce $K[Pt(R_2SO)I_3]$ or $Pt(R_2SO)_2I_2$ as observed in the chloro system. The product is a brown insoluble compound, which forms quite rapidly. An earlier low field ^1H NMR study by our group [7] has suggested that the iodo-bridged dimer $\{Pt(R_2SO)I\}_2(\mu\text{-}I)_2$ is formed. We have restudied these reactions with several sulfoxide ligands in order to confirm the structures of the dimers. We have now characterized mainly by multinuclear NMR spectroscopy several of these compounds. We were successful in obtaining crystals with a few ligands, and these were studied by crystallographic methods.

The reactions of these iodo-bridged dinuclear species with pyrimidine were then studied and the results were compared with those obtained in the chloro system.

2. Experimental

$K_2[PtCl_4]$ was obtained from Johnson Matthey Inc. and it was purified by recrystallization in water before use. The sulfoxide ligands, CD_2Cl_2 and pyrimidine were purchased from Aldrich except di-*n*-propylsulfoxide, which was bought from Phillips Petroleum. $CDCl_3$ was obtained from CDN Isotopes.

The melting and decomposition points were measured on a Fisher–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 280 cm^{-1}. All the NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 on a Varian Gemini 300BB spectrometer operating at 300.075, 75.462 and 64.400 or 64.335 MHz for ^1H, ^{13}C and ^{195}Pt, respectively. The residual chloroform or dichloromethane peaks were used as an internal standard for the ^1H (7.24 or 5.32 ppm) and ^{13}C (77.00 or 53.80 ppm) NMR spectra. For ^{195}Pt, the external references were $K[Pt(DMSO)Cl_3]$ (in D_2O, adjusted at −2998 ppm from $Na_2[PtCl_6]$), *cis*-$Pt(TMSO)_2Cl_2$ (in $CDCl_3$ adjusted at −3450 ppm from $Na_2[PtCl_6]$) or $K_2[Pt(CN)_4]$ (in D_2O adjusted at −4705 ppm from $Na_2[PtCl_6]$).

The crystals selected for crystallographic studies were examined under a polarizing microscope for homogeneity. The X-ray diffraction measurements were done on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation, except for **I**, which was measured with Cu Kα ($\lambda = 1.54178$ Å) radiation. 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 [8] program. The coordinates of the Pt atoms were determined by direct methods or from Patterson map calculations. All the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structures was done on F^2 by full-matrix least-squares analysis. The hydrogen atom positions were fixed in their calculated position with $U_{eq} = 1.2\ U_{eq}$ (or 1.5 for methyl groups) of the carbon to which they are bonded. Corrections were made for absorption (Gaussian integration except for **V** (empirical Ψ scan)), Lorentz and polarization effects. In crystal **I**, the terminal C atoms on both propyl chains were found to be disordered on two positions. In crystal **III**, the atoms Pt, I1, I2, S, O and N1 are all located on a mirror. Therefore, N3 is disordered on both sides of the mirror plane. The residual peaks were located in the close environment of the platinum atoms. The calculations were done using the Siemens SHELXTL system [8]. The pertinent data are summarized in Table 1.

2.1. $I(R_2SO)Pt(\mu\text{-}I)_2Pt(R_2SO)I$

These compounds were synthesized according to the published method [7] with slight modifications. One mmole of $K_2[PtCl_4]$ dissolved in water was added to a solution containing ~8 mmol of KI dissolved in a minimum quantity of water. The mixture was stirred for 20 min and the solution was filtered directly on the sulfoxide (~2.5 mmol) dissolved in water. The mixture was stirred for about 1 h, and then filtered. The precipitate was washed with water, dried, and washed with ether.

2.1.1. $I(DMSO)Pt(\mu\text{-}I)_2Pt(DMSO)I$

Yield, 28%; m. p. 109–202 °C dec. *Anal*. C, 4.32% (Calc. 4.56); H, 0.75% (Calc. 1.15%); S, 5.62% (Calc. 6.08). IR (cm^{-1}): 2992m, 2903w, 1412m, 1311m, 1291sh, 1263w, ν(S–O) 1126s, 1020s, 970m, 728w, 685m, (νPt–S) 431s, 369m. ^1H NMR (ppm in $CDCl_3$): H_α 3.619s $^3J(^{195}Pt-^1H) = 26$ Hz, 3.614s. ^{13}C NMR (ppm): C_α 48.29, 47.79.

2.1.2. $I(TMSO)Pt(\mu\text{-}I)_2Pt(TMSO)I$

Yield, 30%; m. p. 146–174 °C dec. *Anal*. C, 8.06% (Calc. 8.69); H, 0.95% (Calc. 1.46%); S, 5.44% (Calc. 5.80). IR (cm^{-1}): 2970w, 2935w, 1439w, 1402m. 1305w,

Table 1
Experimental details and crystal data of the compounds $I(R_2SO)Pt(\mu\text{-}I)_2PtI(R_2SO)$ (R = n-Pr (**I**) and Bz (**II**)) and compounds *trans*-$Pt(R_2SO)(pm)I_2$ (R = Me (**III**), n-Pr (**IV**) and $R_2 = C_4H_8$ (**V**)

	I	**II**	**III**	**IV**	**V**
Formula	$C_{12}H_{28}I_4O_2S_2Pt_2$	$C_{28}H_{28}I_4O_2S_2Pt_2$	$C_6H_{10}I_2N_2OSPt$	$C_{10}H_{18}I_2N_2OSPt$	$C_8H_{12}I_2N_2OSPt$
Formula weight	1166.24	1358.40	607.11	663.21	633.15
Space group	$P2_1/n$	I_4/m	$Pnma$	$P\bar{1}$	$P2_1/n$
a (Å)	9.043(2)	14.155(2)	13.1910(10)	5.7244(7)	12.027(2)
b (Å)	15.405(6)	14.155(2)	8.6630(10)	9.9312(12)	8.915(2)
c (Å)	10.169(2)	17.454(4)	11.1530(10)	14.7647(17)	13.995(4)
α (°)				90.51(1)	
β (°)	104.60(2)			95.21(1)	110.55(2)
γ (°)				100.46(1)	
Volume (Å^3)	1370.9(7)	3497.2(9)	1274.5(2)	821.75(17)	1405.2(5)
Z	2	4	4	2	4
$F(000)$	1032	2448	1072	600	1128
ρ_{calc} (Mg m^{-3})	2.825	2.580	3.164	2.680	2.993
μ (Mo Kα) (mm^{-1})	55.621(Cu Kα)	11.665	15.987	12.410	14.507
Reflections collected	2008	8826	2145	5219	3381
Independent reflections (R_{int})	1652 (0.1502)	2080 (0.0583)	1971 (0.045)	4775 (0.0215)	3233 (0.0533)
Observed reflections ($I > 2\sigma(I)$)	855	1674	1461	3889	2653
R_1 ($I > 2\sigma(I)$)	0.0696	0.0350	0.0437	0.0364	0.0473
wR_2 (all data)	0.1524	0.0748	0.1237	0.0953	0.0987
S	1.071	1.061	1.051	1.018	1.038

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

1260w, ν(S–O) 1131s, 1070m, 1020w, 995w, 951w, 875w, 776w, 650w, 557m, 364w. ^{1}H NMR (ppm in $CDCl_3$): H_α 4.289ddd, $J = 14.1$, 7.4, 6.8; 4.267ddd, $J = 13.3$, 6.9, 6.2; 3.589ddd, $J = 12.4$, 6.9, 5.9; 3.568ddd, $J = 12.5$, 7.0, 6.6; H_β 2.377m, 2.183m. ^{13}C NMR (ppm): C_α 61.75, 61.54, C_β 26.22, 26.08.

2.1.3. I(DPrSO)Pt(μ-I)$_2$Pt(DPrSO)I

Yield, 58%; m. p.146–190 °C dec. IR (cm^{-1}): 2957m, 2925sh, 2866sh, 1458m, 1403m, 1382sh, 1344w, 1297w, 1250m, 1217w, ν(S–O) 1135s, 1129s, 1122s, 1066m, 860w, 750m, 651w, 497w, 444m. ^{1}H NMR (ppm in $CDCl_3$): H_α 3.860ddd $J = 12.7$, 11.0, 5.5 Hz, 3.842ddd $J = 12.8$, 11.2, 5.6 Hz, 3.399ddd $J = 11.7$, 10.5, 5.3 Hz, 3.356ddd $J = 11.6$, 10.4, 5.2 Hz, H_β 2.279m, 2.030m, H_γ 1.193t $J = 7.5$ Hz, 1.184t $J = 7.5$ Hz. ^{13}C NMR (ppm): C_α 59.75, 59.33, C_β 17.25, 17.22, C_γ 12.88.

2.1.4. I(DBuSO)Pt(μ-I)$_2$Pt(DBuSO)I

Yield, 53%; m. p.132–184 °C dec. IR (cm^{-1}): 2956s, 2928s, 2864m, 1464s, 1400s, 1360w, 1344w, 1314w, 1280w, 1237m, 2101w, 1183sh, ν(S–O) 1126s, 1091sh. 1078m, 969w, 788w, 737w, 660w, 499w, 454m, 405w. ^{1}H NMR (ppm in $CDCl_3$): H_α 3.894ddd $J = 12.1$, 12.1, 5.8, 3.876ddd $J = 12.1$, 12.1, 5.9 Hz, 3.417ddd $J = 11.8$, 11.6, 4.8 Hz, 3.378ddd $J = 12.0$, 11.8, 4.8 Hz, H_β 2.234m, 1.959m, H_γ 1.604sextuplet $J = 7.3$ Hz, 1.598sextuplet $J = 7.4$ Hz, H_δ 1.033t $J = 7.4$ Hz, 1.021t $J = 7.5$ Hz. ^{13}C NMR (ppm): C_α 57.97, 57.55, C_β 25.22, C_γ 21.75, C_δ 13.79.

2.1.5. I(DBzSO)Pt(μ-I)$_2$Pt(DBzSO)I

Yield 70%. IR (cm^{-1}): 3062w, 3032m, 2964w, 2915w, 1493s, 1452s, 1409m, 1170m, ν(S–O) 1112s 1073m, 1031s, 916m, 886w, 773s, 695s, 477s, 410w. ^{1}H NMR (ppm in CD_2Cl_2): CH_2 4.68dd $J = 12.9$, 3.0 Hz, 5.12dd $J = 12.6$, 4.8 Hz, Ph 7.5m. ^{13}C NMR (ppm): CH_2 62.23, 62.61, C_{phenyl} 129.21, 129.26, 129.85, 129.90, 132.12, 132.19.

2.1.6. I(MeBzSO)Pt(μ-I)$_2$Pt(MeBzSO)I

Yield 70%. IR (cm^{-1}): 3003m, 2912m, 1492m, 1451s, 1398s, 1297m, 1150s, ν(S–O) 1115s 1070w, 1026w, 963s, 866w, 763s, 644s, 586w, 481s, 445m, 420m, 390w. ^{1}H NMR (ppm in CD_2Cl_2): CH_3 3.493s $^3J(^{195}Pt-^1H) = 25$ Hz, 3.484s $^3J(^{195}Pt-^1H) = 25$ Hz, CH_2 5.026m, 4.809m, Ph 7.49m. ^{13}C NMR (ppm): CH_3 47.50, 45.11, CH_2 67.6, 65.3, C_{phenyl} 132.0, 129.6, 129.2, 120.08.

2.2. trans-Pt(R$_2$SO)(pm)I$_2$

The iodo-bridged dimers $I(R_2SO)Pt(\mu\text{-}I)_2Pt(R_2SO)I$ were dissolved in a minimum quantity of CH_2Cl_2. A slight excess of pyrimidine (dissolved in a minimum quantity of CH_2Cl_2) was slowly added to the dimer solution and the mixture was stirred between 15 and 60 min. The solution was then evaporated to dryness and the residue washed with ether and dried.

2.2.1. trans-Pt(DMSO)(pm)I$_2$

Yield 60%. M.p. 143–214 °C dec. IR (cm^{-1}): pm (vibration number [9,10]): 3080w (8), 3048w (2), 1591s, 1555w (9,10), 1467w (22), 1408s (23), 1226w (3), 1172w

(17), 1070w, 1055w (14), 1026m (1), 976w (5), 820w (12), 729w (13), 695w (4), 638w (6), ν(S–O) 1120s, ν(Pt–S) 437w. ^{1}H NMR (ppm in CD_2Cl_2): H_2 9.441s $^3J(^{195}Pt-^1H) = 21$ Hz, H_4 8.773dd $J = 5.0$, 2.3, H_5 7.470ddd $J = 6.0$, 4.8, 1.2 Hz, H_6 8.982ddd $J = 5.7$, 2.3, 0.9 Hz, $^3J(^{195}Pt-^1H) = 30$ Hz, H_α 3.860s $^3J(^{195}Pt-^1H) = 23$ Hz. ^{13}C NMR (ppm): C_2 161.94, C_4 159.17, C_5 122.61 $^3J(^{195}Pt-^{13}C) = 27$ Hz, C_6 160.54, C_α 51.83 $^2J(^{195}Pt-^{13}C) = 69$ Hz.

2.2.2. trans-Pt(TMSO)(pm)I_2

Yield 61%. M. p. 121–209 °C dec. IR (cm^{-1}): pm: 3060w (2), 1593s, 1557m (9,10), 1468m (22), 1408s (23), 1225w (3), 1171w (17), 1073s, 1052sh (14), 1025w (1), 813w (12), 698m (4), 639m (6), ν(S–O) 1142s, ν(Pt–S) 444w. ^{1}H NMR (ppm in CD_2Cl_2): H_2 9.468s $^3J(^{195}Pt-^1H) = 22$ Hz, H_4 8.783dd $J = 5.0$, 2.3 Hz, H_5 7.474ddd $J = 5.9$, 4.7, 1.3 Hz, H_6 9.021ddd $J = 6.0$, 2.1, 1.1 Hz, $^3J(^{195}Pt-^1H) = 30$ Hz, H_α 4.067ddd $J = 14.1$, 7.1, 7.1, 3.911m, H_β 2.306m, 2.161m. ^{13}C NMR (ppm): C_2 161.95, C_4 159.14, C_5 122.64 $^3J(^{195}Pt-^{13}C) = 30$ Hz, C_6 160.52, C_α 64.23 $^2J(^{195}Pt-^{13}C) = 70$ Hz, C_β 25.43 $^3J(^{195}Pt-^{13}C) = 27$ Hz.

2.2.3. trans-Pt(DPrSO)(pm)I_2

Yield 75%. M.p. 112 °C. IR (cm^{-1}): pm: 3084w (8), 3046m (2), 1593s, 1557m (9,10), 1464m (22), 1409m (23), 1223w (3), 1170w (17), 1074m, 1055w (14), 1024w (1), 814w (12), 738w (13), 699m (4), 637m (6), ν(S–O) 1127s, ν(Pt–N) 512m, ν(Pt–S) 453m. ^{1}H NMR (ppm in CD_2Cl_2): H_2 9.449s $^3J(^{195}Pt-^1H) = 21$ Hz, H_4 8.764dd $J = 5.1$, 2.1 Hz, H_5 7.459ddd $J = 6.0$, 4.9, 1.3 Hz, H_6 8.990ddd $J = 5.9$, 2.3, 1.1 Hz $^3J(^{195}Pt-^1H) = 32$ Hz, H_α 4.050ddd $J = 12.8$, 11.1, 5.3 Hz, 3.592ddd $J = 12.8$, 11.1, 5.1 Hz, H_β 2.261dddq $J = 15.1$, 10.9, 7.4, 5.3 Hz, 2.082dddq $J = 15.1$, 11.0, 7.4, 5.3 Hz, H_γ 1.213t $J =$ 7.4Hz. ^{13}C NMR (ppm): C_2 161.89, C_4 159.04, C_5 122.49 $^3J(^{195}Pt-^{13}C) = 26$ Hz, C_6 160.53, C_α 61.71 $^2J(^{195}Pt-^{13}C) = 56$ Hz, C_β 17.57, C_γ 12.90.

2.2.4. trans-Pt(DBuSO)(pm)I_2

Yield 49%. M.p. 155–193 °C dec. IR (cm^{-1}): pm: 3085w (8), 3048w (2), 1594m, 1557w (9,10), 1468m (22), 1402s (23), 1229w (3), 1169w (17), 1077sh, 1057sh (14) 1024sh (1), 740w (13), 699m (4), 638w (6), ν(S–O) 1130s, ν(Pt–N) 499w, ν(Pt–S) 454m. ^{1}H NMR (ppm in CD_2Cl_2): H_2 9.440s $^3J(^{195}Pt-^1H) = 20$ Hz, H_4 8.753dd $J = 5.1$, 2.1 Hz, H_5 7.453ddd $J = 5.9$, 5.0, 1.1 Hz, H_6 8.983ddd $J = 5.9$, 2.2, 1.0 Hz $^3J(^{195}Pt-^1H) = 30$ Hz, H_α 4.064ddd $J = 12.7$, 11.3, 5.0 Hz, 3.599ddd $J = 12.8$, 11.1, 5.1 Hz, H_β 2.198m, 2.000m, H_γ 1.618sextuplet $J = 7.3$ Hz, H_δ 1.027t $J = 7.2$ Hz. ^{13}C NMR (ppm): C_2 161.88, C_4 159.03, C_5 122.48 $^3J(^{195}Pt-^{13}C) = 26$ Hz, C_6 160.55, C_α 59.89 $^2J(^{195}Pt-^{13}C) = 56$ Hz, C_β 25.54 $^3J(^{195}Pt-^{13}C) = 15$ Hz, C_γ 21.76, C_δ 13.85.

2.2.5. trans-Pt(DBzSO)(pm)I_2

Yield 65%. IR (cm^{-1}): 3060w, 3032w, 2970w, 2920w, 1588s, 1503m, 1491m, 1451m, 1404s, 1375m, 1330m, 1170m, ν(S–O) 1129s, 872m, 695s, 479m. ^{1}H NMR (ppm in $CDCl_3$): CH_2 4.58d $J = 12.6$ Hz, 5.00d $J = 12.9$ Hz, 5.20d $J = 12.9$ Hz, 5.48d $J = 12.3$ Hz, Ph 7.45m, H_2 9.677s, H_4 8.70m, H_5 7.66m, H_6 9.19m. ^{13}C NMR (ppm): C_2 163.49, C_4 157.60, C_5 121.80 $^3J(^{195}Pt-^{13}C) =$ 30 Hz, C_6 162.00, C_{phenyl} 128.36, 128.95, 130.11, 131.7.

2.2.6. trans-Pt(MeBzSO)(pm)I_2

Yield 65%. IR (cm^{-1}): 3052w, 3002w, 2970w, 2922w, 1590s, 1553m, 1495w, 1465w, 1451w, 1405s, 1150m, ν(S–O) 1110s, 1067w, 973m, 962m, 871w, 766m, 696s, 636w, 478m, ν(Pt–S) 446m. ^{1}H NMR (ppm in CD_2Cl_2): CH_3 3.59s $^3J(^{195}Pt-^1H) = 23$ Hz, CH_2 5.07dd $J = 13.8$, 1.2 Hz, (second peak hidden by solvent), Ph 7.49m, H_2 9.34s $^3J(^{195}Pt-^1H) = 22$ Hz, H_4 8.69dd, $J = 5.1$, 2.4 Hz, H_5 7.50dd $J = 5.1$, 2.4 Hz, H_6 8.96ddd $J = 5.7$, 2.1, 0.9 Hz, $^3J(^{195}Pt-^1H) = 34$ Hz. ^{13}C NMR (ppm): CH_3 47.57 $^2J(^{195}Pt-^{13}C) = 70.7$ Hz, CH_2 67.61 $^2J(^{195}Pt-^{13}C) =$ 63.6 Hz, Ph 129.08, 129.18, 129.63, 131.89, C_2 161.67 $^2J(^{195}Pt-^{13}C) = 15$ Hz, C_4 158.96, C_5 122.45 $^3J(^{195}Pt-^{13}C) = 33$ Hz, C_6 160.30 $^2J(^{195}Pt-^{13}C) = 15$ Hz.

2.2.7. trans-Pt(MePhSO)(pm)I_2

Yield 65%. IR (cm^{-1}): 3082m, 3062m, 3020m, 3000m, 2915w, 1585s, 1548s, 1463m, 1438m, 1398s, 1302w, 1225w, 1170m, ν(S–O) 1135s, 1084m, 1062m, 1053m, 1022s, 957s, 820s, 757m, 723m, 698s, 640s, 517s, 488m, 412w, 363w. ^{1}H NMR (ppm in $CDCl_3$): CH_3 4.11 $^3J(^{195}Pt-^1H) = 24$ Hz, Ph 7.45m, H_2 9.52s $^3J(^{195}Pt-^1H) = 24$ Hz, H_4 8.78dd, $J = 4.9$, 2.1 Hz, H_5 7.64m, H_6 9.04ddd $J = 6.2$, 2.0, 1.0 Hz, $^3J(^{195}Pt-^1H) =$ 33 Hz. ^{13}C NMR (ppm): CH_3 55.49, Ph 125.38, 129.31, 129.93, 133.0, C_2 161.98, C_4 158.78, C_5 122.22, C_6 160.44.

3. Results and discussion

3.1. Complexes I(R_2SO)Pt(μ-I)$_2$Pt(R_2SO)I

The aqueous reaction of $K_2[PtI_4]$ with sulfoxides does not produce $K[Pt(R_2SO)I_3]$ or $Pt(R_2SO)_2I_2$ as in the analogous chloro system. The reaction was studied with R_2SO = DMSO, tetramethylenesulfoxide (TMSO), di-*n*-propylsulfoxide (DPrSO), di-*n*-butylsulfoxide (DBuSO), dibenzylsulfoxide (DBzSO) and benzylmethylsulfoxide (MeBzSO). A few experiments were also done on methylphenylsulfoxide (MePhSO), although the products were not very stable. The reaction produces a dark red precipitate which has been characterized by IR and multinuclear magnetic resonance spectroscopies and a few by elemental analysis and X-ray diffraction.

A low field ^{1}H NMR study of this reaction was done many years ago by our research group and we had suggested that the results were consistent with iodo-bridged dinuclear species [7].

In the present study, the ^{195}Pt and ^{1}H NMR results have shown that there are two Pt species in solution. The crystallographic results have shown that one of the compound is the iodo-bridged dimer $I(R_2SO)Pt(\mu\text{-}I)_2Pt(R_2SO)I$, where the two sulfoxide ligands are in *trans* position. Only the DPrSO (Fig. 1) and DBzSO (Fig. 2) compounds gave crystals suitable for crystallographic studies and both crystals were found to have the *trans* geometry. The elemental analysis confirmed the chemical composition. The ^{195}Pt NMR results have shown the presence of two signals separated by about 106 ppm (Table 2). We suggest at this moment that the second species is the same dimer but with a *cis* configuration of the two sulfoxide ligands.

$$2K_2[PtI_4] + 2R_2SO \rightarrow I(R_2SO)Pt(\mu - I)_2Pt(R_2SO)I + 4KI$$

The ^{195}Pt NMR spectra have shown the presence of two signals at average values of −4827 and −4933 ppm, the lower field peak being slightly more intense. Therefore, we have assigned the higher field signal to the *cis* isomer and the lower field one to the *trans* compound. Although there are no example in the literature on ^{195}Pt NMR spectroscopy of such compounds, the chemical shifts seem to be observed in the expected region. The chemical shift of $K_2[PtI_4]$ was reported at −5208 ppm [11], while the one of $K[Pt(NH_3)I_3]$ was found at −4255 ppm [11]. We have not found any report in the literature on a $Pt(II)I_3S$ species. The signals of the TMSO complexes, which contain a four-membered ring were observed at slightly lower fields than the others (Table 2).

The IR spectra have shown the expected sulfoxide vibrations. The ν(S–O) vibrations absorb at higher energy ($\sim$1125 cm^{-1}) than in free sulfoxides, since the ligands are bonded to Pt by the S atom. The ν(Pt–S) vibrations [6,12–15] were found around 430 cm^{-1}.

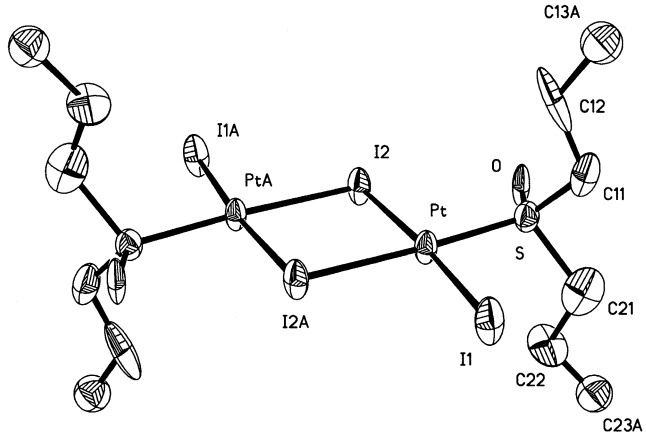


Fig. 1. Labeled diagram of the dimer $(Pt(DPrSO)I)_2(\mu\text{-}I)_2$ (**I**). The ellipsoids correspond to 30% probability. Only the main component is shown for each terminal C atoms.

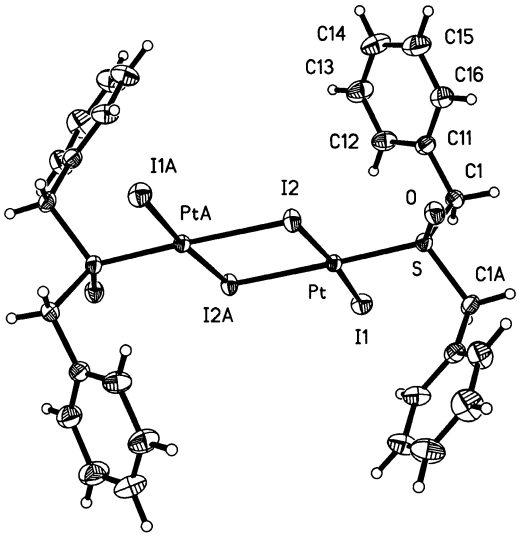


Fig. 2. Labeled diagram of the dimer $(Pt(DBzSO)I)_2(\mu\text{-}I)_2$ (**II**). The ellipsoids correspond to 25% probability.

Table 2
^{195}Pt chemical shifts (ppm) of the complexes $(R_2SO)IPt(\mu\text{-}I)_2Pt(R_2SO)I$

R_2SO	δ (ppm)		$\Delta\delta$ (ppm)	$^{3}J(^{195}Pt-^{1}H)$ (Hz)
DMSO	−4815	−4921	106	26
TMSO	−4760	−4869	109	
DPrSO	−4851	−4957	106	
DBuSO	−4850	−4957	107	
DBzSO	−4855	−4959	104	
MeBzSO	−4832	−4938	106	25(Me)

The ^{1}H and ^{13}C chemical shifts of the sulfoxide ligands are presented in the Section 2 along with the coupling constants. Two series of signals were observed for each product. The more intense series was assigned to the *trans* isomers. The multiplicity of the signals and the coupling constants $J(^{1}H-^{1}H)$ are similar to those determined in the complexes *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$ [4] and in the pyrimidine-bridged dimers $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ [5]. The ^{1}H spectrum of the DMSO iodo-bridged dimer showed only one peak for the methyl groups for each isomer, but for TMSO, all the geminal methylene protons possess different chemical environments. Therefore, there are two signals for each isomer. Each α proton consists of a doublet of doublets of doublets, with J values of 13.1, 7.1 and 6.4 Hz. For the β protons, the separation between the two isomers is not well resolved. For the DPrSO and DBuSO complexes, the geminal methylene protons have also different chemical environments due to limited rotation of the two alkyl chains. Each α proton consists again of

a doublet of doublets of doublets, with J values of 12.1, 10.9 and 5.4 Hz. The separation between the signals of the geminal protons decreases as the distance from the coordination site increases. The signals of the H_γ protons in the DBuSO complex consists of a sextuplet for each isomer (the two H_β are felt as equivalent). The DBzSO and MeBzSO complexes decompose in $CDCl_3$ producing I_2. The deuterated solvent was purified by neutralizing, but the dimers still decompose very rapidly. They were measured in CD_2Cl_2 but there was also some decomposition, although it was slower. For these two compounds, free sulfoxide could be detected in ^1H and ^{13}C NMR spectroscopy.

The sulfoxide proton signals are often multiplets and consequently, the ^{195}Pt satellites are weak and overlap with the other signals, except for DMSO and MeBzSO. $^3J(^{195}Pt-^1H_\alpha)$ values of 26 Hz (DMSO) and 25 Hz (MeBzSO) were measured.

The ^{13}C NMR chemical shifts are in agreement with those reported for Pt(II)–sulfoxide [4,5,16] complexes. We have suggested in the past the presence of inverse polarization of the π-electrons in the S=O bond in complexes of the types $K[Pt(R_2SO)Cl_3]$ [16], $Pt(R_2SO)$-$(pm)Cl_2$ [4] and $\{Pt(R_2SO)Cl_2\}_2(\mu\text{-pm})$ [5]. Bonding of the sulfoxide ligand to the metal atom would reduce the π-electron 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 [17] and Pt–carboxylate complexes [18]. The chemical shifts in ^{13}C NMR spectroscopy are particularly dependent on such mesomeric effects. The coupling constants $^2J(^{195}Pt-^{13}C_\alpha)$ and $^3J(^{195}Pt-^{13}C_\beta)$ could not be determined, probably because of overlap of the signals due to the presence of two isomers in solution, and in some cases, the presence of free ligand (when decomposition occurred in the NMR solvent).

The crystal structures of the two dimers (R = n-Pr and Bz) will be discussed below.

3.2. Complexes trans-Pt(R2SO)(pm)I2

The reactions of the iodo-bridged dimeric species with a slight excess of pyrimidine in dichloromethane produced monomers identified as *trans*-$Pt(R_2SO)(pm)I_2$.

$$I(R_2SO)Pt(\mu-I)_2Pt(R_2SO)I + 2pm \rightarrow 2\ \textit{trans}\text{-}Pt(R_2SO)(pm)I_2$$

The products were characterized by IR and multinuclear NMR spectrocopies. The DBzSO complex was quite unstable in $CDCl_3$ and CD_2Cl_2. The IR spectrum of pyrimidine has been reported and our assignments (Section 2) 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 the free sulfoxides, since the ligands are bonded to Pt by the S atom. The ν(S–O) energies are identical to those observed in the dimeric species described above and in the *cis* and *trans* analogous chloro compounds [4]. One absorption band observed around 450 cm^{-1} was assigned to a ν(Pt–S) vibration as suggested in the literature [6,12–15], while a band around 500 cm^{-1} observed in a few complexes was assigned to the ν(Pt–N) vibration, based also on published results [19,20].

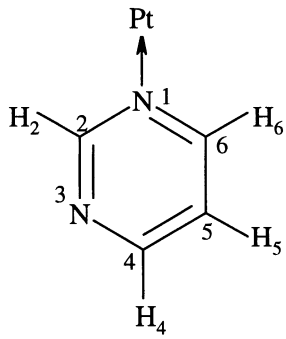
The ^{195}Pt NMR spectra of the complexes *trans*-$Pt(R_2SO)(pm)I_2$ were measured in $CDCl_3$ or CD_2Cl_2 and showed only one signal betweem −4387 and −4438 ppm. These values are at much higher fields than the corresponding chloro analogues *trans*-$Pt(R_2SO)(pm)Cl_2$ (about −3060 ppm) [4]. The ^{195}Pt chemical shifts are summarized in Table 3 and they are close to the one reported for *cis*-$Pt(DMSO)(NH_3)I_2$ (−4405 ppm [21]). The ^{195}Pt NMR chemical shifts do not seem to vary very much with the substituents on the sulfoxide ligand.

The pyrimidine signals of the complexes will first be discussed. The chemical shifts are shown in Section 2. The coupling constants with ^{195}Pt are listed in Table 3. Free pyrimidine is a symmetric molecule (C_{2v} symmetry) which shows three signals in ^1H and ^{13}C NMR. The most deshielded signal is H_2, then H_4, while H_5 is the most shielded. The values have already been reported in CD_2Cl_2 [4] and other solvents [22,23]. The shielding order is the same in ^{13}C NMR.

When pyrimidine is bonded to Pt(II), it is no longer symmetric (Scheme 1) and four different signals will be observed. The deshielding order is now 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, since H_2 couples with the two neighboring ^{14}N nuclei, which possess a large

Table 3
^{195}Pt NMR chemical shifts (ppm) of the complexes *trans*-$Pt(R_2SO)(pm)I_2$, $J(^{195}Pt-^1H)$ and $J(^{195}Pt-^{13}C)$ coupling constants (Hz)

R_2SO	δ(Pt)	$^3J(^{195}Pt-H_\alpha)$	$^3J(^{195}Pt-H_2)$	$^3J(^{195}Pt-H_6)$	$^3J(^{195}Pt-C_5)$	$^2J(^{195}Pt-C_\alpha)$	$^3J(^{195}Pt-C_\beta)$
DMSO	−4387	23	21	30	27	69	
TMSO	−4427		22	30	30	70	27
DPrSO	−4404		21	32	26	56	
DBuSO	−4399		20	30	26	56	15
MeBzSO	−4413	23(Me)	22	34	33	71(Me), 64	
MePhSO	−4438	24	24	33			



Scheme 1.

quadripolar moment, leading to the broadening of the signal.

The pyrimidine proton signals are shifted towards lower field upon coordination, but the shifts are slightly smaller than in the corresponding chloro complexes [4]. The protons H_2 and H_6 are the most affected by coordination as expected. The pyrimidine ^{13}C signals were observed at lower fields than the corresponding chloro analogues [4], probably due to the greater polarizability of iodide.

In ^{1}H and ^{13}C NMR, satellites arising from coupling with the ^{195}Pt nucleus are observed for H_2, H_6 and C_5 (^{3}J) of the pyrimidine ligand (Table 3). The $^{3}J(^{195}Pt-^{1}H_2)$ are smaller (20–24 Hz) than the $^{3}J(^{195}Pt-^{1}H_6)$ coupling constants (30–34 Hz). The couplings $^{3}J(^{195}Pt-^{13}C_5)$ are between 26 and 33 Hz. These values are similar to those observed in *trans*-$Pt(R_2SO)(pm)Cl_2$ [4]. Furthermore, in the MeBzSO complex, $^{2}J(^{195}Pt-^{13}C_2)$ and $^{2}J(^{195}Pt-^{13}C_6)$ coupling constants of 15 Hz could be well observed.

The chemical shifts of the sulfoxide ligands are presented in Section 2. The multiplicity of the signals and the coupling constants $J(^{1}H-^{1}H)$ are identical to those determined in the complexes *cis*- and *trans*-$Pt(R_2SO)(pm)Cl_2$ [4]. For TMSO, all the geminal methylene protons possess different chemical environments. For the other complexes (except DMSO), the geminal methylene protons have also different chemical environments due to limited rotation. The separation between the signals of the geminal protons decreases as the distance from the coordination site increases. The α protons are more deshielded than in the corresponding chloro compounds. The sulfoxide ^{13}C signals were observed at much lower fields than the corresponding chloro analogues [4]. The inversed polarization of the S=O bond seems to be much less important in the iodo compounds, probably since the electronegativity of iodide is much smaller than the one of chloride.

The sulfoxide proton signals are often multiplets and consequently, the ^{195}Pt satellites overlap with the other signals, except for DMSO, MeBzSO and MePhSO. $^{3}J(^{195}Pt-^{1}H_\alpha)$ values of 23–24 Hz were measured. In ^{13}C NMR, the coupling constants $^{2}J(^{195}Pt-^{13}C_\alpha)$ are between 56 and 70 Hz (Table 3), about 7–10 Hz larger than those of the chloro analogues. A few coupling constants $^{3}J(^{195}Pt-^{13}C_\beta)$ were observed between 15 and 27 Hz, in agreement with the values reported for the $K[Pt(R_2SO)Cl_3]$ complexes [16].

3.3. Crystal structures

The crystal structures of the DPrSO (**I**) and DBzSO (**II**) iodo-bridged dinuclear species were determined (Figs. 1 and 2). Selected bond distances and angles for the two structures are shown in Table 4. The results are more precise for the DBzSO compound, since crystal **I** was measured with Cu Kα radiation and it was lost before it could be remeasured with Mo Kα radiation. No other adequate crystal could be prepared. The bridging Pt–I bond in *trans* position to the R_2SO ligand (2.626(3) for **I** and 2.6216(7) Å for **II**) is slightly longer than the one in *trans* position to the terminal iodo ligand (2.596(3), and 2.6011(7) Å). The large *trans* influence of sulfoxides is well known. The terminal Pt–I bonds are 2.586(3) and 2.6110(7) Å, while the Pt–S bonds are 2.199(9) and 2.224(2) Å for **I** and **II**, respectively.

The DPrSO dimer (**I**) contains an inversion center, while in the DBzSO crystal (**II**), the atoms Pt, I1, I2, S and O (and their symmetric atoms) are all on a mirror plane. Therefore, except for the C and H atoms, all the atoms in **II** are in a plane. The coordination around the Pt atom is square planar although there are some deviations in the angles. The I2–Pt–I2A angles are reduced to 85.04(8) for **I** and to 83.65(2)° for **II**, because

Table 4
Selected bond distances (Å) and angles (°) in crystals **I** to **II**

Crystal	**I**	**II**
Bond lengths		
Pt–I1 (terminal)	2.586(3)	2.6110(7)
Pt–I2 (bridging, *trans* to **I**)	2.596(3)	2.6011(7)
Pt–I2A (bridging, *trans* to R_2SO)	2.626(3)	2.6216(7)
Pt–S	2.199(9)	2.224(2)
S–O	1.43(2)	1.471(7)
Bond angles		
I1–Pt–I2	173.79(10)	173.94(2)
I1–Pt–I2A	88.76(9)	90.29(2)
I2–Pt–I2A	85.04(8)	83.65(2)
S–Pt–I1	94.1(2)	93.34(6)
S–Pt–I2	92.1(2)	92.72(6)
S–Pt–I2A	176.8(2)	176.37(6)
Pt–I2–PtA	94.96(8)	96.35(2)
Pt–S–O	117.5(10)	115.4(3)
Pt–S–C	113(2), 118(2)	111.9(2)
C–S–C	96(3)	100.9(4)
O–S–C	102(2), 108(2)	107.8(3)
S–C–C	111(3), 115(4)	112.6(4)

of the strain inside the four membered ring. The Pt–I2–PtA angle is 94.96(8) for **I** and 96.35(2)° for **II**. In crystal **I**, the O atom is not far from the coordination plane (deviation = 0.120 Å), while it is in the crystallographic plane in crystal **II**. This is common for Pt–sulfoxide structures (especially the more hindered ones), since this conformation reduces the steric hindrance caused by the R groups on the sulfoxides.

The crystal structures of three compounds of the type *trans*-Pt(R_2SO)(pm)I_2 were determined. The sulfoxides are DMSO (**III**), DPrSO (**IV**) and TMSO (**V**). Labeled diagrams of the structures are shown in Figs. 3–5. Selected bond distances and angles are listed in Table 5. The Pt–I bonds are between 2.5940(11) and 2.6135(7) Å. They seem slightly larger for the di-*n*-propylsulfoxide complex (**IV**), where the steric hindrance is the largest. The Pt–S bond seems also slightly larger for the DPrSO compound (2.2312(13) Å) than for the others (2.215(3) and 2.216(3) Å). The Pt–N located in *trans* position to the sulfoxides are between 2.042(9) and 2.067(5) Å. These distances are similar to those observed in the corresponding *trans* TMSO chloro complex (2.063(5) Å [4], and larger than those observed in the corresponding *cis* isomers, where the Pt–N bond is in *trans* position to a chloro ligand (ave. 2.028 Å [4]). It is much larger than the value reported for *trans*-Pt$(pm)_2X_2$ (ave. 2.011(6) Å) [1], where the Pt–N bonds are in *trans* position to pyrimidine.

The angles around the Pt atoms are close to the values expected for square-planar coordination, but there are slight deformations due to the bulky sulfoxide. The S–Pt–I angles are slightly larger (ave. 93.21°), while the N–Pt–I are the smallest (ave. 86.88°). The best planes were calculated through the Pt coordination plane and through the pyrimidine ligand. The dihedral angles between the Pt and the pyrimidine planes are 88.6(6)° for **III**, 75.2(2)° for **IV**, and 84.6(3)° for **V**.

In the DMSO complex (**III**), the oxygen atom of the sulfoxide ligand is in the crystallographic mirror coordination plane, while in the DPrSO crystal (**IV**) it is located 0.622(5) Å out of the coordination plane. In the TMSO compound, where the steric hindrance is the smallest (angle C–S–C = 92.9(6)°), the deviation of the O atom from the coordination plane is much greater (1.378(10) Å).

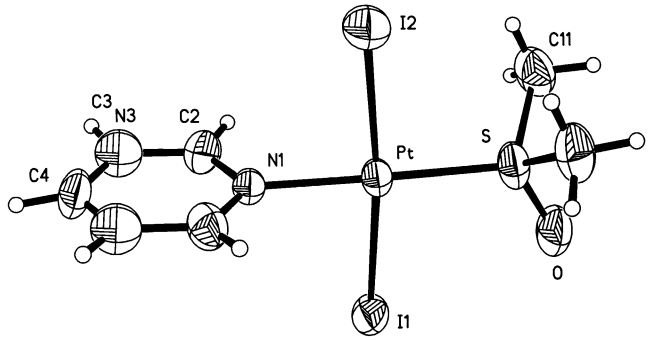


Fig. 3. Labeled diagram of *trans*-Pt(DMSO)(pm)I_2 (**III**). The ellipsoids correspond to 30% probability.

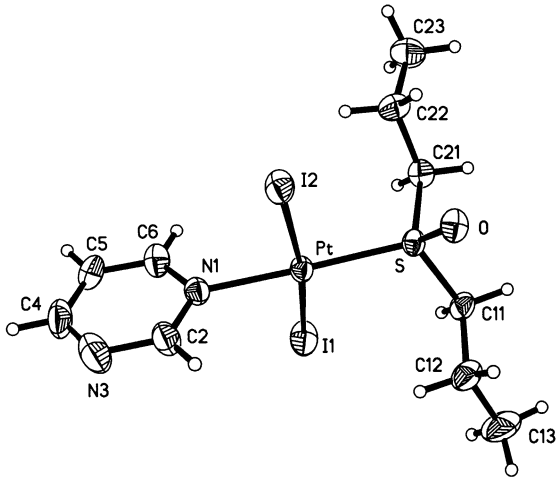


Fig. 4. Labeled diagram of *trans*-Pt(DPrSO)(pm)I_2 (**IV**). The ellipsoids correspond to 30% probability.

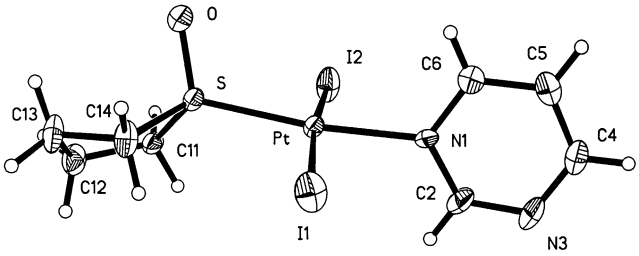


Fig. 5. Labeled diagram of *trans*-Pt(TMSO)(pm)I_2 (**V**). The ellipsoids correspond to 30% probability.

The S atom in the sulfoxide ligands is in an approximate tetrahedral environment. The C–S–C angles (101.7(8)° for DMSO, 101.2(3)° for DPrSO and 92.9(6)° for TMSO) are smaller than the other angles as observed in other Pt–R_2SO structures [4,5,24]. The bond distances and angles of the different sulfoxide ligands are normal. The S–O bond lengths are 1.462(11) (**III**), 1.470(4) (**IV**) and 1.471(9) Å (**V**). The S–C bond might depend on the lengths of the alkyl chains. The average values are 1.771(11) Å for the DMSO compound, 1.795(6) Å for the DPrSO complex and 1.790(13) Å for the TMSO compound. The conformation of the TMSO ligand in crystal **V** is of the envelope type.

The pyrimidine bonds and angles agree well with the values reported for the free ligand [25], for the complexes *trans*-Pt$(pm)_2X_2$ [1], for *cis*- and *trans*-Pt(R_2SO)(pm)Cl_2 [4] and the pyrimidine-bridged dimers $(Pt(R_2SO)Cl_2)_2$(μ-pm) [5]. In the DMSO complex, the pyrimidine N3 atom is equally disordered on two positions. Therefore, the distances are not given in Table 5. The angle N–C–N is larger (ave. 124.3(9)°) than the other internal angles as reported in the above

Table 5
Selected bond distances (Å) and angles (°) in crystals **III** to **V**

Crystal	**III**	**IV**	**V**
Bond lengths			
Pt–I	2.5956(11)	2.6135(7)	2.5940(11)
	2.6058(10)	2.6125(7)	2.5990(11)
Pt–S	2.215(3)	2.2312(13)	2.216(3)
Pt–N	2.042(9)	2.067(5)	2.047(9)
S–O	1.462(11)	1.470(4)	1.471(9)
S–C (ave.)	1.771(11)	1.795(6)	1.790(13)
N–C (ave.)	1.348(10)*	1.341(10)	1.32(2)
C–C (pm, ave.)	*	1.333(11)	1.36 (2)
C–C (R_2SO, ave.)		1.515(10)	1.51(2)
Bond angles			
I–Pt–I	174.02(4)	172.09(2)	172.22(4)
S–Pt–I	93.99(11)	95.00(4)	96.60(8)
	91.99(11)	92.24(4)	89.44(8)
N–Pt–I	87.2(3)	86.8(2)	85.7(2)
	86.9(3)	85.9(2)	88.8(2)
N–Pt–S	178.9(3)	178.6(2)	173.7(2)
Pt–S–O	118.1(5)	117.5(2)	112.0(4)
Pt–S–C (ave.)	110.5(4)	111.3(2)	116.5(5)
Pt–N–C (ave.)	120.6(5)	121.2(5)	121.8(9)
C–S–C	101.7(8)	101.2(3)	92.9(6)
C–S–O (ave.)	107.3(5)	107.1(3)	108.7(7)
C–N1–C	118.6(10)	117.6(5)	116.4(11)
N–C2–N	*	121.6(7)	126.9(14)
C–N3–C	*	117.7(7)	116.7(12)
N–C–C (ave.)	*	122.3(7)	120.3(13)
C–C–C (pm)	*	118.3(7)	119.2(13)

*, Disorder on N3 and C5.

references. The average C–N1–C angle is 117.5(9)°. The binding of pyrimidine 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 [26,27]. 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.

No H-bonding is expected in these types of structures. The molecules are held together in the crystals by van der Waals forces.

4. Conclusion

The reaction of $K_2[PtI_4]$ with sulfoxides produced a dinuclear iodo-bridged complex $I(R_2SO)Pt(\mu\text{-}I)_2Pt(R_2SO)I$. This reaction is very different from the analogous chloro compounds. The crystal structures of the di-*n*-propysulfoxide and the dibenzylsulfoxide complexes were determined by X-ray diffraction. Crystal structures of this type of iodo-bridged Pt complexes have not been reported yet in the literature. The results have shown that the two sulfoxide ligands in the two crystals have the *trans* configuration. Multinuclear magnetic resonance spectroscopy has shown the presence of two compounds in $CDCl_3$ or CD_2Cl_2. The most intense resonance was assigned to the *trans* isomer, and the second signal to the *cis* dimeric compound. In chloroform and in dichloromethane, the compounds decompose producing iodine. It is not soluble in most other solvents. Several attempts to obtain *cis* crystals adequate for crystallographic analysis were not successful. Decomposition probably occurs before crystals can be obtained.

The reactions of these iodo-bridged dimers with pyrimidine were studied. Complexes of the type *trans*-$Pt(R_2SO)(pm)I_2$ were isolated and characterized by infrared and multi-NMR spectroscopies. Contrary to the chloro system, these compounds do not isomerize to the *cis* isomers. We have made several isomerization attempts in different solvents. In chloroform and in dichloromethane, the compounds slowly decompose and they are very sparingly soluble in most other solvents.

The crystal structures of three complexes *trans*-$Pt(R_2SO)(pm)I_2$ were studied by crystallographic methods confirming the NMR results. Sulfoxides have clearly a larger *trans* influence than iodides, 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.

5. Supplementary material

The CIF tables of the five crystal structure determinations have been deposited at the Cambridge Data File Centre. The deposit numbers are: CCDC 190689-190693. 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).

Acknowledgements

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of the project.

References

[1] F.D. Rochon, P.C. Kong, R. Melanson, Can. J. Chem. 59 (1981) 195.
[2] G.V. Fazakerley, K.R. Koch, Inorg. Chim. Acta 36 (1979) 13.
[3] W. Kaufmann, L.M. Venanzi, A. Albinati, Inorg. Chem. 27 (1988) 1178.
[4] N. Nédélec, F.D. Rochon, Inorg. Chim. Acta 319 (2001) 95.

[5] N. Nédélec, F.D. Rochon, Inorg. Chem. 40 (2001) 5236.
[6] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.
[7] P.C. Kong, F.D. Rochon, Inorg. Chim. Acta 37 (1979) L457.
[8] XSCANS and SHELXTL (PC, version 5) programs, Bruker Analytical X-Ray Systems, Madison, WI, 1995.
[9] R.C. Lord, A.L. Marston, F.A. Miller, Spectrochim. Acta 9 (1957) 113.
[10] D.J. Brown, The Chemistry of Heterocyclic Compounds. The Pyrimidines, vol. 16 (Chapter 13), Wiley, New York, 1962.
[11] Y. Qu, N. Farrell, M. Valsecchi, L. de Greco, S. Spinelli, Magn. Res. Chem. 31 (1993) 920.
[12] 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.
[13] Y.N. Kukushkin, V.N. Spevak, Russ. J. Inorg. Chem. 18 (1973) 240.
[14] Y.N. Kukushkin, I.V. Pakhomova, Russ. J. Inorg. Chem. 16 (1971) 226.
[15] B.F.G. Johnson, R.A. Walton, Spectrochim. Acta 22 (1966) 1853.
[16] C. Bensimon, M.Sc. Thesis, Université du Québec à Montréal, Montréal, Canada, 1986.
[17] D.G. Cooper, J. Powell, Inorg. Chem. 16 (1977) 142.
[18] F.D. Rochon, L. Gruia, Inorg. Chim. Acta 306 (2000) 193.
[19] Y.N. Kukushkin, N.V. Ivannikova, K.A. Khokhryakov, Russ. J. Inorg. Chem. 15 (1970) 1595.
[20] K. Nakamoto, P.J. McCarthy, J. Fujita, R.A. Condrate, G.T. Behnke, Inorg. Chem. 4 (1965) 36.
[21] S.J.S. Kerrison, P.J. Sadler, J. Chem. Soc., Chem. Commun. (1977) 861.
[22] D.J. Brown, R.F. Evans, T.J. Batterham, The Chemistry of Heterocyclic Compounds. The Pyrimidines, Supplement 1, vol. 16 (Chapter 13), Wiley, New York, 1970.
[23] G.S. Reddy, R.T. Hobgood, Jr., J.H. Goldstein, J. Am. Chem. Soc. 84 (1962) 336.
[24] (a) R. Melanson, C. de la Chevrotière, F.D. Rochon, Acta Crystallogr., C 41 (1985) 1428;
(b) R. Melanson, F.D. Rochon, Acta Crystallogr., C 43 (1987) 1869;
(c) L. Antolini, U. Folli, D. Iarossi, L. Schenetti, F. Taddei, J. Chem. Soc., Perkin Trans. 2 (1991) 955;
(d) J. Ebbighausen, N. Farrell, K. Lövqvist, Å. Oskarsson, Acta Crystallogr., C 52 (1996) 1091.
[25] P.J. Wheatley, Acta Crystallogr. 13 (1960) 80.
[26] S. Furberg, J.B. Aas, Acta Chem. Scand. A29 (1975) 713.
[27] C. Singh, Acta Crystallogr. 19 (1965) 861.