Acta Chemica Scandinavica, 1996: 50: 1069–1073
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

trans-Influence on Bond Distances in Platinum(II) Complexes. Structures of *trans*-[PtPhI(Me_2S)$_2$] and *trans*-[PtI$_2$(Me_2S)$_2$]

Karin C. Lövqvist[a], Ola F. Wendt*[,a] and Johann G. Leipoldt†[,b]

[a]Inorganic Chemistry 1, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden, and
[b]Department of Chemistry, University of Orange Free State, Bloemfontein 9300, South Africa

Lövqvist, K. C., Wendt, O. F. and Leipoldt, J. G., 1996. *trans*-Influence on Bond Distances in Platinum(II) Complexes. Structures of *trans*-[PtPhI(Me_2S)$_2$] and *trans*-[PtI$_2$(Me_2S)$_2$]. – Acta Chem. Scand. 50: 1069–1073. © Acta Chemica Scandinavica 1996.

trans-[Iodophenylbis(dimethylsulfide)platinum(II)] and *trans*-[diiodobis(dimethylsulfide)platinum(II)] have been synthesized and their crystal structures determined. Both compounds are monoclinic: *trans*-[PtPhI(Me_2S)$_2$] crystallizes in $P2_1/c$ with $a = 8.7126(4)$, $b = 18.779(1)$, $c = 9.1054(4)$ Å, $\beta = 105.444(7)°$ and $Z = 4$ and *trans*-[PtI$_2$(Me_2S)$_2$] in $C2/c$ with $a = 15.641(2)$, $b = 6.046(1)$, $c = 12.845(2)$ Å, $\beta = 101.67(1)$ and $Z = 4$. The structures were refined to $R = 0.054$ and $R = 0.039$, respectively. The coordination geometry around platinum is slightly distorted square-planar in both cases. In the *trans*-diiodo complex, the Pt–I distance is 2.6039(8) Å. When iodide is coordinated *trans* to the phenyl the Pt–I distance is 2.712(1) Å. This increase of 0.108 Å reflects a large ground state *trans* influence of phenyl compared to iodide. The complexes maintain their *trans* configurations in solution as shown by NMR and Raman spectroscopy.

The present work is part of investigations aiming to correlate kinetic properties with structural parameters for Pt^{II} complexes of the type *trans*-[PtXY(Me_2S)$_2$]. The substitution of chloride by iodide in the complex *trans*-[PtPhCl(Me_2S)$_2$] has been studied in methanol solution under pseudo-first-order conditions using a stopped-flow technique.[1] The crystal structure of the substrate has been determined previously[2] and the structure of the reaction product, *trans*-[PtPhI(Me_2S)$_2$], in the solid state and in solution is reported here.

The bond length Pt–Y in a complex *trans*-[PtXY(Me_2S)$_2$] may be tuned by varying the ligand X in a *trans* position to Y. These bond-length changes reflect the ground-state *trans*-influence of X on the Pt–Y bond length. The ligands X may thus be arranged in a series of increasing *trans*-influence[2] and it has been shown that for ligands with predominantly σ-bonding properties, the *trans*-influence runs approximately parallel to the kinetic *trans*-effect, i.e. the lability of Y.[3] The ground-state *trans*-influence is thus one important parameter (among others) for determining the reactivity of a complex, and it can be conveniently studied in the solid state by single-crystal X-ray diffraction.[4] The *trans*-influence of different ligands on the Pt–Cl distance has been extensively studied,[2] but data for other halides are scarce. We here report the structure of *trans*-[PtI$_2$(Me_2S)$_2$] in order to compare the *trans*-influence of phenyl with that of iodide.

Experimental

Syntheses. trans-[PtPhI(Me_2S)$_2$] (**1**): PtPhCl(Me_2S)$_2$,[2] (65.6 mg (0.152 mmol)) was dissolved in 3–4 ml of acetone. A solution of 25.3 mg (0.169 mmol) of NaI (Merck, Pa) in 3–4 ml of acetone was added. Off-white crystals of NaCl precipitated almost immediately and were filtered off. The solution was allowed to stand at room temperature until the solvent had evaporated. Yellow crystals (57 mg, 72%) of PtPhI(Me_2S)$_2$ were formed. ^{1}H-NMR: δ 2.32 (s, $^3J_{Pt-H}$ 58.2 Hz, 12 H) δ 6.92–7.12 (m, 3 H) δ 7.27–7.50 (m, 2 H).

trans-[PtI$_2$(Me_2S)$_2$] (**2**): Recrystallization of [PtI$_2$(Me_2SO)$_2$] prepared as described elsewhere[5] from Me_2S (Merck, zS) gave *trans*-[PtI$_2$(Me_2S)$_2$] as red–brown crystals. ^{1}H-NMR: δ 2.71 (s, $^3J_{Pt-H}$ 44.7 Hz).

Spectroscopic measurements. NMR spectra were recorded on a Varian Unity 300 spectrometer or a Varian XL-200 spectrometer. The ^{195}Pt-NMR spectrum of **2** was recorded in a 10 mm probe at 64.140 MHz field with WALTZ-16 proton decoupling. The sample was a 20 mM solution in $CHCl_3/CDCl_3$. An aqueous solution of K_2PtCl_4 (δ −1639 ppm) was used as external reference.

---

* To whom correspondence should be addressed.
† Deceased 1994.

The ^{1}H-NMR spectrum of **1** was recorded in CD_3OD in a 5 mm probe at 299.949 MHz using the residual peak from CD_2HOD (δ 3.35 ppm) as internal reference. The complex was prepared *in situ* by adding a tenfold excess of iodide to the chloride complex. The ^{1}H-NMR spectrum of **2** was recorded in $CDCl_3$ at 200.057 MHz using the residual peak of $CHCl_3$ (δ 7.26 ppm) as internal reference. Raman spectra were recorded on a Bio-Rad FT-Raman spectrometer.

Structure determinations. Intensity data were collected at room temperature employing monochromated Mo $K\alpha$ radiation. Three standard reflexions were measured at regular intervals. The variation in the standard reflexions was random and within 2%. Laue class and systematic extinctions are consistent with the space group $P2_1/c$ for **1** and $C2/c$ or Cc for **2**. The centrosymmetric space group $C2/c$ was chosen for **2** and this choice is supported by the LS calculations. Unit-cell dimensions were obtained from 50 ($14<\theta<21°$) **1** and 24 ($14<\theta<26°$) **2** θ-values, determined as $\theta_{hkl}=(\omega_{hkl}-\omega_{\bar{h}\bar{k}\bar{l}})/2$. The Pt atom in **1** was found with the Patterson method and in **2** the starting model was achieved by a combination of SAPI91[6] and DIRDIF92.[7] Difference Fourier methods revealed the remaining atoms and the structures were refined by full-matrix least-squares calculations using the TEXSAN crystallographic software package.[8] The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with weights $w=4F_o^2/\sigma^2(F_o^2)$. I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects, the latter by the method based on integration of the crystal shape. The intensities were measured with ω–2θ scans. Reflections with $I<3\sigma(I)$ were considered insignificantly different from the background and excluded in the calculations. All non-hydrogen atoms were refined anisotropically. In **1** the hydrogen atoms in the phenyl ring were placed at calculated positions and included in the structure factor calculations. The methyl hydrogens could not be located. The residual maximum and minimum peaks found in the final difference Fourier map were located at distances of 1.20 Å or shorter to the platinum atoms in both structures. Information concerning the collection and reduction of the data is given in Table 1 and atomic parameters in Tables 2 and 3.

Results and discussion

Description of the structures.

trans-*[PtPhI(Me$_2$S)$_2$] (1).* The compound consists of van der Waals packed complexes. The closest non-hydrogen intermolecular contact is between C(11)···C(22), 3.57(3) Å. The coordination around platinum(II) is distorted square-planar with one σ-bonded phenyl group, one iodide and two thioether molecules bonded via their sulfur atoms in a *trans* configuration. Bond

Table 1. Crystal data, collection and reduction of intensity data and least-squares refinement of the two crystals of *trans*-[PtPhI(Me$_2$S)$_2$] and *trans*-[PtI$_2$(Me$_2$S)$_2$].

Compound	*trans*-[PtPhI(Me$_2$S)$_2$]	*trans*-[PtI$_2$(Me$_2$S)$_2$]
Mol wt	523.36	573.16
Diffractometer type	CAD 4	Huber
Space group	$P2_1/c$	$C2/c$
a/Å	8.7126(4)	15.641(2)
b/Å	18.779(1)	6.046(1)
c/Å	9.1054(4)	12.845(2)
β/°	105.444(7)	101.67(1)
V/Å^3	1436.0(1)	1189.6(3)
Z	4	4
D_x/g cm^{-3}	2.42	3.20
μ/mm^{-1}	12.25	17.23
Crystal size/mm	0.29 × 0.17 × 0.12	0.25 × 0.15 × 0.15
λ/Å	0.71069	0.71069
Range of transmission factors	0.28–0.42	0.40–0.68
Secondary extinction coeff.	5.18×10^{-7}	6.89×10^{-7}
θ-interval	1.50–27.50	3.00–28.00
ω-2θ scan width, Δω/°	0.74 + 0.34 tan θ	0.70 + 0.50 tan θ
$\sigma(I)/I$ requested in a scan	0.028	0.028
No. measured reflexions	3634	2090
No. unique reflexions	3434	2035
No. reflexions used in the refinements, m	2381	1234
No. variables, n	128	44
hkl range	$-11\leqslant h\leqslant 11$, $0\leqslant k\leqslant 24$, $0\leqslant l\leqslant 11$	$0\leqslant h\leqslant 20$, $0\leqslant k\leqslant 8$, $-16\leqslant l\leqslant 16$
$R=\Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$	0.054	0.039
$R_w=[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.063	0.051
$S=[\Sigma w(\|F_o\|-\|F_c\|)^2/(m-n)]^{1/2}$	2.28	1.88
$(\Delta/\sigma)_{max}$	0.001	0.003
$\Delta\rho_{max/min}$	2.23/−2.98	2.14/−1.90

Table 2. Positional parameters and B_{eq} for *trans*-$[\mathrm{PtPhI(Me_2S)_2}]$.

Atom	*x*	*y*	*z*	B_{eq}
Pt	0.01800(6)	0.11608(3)	0.18177(6)	2.57(2)
I	0.2840(1)	0.08161(6)	0.4026(1)	4.19(4)
S(1)	0.1868(5)	0.1649(2)	0.0546(5)	3.9(1)
S(2)	−0.1259(4)	0.0578(2)	0.3202(4)	3.3(1)
C(1)	−0.1728(17)	0.1452(7)	0.0204(15)	3.1(5)
C(2)	−0.2318(19)	0.1027(7)	−0.1132(17)	3.6(6)
C(3)	−0.3650(18)	0.1229(10)	−0.2239(16)	4.4(7)
C(4)	−0.4521(20)	0.1844(12)	−0.2087(21)	5.5(8)
C(5)	−0.3968(19)	0.2249(8)	−0.0782(19)	4.3(7)
C(6)	−0.2595(19)	0.2048(8)	0.0332(17)	3.9(6)
C(11)	0.2499(25)	0.0882(10)	−0.0403(25)	6(1)
C(12)	0.0851(24)	0.2143(10)	−0.1176(21)	6(1)
C(21)	−0.1096(25)	0.1078(9)	0.4978(19)	5.3(8)
C(22)	−0.3428(21)	0.0622(10)	0.2405(27)	6(1)
H(1)	−0.1781	0.0600	−0.1254	4.3
H(2)	−0.3993	0.0947	−0.3132	5.3
H(3)	−0.5452	0.1976	−0.2851	6.6
H(4)	−0.4526	0.2667	−0.0641	5.2
H(5)	−0.2248	0.2336	0.1215	4.7

Table 3. Positional parameters and B_{eq} for *trans*-$[\mathrm{PtI_2(Me_2S)_2}]$.

Atom	*x*	*y*	*z*	B_{eq}
Pt	3/4	1/4	1/2	2.28(2)
I	0.59453(5)	0.2981(2)	0.38271(6)	3.97(4)
S	0.7007(2)	0.0803(5)	0.6380(2)	3.2(1)
C(1)	0.6008(10)	0.2178(23)	0.6621(12)	4.7(6)
C(2)	0.6548(11)	−0.1813(23)	0.5858(12)	5.2(7)

Table 4. Distances (in Å) and angles (in °) in *trans*-$[\mathrm{PtPhI(Me_2S)_2}]$ and *trans*-$[\mathrm{PtI_2(Me_2S)_2}]$.

trans-$[\mathrm{PtPhI(Me_2S)_2}]$		*trans*-$[\mathrm{PtI_2(Me_2S)_2}]$	
Pt–I	2.712(1)	Pt–I	2.6039(8)
Pt–S(1)	2.291(4)	Pt–S	2.310(2)
Pt–S(2)	2.281(4)		
Pt–C(1)	1.98(1)		
S(1)–C(11)	1.84(2)	S–C(1)	1.81(1)
S(1)–C(12)	1.83(2)	S–C(2)	1.82(1)
S(2)–C(21)	1.84(1)		
S(2)–C(22)	1.84(2)		
C(1)–C(2)	1.43(2)		
C(1)–C(6)	1.37(2)		
C(2)–C(3)	1.37(2)		
C(3)–C(4)	1.41(3)		
C(4)–C(5)	1.39(3)		
C(5)–C(6)	1.40(2)		
I–Pt–S(1)	86.2(1)	I–Pt–S′	85.65(6)
I–Pt–S(2)	87.9(1)	I–Pt–S	94.35(6)
I–Pt–C(1)	177.7(4)	I–Pt–I	180
S(1)–Pt–S(2)	173.0(1)	S–Pt–S	180
S(1)–Pt–C(1)	92.3(4)		
S(2)–Pt–C(1)	93.8(4)		
Pt–S(1)–C(11)	103.7(7)	Pt–S–C(1)	105.4(4)
Pt–S(1)–C(12)	113.9(7)	Pt–S–C(2)	111.7(4)
C(11)–S(1)–C(12)	97.6(9)	C(1)–S–C(2)	99.4(6)
Pt–S(2)–C(21)	108.4(6)		
Pt–S(2)–C(22)	114.8(6)		
C(21)–S(2)–C(22)	99(1)		
Pt–C(1)–C(2)	121(1)		
Pt–C(1)–C(6)	122(1)		
C(2)–C(1)–C(6)	116(1)		
C(1)–C(2)–C(3)	121(1)		
C(2)–C(3)–C(4)	122(1)		
C(3)–C(4)–C(5)	117(1)		
C(4)–C(5)–C(6)	121(2)		
C(1)–C(6)–C(5)	123(1)		
S(2)–Pt–C(1)–C(2)	−93(1)		
S(2)–Pt–C(1)–C(6)	84(1)		
I–Pt–S1–C(11)	82.5(7)	I–Pt–S–C(1)	−67.4(5)
I–Pt–S1–C(12)	−172.6(7)	I–Pt–S–C(2)	39.6(5)
I–Pt–S2–C(21)	67.1(7)		
I–Pt–S2–C(22)	176.6(8)		
C(1)–Pt–S(2)–C(22)	−1.8(9)		
C(1)–C(2)–C(3)–C(4)	−2(2)		
Pt···Pt	5.433(1)	Pt···Pt	6.046(1)

distances and bond angles are given in Table 4. One methyl group on each $\mathrm{Me_2S}$ molecule is oriented in an eclipsed configuration to the carbon bonded to platinum, while the two methyl groups on the other $\mathrm{Me_2S}$ molecule point at separate sides of the coordination plane (Fig. 1). These orientations avoid disturbing interference with the iodide ligand. The eclipsed conformation also causes the sulfur atoms to move somewhat toward the iodide giving I–Pt–S angles somewhat smaller, and C–Pt–S angles somewhat larger than the expected 90°. The largest deviations from the least-squares plane through $\mathrm{PtCIS_2}$, 0.075(4) and 0.063(4) Å, are shown by the sulfur atoms. The phenyl group is approximately perpendicular to the coordination plane; the dihedral angle between the least-squares planes is 96°.

In the pseudo-octahedral positions relative to the coordination plane there is one methyl group with Pt···C(12), 3.64(2) Å and one hydrogen from the phenyl group, Pt···H(C2), 3.7 Å (Fig. 2). This is somewhat similar to the packing of the complexes in *trans*-$[\mathrm{PtPhCl(Me_2S)_2}]$.[3] However, the Pt···H distance found in the chloro analogue is shorter, about 3.0 Å. The shortest Pt···Pt distance is 5.433(1) Å. Selected distances and angles are given in Table 4.

trans-$[\mathrm{PtI_2(Me_2S)_2}]$ *(2).* This compound consists of van der Waals packed square-planar complexes of $[\mathrm{PtI_2(Me_2S)_2}]$, where the sulfurs in the two thioether molecules and the iodides are in a *trans* configuration (Fig. 3). The shortest intermolecular distances 3.95(2) and 3.96(1) Å are observed between C(1)···C(2)′ and Pt···C(1)′, respectively, in a distorted octahedral position to platinum creating a chain of complexes (Fig. 4). The platinum atom is located on an inversion centre resulting in a strictly planar coordination geometry. The methyl groups are oriented in a staggered conformation relative to the iodide ligands. The deviation from the expected 90° of the angles I–Pt–S, 94.35(6) and 85.65(6)°, respectively, is probably caused by a steric repulsion between the methyl groups and iodide. The closest Pt···Pt distance, 6.046(1) Å, is equal to the shortest unit cell axis.

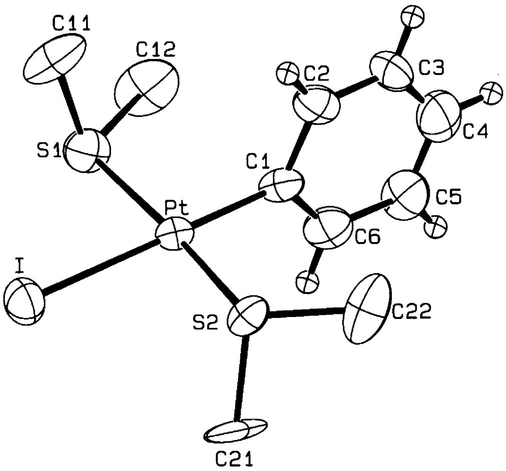

Fig. 1. Ortep drawing with atomic numbering of *trans*-[PtPhI(Me$_2$S)$_2$] (**1**). The ellipsoids denote 50% probability.

Selected bond distances, bond angles and torsion angles are given in Table 4.

Bond length variations. The flexible rotational conformation of the Me$_2$S ligands found in these complexes has also been observed in *trans*-[PtPhCl(Me$_2$S)$_2$].[3] This flexibility indicates a relatively small energy barrier for rotation around the Pt–S bond. The observed variation in the Pt–S distances, 2.281(4) and 2.291(4) Å in **1**; 2.310(2) Å in **2**, might be due to this flexibility. However, the difference in the Pt–S distances in **1** compared to **2** may also reflect a difference in *cis*-influence of the phenyl group compared to an iodide. The latter idea that the phenyl group has a different *cis*-influence is further supported by the differences in Pt–S distances observed in *trans*-[PtPhCl(Me$_2$S)$_2$] ranging between 2.279(4) and 2.298(3) Å,[2] and in *trans*-[PtI$_2$(tht)$_2$],[9] 2.310(1) and 2.309(1) Å, which are comparable to those observed in *trans*-[PtPhI(Me$_2$S)$_2$] and *trans*-[PtI$_2$(Me$_2$S)$_2$], respectively.

The Pt–I distance in **2**, 2.6039(8) Å is not significantly different from those observed in *trans*-[PtI$_2$(tht)$_2$] 2.606(2) and 2.616(1) Å,[9] or those in [PtI$_4$]$^{2-}$, 2.606(2) and 2.616(1) Å.[10] In **1** the Pt–I distance is substantially longer, 2.712(1) Å, which certainly reflects a larger *trans*-influence of a phenyl compared with an iodide.

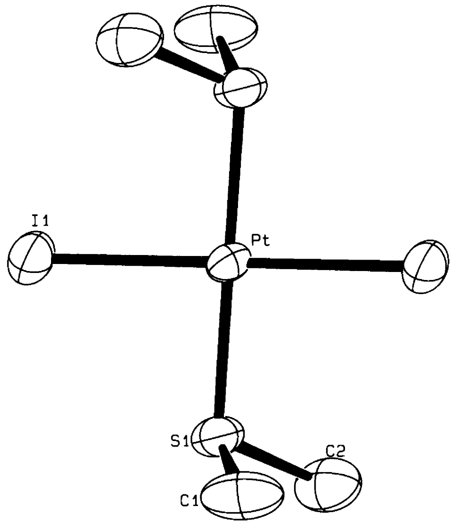

Fig. 3. Ortep drawing with atomic numbering of *trans*-[PtI$_2$(Me$_2$S)$_2$] (**2**). The ellipsoids denote 50% probability.

The observed Pt–C distance in *trans*-[PtPhI(Me$_2$S)$_2$], 1.98(1) Å, is not significantly different from other Pt–C(phenyl) distances observed *trans* to a chloride[2] ligand, 1.99(1)–2.004(5) Å. It is, however, somewhat longer than that observed *trans* to a peroxo group, 1.93(1) in *trans*-[PtPh(OO-Bu^t)(PPh$_3$)$_2$], indicating a somewhat smaller *trans*-influence of the peroxo group as compared with the halides. When the phenyl is *trans* to a sulfur-bonded ligand like dimethyl sulfide in *cis*-[PtPh$_2$(Me$_2$S)$_2$][11] and dimethyl sulfoxide in *cis*-[PtPh$_2$(Me$_2$SO)$_2$][12] the Pt–C distance is slightly longer than those found *trans* to the halide ligands, 2.036(7), 2.010(7) and 2.043(5), 2.049(6) Å, respectively. In *trans*-[PtPh$_2$(PPh$_3$)$_2$][13] the Pt–C distance *trans* to phenyl is 2.080(8) Å, which is significantly longer compared to halogen as a *trans* ligand. This indicates that the *trans*-

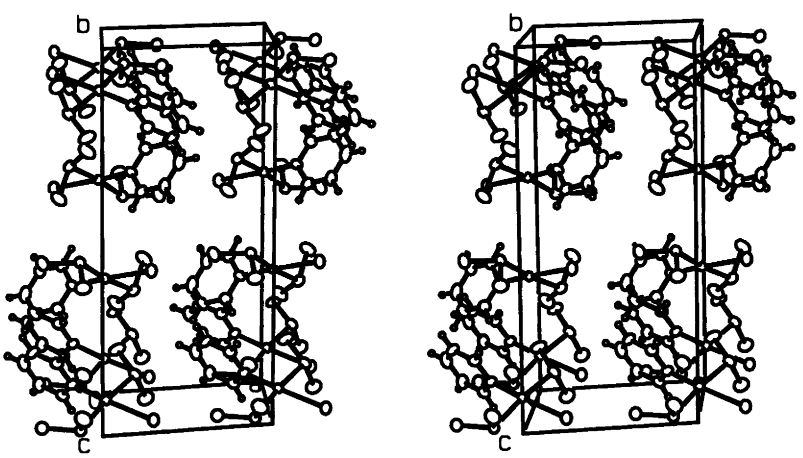

Fig. 2. Stereo view of the packing in *trans*-[PtPhI(Me$_2$S)$_2$] (**1**). The ellipsoids denote 30% probability.

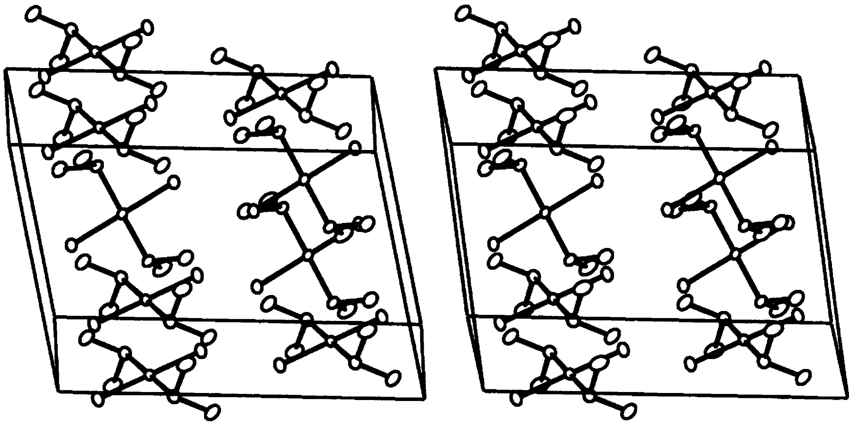

Fig. 4. Stereo view of the packing in *trans*-[PtI$_2$(Me$_2$S)$_2$] (**2**). The ellipsoids denote 30% probability.

influence on the Pt–C(phenyl) bond decreases in the order Ph > S > Cl, I > OO(peroxo group).

Structures based on NMR and Raman spectra. The ^{1}H-NMR spectrum of **1** shows the presence of only one type of Me$_2$S molecules. This fact together with the large $^3J_{\mathrm{Pt-H}}$ value shows that the *trans* configuration is maintained in solution.[14] It is more difficult to decide the configuration of **2** from its ^{1}H-NMR spectrum. However, the Raman spectra of **2** in the solid state and in CH$_2$Cl$_2$ solution both display a band at 149 cm^{-1}. This band is very intense in the solid state and can most certainly be assigned to the symmetric ν(Pt–I). The IR-spectrum of **2** displays a Pt–I vibration at 188 cm^{-1}.[15] The absence of this band (due to the asymmetric stretching) in the Raman solution spectra shows that the *trans*-configuration is maintained in solution. The ^{195}Pt-NMR spectrum of **1** with a metal resonance of −4225 ppm has been reported earlier.[1] The spectrum of **2** consists of a singlet at −4796 ppm in good agreement with the reported value of −4805 ppm.[16] It can be noted that replacing an iodide with a phenyl gives a shift to lower field, whereas the opposite is true, when the halide in the corresponding dichloro and dibromo complexes is replaced by phenyl.[1,17] It may be concluded that the molecular structures of *trans*-[PtPhI(Me$_2$S)$_2$] and *trans*-[PtI$_2$(Me$_2$S)$_2$] in the solid state are maintained in solution. The ground-state *trans*-influence on a Pt–I bond length is Ph > I and on a Pt-C bond length Ph > S > Cl, I > OO(peroxo).

Acknowledgement. We thank Prof. L. I. Elding and Dr. Å. Oskarsson for valuable discussions of this work. It was supported financially by the Swedish Natural Science Research Council (NFR) and the Crafoord Foundation through grants to L. I. Elding and Å Oskarsson and through a travel grant to J. G. L. for a visiting professorship at Lund in 1992 (NFR).

References

1. Wendt, O. F., Oskarsson, Å., Leipoldt, J. G. and Elding, L. I. *To be published.*
2. Kapoor, P., Kukushkin, V. Y., Lövqvist, K. and Oskarsson, Å. *J. Organomet. Chem.* (1996). *In press.*
3. Zumdahl, S. S. and Drago, R. S. *J. Am. Chem. Soc. 90* (1968) 6669.
4. Appleton, T. G., Clark, H. C. and Manzer, L. E. *Coord. Chem. Rev. 10* (1973) 335.
5. Lövqvist, K. *Acta Crystallogr., Sect C2* (1996). *In press.*
6. Fan Hai-Fu. *Structure Analysis Programs with Intelligent Control*, Rigaku Corporation, Tokyo, Japan 1991.
7. Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. and Smykalla, C. *The DIRDIF Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, Netherlands 1992.
8. Molecular Structure Corporation. *TEXSAN. Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 1989.
9. Oskarsson, Å., Norén, B., Svensson, C. and Elding, L. I. *Acta Crystallogr., Sect. B46* (1990) 748.
10. Olsson, L.-F. and Oskarsson, Å. *Acta Chem. Scand. 43* (1989) 811.
11. Alibrandi, G., Bruno, G., Lanza, S., Minniti, D., Romeo, R. and Tobe, M. L. *Inorg. Chem. 26* (1987) 185.
12. Bardi, R., Del Pra, A., Piazzesi, A. M. and Trozzi, M. *Cryst. Struct. Commun. 10* (1981) 301.
13. Ertl, J., Debaerdemaeker, T. and Brune, H. A. *Chem. Ber. 115* (1982) 3860.
14. Miyamoto, T. *J. Organomet. Chem.* 134 (1977) 335.
15. Allkins, J. R. and Hendra, P. J. *J. Chem. Soc. A* (1967) 1326.
16. Calculated from the value −272 ppm (to high frequency of 21.4 MHz) reported in Ref. 17. The value is also given in Pregosin, P. S. *Coord. Chem. Rev., 44,* (1982) 247 where it is erroneously reported to be −5789 ppm.
17. Goggin, P. L., Goodfellow, R. J., Haddock, S. R., Taylor, B. F., Marshall, I. R. H. *J. Chem. Soc., Dalton Trans* (1976) 459.

Received January 4, 1996.