

Trans influence in platinum(II) complexes. Phenylation of Pt(II) dialkylsulfide complexes by BPh_4^- and SnPh_3H . Crystal structures of two polymorphs of *trans*-chlorobis(dimethylsulfide)(phenyl)platinum(II)

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Abstract

Two methods of phenylation of platinum(II) complexes are described, one by heating $[\text{PtCl}(\text{dms})_3](\text{BPh}_4)$ and another starting from triphenyltin hydride and $[\text{PtCl}_2(\text{dms})_2]$, dms = dimethylsulfide. Two different polymorphs of *trans*- $[\text{PtPhCl}(\text{dms})_2]$ are obtained, one monoclinic and one triclinic. The monoclinic form contains two crystallographically different complexes. The main difference between the molecular geometries in the polymorphs is the orientation of the dms ligands. Distances found are Pt–Cl, 2.403–2.420; Pt–S, 2.279–2.298 and Pt–C, 1.99–2.00 Å. A comparison of some Pt–Cl bond distances obtained from the literature reveals that the *trans* influence increases in the following order: $\text{Cl} < \text{S} \leq \text{Sn}$, $\text{P} < \text{C}$, $\text{H} < \text{Si}$.

Keywords: Platinum(II); X-ray diffraction; Crystal structure; Thioether complexes; Phenylation; *Cis-trans* influence; Polymorphs

1. Introduction

The present work is part of an investigation aiming to correlate kinetic, thermodynamic and structural properties of Pt(II)-complexes of the type *trans*- $[\text{PtClX}(\text{dms})_2]$, where dms = dimethylsulfide and X is a ligand with a large *trans* influence [1]. The *cis* and *trans* influences on the Pt–Cl bond are defined as the abilities of the ligands in *cis* and *trans* positions to affect the Pt–Cl bond length [2–4] and the *cis* and *trans* influences are expected to run approximately parallel to the *trans* effect, i.e. the lability of Cl. The lability of Cl may thus at least partly be tuned by the *trans* influence of X and the bulkiness of the thioether ligands (associative reaction mechanism).

In previous communications we have shown that the

trans influence on a bond distance may dominate over other factors, such as packing forces and *cis* influence [5,6]. In *trans*- $[\text{PtClX}(\text{dms})_2]$, the Pt–Cl distances are 2.30 and 2.31 Å for X = Cl and dms, respectively [7,23]. Pt(II) is a soft metal acceptor and thus prone to form more strong bonds with soft donor atoms than with hard ones. This will affect the bond in *trans* position, and it is anticipated that the *trans* influence is correlated to the hard/soft properties of the donor atoms involved. Therefore we have tried to synthesize complexes with X ligands having the soft donor atoms C or Sn. This paper reports two synthetic routes for the complex *trans*- $[\text{PtPhCl}(\text{dms})_2]$ and the crystal structures of two polymorphs.

2. Experimental

2.1. Synthesis of *trans*- $[\text{PtPhCl}(\text{dms})_2]$ by thermal conversion of $[\text{PtCl}(\text{thioether})_3](\text{BPh}_4)$, thioether = dimethyl sulfide or 1,4-thioxane

$[\text{PtCl}(\text{dms})_3](\text{BPh}_4)$ was prepared according to Morita and Bailar [8]. $[\text{PtCl}(\text{dms})_3](\text{BPh}_4)$ (0.210 g) was placed in a 30 ml beaker. The complex was heated for 3 h at

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95°C. The mass loss on heating was 0.060 g (29%). The crude product was washed with diethylether, recrystallised from ethanol and dried in air at room temperature. The yield of *trans*-[PtPhCl(dms)₂] was 0.070 g (57%, based on Pt).

The m.p. is 137°C (lit. 92°C [9]). Anal. Found: C, 27.4; H, 4.0; Cl, 8.4. C₁₀H₁₇ClPtS₂ Calc.: C, 27.8; H, 4.0; Cl, 8.2%. ¹H NMR spectrum in CD₂Cl₂ gave δ_{SMe} 2.33 ppm; ³J_{PH} = 57 Hz (lit. 2.3 ppm; ³J_{PH} = 57 Hz [9]). IR spectrum in Nujol gave ν_{PCl} 272 cm⁻¹. Colorless crystals suitable for an X-ray single crystal study were obtained by rapid recrystallisation from boiling ethanol. A single crystal selected for the structure determination turned out to be monoclinic (*P*2₁/*n*), this phase is denoted polymorph 1 below.

Thermal breakdown of [PtCl(dms)₃](BPh₄) can also be carried out in nitromethane solution. [PtCl(dms)₃](BPh₄) (0.345 g) was dissolved in 8 ml nitromethane and heated to 100°C for 3 h. The solvent was removed in vacuo and the residue was recrystallised from ethanol. The yield of *trans*-[PtPhCl(dms)₂], 61%, is about the same as in the case of the solid state reaction, 57%.

2.2. Synthesis of *trans*-[PtPhCl(dms)₂] from triphenyltin hydride and [PtCl₂(dms)₂]

Triphenyltin hydride (0.17 g, 0.48 mmol) was added to a suspension of [PtCl₂(dms)₂] (0.20 g, 0.51 mmol) in 10 ml benzene. Immediately the color of the solution became orange–brown. It was left under stirring overnight and a dark brown solid separated. The benzene was removed under vacuum and the product was redissolved in 20 ml of benzene and filtered. The dark brown filtrate was left to evaporate; it gave a dark brown solid which was washed with acetone to give pale yellow crystals suitable for single crystal X-ray diffraction, and a brown acetone solution. The pale yellow crystals were analysed by single crystal X-ray diffraction and they turned out to be two different polymorphs of *trans*-[PtPhCl(dms)₂], the previously obtained polymorph 1 and a second one, denoted polymorph 2, triclinic *P* $\bar{1}$. The acetone solution was evaporated, resulting in a brown solid. ¹H NMR spectrum in CD₂Cl₂ shows that the brown solid does not contain the starting material but, apart from signals of *trans*-

Table 1

Crystal data, collection and reduction of intensity data and least-squares refinement of the two polymorphs of *trans*-[PtCl(dms)₂Ph]

Compound	1	2
Mol. wt	431.91	431.91
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.106(1)	7.9076(6)
<i>b</i> (Å)	13.046(3)	8.9994(6)
<i>c</i> (Å)	20.939(2)	9.998(1)
α (°)	90	85.88(1)
β (°)	94.39(1)	80.600(9)
γ (°)	90	76.668(7)
<i>V</i> (Å ³)	2752.4(6)	682.56(9)
<i>Z</i>	8	2
<i>D</i> _x (g cm ⁻³)	2.084	2.101
μ (mm ⁻¹)	10.76	10.84
Crystal size (mm ³)	0.2 × 0.18 × 0.19	0.25 × 0.22 × 0.05
λ (Å)	0.71069	0.71069
Range of transmission factors	0.17–0.25	0.13–0.44
θ-interval	3.00–25.00	3.00–28.00
ω–2θ scan width, Δω (°)	0.7 + 0.5 tan θ	1.00 + 0.5 tan θ
σ(<i>I</i>)/ <i>I</i> requested in a scan	0.028	0.028
Number of measured reflections	5179	3483
Number of unique reflections	5038	3276
Number of reflections used in the refinements, <i>m</i>	3443	2722
Number of variables, <i>n</i>	253	147
<i>h</i> , <i>k</i> , <i>l</i> range	–12 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 24	–10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 11, –13 ≤ <i>l</i> ≤ 13
<i>R</i> _{int}	0.043	0.053
<i>R</i> = Σ(<i>F</i> _o – <i>F</i> _c)/Σ <i>F</i> _o	0.038	0.025
<i>R</i> _w = [Σw(<i>F</i> _o – <i>F</i> _c) ² /Σ <i>F</i> _o ²] ^{1/2}	0.051	0.028
<i>S</i> = [Σw(<i>F</i> _o – <i>F</i> _c) ² /(<i>m</i> – <i>n</i>)] ^{1/2}	1.86	1.12
(Δ/σ) _{max}	0.01	0.04
ρ _{max} /min	0.81/–2.39	0.69/–1.11

[PtPhCl(dms)₂] (δ 2.28 ppm; $^3J_{\text{PtH}} = 57$ Hz), another group of peaks (δ 2.54 ppm; $^3J_{\text{PtH}} = 50$ Hz) can tentatively be attributed to *cis*-[PtPhCl(dms)₂]. So far we have not been able to isolate the second compound in the brown solid.

2.3. Structure determinations of the two polymorphs of *trans*-[PtPhCl(dms)₂]

A single crystal for the structure determination of polymorph **1** was selected from the batch obtained via thermal conversion of [PtCl(dms)₃]BPh₄, while a crystal of polymorph **2** was selected from the synthesis starting from triphenyltin hydride and [PtCl₂(dms)₂]. The intensity data were collected at room temperature employing monochromated Mo K α radiation. Two and three standard reflections were measured at regular intervals (120 min) for polymorphs **1** and **2** respectively. The variation in the standards was within 2%. Laue class and systematic extinctions are consistent with the space group $P2_1/n$ for **1** and $P\bar{1}$ for **2**. Unit cell dimensions were obtained from 49 ($7 < \theta < 19^\circ$) (**1**) and 50 ($7 < \theta < 22^\circ$) (**2**) θ -values, determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$. The Pt atoms in **1** were found by direct methods and in **2** with the Patterson method. Difference Fourier methods revealed the rest of the

structures, and they were refined by full-matrix least-squares calculations using the TEXSAN crystallographic software package of Molecular Structure Corporation [10]. The function minimised was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 4F_o^2/\sigma^2(F_o)$. I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects, the latter based on path lengths obtained by integration of the crystal shape. The intensities were measured with ω - 2θ scans. Reflections with $I < 2\sigma(I)$ (**1**) and $I < 3\sigma(I)$ (**2**) 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 the methyl hydrogens were not located. In **2** all hydrogen atoms in the phenyl ring were found and their positions were refined, as well as the isotropic temperature factors. Some hydrogen atoms were located in the methyl groups and the rest were placed at calculated positions. These hydrogen atom parameters were not refined. Information concerning the collection and reduction of the data is given in Table 1 and atomic coordinates in Tables 2 and 3. Tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

Phase analyses of the solid compounds obtained from

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$), $B_{\text{eq}} = (8\pi^2/3)\sum_i U_{ij}a_i^*a_j^*a_i a_j$ for polymorph **1** of *trans*-[PtCl(dms)₂Ph]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Pt(1)	0.53101(5)	0.10229(4)	0.12684(2)	2.90(2)
Pt(2)	0.47559(5)	0.13191(4)	0.38665(2)	2.89(2)
Cl(1)	0.7467(3)	0.0629(3)	0.0923(2)	4.8(2)
Cl(2)	0.2579(4)	0.1554(3)	0.4231(2)	6.1(2)
S(1)	0.5695(3)	0.2754(2)	0.1368(2)	3.7(1)
S(2)	0.4656(4)	-0.0659(3)	0.1273(2)	5.3(2)
S(3)	0.4394(3)	-0.0385(2)	0.3645(2)	3.6(2)
S(4)	0.5410(4)	0.2973(3)	0.4044(2)	5.4(2)
C(1)	0.349(1)	0.133(1)	0.1519(6)	3.5(6)
C(2)	0.326(1)	0.165(1)	0.2143(6)	4.1(7)
C(3)	0.203(2)	0.185(1)	0.2332(7)	5.5(8)
C(4)	0.092(2)	0.173(1)	0.190(1)	6(1)
C(5)	0.112(1)	0.143(1)	0.1272(9)	5.7(9)
C(6)	0.236(1)	0.124(1)	0.1098(7)	4.7(7)
C(7)	0.658(1)	0.1077(9)	0.3599(6)	3.1(5)
C(8)	0.683(1)	0.084(1)	0.2968(6)	3.8(6)
C(9)	0.812(1)	0.068(1)	0.2783(6)	4.1(7)
C(10)	0.916(1)	0.070(1)	0.3224(8)	4.4(7)
C(11)	0.897(1)	0.092(1)	0.3843(7)	4.5(7)
C(12)	0.770(1)	0.114(1)	0.4037(6)	3.8(6)
C(13)	0.521(3)	0.328(1)	0.059(1)	12(2)
C(14)	0.744(2)	0.300(2)	0.143(1)	12(2)
C(15)	0.577(2)	-0.130(1)	0.1829(9)	8(1)
C(16)	0.513(3)	-0.127(1)	0.0550(8)	9(1)
C(17)	0.425(2)	-0.099(1)	0.4410(8)	9(1)
C(18)	0.272(1)	-0.055(1)	0.329(1)	8(1)
C(19)	0.420(2)	0.367(1)	0.451(1)	9(1)
C(20)	0.516(3)	0.360(1)	0.329(1)	11(2)

Table 3

Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) $B_{\text{eq}} = (8\pi^2/3)\sum_i U_{ij}a_i^*a_j^*a_i a_j$ for polymorph 2 of *trans*-[PtCl(dms)₂Ph]

Atom	x	y	z	B_{eq}
Pt	0.01412(2)	0.07996(2)	0.22334(2)	2.58(1)
Cl	−0.1990(2)	0.3071(2)	0.1697(2)	4.46(8)
S(1)	0.2102(2)	0.2093(2)	0.2769(2)	4.20(9)
S(2)	−0.1817(2)	−0.0537(2)	0.1747(1)	3.66(8)
C(1)	0.1903(6)	−0.1085(5)	0.2677(5)	2.7(2)
C(2)	0.3040(7)	−0.1974(6)	0.1676(5)	3.2(3)
C(3)	0.4247(7)	−0.3285(6)	0.1987(6)	3.5(3)
C(4)	0.4354(8)	−0.3728(6)	0.3327(6)	4.0(3)
C(5)	0.3269(8)	−0.2867(7)	0.4344(6)	4.0(3)
C(6)	0.2058(7)	−0.1564(6)	0.4023(5)	3.2(3)
C(11)	0.092(1)	0.377(1)	0.363(1)	8.1(7)
C(12)	0.300(2)	0.290(2)	0.125(1)	13(1)
C(21)	−0.0992(8)	−0.2555(7)	0.1854(7)	4.9(4)
C(22)	−0.348(1)	−0.033(1)	0.3249(9)	6.0(5)

the two syntheses, using the powder method, revealed that both the monoclinic, polymorph 1, and the triclinic, polymorph 2, phases are present in both samples. The relative intensities indicate that polymorph 1 is the more common one in both cases.

2.4. Analytical methods and apparatus

Elemental analyses for C, H and Cl were performed at Mikrokemi AB (Uppsala, Sweden) and Pt was determined gravimetrically by the authors. Melting or decomposition points were determined in capillaries with a Rudolph Grave AB electrothermal melting point apparatus. IR were recorded in Nujol using a Nicolet model 20 SXC-IR spectrometer. ^1H NMR were recorded at 299.4 MHz on a Varian model XL-300. The single X-ray crystallographic data sets were collected on a CAD-4 diffractometer. The powder diffractograms were collected on a Guinier–Hägg focusing powder camera.

3. Results and discussion

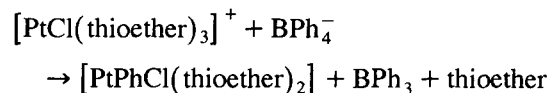
For the preparation of *trans*-[PtPhCl(dms)₂] we have used a method of phenylation with BPh_4^- . The first example of such a phenylation was given by Clark and Dixon [11], who observed that refluxing $[\text{PtCl}_2(\text{PEt}_3)_2]$ with NaBPh_4 in tetrahydrofuran for 40 h gave $[\text{PtPh}_2(\text{PEt}_3)_2]$. Phenylation of metal centers may be divided into two groups.

(i) Interaction of NaBPh_4 with cationic solvento complexes [12,13] proceeds rapidly, also under mild conditions.

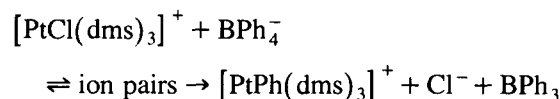
(ii) Reaction of NaBPh_4 with more or less strongly bonded acido ligands [11,14,15].

We have found that complexes of the type $[\text{PtCl}(\text{thioether})_3]^+$, where thioether = dimethyl sulfide

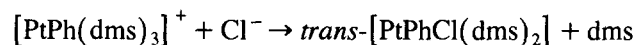
or 1,4-thioxane, which do not contain weakly coordinated ligands, nevertheless are sufficiently electrophilic to abstract a phenyl group from the tetraphenylborate counterion with the displacement of one thioether ligand. The reaction proceeds both in the solid state and in nitromethane solution:



Rate constants and activation parameters for this process in nitromethane solution have been determined by Olsson [16] using ^1H NMR and stopped flow technique. The following mechanism was proposed:



These steps are followed by a ligand substitution reaction:



Baird [17] reported that $[\text{PtCl}(\text{SnPh}_3)(\text{PPh}_3)_2]$ could be prepared by either treating *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with lithium triphenyltin or $[\text{PtCl}(\text{H}(\text{PPh}_3)_2)]$ with triphenyltin nitrate. He claims that refluxing $[\text{PtCl}(\text{SnPh}_3)(\text{PPh}_3)_2]$ in a polar solvent gives the complex $[\text{PtPhCl}(\text{PPh}_3)_2]$. Eaborn et al. [18] found that the complex $[\text{PtCl}(\text{SnPh}_3)(\text{PPh}_3)_2]$ did not change on refluxing, but that the synthesis with $[\text{PtCl}(\text{H}(\text{PPh}_3)_2)]$ and triphenyltin nitrate gave a mixture of three complexes, $[\text{PtCl}(\text{SnPh}_3)(\text{PPh}_3)_2]$, $[\text{PtPhCl}(\text{PPh}_3)_2]$ and an unidentified *cis*-bis(phosphine) complex. In our synthesis with $[\text{PtCl}_2(\text{dms})_2]$ and triphenyltin hydride in benzene, we were only able to crystallize the *trans*- $[\text{PtPhCl}(\text{dms})_2]$ compound.

Both polymorphs are composed of discrete van der

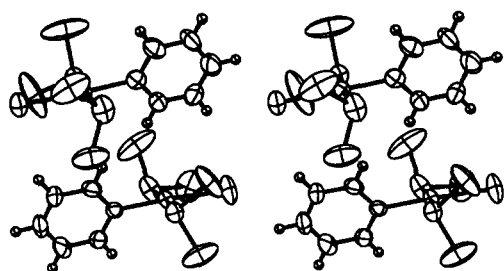


Fig. 1. Stereo picture of polymorph 1 showing two independent complexes related by a pseudo inversion center, the upper complex contains Pt(1) and the lower Pt(2). The ellipsoids are drawn at 50% probability.

Waals packed *trans*-[PtPhCl(dms)₂] complexes (Figs. 1 and 2). The Pt atom is coordinated by one chlorine atom, one phenyl ring and two dms molecules in a distorted square planar configuration. Structure 1 is

composed of two crystallographically independent complexes arranged in pairs around a pseudoinversion center (Fig. 1). The orientations of the dms molecules and the phenyl rings are slightly different in the two complexes (Table 4). In 2 there is only one independent complex, and in this structure, pairs of complexes are related by a true inversion center (Fig. 4) similar to the packing found in 1. The shortest Pt...Pt distance is 5.5248(9) Å in 1 and 4.8435(6) Å in 2. The closest intermolecular contact is 2.5 Å in both 1, H(C2)...H(C8)', and 2, H(C6)...H(C6)'. There might be interactions between Pt and a hydrogen atom in the phenyl group of the centro (or pseudocentro) symmetrically related molecule in both 1 and 2 (Tables 4 and 5, Figs. 3 and 4), Pt...H 3.0 Å. In the pseudo octahedral positions on the other side of the coordination plane the closest contacts to platinum are Pt(1)...C(16) 3.81(2) and Pt...C(17) 3.69(2) Å in

Table 4
Distances (Å) and angles (°) with expected standard deviations in parentheses in *trans*-[PtCl(dms)₂Ph] (1)

Pt(1)–Cl(1)	2.404(3)	Pt(2)–Cl(2)	2.403(4)
Pt(1)–S(1)	2.298(3)	Pt(2)–S(3)	2.295(3)
Pt(1)–S(2)	2.291(4)	Pt(2)–S(4)	2.279(4)
Pt(1)–C(1)	1.99(1)	Pt(1)–C(7)	1.99(1)
S(1)–C(13)	1.80(2)	S(2)–C(15)	1.77(2)
S(1)–C(14)	1.79(2)	S(2)–C(16)	1.81(2)
C(1)–C(2)	1.41(2)	C(7)–C(8)	1.40(2)
C(2)–C(3)	1.37(2)	C(8)–C(9)	1.41(2)
C(3)–C(4)	1.39(2)	C(9)–C(10)	1.35(2)
C(4)–C(5)	1.40(2)	C(10)–C(11)	1.36(2)
C(5)–C(6)	1.36(2)	C(11)–C(12)	1.41(2)
C(6)–C(1)	1.40(2)	C(12)–C(7)	1.40(2)
Pt(1)...H(C11)	2.97	Pt(2)...H(C2)	3.05
Pt(1)...Pt(2)	5.5248(9)	Pt(1)...Pt(1) ^a	5.935(1)
Pt(2)...Pt(2) ^b	5.854(1)		
S(1)–Pt(1)–Cl(1)	95.0(1)	S(3)–Pt(2)–Cl(2)	93.0(1)
S(2)–Pt(1)–Cl(1)	93.7(1)	S(4)–Pt(2)–Cl(2)	95.1(1)
S(1)–Pt(1)–C(1)	86.0(4)	S(3)–Pt(2)–C(7)	85.8(3)
S(2)–Pt(1)–C(1)	85.4(4)	S(4)–Pt(2)–C(7)	86.1(4)
S(1)–Pt(1)–S(2)	170.8(1)	S(3)–Pt(2)–S(4)	171.9(1)
C(1)–Pt(1)–Cl(1)	177.7(4)	C(7)–Pt(2)–Cl(2)	177.2(3)
C(1)–C(2)–C(3)	123(1)	C(7)–C(8)–C(9)	122(1)
C(2)–C(3)–C(4)	120(1)	C(8)–C(9)–C(10)	120(1)
C(3)–C(4)–C(5)	119(1)	C(9)–C(10)–C(11)	120(1)
C(4)–C(5)–C(6)	120(1)	C(10)–C(11)–C(12)	121(1)
C(5)–C(6)–C(1)	123(1)	C(11)–C(12)–C(7)	121(1)
C(6)–C(1)–C(2)	115(1)	C(12)–C(7)–C(8)	116(1)
C(13)–S(1)–C(14)	101(1)	C(17)–S(3)–C(18)	100(1)
C(15)–S(2)–C(16)	98(1)	C(19)–S(4)–C(20)	101(1)
C(1)–Pt(1)–S(1)–C(13)	–89(1)	C(7)–Pt(2)–S(3)–C(17)	110.6(9)
C(1)–Pt(1)–S(1)–C(14)	163(1)	C(7)–Pt(2)–S(3)–C(18)	–142.7(8)
C(1)–Pt(1)–S(2)–C(15)	–121.5(9)	C(7)–Pt(2)–S(4)–C(19)	–166.6(9)
C(1)–Pt(1)–S(2)–C(16)	133.3(9)	C(7)–Pt(2)–S(4)–C(20)	85(1)

^a 1 – x, – y, – z.

^b 1 – x, – y, 1 – z.

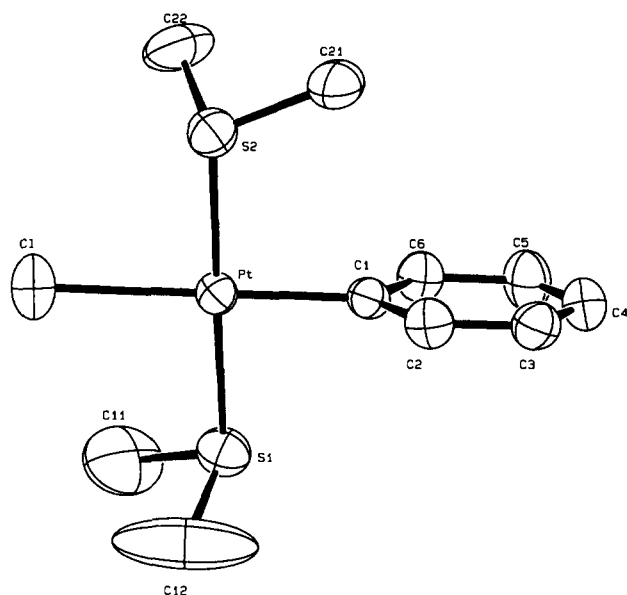


Fig. 2. Molecular structure of polymorph 2 showing the atomic numbering. The ellipsoids are drawn at 50% probability.

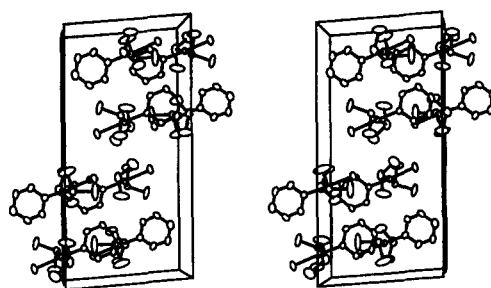


Fig. 3. Stereo packing diagram showing the unit cell content in 1 viewed along the *b* axis. The ellipsoids are drawn at 30% probability.

polymorph 1 and Pt $\cdots$ S(2) 3.988(2) Å in polymorph 2.

The conformations of the three complexes are somewhat different, showing high geometrical flexibility. The least-squares planes through the phenyl groups are

Table 5

Distances (Å) and angles (°) with expected standard deviations in parentheses in *trans*-[PtCl(dms)₂Ph] (2)

Pt–Cl	2.420(1)		
Pt–S(1)	2.289(2)		
Pt–S(2)	2.296(1)		
Pt–C(1)	2.004(5)		
S(1)–C(11)	1.776(8)		
S(1)–C(12)	1.752(9)		
C(1)–C(2)	1.393(7)	C(2)–H(C2)	0.94(5)
C(2)–C(3)	1.387(7)	C(3)–H(C3)	0.96(6)
C(3)–C(4)	1.380(8)	C(4)–H(C4)	0.97(8)
C(4)–C(5)	1.376(8)	C(5)–H(C5)	0.93(5)
C(5)–C(6)	1.387(7)	C(6)–H(C6)	0.98(6)
C(6)–C(1)	1.399(7)		
Pt $\cdots$ H(C6) ^a	3.00(6)		
Pt $\cdots$ Pt ^a	4.8435(6)		
Pt $\cdots$ Pt ^b	5.5969(7)		
S(1)–Pt–Cl	95.08(6)		
S(2)–Pt–Cl	85.95(5)		
S(1)–Pt–C(1)	85.0(1)		
S(2)–Pt–C(1)	93.9(1)		
S(1)–Pt–S(2)	178.51(5)		
C(1)–Pt–Cl	179.9(1)		
C(1)–C(2)–C(3)	122.1(5)		
C(2)–C(3)–C(4)	119.7(5)		
C(3)–C(4)–C(5)	119.9(5)		
C(4)–C(5)–C(6)	120.0(5)		
C(5)–C(6)–C(1)	121.7(1)		
C(6)–C(1)–C(2)	116.6(4)		
C(11)–S(1)–C(12)	100.7(6)		
C(21)–S(2)–C(22)	99.2(4)		
C(1)–Pt–S(1)–C(11)	–142.3(4)		
C(1)–Pt–S(1)–C(12)	109.7(6)		
C(1)–Pt–S(2)–C(21)	–3.2(3)	C(1) $\cdots$ C(21)	3.136(8)
C(1)–Pt–S(2)–C(22)	102.8(3)	C(1) $\cdots$ H(C21)	2.74

^a – *x*, – *y*, – *z*.

^b – *x*, – *y*, 1 – *z*.

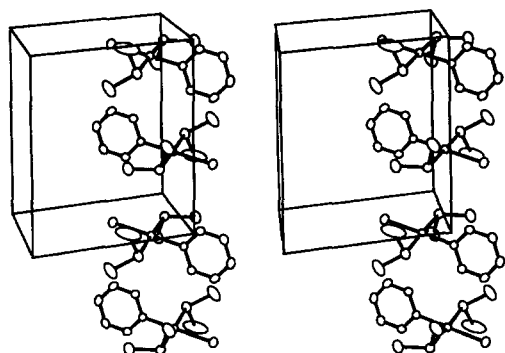


Fig. 4. Stereo packing diagram showing the content in two unit cells in **2** viewed along the *a* axis. The ellipsoids are drawn at 30% probability.

approximately perpendicular to the coordination planes, in **1** the dihedral angles are 68–70° and in **2** 78°. The rotation barrier for the phenyl group will probably also prevent a rotation of this group in solution media, but it is certainly free to rotate slightly, at least in the interval $90 \pm 20^\circ$. The dms ligands show a much larger orientational freedom. In polymorph **1** one of the dms molecules in each complex is staggered with the chlorine atom while the other is in an almost eclipsed conformation with the chlorine atom (Table 4). In poly-

morph **2** one of the dms molecules is also staggered with the chlorine atom while the other is eclipsed with the coordinated carbon atom in the phenyl ring (Table 5, Fig. 2). It is interesting to note that a pyramidal inversion of the dms eclipsed with the chlorine atom in polymorph **1** results in the conformation observed in polymorph **2**, and such inversions have been observed for thioether complexes of Pt(II) in solution [19]. The orientation and size of the thermal ellipsoids of the methyl groups and the conformations adopted indicate several soft energy minima for the orientation of the dms ligands.

The deviations from the least-squares planes through the coordination square, PtCClS₂, is less than 0.08 Å in **1** and 0.02 Å in **2**. The bond angles around Pt are in the range 85–95°, but in **1** the S atoms in both complexes are moved towards the coordinated phenyl carbon atom while in **2** one of the S atoms is moved towards the phenyl carbon and the other towards the chlorine atom (Tables 4 and 5). This indicates fairly soft bond angles around Pt as well as a correlation between the bond angles and the different orientations of the ligands. In solution the rotational barrier for dms may thus be lowered by changing the bond angles.

The Pt–C distances, 1.99(1), 1.99(1) and 2.004(5) Å, are not significantly different from other Pt–C(phenyl)

Table 6

Pt–Cl distances in complexes of the type [PtClXYZ].

Complex	Donor atoms in <i>cis</i> positions	Donor atom in <i>trans</i> position	Pt–Cl distance (Å)	Reference
[PtCl ₃ (dms)] [−]	Cl/S	Cl	2.291(3), 2.303(2)	[23]
<i>cis</i> -[PtCl ₂ (phenoselenazine) ₂]	Cl/Se	Se	2.297(4), 2.326(4)	[24]
<i>trans</i> -[PtCl ₂ (1,4-thioxane) ₂]	S/S	Cl	2.300(2)	[25]
[PtCl ₃ PEt ₃] [−]	Cl/P	Cl	2.300(2)	[26]
[PtCl ₄] ^{2−}	Cl/Cl	Cl	2.304(7)	[27]
<i>trans</i> -[PtCl ₂ (Me ₃ GeCH ₂ SeMe) ₂]	Se/Se	Cl	2.305(5)	[28]
<i>trans</i> -[PtCl ₂ (dms) ₂]	S/S	Cl	2.297(5)	[7]
[PtCl ₃ (dms)] [−]	Cl/Cl	S	2.316(2)	[23]
<i>cis</i> -[PtCl ₂ (dms) ₂]	Cl/S	S	2.315(1), 2.319(1)	[29]
<i>cis</i> -[PtCl ₂ (1,4-thioxane) ₂]	Cl/S	S	2.321(2), 2.327(2)	[25]
[PtCl(PEt ₃)(PhC(NH ₂)NOH)(SnCl ₃)]	N/P	Sn	2.325(3)	[30]
[PtCl(NH ₂ C ₆ H ₄ Cl)(PEt ₃)(SnCl ₃)]	N/P	Sn	2.331(3)	[31]
<i>cis</i> -[PtCl(PPh ₃) ₂ (SnCl ₃)]	Sn/P	P	2.333(2)	[32]
<i>cis</i> -[PtCl ₂ (SnCl ₃) ₂] ^{2−}	Cl/Sn	Sn	2.341(4), 2.356(5)	[33]
<i>cis</i> -[PtCl ₂ (PMe ₂ Ph) ₂]	Cl/P	P	2.359(1), 2.355(1)	[34]
[PtCl ₃ PEt ₃] [−]	Cl/Cl	P	2.382(4)	[26]
<i>trans</i> -[PtCl(CH=CH ₂)(PEt ₂ Ph) ₂]	P/P	C	2.398(4)	[35]
<i>trans</i> -[PtClPh(dms) ₂]	S/S	C	2.403(4)–2.420(1)	This work
<i>trans</i> -[PtCl(C≡CPh)(PEt ₂ Ph) ₂]	P/P	C	2.407(5)	[36]
<i>trans</i> -[PtClPh(PPh ₃) ₂]	P/P	C	2.408(5)	[20]
<i>trans</i> -[PtCl(CH ₃)(AsPh ₃) ₂]	As/As	C	2.410(2)	[37]
<i>trans</i> -[PtCl(CH ₃)(PMePh ₂) ₂]	P/P	C	2.412(2)	[38]
<i>trans</i> -[PtClPh(pyridine) ₂]	N/N	C	2.415	[21]
<i>trans</i> -[PtClH(PEtPh ₂) ₂]	P/P	H	2.422(9)	[39]
<i>trans</i> -[PtCl(PPh ₃) ₂ (η ¹ -C ₃ H ₅)]	P/P	C	2.425(2)	[40]
<i>trans</i> -[PtCl(CH ₃)(PPh ₃) ₂]	P/P	C	2.431(3)	[41]
<i>trans</i> -[PtCl(PMe ₂ Ph) ₂ (SiPh ₃)]	P/P	Si	2.465(2)	[42]

distances observed in *trans*-[PtPhCl(PPh₃)₂] {2.00(2)}, *trans*-[PtPhCl(pyridine)₂] {1.999(8)}, and *cis*-[PtPh₂(dms)₂] {2.010(7) and 2.036(7) Å} [20–22].

The Pt–S distances in *trans*-[PtPhCl(dms)₂] range between 2.279(4) and 2.298(3) Å and they cannot be considered as significantly different. However, they are much longer than those observed in [PtCl₃(dms)][–], 2.246(2) Å [23], about the same as in *trans*-[PtCl₂(dms)₂], 2.297(5) Å [7], and in [Pt(dms)₄]²⁺, 2.317–2.321 Å [24], but much shorter than in *cis*-[PtPh₂(dms)₂], 2.370(2)–2.389(2) Å [21]. This reflects an increasing *trans* influence in the series Cl < S < C. However, it should be noticed that these distances may also be affected by different *cis* influences.

The Pt–Cl distances in polymorph 1, 2.403(4) and 2.404(3) Å, are not significantly different but they are possibly shorter than in polymorph 2, 2.420(1) Å. Smaller variations in torsion angles do not normally affect bond distances to Pt [6]. However, in this case the orientation of one of the dms molecules is different in 1 and 2, which could be an explanation for the observed difference. The Pt–Cl distances found in *trans*-[PtPhCl(PPh₃)₂] {2.408(5)} and in *trans*-[PtPhCl(pyridine)₂] {2.414(2)} are not significantly different from those observed in *trans*-[PtPhCl(dms)₂] [20,21].

The Pt–Cl distances in Table 6 range between 2.291 and 2.465 Å, i.e. a variation of 0.17 Å, illustrating the highly significant *trans* influence of different ligands. The distances increase in the following order: Cl[–] < S ≤ Sn(SnCl₃)[–], P < C(sp², sp³), H[–] < Si, which is parallel to the influences found on the Pt–S(thioether) distances shown above. In the literature we have only found crystal structures of platinum complexes with tin as a donor atom with the ligand SnCl₃[–] *trans* to Cl [32,33]. According to IR measurements SnCl₃[–] seems to have a *trans* influence comparable with PPh₃, while SnPh₃[–] shows a larger *trans* influence though still smaller than that found for H[–] [17].

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