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Platinum(II) complexes with the tridentate phosphino-thioether ligand bis(2-diphenylphosphinoethyl)sulfide, $(PPh_2CH_2CH_2)_2S$. X-ray crystal structures of $[Pt\{(PPh_2CH_2CH_2)_2S\}CI]ClO_4$ and $[Pt\{(PPh_2CH_2CH_2)_2S\}I]I$

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Abstract

A series of new four coordinate Pt(II) complexes with the potentially tridentate chelate ligand bis(2-diphenylphosphinoethyl)sulfide (PSP) have been synthesized and characterized and the X-ray crystal stuctures of $[Pt(PSP)CI]ClO_4$ and [Pt(PSP)I]Iwere determined. The spectroscopic data are consistent with the general formula $[Pt(PSP)X]^{n+}$ with $X = Cl^-$, Br^- , I^- , SCN^- , CN^- , thiourea or PPh₃ where all the three donor atoms in PSP are coordinated to platinum in all the complexes. Both the crystal structures show that the coordination sphere of the tridentate chelate system is strongly tetrahedrally distorted from a square planar geometry. The larger iodide ligand appears to cause a greater distortion. The potentially larger *trans* influence of iodide shows no effect on the structure of the, apparently, rigid Pt(PSP) moiety, whereas the *trans* influence of the chelating sulfur donor appears to be large which is reflected in unusually long platinum–halogen distances. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Platinum(II) phosphine complexes; Phosphathia chelate ligand; Crystal structures; Trans influence

1. Introduction

The coordination chemistry of acyclic and macrocyclic chelate ligands containing both phosphorus and sulfur donor atoms have received a considerable interest and the platinum metal complexes of these phosphathia ligands have been investigated by several research groups. Thus, the dependence of the redox properties of the complexes and the coordinating abilities of the ligands on the geometrical arrangement of P and S donor groups have been the subject of a series of investigations [1-10]. Recently, improved catalysts for carbonylation of methanol using rhodium complexes with chelating phosphathia ligands have also been reported [11].

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Prior to this work on Pt(II) complexes with the potentially tridentate phosphino-thioether ligand bis(2-diphenylphosphinoethyl)sulfide (PSP), a series of transition metal complexes with this ligand have been reported in the literature [1,2,12,13], including X-ray crystal structures of Ni(II) [14], Ag(I) [15,16] and Hg(II) [17] PSP complexes. In all the reported PSP complexes with Ni(II), Pd(II) and Pt(II) the ligand is found to act as a tridentate chelating ligand. Pt(II) and Pd(II) complexes with the closely related chelate ligand P-S(O)–P¹ have also been synthesized and characterized recently [3,4].

As a part of our studies on rates and equilibria of Pt(II) complexes containing tridentate chelate ligands we have synthesized and characterized a series of $[Pt(PSP)X]^{n+}$ complexes with $X = Cl^-$, Br^- , I^- , SCN^- , CN^- , thiourea (tu) or PPh₃ and determined the X-ray crystal structures of $[Pt(PSP)Cl]ClO_4$ and [Pt(PSP)I]I.

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¹ P–S(O)–P is (PPh₂CH₂CH₂)₂SO.

2. Experimental

ligand bis(2-diphenylphosphinoethyl)sulfide The (PSP) was purchased from Argus Chemicals, Italy and used as received. K₂PtCl₄ was obtained from Chempur and K¹³CN (90 atom[%] ¹³C) from Merck, Sharp & Dohme Isotopes, Montreal, Canada. All other reagents were AR grade. Doubly distilled water was used throughout and all other solvents were HPLC grade. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Varian 300 MHz Gemini spectrometer at 300, 75.46 and 121.49 MHz, respectively. ¹H and ¹³C chemical shifts are referenced to TMS and positive ³¹P chemical shifts are downfield from 85% H₃PO₄ external standard. IR spectra were measured both as KBr discs and Nujol mulls using a Perkin-Elmer 1720 (FT-IR) spectrometer at 1 cm⁻¹ resolution. Within the experimental accuracy both methods gave identical results for each sample. FAB mass spectra were recorded on a Kratos MS 50 TC. UV-Vis spectra were recorded on a Shimadzu UV-3100. Elemental analyses were performed by the Microanalytical Laboratory of the H.C. Ørsted Institute, Copenhagen University and by Atlantic Microlab, Norcross, GA, USA.

Caution: Those of the complexes isolated as perchlorate salts were treated as potential explosives.

2.1. Syntheses

2.1.1. [*Pt*(*PSP*)*Cl*]*Cl* (1)

The procedure for synthesizing [Pt(PSP)Cl]Cl is a modification of the literature method [1]. To K_2PtCl_4 (1.81 g, 4.36 mmol) in 20 ml water were added 20 ml CH₃CN. The solution was heated to 70°C for 15 min. A suspension of the PSP ligand (2.00 g, 4.36 mmol) in 50 ml CH₃CN was added dropwise to the warm solution and the mixture was refluxed for 15 min. After evaporation of all the solvent, the crude, bright yellow product [Pt(PSP)Cl]Cl was redissolved in 80 ml CH₂Cl₂, leaving some KCl which was filtered off before removing the solvent under reduced pressure. Yield: 2.87 g, 91%.

A portion of the crude [Pt(PSP)Cl]Cl (1.13 g, 1.56 mmol) was dissolved in 5 ml CHCl₃ and added 15 ml methanol. This solution was added dropwise to 500 ml diethyl ether with rapid stirring. The resulting white product was collected by filtration, washed with diethyl ether and dried in vacuo ($< 10^{-3}$ atm.). Yield: 1.03 g, 91%. FAB MS: m/z 689 [Pt(PSP)Cl]⁺ (100%).

The recrystallized [Pt(PSP)Cl]Cl (1) gives FAB MS and ${}^{31}P{}^{1}H$ NMR spectra identical to those of the purified product 1a described below. Several batches of 1 were made, since [Pt(PSP)Cl]Cl was used as the starting material in the syntheses of 1a-7.

2.1.2. [Pt(PSP)Cl]ClO₄ (1a)

[Pt(PSP)Cl]Cl (1) (1.29 g, 1.78 mmol) was dissolved in 15 ml CH₂Cl₂ and 75 ml methanol. A saturated methanolic solution of LiClO₄ was added dropwise until precipitation started and the cloudy solution was added dropwise to 200 ml diethyl ether with rapid stirring. The white microcrystals were collected, redissolved in 500 ml methanol followed by addition of a saturated LiClO₄ methanolic solution until cloudiness. Addition of an equivolume of water caused precipitation of the product which was isolated, washed with ice cold water and dried in vacuo. Yield: 1.10 g, 85%.

Anal. Calc. for [Pt(PSP)Cl]ClO₄, $C_{28}H_{28}PtCl_2O_4P_2S$: C, 42.65; H, 3.58; Cl, 8.99; S, 4.07. Found: C, 42.47; H, 3.54; Cl, 9.63; S, 3.90%. UV–Vis (20% v/v methanol/ water): λ_{max} (log ε): 254 (4.31); 293 (3.97) nm. FAB MS: m/z 689 [Pt(PSP)Cl]⁺ (100%).

2.1.3. [Pt(PSP)Br]Br (2)

[Pt(PSP)Cl]Cl (1) (310 mg, 0.43 mmol) was dissolved in 120 ml methanol and 40 ml water. KBr (540 mg, 4.50 mmol) in 20 ml 50% v/v methanol/water was added dropwise and the mixture was left for 24 h. The volume was reduced to 70 ml and after cooling the concentrated solution to 0°C the crude product of **2** was collected by filtration and washed with water. Yield: 238 mg, 68%.

A portion of the crude product of **2** (136 mg, 0.17 mmol) was redissolved in 100 ml methanol and 2.5 ml 2.0 M KBr in 50% v/v methanol/water mixture was added, followed by 50 ml of water. The volume was reduced to 50 ml and the white product was collected by filtration, washed with water followed by diethyl ether and dried in vacuo. Yield: 83 mg, 61%.

Anal. Calc. for [Pt(PSP)Br]Br·2H₂O, C₂₈H₂₈PtBr₂P₂S· 2H₂O: C, 39.59; H, 3.80; Br, 18.81; S, 3.77. Found: C, 39.79; H, 3.59; Br, 19.07; S, 3.64%. UV–Vis (20% v/v methanol/water): λ_{max} (log ε): 260 (4.29); 305 (3.78) nm. FAB MS: m/z 733 [Pt(PSP)Br]⁺ (100%).

2.1.4. [Pt(PSP)I]I (3)

After dissolving [Pt(PSP)Cl]Cl (1) (158 mg, 0.22 mmol) in 70 ml methanol, 35 ml water were added, followed by dropwise addition of NaI (92 mg, 0.61 mmol) dissolved in 30 ml 50% v/v methanol/water. Precipitation of the yellow product started before all the NaI solution had been added. After 24 h, the volume was reduced to 40 ml and the product was collected by filtration, washed with water and dried in vacuo. Yield: 174 mg, 88%.

Anal. Calc. for [Pt(PSP)I]I, $C_{28}H_{28}PtI_2P_2S$: C, 37.06; H, 3.11; I, 27.97; S, 3.53. Found: C, 37.02; H, 3.12; I, 27.69; S, 3.56%. UV–Vis (20% v/v methanol/water): λ_{max} (log ε): 268 (4.18); 340 (3.47) nm. FAB MS: m/z780 [Pt(PSP)I]⁺ (100%).

2.1.5. [Pt(PSP)(CNS)]SCN (4)²

[Pt(PSP)Cl]Cl (1) (371 mg, 0.51 mmol) was dissolved in 180 ml methanol and 60 ml water. NH_4SCN (191 mg, 2.51 mmol) in 25 ml 75% v/v methanol/water was added and the mixture was left for 1 h. The volume was reduced to 75 ml and the yellow precipitate was afterwards collected by filtration, washed with water followed by diethyl ether and dried in vacuo. Yield: 270 mg, 68%.

Anal. Calc. for [Pt(PSP)(CNS)]SCN·0.5H₂O, $C_{30}H_{28}$ -PtP₂S₃N₂·0.5H₂O: C, 46.27; H, 3.75; N, 3.60. Found: C, 46.09; H, 3.60; N, 3.65%. UV–Vis (20% v/v methanol/ water): λ_{max} (log ε): 275 (4.18); 345 (3.31) nm. FAB MS: m/z 711 [Pt(PSP)(CNS)]⁺ (100%). IR: v(CN); 2124 (s), 2097 (s), 2054 (s) cm⁻¹.

2.1.6. [*Pt*(*PSP*)*CN*]*ClO*₄ (5)

[Pt(PSP)Cl]Cl (1) (197 mg, 0.27 mmol) was dissolved in 150 ml methanol and added 150 ml water. Over 5 h, a solution of KCN (19 mg, 0.29 mmol) in 100 ml 50% v/v methanol/water was added dropwise. The reaction mixture was filtered to remove traces of insoluble byproducts before reducing the volume to 150 ml. Addition of 25 ml saturated aqueous LiClO_4 solution caused slow precipitation of the white microcrystals, which were collected by filtration after cooling to 0°C. The isolated product was washed with ice cold water followed by diethyl ether and dried in vacuo. Yield: 105 mg, 50%.

Anal. Calc. for [Pt(PSP)CN]ClO₄·0.5H₂O, $C_{29}H_{28}$ -PtClP₂SNO₄·0.5H₂O: C, 44.20; H, 3.71; N, 1.78. Found: C, 44.15; H, 3.54; N, 1.67%. UV–Vis (20% v/v methanol/water): λ_{max} (log ε): 247 (4.42); 269 (sh), 276 (sh) nm. FAB MS: m/z 679 [Pt(PSP)CN]⁺ (100%). IR: v(CN); 2144 (s) cm⁻¹.

2.1.7. $[Pt(PSP)(tu)](ClO_4)_2$ (6)

[Pt(PSP)Cl]Cl (1) (218 mg, 0.30 mmol) was dissolved in 100 ml methanol and added 50 ml water. Thiourea (tu) (68 mg, 0.90 mmol) in 10 ml water was added, causing a colour change from colourless to yellow. After 30 min, 10 ml saturated aqueous LiClO₄ solution were added and the mixture was left at 5°C for 24 h during which bright yellow microcrystals separated out. These were collected by filtration and washed with ice cold water followed by diethyl ether and dried in vacuo. Yield: 180 mg, 64%.

Anal. Calc. for [Pt(PSP)(tu)](ClO₄)₂·0.5H₂O, C₂₉H₃₂-PtCl₂P₂S₂O₈N₂·0.5H₂O: C, 37.15; H, 3.55; N, 2.99; Cl, 7.56; S, 6.84. Found: C, 37.22; H, 3.59; N, 2.87; Cl, 7.55; S, 6.87%. UV–Vis (20% v/v methanol/water): λ_{max} (log ε): 268 (4.16); 335 (3.58) nm. FAB MS: m/z829 {[Pt(PSP)(tu)](ClO₄)} + (34%), 728 {[Pt(PSP)(tu)-(-H)³]} + (100%), 653 {[Pt(PSP)]} + (33%).

2.1.8. $[Pt(PSP)(PPh_3)](ClO_4)_2$ (7)

[Pt(PSP)Cl]Cl (1) (301 mg, 0.42 mmol) was dissolved in 5 ml CH₂Cl₂ and 15 ml methanol and added PPh₃ (548 mg, 2.09 mmol) in 10 ml acetone. After 24 h, the volume was reduced to 5 ml under reduced pressure and to the concentrated solution were added 2 ml of a saturated methanolic LiClO₄ solution, which caused precipitation of white microcrystals. The crude product of 7 was collected by filtration, redissolved in 200 ml methanol and to the mixture were added 10 ml saturated methanolic LiClO₄ solution. The final white product was collected by filtration, washed with water followed by diethyl ether and dried in vacuo. Yield: 275 mg, 59%.

Anal. Calc. for [Pt(PSP)(PPh₃)](ClO₄)₂, C₄₆H₄₃PtCl₂-P₃SO₈: C, 49.56; H, 3.89; Cl, 6.36; S, 2.88. Found: C, 49.54; H, 3.85; Cl, 6.40; S, 2.85%. UV–Vis (20% v/v methanol/water): λ_{max} (log ε): 258 (4.38); 276 (sh) nm. FAB MS: m/z 1015 {[Pt(PSP)(PPh₃)](ClO₄)} + (74%), 915 {[Pt(PSP)(PPh₃)]} + (52%), 653 {[Pt(PSP)]} + (100%).

2.2. Crystal structure determinations

Crystals of $[Pt(PSP)Cl]ClO_4$ and [Pt(PSP)I]I were grown by slow diffusion of diethyl ether into solutions of **1a** or **3** in 30% v/v chloroform/methanol. The crystals of **1a** were colourless and of suitable size for X-ray analysis, whereas **3** crystallized as bright yellow needles, which had to be cut to obtain a suitable size.

X-ray diffraction data were collected on a Siemens SMART CCD diffractometer at 120 K using Mo Ka radiation. Data were corrected for Lorentz and polarization effects and absorption (empirically) using SAINT and SADABS in SMART software [18]. For both complexes 1a and 3 the unit cell parameters were determined from 4096 reflections. Crystal data and details on data collections and refinements are presented in Table 1. The structures were determined and refined by use of the programs included in the Xtal 3.2 system [19]. The coordinates of the platinum atoms in the structures of 1a and 3 were deduced from the Patterson function and all the remaining non-hydrogen atoms were localized from successive difference Fourier maps. The structure of 1a was refined by full-matrix leastsquares calculations (CRYLSQ) [20] with anisotropic displacement parameters for all non-hydrogen atoms. For the hydrogen atoms a fixed isotropic temperature factor ($U_{iso} = 0.035 \text{ Å}^2$) was used and only the coordinates were allowed to vary. The structure of 3 was refined by full-matrix least-squares calculations (CRYLSQ) with anisotropic displacement parameters

 $^{^{2}}$ With the nomenclature 'CNS' we do not specify the coordination mode of thiocyanate.

 $^{^{3}}$ (-H) is defined as one proton abstracted from the complex.

for the platinum, phosphorus, sulfur and iodine atoms. The hydrogen atoms were included in the calculations but the coordinates were not allowed to vary. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*, Vol. IV, 1974.

The thermal vibrations of the perchlorate counter anion in **1a** were moderate and allowed a good determination of positions for all the atoms in the anions. The final *R* value for **1a** was 0.038. In **3** the thermal parameter $U_{\rm iso}$ for the iodide counter anion was large $(U_{\rm iso} = 0.099 \text{ Å}^2)$ and we find that this probably contributes to the rather large final *R* value 0.116 for **3**. For comparison, the thermal parameter for the coordinated iodide was found to be significantly smaller $(U_{\rm iso} = 0.032 \text{ Å}^2)$. The distances (0.77-1.37 Å) between the biggest tops in $\Delta \rho$ -map and the nearest atoms,

Table 1

Crystal data and details of structure determinations for $[Pt(PSP)CI]CIO_4$ (1a) and [Pt(PSP)I]I (3)

Complex	1a	3
Crystal data		
Formula	C28H28Cl2O4P2PtS	C ₂₈ H ₂₈ I ₂ P ₂ PtS
Molecular weight	788.522	907.428
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_{1}/c$
a (Å)	9.2311(2)	18.684(2)
$b(\mathbf{A})$	8.8196(2)	7.231(1)
$c(\mathbf{A})$	35.8466(7)	22.969(1)
β (°)	92.609(1)	106.500(5)
$V(A^3)$	2915.4(1)	2975.2(2)
Z	4	4
$D_{\rm calc}$ (g cm ⁻³)	1.797	1.945
F(000)	1544	1704
$\mu ({\rm mm}^{-1})$	5.218	6.729
Crystal size (mm)	0.24×0.075	0.0275×0.147
•	$\times 0.035$	$\times 0.147$
Data collection		
Temperature (K)	120	120
Wavelength (Mo Kα) (Å)	0.71073	0.71073
Scan type	ω	ω
T_{\min}, T_{\max}	0.7444, 0.9265	0.5968, 0.8716
θ (°)	3–29	1–26
Data set (hkl)	0:12, 0:12, -49:49	0:23, 0:9, -28:27
No. reflections measured	20293	31341
No. independent reflections	7676 ($R_{\rm int} = 0.027$)	5151 ($R_{\rm int} = 0.093$)
No. observed reflections	6681 $[I > 2.5\sigma(I)]$	4341 $[I > 2.5\sigma(I)]$
Refinement		
No. refined parameters	427	167
R	0.038	0.116
wR	0.039	0.116
GOF	1.50(1)	2.09(2)
W	$< 1/\sigma^{2} (F)$	$< 1/\sigma^{2} (F)$
$\Delta/\sigma_{\rm av}, \ \Delta/\sigma_{\rm max}$	0.0721, 0.836	0.00086, 0.0143
$\Delta \rho_{\rm max}$, $\Delta \rho_{\rm min}$ (e Å ⁻³)	1.20, -1.54	4.28, -4.43

platinum and the iodide counter anion, indicate that the residual electron density in **3** is artificial.

3. Results and discussion

3.1. Syntheses

The chloro complexes 1 and 1a were synthesized by a modified literature method [1]. Substitution of Cl⁻ from [Pt(PSP)Cl]⁺ with the appropriate nucleophile X⁻ in aqueous methanolic solution gave the desired products 2–4 [Pt(PSP)X]X, $X = Br^-$, I⁻ or SCN⁻ and 5–6 [Pt(PSP)Y](ClO₄)_n with Y = CN⁻ (n = 1) or tu (n = 2). Due to the low solubility of PPh₃ in water/methanol mixtures the preparation of 7 was performed in organic solvents. To the best of our knowledge, only three Pt(II) complexes with PSP have previously been synthesized [1], namely [Pt(PSP)Cl]ClO₄, [Pt(PSP)I]I and [Pt(PSP)I]ClO₄. We extended the characterization of the first two compounds by NMR, FAB MS and X-ray analysis.

Elemental analyses for 1a-7 all gave satisfactory results. FAB mass spectra reveal {[Pt(PSP)X]}⁺ peaks with the expected isotopic distribution for the complexes 1-5. The two complexes 6 and 7 reveal peaks with correct isotopic distribution for {[Pt(PSP)X]-ClO₄}⁺, X = tu or PPh₃ and also for the ions formulated as {[Pt(PSP)]}⁺, {[Pt(PSP)(tu)(-H)]}⁺ and {[Pt(PSP)PPh₃]}⁺. UV-Vis spectra of 1a-7 were recorded with 20% v/v methanol/water solutions at 23.7°C.

3.2. Crystal and molecular structures

3.2.1. $[Pt(PSP)Cl]ClO_4$ (1a)

The crystal of [Pt(PSP)Cl]ClO₄ (1a) which was used for single crystal X-ray diffraction was found to crystallize in the monoclinic space group $P2_1/n$. The molecular structure of the cation [Pt(PSP)Cl]⁺ with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and bond angles are given in Tables 2 and 3, respectively.

The molecular structure of **1a** confirms that the PSP ligand acts as a tridentate chelating ligand, coordinating to platinum through the sulfur and both phosphorus atoms and that the chlorine atom occupies the fourth coordination site.

The Pt–P bond lengths (Pt–P(1) = 2.317(1) Å, Pt–P(2) = 2.315(1) Å) are close to values given in the literature for Pt(II) complexes with two mutually *trans* –PPh₂ moieties [3,21–24]. The Pt–S distance (Pt–S = 2.254(1) Å) is also within the range normally observed for thioether donor groups in Pt(II) complexes with Cl⁻ in the *trans* position [25–31]. There is a general tendency towards slightly shorter Pt–S bond distances



Fig. 1. ORTEP plot of $[Pt(PSP)Cl]ClO_4$ (1a) with adopted numbering scheme.

Table 2 Selected bond distances (Å) for [Pt(PSP)Cl]ClO₄ (1a)

Pt-P(1)	2.317(1)	Pt-P(2)	2.315(1)
Pt-S	2.254(1)	Pt-Cl(1)	2.347(1)
P(1)–C(2)	1.860(5)	P(2)–C(4)	1.836(5)
P(1)–C(11)	1.815(5)	P(2)-C(31)	1.821(5)
P(1)-C(21)	1.820(5)	P(2)-C(41)	1.822(5)
S-C(1)	1.837(6)	S-C(3)	1.834(5)

Table 3

Selected bond angles (°) for [Pt(PSP)Cl]ClO₄ (1a)

P(1)-Pt-P(2)	161.14(4)	S-Pt-Cl(1)	175.85(4)	
P(1)–Pt–S	85.67(4)	P(2)-Pt-S	86.44(4)	
P(1)-Pt-Cl(1)	93.11(4)	P(2)-Pt-Cl(1)	95.88(4)	
Pt-P(1)-C(2)	106.0(2)	Pt-P(2)-C(4)	105.5(2)	
Pt–P(1)–C(11)	120.9(2)	Pt-P(2)-C(31)	123.7(2)	
Pt-P(1)-C(21)	107.8(2)	Pt-P(2)-C(41)	108.4(2)	
C(2)–P(1)–C(11)	106.0(2)	C(4)-P(2)-C(31)	106.2(2)	
C(2)–P(1)–C(21)	108.4(2)	C(4)-P(2)-C(41)	105.6(2)	
C(11)–P(1)–C(21)	107.3(2)	C(31)–P(2)–C(41)	106.2(2)	
C(1)-S-C(3)	103.6(2)			

in complexes where the thioether group is part of a chelate ring compared with complexes having monodentate thioether ligands [25], and accordingly the Pt–S distance in **1a** is in the lower end of the platinum– thioether range. In contrast to the Pt–P and Pt–S distances, which appear in the normal ranges, the Pt–Cl(1) bond in **1a** (Pt–Cl(1) = 2.347(1) Å) is longer than most Pt–Cl bond distances found for chloride *trans* to a thioether in Pt(II) complexes [25–31].

The coordination sphere for platinum is tetrahedrally distorted from planar geometry, with two phosphorus atoms on one side (0.21/0.20 Å) of the least-squares plane defined by (P(1),P(2),S,Cl(1)) and with the sulfur (-0.21 Å) and chlorine (-0.21 Å) atoms on the opposite side. Platinum is displaced 0.13 Å from the

least-squares plane and to the same side as the sulfur and chlorine atoms. The S–Pt–Cl(1) angle is 175.85(4)° which is relatively close to the ideal 180°. In contrast, the P(1)–Pt–P(2) angle is found to be only 161.14(4)°, probably as a result of ring strain in the tridentately bonding PSP ligand. Further, the small P–Pt–S angles for the two adjacent five-membered chelate rings (P(1)–Pt–S = 85.67(4)°, P(2)–Pt–S = 86.44(4)°) also display the strained coordination geometry of the rings, as generally observed in five-membered phosphine chelate rings [3,7,22,23]. The bond distances and angles within the PSP ligand are all in the ranges normally observed for thioether and phosphine ligands [14–17,21–23].

It is seen that the span for the Pt-P-C angles is rather large, 105.5(2)-123.7(2)°, which is not unusual [14,23]. The bond angles to the aliphatic carbons are at the lower end of the span $(Pt-P(1)-C(2) = 106.0(2)^{\circ})$, $Pt-P(2)-C(4) = 105.5(2)^{\circ}$). From the molecular structure it is seen that each phosphine group has one phenyl ring positioned on each side of the least-squares plane defined by the four donor atoms. The small P(1)-Pt-P(2) angle might cause each phosphine group to display the largest Pt-P-C angle to the phenyl ring positioned on the same side of the least-squares plane as the chlorine atom $(Pt-P(1)-C(11) = 120.9(2)^{\circ})$, $Pt-P(2)-C(31) = 123.7(2)^{\circ}$, although we cannot exclude the possibility that the Pt–P–C angles $> 120^{\circ}$ are just effects of crystal packing demands. If some steric repulsion exists between the chlorine atom and two phenyl rings in close proximity, this could probably also contribute to give the large observed Pt-P-C angles. The angles to the two phenyl rings on the opposite side of the least-squares plane are significantly smaller, 107.8(2) and 108.4(2)°, respectively.

3.2.2. [Pt(PSP)I]I (3)

The crystals of [Pt(PSP)I]I (3) are monoclinic belonging to the space group $P2_1/c$. The molecular structure of the cation [Pt(PSP)I]⁺ with the atomic numbering scheme is shown in Fig. 2. Selected bond distances are given in Table 4 and selected bond angles in Table 5.

The $[Pt(PSP)I]^+$ cation is four coordinate, with one iodine, I(1), coordinated to the metal center and with PSP acting as a tridentate ligand. The iodide counter anion, I(2), is positioned at a non-bonding distance (4.040(3) Å) from the nearest platinum atom.

The Pt–P bond distances (Pt–P(1) = 2.294(7) Å, Pt–P(2) = 2.276(8) Å) are shorter than those found in **1a**, but still within the normal range for Pt(II) complexes with two –PPh₂ moieties in a *trans* position [3,21–24].

Although iodide is known to exert a larger *trans* influence on Pt–S bonds than chloride [8,25,26], the two Pt–S bond distances in **1a** (Pt–S = 2.254(1) Å) and **3** (Pt–S = 2.258(6) Å) are nearly identical. That the Pt–S bond in **3** is rather short is seen from comparison with

the range for Pt–S bonds in other Pt(II) complexes having the *trans* iodide–thioether motif (2.262(2)-2.280(5) Å [25,26]. A comparison of the Pt–I bond length in **3** (Pt–I(1) = 2.613(2) Å) with data for the above-mentioned complexes reveals that, as found in **1a**, the platinum–halogen bond is significantly longer than in other



Fig. 2. ORTEP plot of [Pt(PSP)I]I (3) with adopted numbering scheme.

Table 4 Selected bond distances (Å) for [Pt(PSP)I]I (3)

Pt-P(1)	2.294(7)	Pt-P(2)	2.276(8)
Pt-S	2.258(6)	Pt-I(1)	2.613(2)
P(1)–C(2)	1.86(2)	P(2)–C(4)	1.87(2)
P(1)–C(11)	1.75(3)	P(2)–C(31)	1.82(3)
P(1)-C(21)	1.87(2)	P(2)-C(41)	1.83(3)
S-C(1)	1.84(3)	S-C(3)	1.85(3)

Table 5 Selected bond angles (°) for [Pt(PSP)I]I (3)

P(1)-Pt-P(2)	156.6(2)	S–Pt–I(1)	170.3(2)
P(1)–Pt–S	86.6(2)	P(2)–Pt–S	86.6(2)
P(1)–Pt–I(1)	97.7(2)	P(2)-Pt-I(1)	92.6(2)
Pt-P(1)-C(2)	105.8(9)	Pt-P(2)-C(4)	105.4(9)
Pt–P(1)–C(11)	125.2(9)	Pt-P(2)-C(31)	109(1)
Pt-P(1)-C(21)	107.2(8)	Pt-P(2)-C(41)	124(1)
C(2)–P(1)–C(11)	106(1)	C(4)-P(2)-C(31)	103(1)
C(2)–P(1)–C(21)	104(1)	C(4)-P(2)-C(41)	106(1)
C(11)–P(1)–C(21)	106(1)	C(31)–P(2)–C(41)	108(1)
C(1)-S-C(3)	105(1)		

complexes having thioethers *trans* to iodide (2.601(1) - 2.602(2) Å) [25,26].

The structure of **3** shows an increased distortion relative to **1a**, which seems to reflect the larger steric demands of the iodide. Thus, the deviations from the least-squares plane defined by (P(1), P(2), S, I(1)) are: P(1), 0.33 Å; P(2), 0.44 Å; S, -0.40 Å; I(1), -0.02 Å and Pt, -0.03Å from which it is seen that **3** is also tetrahedrally distorted from planar geometry. The larger distortion in **3** is also evident from the smaller angles for the *trans* donors, with S-Pt-I(1) = 170.3(2)° and P(1)-Pt-P(2) only 156.6(2)°. As expected, the P-Pt-S angles of the five-membered chelate rings are smaller than 90° (P(1)-Pt-S = 86.6(2)°, P(2)-Pt-S = 86.6(2)°), while the two P-Pt-I(1) angles are 97.7(2) and 92.6(2)°. The distances and angles within the coordinated PSP ligand in **3** are close to those found in **1a**.

Like in 1a the two phenyl rings in each phosphine group are on either side of the least-squares plane. The small P(1)–Pt–P(2) angle in 3 results in even larger Pt–P– C angles to the two phenyl rings closest to the iodine atom (Pt–P(1)–C(11) = $125.2(9)^\circ$, Pt–P(2)–C(41) = 124-(1)°) when compared to the corresponding angles in 1a.

A stereo view of the unit cell (see Fig. 3) reveals that the large thermal vibrations of the counter anion, I(2),



Fig. 3. Stereo view of the unit cell in [Pt(PSP)I]I (3).

Table 6			
${}^{31}P{}^{1}H{}$	NMR	data	a

Compound	$\delta^{31} P\{^{1}H\}$ (ppm)	$^{1}J(\text{PtP})$ (Hz)	∆ (ppm)
PSP ^b	-16.4		
[Pt(PSP)Cl]Cl (1)	38.9	2547	55.3
$[Pt(PSP)Cl]ClO_4$ (1a)	38.7	2538	55.1
[Pt(PSP)Br]Br (2)	39.0	2519	55.4
[Pt(PSP)I]I (3)	39.0	2473	55.4
[Pt(PSP)(CNS)]SCN (4)	40.5	2459	56.9
	44.1	2515	60.5
$[Pt(PSP)CN]ClO_4$ (5)	39.7	2417	56.1
$[Pt(PSP)(tu)](ClO_4)_2^{\circ}$ (6)	38.9	2551	55.3
$[Pt(PSP)(PPh_3)](ClO_4)_2 ^{\circ} (7)$	44.5	2402	60.9
	10.0	3270	

^a In CDCl₃ solution at 293 K, unless otherwise stated.

^b In agreement with δ –16.4 in CD₃CN [2].

^c In DMSO-d₆ solution at 293 K, due to the low solubility in CDCl₃.

are mainly directed towards one of the phenyl rings, (C(41)-C(46)), resulting in larger thermal vibrations of C(45) (see Fig. 2).

3.3. NMR and IR spectra

In the ³¹P{¹H} NMR spectra of the platinum complexes 1–7, all ³¹P resonances are singlets with satellites of 17% intensity, corresponding to the natural abundance of the ¹⁹⁵Pt isotope, and hence in accordance with the two PSP phosphine groups in each complex being chemically equivalent and both coordinated to platinum. The spectra of 1–3 and 5–6 show just one ³¹P resonance, while two singlets are observed in the spectra of 4 and 7 (see discussion below). The ¹J(PtP) range for 1–7 (see Table 6) is in good agreement with literature data for Pt(II) complexes having two mutually *trans* –PPh₂ moieties [3,21,32,33] and is support for the *trans* –PPh₂ configuration observed in the crystal structures of **1a** and **3**.

The range of the coordination chemical shift Δ is found to be 55.1–60.9 ppm for 1–7, where Δ is defined as the difference in ³¹P chemical shift between the complex and the free PSP ligand. The observed range of Δ is indicative of phosphines being part of a fivemembered chelate ring [6,10,34], thus consistent with the PSP ligand binding tridentately to platinum in all the prepared complexes.

As mentioned above, the spectrum of 7 shows two ³¹P singlets, both having ¹⁹⁵Pt satellites, and with a relative intensity 2:1 for the two resonances at δ 44.5 and 10.0, respectively. From this intensity ratio and the observed δ ³¹P range of **1**–**6**, the downfield resonance at δ 44.5 is easily assigned to the PSP ligand and the δ 10.0 resonance to the coordinated PPh₃ group. Both the chemical shift and the ¹*J*(PtP) (3270 Hz) of the PPh₃ ligand are similar to data for Pt(II) having PPh₃ *trans*

to a thioether group [26]. No coupling of PPh₃ with PSP is observed in the spectrum, which might indicate that ${}^{2}J(-PPh_{2},PPh_{3})$ is <2 Hz.

In the ${}^{31}P{}^{1}H{}$ spectrum of [Pt(PSP)(CNS)]SCN (4) two ³¹P resonances with ¹⁹⁵Pt satellites are observed at δ 44.1 and 40.5 in a ca. 6:1 intensity ratio, thus indicating the presence of two different complexes in solution. From Δ data, it is evident that in both complexes PSP is tridentately coordinated. More conclusive evidence comes from the IR spectra of crystalline [Pt(PSP)-(CNS)]SCN (4), where three bands are observed in the v(CN) region, the lowest frequency at 2054 cm⁻¹ being close to the reported value for salts containing the SCN⁻ ion [33,35,36]. At higher frequencies a sharp band at 2124 cm⁻¹, assigned to the -SCN isomer, is observed along with a broader band at 2097 cm⁻¹, assigned to the -NCS isomer. This assignment is made from the general observation that S-bonded thiocyanate results in higher v(CN) and sharper bands than does N-bonded thiocyanate [35,37]. Thus, IR reveals that the solid sample of 4 contains both the N- and S-bonded thiocyanate with the values of 4 being close to literature data for Pt(II) and Pd(II) thiocyanato complexes [33,37-41]. Consistent with these IR results, the ${}^{31}P{}^{1}H$ data of 4 can be explained by the presence of both N- and S-bonded thiocyanato complexes in solution. In our case, it is not possible to specifically assign the ³¹P resonances to the two linkage isomers, since chemical shifts alone do not indicate the coordination mode of thiocyanate [41]. Though, data from the sterically comparable complex [Pt(triphos⁴)(CNS)]⁺ show that S-bonded thiocyanate results in a larger chemical shift for the -PPh₂ group than does N-bonded thiocyanate [32,42].

⁴ Triphos is bis(2-diphenylphosphinoethyl)phenylphosphine.

The kinetics and thermodynamics of linkage isomerism in $[Pt(PSP)(CNS)]^+$ are currently under investigation in this group to clarify how, e.g., steric, electronic and medium effects influence the coordination mode of the thiocyanate ligand in Pt(II) complexes having the *trans* thioether-CNS donor group motif.

Table 7 presents ¹H NMR data of the free PSP ligand and the complexes **1a**–7. The spectrum of the free PSP ligand in CDCl₃ shows a multiplet in the aromatic region for the phenyl ring protons, δ 7.25–7.45 (m, 20H) and two multiplets in the aliphatic region due to the two different methylene groups; δ 2.20–2.35 (m, PCH₂, 4H), δ 2.50–2.65 (m, SCH₂, 4H).

Common for all the ¹H NMR spectra of the complexes 1a-7 is the presence of four groups of multiplets in the aliphatic region, each integrating to 2H (see Fig. 4). This suggests that the eight aliphatic protons are pairwise equivalent. If the $\delta - \lambda$ conformation of the two five-membered chelate rings observed in both crystal structures of 1a and 3 persists in solution, the symmetry would allow the four protons in each chelate ring to be distinguishable

Table 7 ¹H NMR data ^a

and pairwise identical to the proton equally positioned in the other chelate ring. This 'frozen' $\delta - \lambda$ conformation may arise from the strained geometry of the coordinated PSP ligand, which probably does not allow free $\delta - \lambda$ conformational interconversions. A similar pattern of multiplets for protons in a five-membered -PCH₂CH₂Schelate ring is observed in [Pd(P-S(O)-P)Cl]ClO₄ [4], where it is assumed that a conformational 'interlocking' of the $\delta - \lambda$ ring conformation exists due to steric repulsion between the S=O group and -SCH₂- protons. In the present case, we cannot exclude the possibility that a simultaneous $\delta - \lambda$ conformational exchange process for both rings could occur on the NMR time scale. However, a fast change from $\delta - \lambda$ to either $\delta - \delta$ or $\lambda - \lambda$ is unlikely, since this would average out the resonances of protons attached to the same carbon atoms, resulting in only two aliphatic multiplets.

In the aromatic region of the ¹H NMR spectra for **1a–5** two multiplets are seen, one around δ 7.45–7.70 (m, 12H) and one δ 7.70–7.90 (m, 8H). For **6** only one multiplet is observed, δ 7.50–7.80 (m, 20H), along with

Compound	δ Aliphatic protons (ppm)		δ Aromatic protons (ppm)	
PSP	2.20-2.35 (m, 4H)	2.50-2.65 (m, 4H)	7.25–7.45 (m, 20H)	
1a	2.55–2.70 (m, 2H)	3.30-3.60 (m, 2H)	7.45–7.60 (m, 12H)	
	3.05–3.20 (m, 2H)	4.00-4.30 (m, 2H)	7.75–7.90 (m, 8H)	
2	2.65-2.80 (m, 2H)	3.40-3.60 (m, 2H)	7.45–7.60 (m, 12H)	
	3.20-3.35 (m, 2H)	4.30-4.80 (m, 2H)	7.75–7.90 (m, 8H)	
3	2.60–2.80 (m, 2H)	3.40-3.65 (m, 2H)	7.45–7.60 (m, 12H)	
	3.15-3.35 (m, 2H)	3.75-4.25 (m, 2H)	7.70–7.85 (m, 8H)	
4	2.70–2.90 (m, 2H)	4.00-4.40 (m, 2H)	7.45–7.65 (m, 12H)	
	3.40-3.80 (m, 4H)		7.70–7.80 (m, 8H)	
5	2.65–2.80 (m, 2H)	3.60-3.90 (m, 2H)	7.45–7.60 (m, 12H)	
	3.00-3.20 (m, 2H)	3.95-4.35 (m, 2H)	7.70–7.90 (m, 8H)	
6 ^b	2.90-3.10 (m, 2H)	3.60-4.10 (m, 4H)	7.50–7.80 (m, 20H)	
	3.35–3.55 (m, 2H)		(7.90–8.20 (tu)) °	
7 ^b	2.95-3.15 (m, 2H)	3.65-3.85 (m, 2H)	6.90-7.80 (m, 35H)	
	3.20-3.40 (m, 2H)	3.95-4.15 (m, 2H)		

^a In CDCl₃ solution at 293 K, unless otherwise stated. m = multiplet.

^b In DMSO-d₆ solution at 293 K, due to the low solubility in CDCl₃.

^c Broad resonance from the coordinated thiourea ligand.



Fig. 4. ¹H NMR spectrum of [Pt(PSP)I]I (3) in CDCl₃, showing the resonances in the aliphatic region of the spectrum.

Table 8			
${}^{13}C{}^{1}H{}$	NMR	data	a

Compound	ppm Hz	δ C _{ipso} (¹ J(PC)) ^b	δC_{ortho} (² J(PC)) ^b	δ C _{meta} (³ J(PC)) ^b	$\delta \mathrm{C}_{para}$	$\begin{array}{c} \delta \ \mathrm{PCH}_2 \\ (^1J(\mathrm{PC}))^{\mathrm{\ b}} \end{array}$	$\delta \text{ SCH}_2$
PSP		137.9 d (13)	132.7 d (19)	128.6 d (7)	128.8 s	28.3 d (15)	28.0 d (22)
	(1) ^c	128.3 t (57)	133.5 t (13)	129.4 t (11)	132.4 s	31.3 t (36)	36.8 s
1a	(2) °	127.6 t (57)	133.2 t (13)	129.3 t (11)	132.3 s		
	(1)–(2) ^c	51 Hz	22 Hz	11 Hz	12 Hz		
	(1)	127.4 t (59)	133.6 t (13)	129.4 t (11)	132.5 s	33.7 t (36)	39.0 s
2	(2)	127.0 t (59)	133.5 t (13)	129.4 t (11)	132.4 s		
	(1)–(2)	28 Hz	3 Hz	2 Hz	10 Hz		
	(1)	127.4 t (60)	134.0 t (13)	129.4 t (11)	132.6 s	35.4 t (36)	38.0 s
3	(2)	127.4 t (60)	133.7 t (13)	129.3 t (11)	132.4 s		
	(1)–(2)	0 Hz	24 Hz	3 Hz	12 Hz		
	(1)	125.6 t (59)	133.8 t (14)	129.7 t (11)	133.1 s	35.6 t (38)	37.7 s
4	(2)	125.2 t (59)	133.3 t (14)	129.7 t (11)	132.9 s		
	(1)–(2)	29 Hz	33 Hz	5 Hz	13 Hz		
	(1)	127.3 t (61)	133.3 t (14)	130.0 t (12)	133.0 s	33.7 t (38)	36.5 s
5	(2)	126.2 t (61)	133.1 t (14)	129.9 t (12)	132.9 s		
	(1)–(2)	84 Hz	17 Hz	7 Hz	15 Hz		
	(1)	127.9 t (58)	133.3 t (13)	129.4 t (11)	132.6 s	33.1 t (36)	36.4 s
6 ^d	(2)	127.2 t (58)	133.1 t (13)	129.2 t (11)	132.3 s		
	(1)–(2)	53 Hz	15 Hz	15 Hz	22 Hz		
7 ^d		125.6 d (86)	134.2 d (12)	128.5 d (11)	132.2 s	_ e	34.7 s

^a In CDCl₃ solution at 293 K, unless otherwise stated. s = singlet, d = doublet, t = virtual 1:2:1 triplet.

^b These coupling constants are for **1a–6** the sum $|{}^{n}J(PC) + {}^{n+2}J(P'C)|$, though for n > 1, the ${}^{n+2}J(P'C)$ is usually very small [44].

 c (1) and (2) denotes first and second virtual 1:2:1 triplet/singlet, respectively, and (1)–(2) denotes the difference in chemical shift in Hz between (1) and (2).

^d In DMSO-d₆ solution at 293 K, due to the low solubility in CDCl₃.

^e Not observed, probably masked by the DMSO-d₆ resonance.

a broad resonance δ 7.90–8.20 from the protons on the coordinated thiourea ligand. The spectrum of 7 is more complex with four overlapping multiplets, δ 6.90–7.80 (m, 35H), arising from the phenyl group protons from both PSP and PPh₃.

¹³C{¹H} NMR spectra of the free PSP ligand and the complexes 1a-7 have been recorded and the results are presented in Table 8. In the spectrum of the free ligand all the carbon resonances appear as doublets due to coupling with ³¹P, except that of the phenyl ring C_{para}, which is seen as a singlet.

In all the complexes, except $[Pt(PSP)(PPh_3)](ClO_4)_2$ (7), the ${}^{13}C{}^{1}H$ resonances of PCH₂ and the phenyl ring carbons Cipso, Cortho and Cmeta are seen as 1:2:1 triplets and SCH_2 and C_{para} as single lines, broadened due to unresolved couplings. We believe that the most probable explanation for this splitting of the ¹³C{¹H} resonances is the virtual coupling of the trans phosphine system. The observation of ¹³C{¹H} 1:2:1 triplets in platinum and palladium bis-phosphine complexes is known to indicate that the two identical phosphines are in trans position [21,43,44]. The magnitude of the $|{}^{n}J(PC) + {}^{n+2}J(P'C)|$ coupling constants are in accordance with those reported for other ¹³C virtual triplets in Pt(II) trans phosphine complexes [44,45]. Due to the presence of one more I = 1/2 nucleus a similar 1:2:1 pattern is not observed in the spectrum of complex 7. The resonances of Cipso, Cortho

and C_{meta} are seen as doublets while C_{para} show up as a singlet and the PPh₃ phenyl rings only give rise to broad resonances.

A special feature in the ${}^{13}C{}^{1}H$ spectra of the complexes 1a-6 compared to other *trans* bis-phosphine Pt(II) complexes is that two 1:2:1 triplets are found in a 1:1 ratio for C_{ipso} , C_{ortho} and C_{meta} along with two broadened singlets for the C_{para} (see Fig. 5). This is not observed for the methylene carbons, which just show one 1:2:1 triplet from PCH₂ and a broadened singlet from SCH₂. When the integrals of the aromatic ¹³C resonances are compared with those of the methylene groups, it is seen that each of the two 1:2:1 triplets from Cortho and Cmeta integrates to four carbon nuclei. Among the plausible explanations for the presence of two virtual triplets for C_{inso} , C_{ortho} and C_{meta} instead of just the expected one, and likewise two singlets for C_{para} , we tend to believe that each of the triplets/singlets results from the pair of phenyl rings positioned on the same side of the least-squares donor atom plane. Thus, the two phenyl rings on each phosphine could be chemically non-equivalent due to variations in the close environment resulting from one of the phenyl rings being in the close proximity of the monodentate ligand occupying the fourth coordination site. The spectra of $[Pt(PSP)Cl]ClO_4$ (1a) in DMSO-d₆ at 20, 50 and 80°C all show the same pattern of virtual 1:2:1 triplets and broadened singlet, therefore suggesting a



Fig. 5. ¹³C{¹H} NMR spectrum of [Pt(PSP)Cl]ClO₄ (1a) in CDCl₃, showing the resonances in the aromatic region of the spectrum.

rigid conformation of the chelate rings in solution, as was suggested from the ¹H NMR data above.

In [Pt(PSP)(tu)](ClO₄)₂ (6) the ¹³C{¹H} resonance from the thiourea carbon is observed as a low intensity singlet at δ 171.8, compared with δ 183.4 of the uncoordinated thiourea in DMSO-d₆. This deshielding (10–15 ppm) of the ¹³C nucleus upon coordination agrees with data from sulfur-bonded Pt(II) thiourea complexes [46], so our NMR data show no indication of *N*-bonded thiourea. Unfortunately, the use of IR for studying the bonding mode of thiourea in **6** was limited due to masking from the PSP ligand of ν (CS) stretching frequencies.

In the ¹³C{¹H} NMR spectra of **4** and **5** no resonances from the coordinated SCN⁻ or CN⁻ ligands were observed due to the well-known relaxation phenomena [47]. ¹³C{¹H} NMR spectra of a sample of **5** prepared as in section 2.1.5 using 90 atom% enriched ¹³C cyanide showed the ¹³CN triplet at δ 115.0, ²*J*(PC) 24 Hz, and with corresponding ¹⁹⁵Pt satellites, ¹*J*(PtC) 1303 Hz, typical for cyanide coordinated to Pt(II) [47]. These observations are in accordance with IR data, where the spectrum of [Pt(PSP)CN]ClO₄ (**5**) showed one ν (CN) stretching frequency at 2144 cm⁻¹, corresponding to the formula and with the value found in the normal range for cyanide coordinating to Pt(II) [10,32,35,38].

4. Conclusions

The X-ray crystal structures of 1a and 3 show that both complexes are four coordinate with the PSP ligand tridentately coordinating through the sulfur and the two phosphorus atoms. The spectroscopic data are consistent with these crystal data and show that for all the complexes, including those containing the very *trans* labilizing CN^- and PPh_3 , all three donor atoms of PSP are bonded to platinum. Furthermore, the data strongly indicate that the conformations of the fused chelate rings also persist in solution, and this may be caused by a significant ring strain in the five-membered chelate due to the presence of the bulky donor atoms. Such ring strain is further reflected in the small bite angles of the PSP ligand and in the large distortion from square planar geometry, which is seen to be further enhanced when chloride is replaced by iodide.

Ring strain may also be responsible for the observation that when comparing the chloro with the iodo complex the larger *trans* influence of the iodide is not reflected in an increased Pt–S bond distance. In contrast, the structural data of the two complexes show unexpectedly long Pt-halogen distances, which suggest that the *trans* influence of the PSP sulfur donor is larger than that of a monodentate thioether.

5. Supplementary material

Atomic coordinates, bond lengths and angles and thermal parameters for **1a** and **3** have been deposited at the Cambridge Crystallographic Data Center, deposition numbers CCDC 133384 for **1a** and 133383 for **3**.

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