A STUDY OF THE BONDING BETWEEN PLATINUM(II) AND THE GROUP VI DONOR LIGAND IN THE ISOSTRUCTURAL COMPLEXES CHLOROPENTAFLUOROPHENOLATO-o-VINYL-N,N-DIMETHYLANILINEPLATINUM(II) AND CHLOROPENTAFLUOROTHIOPHENOLATO-o-VINYL-N,N-DIMETHYLANILINEPLATINUM(II)

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Summary

The molecular structures of $Pt(VMN)Cl(OC_6F_5)$, and $Pt(VMN)Cl(SC_6F_5)$, (VMN = $o\text{-}Me_2NC_6H_4CH=CH_2$) have been determined from single crystal X-ray diffraction data. Both complexes crystallize in the $P\bar{1}$ space group with lattice constants a 8.661(4), b 10.458(8), c 10.102(8) Å, and a 8.724(3), b 10.385(5), c 10.414(8) Å, respectively. Least squares refinements gave conventional R values of 0.033, and 0.045. The molecules are essentially isostructural and the coordination geometries have been used in conjunction with platinum—olefinic hydrogen coupling constants to reveal a small but significant degree of π-bonding between platinum(II) and the thiol sulphur.

Introduction

Evidence for and against the existence of π-bonding between metals and ligands coordinated through sulphur atoms is scarce [1,2]. To assess the π-acceptor ability, if any, of sulphur when bonded to platinum in a thiophenolato complex we have prepared the compounds chloropentafluorophenolato-o-vinyl-N,N-dimethylanilineplatinum(II) (I) and chloropentafluorothiophenolato-o-vinyl-N,N-dimethylanilineplatinum(II) (II) which differ only in their Group VI donor atoms. The phenolato compound has a coordinated oxygen atom, which is incapable of acting as a π-acceptor, and was used for the purpose of comparison with the sulphur-containing compound.

The crystal structures of both complexes have been determined, and their ^{1}H NMR spectra analysed. This information has enabled us to comment on the nature of the Pt—S bond.

Experimental

o-Vinyl-*N*,*N*-dimethylaniline (VMN) was made from indoline by the method of Booth, King and Parrick [3]. Thallium(I) pentafluorophenolate and pentafluorothiophenolate were synthesized by the reaction of thallium(I) ethoxide with the appropriate phenol or thiophenol [4].

Pt(VMN)Cl$_2$, dichloro-*o*-vinyl-*N*,*N*-dimethylanilineplatinum(II), was prepared by the following method. Zeise's salt (2.2 g, 5.7 mmol) [5] was dissolved in dry tetrahydrofuran (40 ml) and a solution of *o*-vinyl-*N*,*N*-dimethylaniline (0.9 g, 6.1 mmol) in dry chloroform (50 ml) was added dropwise to the stirred solution. The mixture was then refluxed for 30 minutes and filtered, while still hot, to remove the precipitated potassium chloride. The filtrate was reduced in volume to ca. 10 ml and dry methanol (15 ml) added. After refrigeration overnight a pale yellow microcrystalline solid was collected, washed with methanol, and air dried. The yield of Pt(VMN)Cl$_2$ was 1.85 g, 4.5 mmol, 78.9%; m.p. 206—209°C (dec.). Analysis: Found: C, 29.04; H, 3.23; N, 3.36; Cl, 17.4. C$_{10}$H$_{13}$NCl$_2$Pt calcd.: C, 29.07; H, 3.17; N, 3.39; Cl, 17.2%.

Infrared absorptions at 340(s) and 311(s) cm^{-1} are attributed to the platinum—chlorine stretching vibrations.

To synthesize Pt(VMN)Cl(OC$_6$F$_5$), chloropentafluorophenolato-*o*-vinyl-*N*,*N*-dimethylanilineplatinum(II) (I), Pt(VMN)Cl$_2$ (0.41 g, 1.0 mmol) was dissolved in dry chloroform (40 ml) and solid thallium(I) pentafluorophenolate (0.40 g, 1.1 mmol) added. The mixture was stirred at room temperature for an hour then filtered through Kieselguhr to remove the precipitated thallium(I) chloride and any unreacted thallium(I) pentafluorophenolate. Rapid evaporation of the solvent at room temperature, under reduced pressure (10 ml final volume), followed by treatment with methanol (15 ml) and refrigeration overnight, produced an off-white microcrystalline solid in a yellow-brown solution. The solid was collected, washed with methanol, and air dried. Yield 0.37 g, 0.66 mmol, 66.0%; m.p. 176—178°C (dec.). Analysis: Found: C, 34.35; H, 2.44; N, 2.44; Cl, 6.2. C$_{16}$H$_{13}$NClF$_5$OPt calcd.: C, 34.26; H, 2.34; N, 2.50; Cl, 6.3%.

Pt(VMN)Cl(SC$_6$F$_5$) (II) was prepared in a similar manner as yellow needles, m.p. 185—187°C (dec.). Analysis: Found: C, 33.27; H, 2.40; N, 2.20; Cl, 6.5; S, 5.2. C$_{16}$H$_{13}$NClF$_5$SPt calcd.: C, 33.31; H, 2.27; N, 2.43; Cl, 6.2; S, 5.6%.

The observation of a single platinum—chlorine infrared absorption (346 cm^{-1}, I; 339 cm^{-1}, II) confirms the presence of one chlorine in each compound.

Crystals of I and II suitable for X-ray structure analysis were grown from chloroform at −20°C.

The ^{1}H NMR spectra of the platinum(II) complexes I and II were recorded on a Varian HA100 100 MHz spectrometer using DMF-*d*$_7$ solution with TMS as internal standard.

Infrared spectra of the complexes were recorded in Nujol mull on a Perkin—Elmer PE457 grating infrared spectrophotometer calibrated with polystyrene film. The frequencies recorded are believed to be accurate to ±2 cm^{-1}.

Melting points were recorded in air on a Reichert hot stage melting point apparatus with microscope, and are corrected.

Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, CSIRO, University of Melbourne.

TABLE 1

CRYSTAL DATA AND DATA COLLECTION PARAMETERS

	$PtCl(NC_{10}H_{13})(OC_6F_5)$ (I)	$PtCl(NC_{10}H_{13})(SC_6F_5)$ (II)
a	8.661(4) Å	8.724(3) Å
b	10.458(8) Å	10.385(5) Å
c	10.102(8) Å	10.414(8) Å
α	104.54(4)°	102.47(4)°
β	102.68(3)°	104.48(3)°
γ	93.57(2)°	92.47(3)°
Volume	857.4 Å³	887.6 Å³
Mol. wt.	560.83	576.89
D_{obs} (by flotation)	2.15 g cm⁻³	2.15 g cm⁻³
D_{calc}	2.17 g cm⁻³	2.16 g cm⁻³
Z	2	2
Space group	$P\bar{1}$	$P\bar{1}$
Crystal shape	Diamond plate	Badly defined plate
Crystal dimensions	0.25 × 0.16 × 0.16 mm	0.15 × 0.10 × 0.08 mm
Linear absorption coefficient for Mo-K_α (λ 0.71069 Å)	87.3 cm⁻¹	86.0 cm⁻¹
Tube take-off angle	2.8°	2.8°
Crystal to counter distance	173 mm	173 mm
Counter aperture	1.8 + 0.35 tan θ	2.0 + 0.35 tan θ
Scan type [a]	$w - 1/3 \theta$	$w - 1/3 \theta$
Scan range	1.2 + 0.35 tan θ	1.5 + 0.35 tan θ
Scan rate [b]	1.3 to 10°/min	1.6 to 10°/min
Intensity standards	3 measured every 8000 s	3 measured every 6000 s
2θ limits	3° to 55°	3° to 50°
Number of reflections measured	3895	3116
Number of reflections measured with $I > 1.5\sigma(I)$ [c]	3071	2242

[a] Determined from reflection profile analyses. [b] Variable, depending on the reflection intensity. [c] $I = PI - 2(B_1 + B_2)$ where PI is the peak intensity, and B_1 and B_2 are the background counts collected for 25% of the total scan time at each end of the scan range; $\sigma(I) = [PI + 4(B_1 + B_2)]^{1/2}$.

Preliminary examination of crystals of complexes I and II by precession and Weissenberg methods revealed neither reciprocal lattice symmetry nor systematic absences. Since $Z = 2$ in each case, space group $P\bar{1}$ was chosen for both I and II. These choices were later confirmed by the successful least squares refinements in that space group. The unit cell data, given in Table 1, were obtained by least squares refinements of the 2θ values of 25 reflections measured with Mo-K_{α_1} radiation (λ 0.70930 Å) in the ranges $36° < 2\theta < 42°$ for I and $28° < 2\theta < 40°$ for II.

Data were collected on an Enraf—Nonius CAD-4 diffractometer using Mo-K_α radiation from a graphite crystal monochromator. The tube take-off angle was 2.8° and the counter was positioned 17.3 cm from the crystal. The data collection parameters for I and II are listed in Table 1. No significant variations in the intensity standards were observed. Both data sets were corrected for Lorentz and polarization effects, and also that of I for absorption effects. Transmission factors ranged from 0.133 to 0.234. An absorption correction was not possible in the case of II owing to the badly defined crystal shape.

TABLE 2

FINAL FRACTIONAL COORDINATES ($\times 10^4$) [a] AND ANISOTROPIC THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) [a,b] FOR COMPLEX 1

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	4587.9(3)	381.1(2)	2672.4(3)	38.7(1)	53.1(2)	52.9(2)	8.3(1)	16.3(1)	21.0(1)
Cl	7128.7(22)	883.4(22)	2488.5(26)	45.8(9)	80.0(13)	99.5(16)	11.9(9)	34.5(10)	35.3(11)
O	4653(6)	2218(5)	3950(6)	60(3)	62(3)	89(4)	-53(2)	32(3)	5(2)
F(2)	7207(7)	3458(5)	6168(5)	105(4)	98(4)	79(3)	-89(3)	8(3)	36(3)
F(3)	8004(7)	5645(6)	6151(6)	103(4)	97(4)	90(4)	-31(3)	7(3)	-0(3)
F(4)	8314(8)	6670(5)	3898(7)	148(6)	66(3)	128(5)	-22(3)	61(4)	21(3)
F(5)	5855(9)	5469(6)	1663(7)	146(6)	105(4)	103(4)	27(4)	38(4)	61(4)
F(6)	4090(7)	3245(7)	1648(6)	89(4)	134(5)	83(4)	3(3)	-8(3)	31(3)
N	2224(6)	32(5)	2762(6)	41(3)	57(3)	60(3)	10(2)	19(3)	16(3)
C(1)	5565(9)	3285(7)	3910(8)	55(4)	55(4)	60(4)	4(3)	24(3)	8(3)
C(2)	6830(10)	3936(7)	5032(8)	67(5)	63(4)	60(5)	5(4)	22(4)	17(4)
C(3)	7760(10)	5060(8)	5033(9)	68(5)	62(4)	68(5)	-7(4)	22(4)	-4(4)
C(4)	7433(12)	5594(7)	3914(10)	90(6)	55(4)	89(6)	2(4)	43(5)	19(4)
C(5)	6186(12)	4969(8)	2786(10)	99(7)	64(5)	78(6)	23(5)	36(5)	29(4)
C(6)	5290(10)	3848(8)	2805(9)	60(5)	70(5)	65(5)	11(4)	14(4)	15(4)
C(7)	2161(10)	64(9)	4227(9)	73(5)	101(6)	69(6)	-17(5)	38(5)	-1(5)
C(8)	1361(9)	1112(7)	2308(11)	55(4)	53(4)	133(8)	16(4)	22(5)	22(5)
C(9)	1438(8)	-1247(6)	1738(7)	49(4)	51(3)	49(4)	2(3)	10(3)	18(3)
C(10)	2262(9)	-1865(7)	812(8)	72(5)	57(4)	56(4)	5(4)	18(4)	23(3)
C(11)	1462(13)	-2989(8)	-285(9)	108(7)	62(5)	62(5)	6(5)	25(5)	14(4)
C(12)	-58(13)	-3481(8)	-332(10)	100(7)	60(5)	77(6)	-14(5)	-6(5)	27(4)
C(13)	-850(10)	-2885(9)	635(10)	64(5)	76(5)	85(6)	-10(4)	7(5)	30(5)
C(14)	-110(9)	-1750(8)	1685(9)	48(4)	70(5)	76(5)	5(3)	15(4)	26(4)
C(15)	3995(9)	-1437(7)	1051(9)	65(5)	60(4)	80(5)	11(4)	40(4)	15(4)
C(16)	5016(10)	-1635(8)	2243(10)	57(4)	65(5)	99(7)	15(4)	29(4)	28(4)

[a] Estimated standard deviations in the least significant figure are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$

TABLE 3

FINAL FRACTIONAL COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) [a] FOR COMPLEX II

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	4376.3(6)	208.5(6)	2606.0(6)	43.9(3)	59.4(3)	52.9(3)	8.8(2)	18.1(2)	15.0(2)
Cl	6889.0(41)	866.0(43)	2562.4(43)	47.3(20)	99.0(30)	89.8(28)	9.1(19)	30.8(19)	23.6(24)
S	4487.0(48)	2232.6(43)	4307.9(44)	63.9(23)	80.0(27)	82.3(28)	-7.9(20)	35.1(21)	-6.6(22)
F(2)	7383(12)	3701(10)	6341(9)	105(7)	103(7)	72(6)	-3(6)	7(5)	26(5)
F(3)	9152(12)	5921(10)	6034(12)	87(7)	89(7)	130(9)	-13(6)	24(7)	-7(6)
F(4)	8462(17)	6650(11)	3712(15)	184(12)	87(8)	200(13)	2(8)	117(11)	40(8)
F(5)	6008(17)	5379(12)	1578(12)	203(13)	137(10)	109(9)	52(9)	61(9)	66(8)
F(6)	4225(4)	3325(12)	1826(10)	117(9)	138(9)	84(7)	18(7)	-17(6)	22(7)
N	1982(12)	-169(10)	2670(10)	60(7)	56(7)	46(6)	3(5)	16(5)	8(5)
C(1)	5731(17)	3485(15)	4088(15)	65(9)	76(10)	69(10)	16(8)	23(8)	30(8)
C(2)	7016(17)	4141(15)	5132(17)	60(9)	64(10)	79(11)	6(8)	14(8)	3(8)
C(3)	7942(19)	5185(16)	5027(18)	73(11)	65(10)	82(11)	15(9)	13(9)	12(9)
C(4)	7588(20)	5006(14)	3852(22)	76(11)	43(8)	131(16)	1(8)	51(11)	14(10)
C(5)	6374(28)	4986(20)	2756(19)	132(17)	89(14)	73(12)	41(13)	40(12)	10(11)
C(6)	5448(19)	3943(17)	2892(19)	64(10)	70(11)	99(14)	26(8)	16(10)	6(10)
C(7)	1851(19)	-300(16)	4000(15)	85(11)	99(12)	62(10)	-3(9)	39(8)	9(9)
C(8)	1054(17)	918(15)	2233(18)	54(9)	69(10)	110(13)	18(7)	7(8)	20(9)
C(9)	1286(16)	-1399(12)	1613(13)	64(8)	53(8)	48(7)	-5(6)	13(6)	17(6)
C(10)	2145(16)	-1897(14)	711(13)	63(9)	65(9)	53(8)	4(7)	11(7)	20(7)
C(11)	1425(23)	-2973(16)	-411(16)	114(15)	72(11)	68(10)	11(10)	23(10)	23(9)
C(12)	-75(23)	-3507(16)	-532(18)	93(13)	74(11)	79(12)	-16(10)	12(10)	17(9)
C(13)	-916(19)	-3023(17)	384(21)	72(10)	77(11)	122(15)	-18(9)	20(11)	42(11)
C(14)	-216(17)	-1946(16)	1473(17)	51(8)	76(10)	94(12)	-22(8)	-1(8)	24(9)
C(15)	3827(18)	-1433(14)	999(15)	80(10)	61(9)	73(10)	20(8)	30(8)	25(8)
C(16)	4913(17)	-1712(13)	2144(16)	63(9)	56(8)	85(10)	11(7)	19(8)	17(8)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.
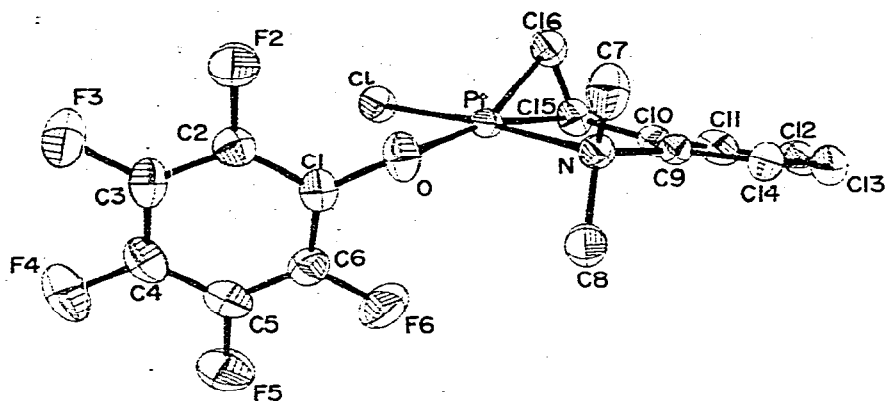
Fig. 1. Perspective view of molecule I showing atom numbering.

Solution and refinement of structures

Both structures were solved by Patterson and heavy-atom methods, and sub-sequently refined by full-matrix least squares. Only the observed data ($I >$ $1.5\sigma(I)$) were used in the refinements. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The weights w were derived from the expression

$$w = (\sigma(F)^2_{\text{statistical}} + \sigma(F)^2_{\text{empirical}})^{-1}$$

where $\sigma(F)_{\text{statistical}}$ is derived from counting statistics, and $\sigma(F)_{\text{empirical}} =$ $(a + b|F_o| + c|F_o|^2 + d|F_o|^3)^{1/2}$. The optimum values for the parameters a, b, c, and d were found to be (-16.96, 1.167, -0.01238, and 0.00004651) for I and (4.369, 0.1176, 0.0001760, and 0.0000) for II. Values of the atomic scattering factors for Pt, Cl, S, O, N, and C were taken from Cromer and Waber [6] and those for H, from Stewart, Davidson, and Simpson [7]. Anomalous scattering terms were included for Pt [8].

Both structures were refined using anisotropic temperature factors and positional parameters for non-hydrogen atoms. The inclusion of anisotropic parameters for the lighter atoms was found to be statistically significant [9]. Difference
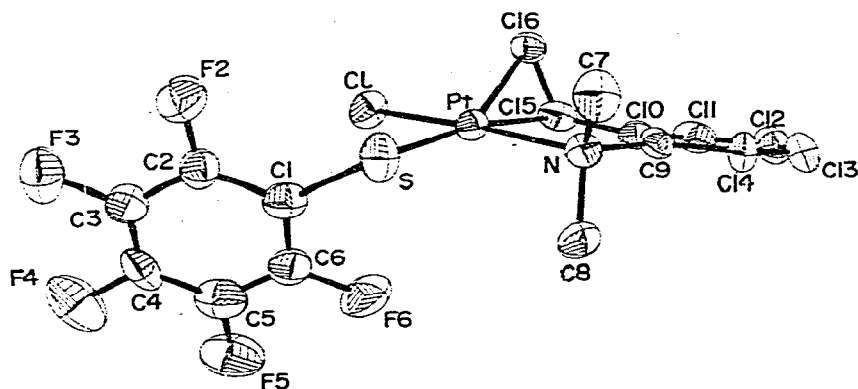

Fig. 2. Perspective view of molecule II showing atom numbering.

TABLE 4

BOND DISTANCES (Å)

	I	II		I	II
(a) Coordination sphere					
Pt—Cl	2.289(2)	2.291(4)	Pt—C(15)	2.123(8)	2.172(15)
Pt—X [a]	2.017(5)	2.304(4)	Pt—C(16)	2.117(8)	2.147(14)
Pt—N	2.083(5)	2.116(10)	Mean Pt—C [b]	2.120(6)	2.160(13)
(b) Pentafluorophenolato and pentafluorothiophenolato ligands					
X—C(1)	1.341(9)	1.747(15)	C(1)—C(2)	1.387(10)	1.382(20)
F(2)—C(2)	1.348(9)	1.353(17)	C(2)—C(3)	1.383(11)	1.364(21)
F(3)—C(3)	1.328(9)	1.318(18)	C(3)—C(4)	1.366(12)	1.356(23)
F(4)—C(4)	1.333(9)	1.354(17)	C(4)—C(5)	1.375(13)	1.363(24)
F(5)—C(5)	1.349(10)	1.343(20)	C(5)—C(6)	1.371(12)	1.376(25)
F(6)—C(6)	1.363(9)	1.351(18)	C(6)—C(1)	1.371(11)	1.396(22)
Mean C—F	1.344(6)	1.344(8)	Mean C—C(Ph)	1.376(5)	1.373(9)
(c) o-Vinyl-N,N-dimethylaniline ligand					
N—C(7)	1.485(10)	1.456(17)	C(12)—C(13)	1.362(13)	1.370(24)
N—C(8)	1.504(9)	1.501(17)	C(13)—C(14)	1.386(12)	1.399(23)
N—C(9)	1.485(8)	1.485(16)	C(14)—C(9)	1.395(9)	1.366(18)
C(9)—C(10)	1.360(9)	1.374(18)	C(10)—C(15)	1.488(11)	1.460(19)
C(10)—C(11)	1.413(11)	1.420(20)	C(15)—C(16)	1.398(12)	1.418(20)
C(11)—C(12)	1.369(13)	1.364(23)			
Mean C—C(Ph)	1.381(9)	1.382(9)			

[a] In this and all subsequent tables, X denotes O and S in I and II respectively. [b] Esd's quoted with mean values are the higher of the biased and unbiased estimates.

Fourier maps calculated during the later stages of the refinements revealed feasible hydrogen atom positions. Hydrogen atoms were subsequently included as fixed contributions using calculated coordinates, and assuming C—H 0.95 Å [10]. Each hydrogen atom was assigned a fixed isotropic thermal parameter which corresponded to the last isotropic value of its attached carbon atom. Both refinements were terminated when the parameter shifts were less than 0.2 σ. The final values of R (= $\Sigma||F_0| - |F_c||/\Sigma|F_0|$) and R_w(= $(\Sigma w(F_0| - |F_c|)^2/\Sigma w|F_0|^2)^{1/2}$) were 0.03 and 0.040 for I, and 0.045 and 0.051 for II. The standard deviations of an observation of unit weight were 0.42 (226 variables and 3071 observations) and 0.52 (226 variables and 2243 observations) for I and II, respectively. No systematic trends were noted in the analyses of $w(|F_0| - |F_c|)^2$ with respect to $|F_0|$, sin θ/λ and Miller indices. Final difference maps showed no significant features.

The final non-hydrogen atomic parameters for I and II are listed in Tables 2 and 3, respectively. Hydrogen atomic parameters and listings of $|F_0|$ and $|F_c|$ values may be obtained from one of the authors (MKC).

Figures 1 and 2 were drawn using Johnson's ORTEP 2 thermal ellipsoid plotting program. The molecular dimensions for I and II are displayed in Tables 3 and 4.

Results and discussion

Description of structures

The structure analyses of molecules I and II show that both contain Pt[II]

TABLE 5

BOND ANGLES (deg)

	I	II		I	II
(a) Coordination sphere					
Cl—Pt—X	90.9(2)	91.1(3)	X—Pt—C(15)	166.0(3)	169.1(4)
Cl—Pt—N	175.7(2)	175.2(3)	X—Pt—C(16)	153.9(3)	150.9(4)
Cl—Pt—C(15)	97.7(2)	96.4(4)	N—Pt—C(15)	83.4(2)	82.2(5)
Cl—Pt—C(16)	87.1(2)	85.3(4)	N—Pt—C(16)	96.3(3)	96.3(5)
X—Pt—N	87.3(2)	89.7(3)	C(15)—Pt—C(16)	38.5(3)	38.3(5)
(b) Pentafluorophenolato and pentafluorothiophenolato ligands					
Pt—X—C(1)	123.0(4)	110.5(5)	F(4)—C(4)—C(3)	121.1(9)	120.8(18)
X—C(1)—C(2)	121.5(7)	121.3(12)	F(4)—C(4)—C(5)	120.5(9)	117.1(20)
X—C(1)—C(6)	123.4(7)	122.9(13)	C(3)—C(4)—C(5)	118.3(8)	122.1(15)
C(2)—C(1)—C(6)	115.0(7)	115.6(14)	F(5)—C(5)—C(4)	119.3(8)	123.1(21)
F(2)—C(2)—C(1)	119.6(7)	120.5(14)	F(5)—C(5)—C(6)	120.4(9)	119.0(20)
F(2)—C(2)—C(3)	117.7(7)	116.6(14)	C(4)—C(5)—C(6)	120.3(8)	117.9(17)
C(1)—C(2)—C(3)	122.6(8)	122.9(16)	F(6)—C(6)—C(1)	118.4(8)	118.4(16)
F(3)—C(3)—C(2)	120.4(8)	122.6(16)	F(6)—C(6)—C(5)	118.1(8)	119.0(17)
F(3)—C(3)—C(4)	119.3(8)	118.5(16)	C(1)—C(6)—C(5)	123.4(8)	122.7(16)
C(2)—C(3)—C(4)	120.3(8)	118.8(15)			
(c) o-Vinyl-N,N-dimethylaniline ligand					
Pt—N—C(7)	109.6(5)	111.4(9)	C(9)—C(10)—C(15)	119.9(7)	120.1(12)
Pt—N—C(8)	107.6(4)	107.5(8)	C(11)—C(10)—C(15)	121.8(7)	120.7(14)
Pt—N—C(9)	110.6(4)	110.3(8)	C(10)—C(11)—C(12)	119.9(8)	119.0(16)
C(7)—N—C(8)	110.3(6)	111.1(12)	C(11)—C(12)—C(13)	121.5(8)	121.9(16)
C(7)—N—C(9)	112.1(5)	110.4(10)	C(12)—C(13)—C(14)	119.5(8)	119.0(15)
C(8)—N—C(9)	106.6(5)	106.0(10)	C(9)—C(14)—C(13)	119.2(8)	120.0(16)
N—C(9)—C(10)	117.1(6)	117.7(11)	Pt—C(15)—C(10)	107.7(5)	108.2(9)
N—C(9)—C(14)	121.1(6)	120.8(13)	Pt—C(15)—C(16)	70.5(5)	69.9(8)
C(10)—C(9)—C(14)	121.7(6)	121.2(13)	C(10)—C(15)—C(16)	117.3(7)	118.6(12)
C(9)—C(10)—C(11)	118.0(7)	118.8(13)	Pt—C(16)—C(15)	71.0(4)	71.8(8)

atoms in approximately square planar environments (see Fig. 1 and 2, and Tables 4 and 5). The olefin group of the o-vinyl-N,N-dimethylaniline ligand is found to occupy the coordination position *trans* to the pentafluorophenolato and pentafluorothiophenolato ligands in I and II respectively.

Comparison with similar systems shows that the coordination geometries around the Pt[II] atoms in I and II are not unusual. The dimensions of I and II (see Fig. 3) compare well with the following bond length ranges taken from some recent structural studies where Pt[II] atoms are coordinated to one or more Cl, N, C=C(olefin), O, or S containing ligands; (a) Pt—Cl, range 2.26 to 2.36 Å [11—24];
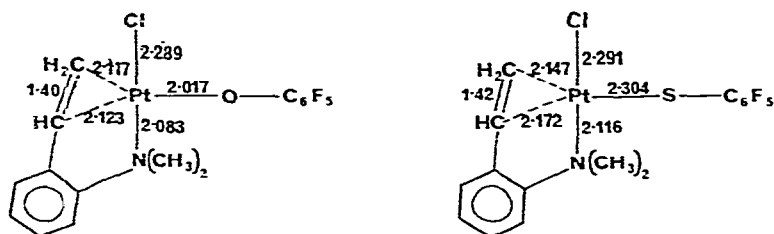
Fig. 3. Comparison of molecular dimensions of molecules I and II in the platinum coordination plane.

(b) Pt—N, range 1.98 to 2.12 Å [17—22]; (c) Pt—C(olefin), range 2.10—2.20 Å [11—16,19]; (d) Pt—O, range 1.97 to 2.07 Å [23,24]; (e) Pt—S, range 2.28 to 2.36 Å [25—27]; (f) C=C(olefin), range 1.35 to 1.44 Å [11—16,19].

A feature of interest in Pt[II]—olefin complexes is the dihedral angle between the principal coordination plane and the plane containing the Pt[II] atom and the olefin carbon atoms. Angles ranging from 67 to 90° have been reported [11—16, 19]. The values obtained for I and II (73.9 and 72.6°) show considerable deviation from the ideal value of 90° which should afford the maximum possible π-interaction between Pt[II] and the π^* orbitals of the olefin. Such deviations are generally considered to result from steric factors in the molecules, and in I and II must result largely from the chelation of the o-vinyl-N,N'-dimethylaniline ligand to the Pt[II] atom. The chelate ring, PtNC(9)C(10)C(15), in both complexes adopts a similar conformation and shows significant deviation from planarity (see Table 6). The olefin carbon atoms do not lie equidistant from the principal coordination plane, C(15) being 0.396 and 0.289 Å below the plane and C(16) being 0.933 and 1.035 Å above the plane in I and II respectively. Other dimensions in molecules I and II are normal and show a close correspondence between equivalent regions.

Comparison of unit cell dimensions (Table 1), unit cell fractional coordinates (Tables 2 and 3), and intermolecular contacts (Table 7) suggests that the gross structural features of both molecules remain almost unaltered on exchange of the donor atom *trans* to the Pt[II]—olefin bond. Extending this comparison to a molecular level (Fig. 1 and 2 and Tables 4 and 5), shows that this similarity is also present to a large degree within the individual molecules of I and II. A further estimate of the structural similarities of I and II can be made by considering planes calculated through various regions of the two molecules and also the dihedral angles between such planes (Table 6). The coordination geometries can be seen to be almost identical, and the only major diffe·ence between the two structures arises in the relative orientations of the pentafluorophenolato and pentafluorothiophenolato ligands with respect to the rest of each molecule. This difference could result from rotation about either the Pt—X or X—C(1) bonds (X = O and S in I and II respectively). Torsion angles calculated about the Pt—X and X—C(1) bonds (Table 8) show clearly that this significant difference in the orientation of the pentafluorophenolato and pentafluorothiophenolato ligands is a result of a 9° rotation about the X—C(1) bond in molecule II relative to molecule I. The dihedral angles between the planes of these ligands and the Pt[II] coordination planes are 85 and 74° for I and II respectively. It is possible that this rotation in II from near perpendicularity, is a consequence of increased intramolecular interactions as the C(1)—X—Pt angle closes from 123.0(4)° in I to 110.5(5)° in II, although this should be partly compensated for by the longer Pt—S bond in II (2.304(4) Å) compared to the Pt—O bond in I (2.017(5) Å).

From the above discussion it appears that the complexes are virtually isostructural, implying that external forces on the two molecules are very similar. This is important, since comparisons of the molecular structures of I and II in the Pt[II] coordination plane must therefore be more valid.

The relevant dimensions in the Pt[II] coordination plane of I and II are shown in Fig. 3. It is obvious that the Pt[II]—Cl bond are experimentally identical (2.289(2) Å for I and 2.291(4) Å for II). It has been suggested that in Pt[II] com-

TABLE 6a

WEIGHTED LEAST SQUARES PLANES [a]

		I	II	Atoms	Distance from plane (Å)	
					I	II
Plane 1	A	1.787	1.878	Pt [b]	0.000(0.2)	0.001(1)
	B	−6.084	−6.868	Cl [b]	−0.010(2)	−0.025(4)
	C	8.613	8.106	X [b]	−0.005(6)	0.000(5)
	D	2.889	2.801	N [b]	−0.132(6)	−0.149(10)
				C(15)	−0.396	−0.289
				C(16)	0.933	1.035
Plane 2	A	7.624	7.536	Pt [b]	0.000	0.000
	B	2.906	3.725	C(15) [b]	0.000	0.000
	C	−6.047	−6.238	C(16) [b]	0.000	0.000
	D	1.993	1.727	X	−0.189	−0.202
Plane 3	A	6.702	6.535	C(1) [b]	0.000(7)	−0.009(14)
	B	−5.437	−6.199	C(2) [b]	−0.005(8)	0.006(14)
	C	−4.449	−4.005	C(3) [b]	0.007(8)	0.007(15)
	D	0.204	0.043	C(4) [b]	−0.005(8)	−0.015(14)
				C(5) [b]	0.001(8)	0.014(17)
				C(6) [b]	0.001(8)	0.002(14)
				X	−0.048	−0.133
Plane 4	A	2.290	2.351	C(9) [b]	−0.014(6)	−0.007(12)
	B	−8.123	−8.278	C(10) [b]	0.023(7)	0.011(13)
	C	7.064	6.610	C(11) [b]	−0.022(9)	−0.010(16)
	D	2.584	2.534	C(12) [b]	−0.004(8)	−0.001(17)
				C(13) [b]	0.014(9)	0.007(17)
				C(14) [b]	0.003(8)	0.000(15)
				pt	0.045	0.030
				N	−0.149	−0.164
				C(15)	0.242	0.212
				C(16)	1.478	1.455
Plane 5	A	1.530	1.587	Pt [b]	0.000(0.2)	0.000(1)
	B	−7.758	−7.996	N [b]	−0.020(6)	−0.026(10)
	C	7.809	6.415	C(9) [b]	0.051(6)	0.065(12)
	D	2.493	2.455	C(10) [b]	−0.066(7)	−0.070(13)
				C(15) [b]	0.054(9)	0.039(14)
				Cl	−0.145	−0.154
				X	−0.417	−0.334
				C(16)	1.294	1.283

[a] Least squares planes are given by the equation $AX + BY + CZ − D = 0$, where X, Y, Z are orthogonal coordinates. [b] Atoms defining weighted least squares plane.

TABLE 6b

DIHEDRAL ANGLES (deg.)

	I	II		I	II
Plane 1—Plane 2	73.9	72.6	Plane 2—Plane 4	102.8	104.6
Plane 1—Plane 3	84.6	73.8	Plane 2—Plane 5	108.1	109.8
Plane 1—Plane 4	16.4	12.8	Plane 3—Plane 4	71.6	63.0
Plane 1—Plane 5	12.3	9.0	Plane 3—Plane 5	78.2	69.3
Plane 2—Plane 3	48.2	58.0	Plane 4—Plane 5	6.5	6.4

TABLE 7

INTERMOLECULAR CONTACTS < 3.7 Å

	Symmetry code [a]	I	II		Symmetry code [a]	I	II
Cl···C(7)	i	3.63	3.65	F(3)···C(12)	iv	3.35	3.38
X···C(4)	ii	3.59	3.50	F(4)···C(14)	v	3.53	3.40
F(2)···C(7)	i	3.69	3.66	F(5)···F(5)	vi	3.23	3.22
F(2)···C(9)	i	3.59	3.65	F(5)···C(16)	vii	3.10	3.19
F(3)···F(3)	iii	3.29	3.16	F(6)···C(12)	viii	3.50	3.56
F(3)···F(4)	iii	3.49	3.39	F(6)···C(13)	viii	3.15	3.17
F(3)···C(3)	iii	3.36	3.14	C(2)···C(6)	ii	3.64	3.69
F(3)···C(4)	iii	3.46	3.25	C(8)···C(12)	viii	3.64	3.55
F(3)···C(8)	ii	3.42	3.51	C(12)···C(12)	ix	3.41	3.51
F(3)···C(11)	iv	3.66	3.65				

[a] Symmetry codes are as follows: (i) $1-x$, $-y$, $1-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $2-x$, $1-y$, $1-z$; (iv) $1+x$, $1+y$, $1+z$; (v) $1+x$, $1+y$, z; (vi) $1-x$, $1-y$, $-z$; (vii) x, $1+y$, z; (viii) $-x$, $-y$, $-z$; (ix) $-x$, $-1-y$, $-z$.

plexes the observed variation in the Pt^{II}—Cl bond distance can be used as a measure of the change in the Pt^{II} radius [28]. In the present case it can therefore be inferred that the Pt^{II} radius has remained constant in I and II, thus providing a basis for assessing other bond length changes in the two molecules. Assuming the accepted value of r(Cl) 0.99 Å [29], a value of $r(Pt^{II})$ 1.30 Å can be calculated for both I and II.

Because pentafluorophenol (pK_a 5.53) [30] is more basic than pentafluoro-thiophenol (pK_a 2.68) [31], it might be expected that the pentafluorophenolato ligand in I would form a stronger σ-bond to Pt^{II} than would the pentafluorothio-phenolato ligand in II. However, it appears that the Pt^{II}—S bond in II (2.304(4) Å) is shortened relative to the sum of the covalent radii, 2.34 Å (r(S) 1.04 Å) [29]. The opposite effect is observed for the Pt^{II}—O bond in I where a relative lengthening has occurred (2.017(5) Å compared to 1.96 Å; r(O) 0.66 Å) [29]. These results imply that the relative strengths of the Pt^{II}—O and Pt^{II}—S bonds cannot be rationalized by σ-effects alone and suggest that the Pt^{II}—S distance is shortened by π-bonding. If this is correct it should have the effect of weakening the π-donor ability of the Pt^{II} atom to the *trans* ligand, the olefin. The two Pt^{II}—C(olefin) bond distances in each molecule, are equal within experimental error (2.123(8) and 2.117(8) Å for I; 2.172(15) and 2.147(14) Å for II). How-

TABLE 8

TORSION ANGLES (deg.)

	I	II
Cl—Pt—X—C(1)	27.2(6)	28.8(6)
N—Pt—X—C(1)	−148.9(6)	−146.5(6)
C(15)—Pt—X—C(1)	−100.9(11)	−105.3(20)
C(16)—Pt—X—C(1)	112.4(8)	111.1(10)
Pt—X—C(1)—C(2)	−113.9(7)	−123.6(11)
Pt—X—C(1)—C(6)	68.9(9)	60.3(13)

ever, the mean value for II (2.160(13) Å) is 0.040(14) Å longer than that for I (2.120(6) Å). This difference is significant at a σ 2.9 level, thus implying that the Pt^{II}—olefin π-interaction has been weakened in molecule II. It follows that the C=C(olefin) bond in II should have more π-character, and therefore be shorter than the corresponding bond in I. In fact, there is no observable difference between the C=C bonds of I and II (1.40(1) and 1.42(2) Å, respectively). However, it is worthy of note that the C=C(olefin) bonds in both I and II are significantly lengthened from the reported average values of 1.334(2) [32] and 1.335(6) Å [33] in two styrene-like systems.

It is also of interest that the Pt^{II}—N bond in II (2.116(10) Å) is significantly longer than the corresponding bond in I (2.083(5) Å). Since the Pt^{II} radius is observed to remain constant and no π-interaction is possible with a sp^3 nitrogen [34], the replacement of the O of I by an S to give II should not directly affect the length of the Pt^{II}—N bonds. However, the lenghtening of the Pt^{II}—C(olefin) bonds in II by 0.04 Å with respect to I might be expected to bring about a corresponding increase in the Pt—N distance in II if the undistorted geometry of the PtNC(9)C(10)C(15) chelate ring is to be maintained. It can be seen from Table 5 that the bond angles around the chelate rings are virtually identical in I and II, thus showing that the geometry of the chelate ring in I is indeed maintained in II by moving the N atom approximately 0.03 Å further from the Pt^{II} atom.

NMR studies

As the coordination geometry in both complexes is virtually identical we have used $J(Pt$—C—H(olefin)$)$ to assess the relative degree of σ-interaction in the platinum—olefin bonds of the two compounds. Other authors [35—37] have shown that in platinum(II)—olefin compounds the symmetry of the complexes is such that the metal → olefin π-bond is not involved in coupling between the metal and the olefinic proton. Such coupling therefore must be transferred through the olefin → metal σ-bond. As mentioned above the pentafluorophenol is expected to be a stronger σ-donor than the pentafluorothiophenol. Consequently the Pt—olefin σ-bond trans to the pentafluorophenolato ligand should be weaker (i.e. $J(Pt$—C—H$)$ should be smaller) than that trans to the analogous sulphur ligand. That this is not so can be seen from the $J(Pt$—C—H$)$ values in Table 9.

TABLE 9

^{1}H CHEMICAL SHIFTS (ppm) AND ^{195}Pt—^{1}H COUPLING CONSTANTS (Hz)

Proton numbering scheme:

	$\delta(1)$	$\delta(2)$	$\delta(3)$	$J(Pt(1))$	$J(Pt(2))$	$J(Pt(3))$
Pt(VMN)Cl(OC$_6$F$_5$)	5.51	4.87	4.12	66.0	69.0	71.0
Pt(VMN)Cl(SC$_6$F$_5$)	5.63	5.03	4.40	46.6	58.0	62.0

It is possible to rationalize this situation if it is assumed that the low-lying empty $3d$-orbitals of the sulphur are capable of accepting π-electron density from the filled $5d(t_{2g})$ orbitals of the platinum. This would reduce the density in the $2p\pi^{*}$ orbitals of the olefin, thereby weakening the platinum $\rightarrow$ olefin π-bond. The synergic relationship between the σ- and π-components of the metal—olefin bond would thus cause a decrease in the strength of the olefin—platinum σ-interaction and hence a lowering of J(Pt—C—H).

Conclusion

Comparison of the structures of I and II shows that the platinum—olefin distance in II is significantly longer than in I. In addition the platinum—sulphur bond of II is shorter than the value calculated from the covalent radius of sulphur and the platinum(II) radius derived from these complexes. In view of the close structural similarity of these compounds, especially in their coordination geometry, we attribute these effects to a small but significant degree of π-back-bonding to the sulphur that cannot be present in the oxygen-containing complex. This is supported by the relative values of the platinum—olefinic hydrogen coupling constants of I and II. It is also consistent with the interaction of the "soft" acid [38], Pt^{2+}, with the relatively (with respect to OR^{-}) "soft" base, SR^{-}.

Since the platinum carries a formal charge of 2+ and the sulphur a single negative charge, we expect the extent of π-back-donation to be small as indeed the X-ray data show. On the other hand the differences in J(Pt—C—H) for the corresponding protons in the two complexes are relatively large (9—19 Hz). This leads us to suggest that in closely related square planar complexes of this type, the platinum—olefinic proton coupling constants are a sensitive probe for indirectly assessing the π-acid character of the ligand *trans* to the olefin.

Acknowledgements

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