The $[PtCl_2(SnCl_3)_2]^{2-}$ Ion: Crystal Structure of Two Salts †

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The crystal structures of $M_2[PtCl_2(SnCl_3)_2]$ [M = $PMePh_3$(1) and $PPh_3(CH_2Ph)$ (2)] have been determined from three-dimensional *X*-ray data collected by counter methods. Compound (1) crystallises in space group $P2_1/n$ with a = 11.815(2), b = 14.172(3), c = 13.848(2) Å, β = 96.56(1)°, and Z = 2. Compound (2) crystallises in space group $P\bar{1}$, with a = 12.722(3), b = 11.518(2), c = 10.674(2) Å, α = 110.73(1), β = 79.86(2), γ = 114.39(1)°, and Z = 1. Both structures were refined by least-squares methods: refinement was halted at R = 0.13 for (1); for (2) refinement was concluded at R = 0.033 for 3 344 reflections with $I/\sigma(I) \geqslant 3.0$. Both crystals contain *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ ions, disordered in such a way as to be pseudo-centrosymmetric. This disordering involves a half-occupied $PtCl_2$ unit appearing on either side of the centre. Simultaneously, one chlorine from each $SnCl_3$ unit changes sides while the other two chlorines appear in average positions with very small displacements between their positions. The Pt–Sn distance (average 2.3556 Å) is significantly shorter than that found in $[Pt(SnCl_3)_5]^{3-}$ (average 2.5530 Å) consistent with the much larger $J(^{195}Pt-^{119}Sn)$ coupling constants in (1) and (2) (27 640 *vs.* 16 030 Hz). The Pt–Cl distance (average 2.296 Å), although not accurately determined, is relatively short. The ^{195}Pt and ^{119}Sn n.m.r. data, the far-i.r. spectral data, and the *X*-ray data, when compared to those of $[Pt(SnCl_3)_5]^{3-}$, suggest a greater amount of Pt–Sn π bonding in the four-co-ordinate than in the five-co-ordinate complex.

The striking n.m.r. properties [1] of the $[PtCl_2(SnCl_3)_2]^{2-}$ ion have led us to examine its molecular structure by *X*-ray methods; it has been studied as the $[PMePh_3]^+$ (1) and the $[PPh_3(CH_2Ph)]^+$ (2) salts.

Experimental

Syntheses.—Methyltriphenylphosphonium chloride and benzyltriphenylphosphonium chloride were prepared by literature methods.[2,3] Methyltriphenylphosphonium and benzyltriphenylphosphonium tetrachloroplatinates(II) were prepared by adding an aqueous solution of the phosphonium salt to an aqueous solution of $K_2[PtCl_4]$. The products, which precipitated immediately as light tan precipitates, were filtered off, washed with methanol and acetone, and air dried. The platinum–tin complexes were prepared as follows.[4]

A mixture of $[PMePh_3]_2[PtCl_4]$ (0.891 g, 1 mmol) and $SnCl_2{\cdot}2H_2O$ (0.451 g, 2 mmol) was covered with acetone (10 cm^3). The acetone supernatant changed from red to yellow-brown as the solids gradually dissolved. After standing for 2 h at room temperature, the solution was filtered to remove undissolved solids. Addition of carbon tetrachloride produced a yellow-brown solid (1.27 g, 99%), m.p. 140—142 °C, in a N_2-filled capillary. Recrystallisation from methanol without heating produced yellow crystals, m.p. 142—143 °C (Found: C, 35.55; H, 2.95; Cl, 22.4. Calc. for $C_{38}H_{36}Cl_8P_2PtSn_2$: C, 35.9; H, 2.85; Cl, 22.3%). Similarly, $[PPh_3(CH_2Ph)]_2[PtCl_2(SnCl_3)_2]$ was prepared in 90% yield and recrystallised from acetone–hexane, m.p. 182—186 °C (decomp.) (Found: C, 42.0; H, 3.20; Cl, 20.15. Calc. for $C_{50}H_{44}Cl_8P_2PtSn$: C, 42.2; H, 3.10; Cl, 19.95%).

Physical Measurements.—Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee 37921. Melting points are uncorrected. Infrared spectra in the region 420—50 cm^{-1} were obtained with a Polytec FIR 30 FT interferometer as Polythene discs. The $^{119}Sn-\{^1H\}$ and $^{195}Pt-\{^1H\}$ n.m.r. spectra were recorded at 37.10 and 21.28 MHz respectively on a JEOL FX-100 spectrometer in Fourier transform mode using saturated $[^2H_6]$acetone solutions. The spectra were recorded at a sweep width of 20 kHz, with 8K data points, pulse widths of 20 μs, and pulse delays of 0.3 (^{119}Sn) or 0.1 s (^{195}Pt). Coupling constants are estimated to be accurate to ±5 Hz and chemical shifts to ±5 p.p.m. Chemical shifts are relative to external $SnMe_4$ and H_2PtCl_6 with upfield shifts negative and downfield shifts positive.

Crystal Structure Analysis.—Both (1) and (2) gave well formed platy crystals which were examined with a Syntex $P2_1$ four-circle diffractometer; Mo-K_α radiation was used throughout (λ = 0.710 69 Å). The maximum 2θ was 50°, with a scan range ±0.95(2θ) around the $K_{\alpha1}$—$K_{\alpha2}$ angles and a scan speed of 1—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections, and showed slight changes during the data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Reflections with $I/\sigma(I) \geqslant 3.0$ were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR;[5] maximum and minimum transmission factors were 0.38—0.76 and 0.46—0.71 for (1) and (2) respectively. The crystal dimensions were 0.40 × 0.25 × 0.06 mm for (1) and 0.25 × 0.25 × 0.10 mm for (2). Additional crystal data are given in Table 1.

Each structure was solved by the heavy-atom Patterson method, locating two independent atoms initially (Sn and ½Pt), in a disordered anion (see Discussion section). For (1) the recognition of this unexpected solution only came after unsuccessful attempts to place a *trans* anion with Pt at the

† Methyltriphenylphosphonium and benzyltriphenylphosphonium *cis*-dichlorobis(trichlorostannato)platinate(II).

Supplementary data available (No. SUP 23426, 38 pp.): atom co-ordinates for (1), thermal parameters and structure factors for (1) and (2). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystal data

Compound	$C_{38}H_{36}Cl_8P_2PtSn_2$	$C_{50}H_{44}Cl_8P_2PtSn_2$
System	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Absences	$h0l; h+l \neq 2n$; $0k0; k \neq 2n$	
a/Å	11.815(2)	12.722(3)
b/Å	14.172(3)	11.518(2)
c/Å	13.848(2)	10.674(2)
α/°	90	110.73(1)
β/°	96.56(1)	79.86(2)
γ/°	90	114.39(1)
U/Å^3	2 303.7(7)	1 331.6(5)
M	1 270.7	1 422.4
Z	2	1
D_c/g cm^{-3}	1.83	1.77
D_m/g cm^{-3}	1.8	1.7
μ(Mo-K_α)/cm^{-1}	45.7	40.8
F(000)	1 192	688
Reflections:		
Total	4 460	4 730
$I/\sigma(I) \geqslant 3.0$	2 374	3 344

it can be concluded that the individual half-atoms lie very close to each other. Within the limited accuracy, the geometry of (1) is identical to that of (2), and it was not felt that the information to be obtained by completing the refinement of (1) would repay the effort required.

Computing was with the *X*-RAY 76 system,[6] on a Burroughs B6700. Scattering factors in the analytical form and anomalous-dispersion factors were taken from ref. 7. Final atomic co-ordinates for (2) are given in Table 2, and bond lengths and angles in Table 3. For (1), only a packing diagram is presented here.

Discussion

The most significant result of the crystal structure analyses is that the $[PtCl_2(SnCl_3)_2]^{2-}$ ion has the *cis* form, as predicted from chemical * and n.m.r.[1] data, but in both the compounds examined it is disordered, and thus pseudo-centrosymmetric. This disorder (illustrated in Figure 1) involves the half-occupied $PtCl_2$ unit appearing either on one or the other side of the centre. Simultaneously, one Cl on each Sn also changes sides, while the other two [Cl(3) and Cl(4)] appear in the

Table 2. Atomic co-ordinates ($\times 10^4$) for (2), with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Pt	5 543.5(4)	4 172.2(4)	9 387.7(4)	C(42)	5 527(6)	8 539(6)	6 241(7)
Sn	3 692.2(4)	3 788.8(5)	8 859.5(4)	C(43)	6 575(6)	9 044(7)	6 831(9)
Cl(1)	7 358(1)	4 415(2)	9 765(2)	C(44)	6 623(7)	9 132(7)	8 140(9)
Cl(2)	4 974(2)	2 163(2)	7 697(2)	C(45)	5 621(8)	8 694(8)	8 879(8)
Cl(3)	2 102(1)	1 892(2)	9 160(2)	C(46)	4 554(6)	8 164(7)	8 314(6)
Cl(4)	3 217(2)	3 692(2)	6 794(2)	H(111)	3 365(51)	9 674(60)	6 359(60)
P(1)	3 135(1)	7 526(1)	6 280(1)	H(112)	3 930(51)	8 863(69)	4 957(60)
C(11)	3 191(5)	8 795(6)	5 594(6)	H(13)	1 303(51)	9 407(59)	6 642(59)
C(12)	2 119(5)	8 473(6)	4 910(6)	H(14)	−355(51)	8 866(59)	5 444(59)
C(13)	1 241(8)	8 846(9)	5 597(8)	H(15)	−462(50)	7 681(59)	3 015(59)
C(14)	261(9)	8 550(12)	4 898(13)	H(16)	1 072(51)	7 105(59)	1 750(59)
C(15)	236(9)	7 907(10)	3 540(12)	H(17)	2 710(51)	7 521(60)	2 988(59)
C(16)	1 135(9)	7 603(8)	2 863(9)	H(22)	1 527(50)	5 215(59)	7 042(59)
C(17)	2 053(7)	7 843(7)	3 539(7)	H(23)	40(50)	5 056(59)	8 778(59)
C(21)	2 015(5)	7 352(6)	7 562(6)	H(24)	−381(51)	7 007(59)	10 203(58)
C(22)	1 365(5)	6 094(6)	7 715(6)	H(25)	781(50)	9 155(59)	10 022(59)
C(23)	507(6)	5 982(8)	8 710(7)	H(26)	2 347(50)	9 454(59)	8 387(59)
C(24)	292(6)	7 093(9)	9 532(7)	H(32)	1 082(51)	5 670(59)	4 861(59)
C(25)	949(6)	8 342(8)	9 400(7)	H(33)	669(51)	3 518(59)	3 055(59)
C(26)	1 817(6)	8 481(7)	8 417(6)	H(34)	2 249(51)	2 736(59)	2 126(59)
C(31)	2 856(5)	5 956(6)	4 973(6)	H(35)	4 195(51)	3 954(59)	3 008(59)
C(32)	1 740(6)	5 260(6)	4 440(6)	H(36)	4 550(50)	5 958(59)	4 832(59)
C(33)	1 530(8)	4 070(7)	3 405(8)	H(42)	5 471(50)	8 362(59)	5 199(59)
C(34)	2 408(9)	3 592(7)	2 888(7)	H(43)	7 297(51)	9 286(59)	6 222(59)
C(35)	3 485(7)	4 255(7)	3 407(7)	H(44)	7 376(50)	9 530(59)	8 604(59)
C(36)	3 711(6)	5 460(6)	4 455(6)	H(45)	5 656(50)	8 764(59)	9 878(59)
C(41)	4 508(5)	8 112(5)	7 001(6)	H(46)	3 790(51)	7 709(59)	8 856(59)

origin. Light atoms were found on successive Fourier syntheses. For (1), refinement was halted at $R = 0.13$ so that an alternative species could be studied, (2), in the vain hope that it might be ordered. For (2), refinement was concluded at $R = 0.033$. Hydrogen atoms were inserted at calculated positions with fixed isotropic thermal parameters, $B = 5.0$ Å^2, and were refined in position only. Final refinement was by least-squares methods in large blocks. A weighting scheme of the form $W = X \cdot Y$ was used, where $X = 1.0$ or $100/F$ for $F > 100.00$, and $Y = 1.0$ or $[(\sin\theta)/\lambda]/0.35$ for $(\sin\theta)/\lambda < 0.35$ or $0.4/[(\sin\theta)/\lambda]$ for $(\sin\theta)/\lambda > 0.4$. This was shown to be satisfactory by a weight analysis. An attempt was made when refinement was nearly complete to refine Cl(1) and Cl(2) as pairs of half-atoms instead of treating these as single anisotropic atoms. This did not give satisfactory convergence, and crystal in averaged positions, but with only a small displacement between their two positions. The key to the disorder lies in Cl(1) and Cl(2). These are the *cis*-chlorines of the $PtCl_2$ unit, with half-occupancy. However, they are simultaneously the third chlorine atom of each tin atom (also half-occupied). The result is that, irrespective of which alternative is present at any

* There has been some discussion in the literature as to whether this compound is the *cis* or the *trans* isomer and whether it isomerises in solution. For the original discussion consult: F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179; J. F. Young, R. D. Gillard, and G. Wilkinson, *ibid.*, p. 5176; J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Commun.*, 1965, 17; and ref. 4. Heating solutions of $[PtCl_2(SnCl_3)_2]^{2-}$ above 40 °C causes disproportionation and formation of red $[Pt(SnCl_3)_5]^{3-}$.[8]

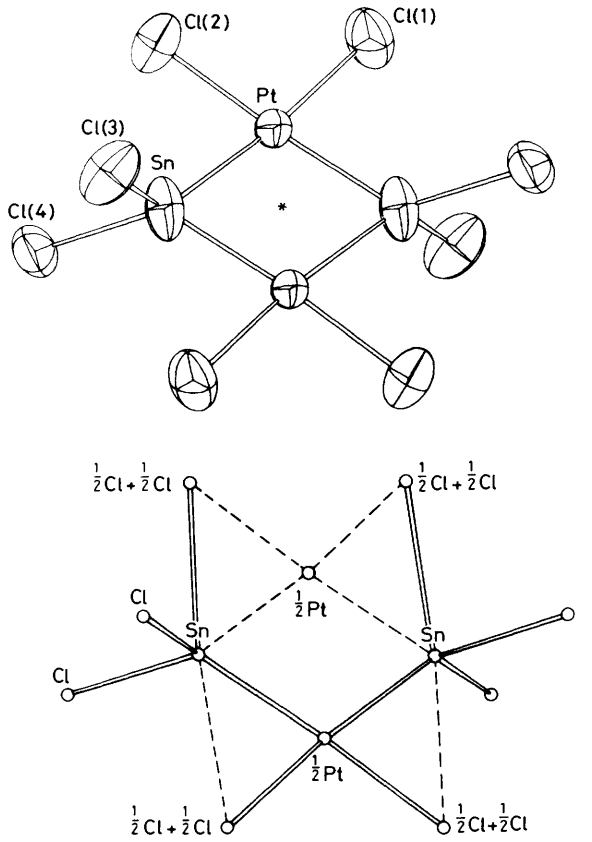

Figure 1. The $[PtCl_2(SnCl_3)_2]^{2-}$ ion in (2) showing the atomic numbering with an interpretation in terms of disordered atoms. The solid bonds show one orientation of the molecule, while the dotted bonds exist in the alternative orientation

Table 3. Bond lengths (Å) and angles (°) in (2) (with estimated standard deviations, e.s.d.s, in parentheses)

Pt–Sn	2.343 7(9)	Sn–Pt–Sn′	111.48(3)
Pt–Sn′	2.367 5(7)	Sn–Pt–Cl(2)	74.44(6)
Pt–Cl(1)	2.299(2)	Sn′–Pt–Cl(1)	72.76(5)
Pt–Cl(2)	2.293(2)	Cl(1)–Pt–Cl(2)	101.32(8)
Sn–Cl(3)	2.364(2)	Pt–Sn–Cl(3)	119.58(7)
Sn–Cl(4)	2.340(2)	Pt–Sn–Cl(4)	124.47(5)
Sn–Cl(2)	2.805(2)	Pt–Sn–Cl(1′)	121.00(4)
Sn–Cl(1′)	2.768(2)	Pt′–Sn–Cl(2)	120.47(4)
P–C(11)	1.824(8)	Cl(3)–Sn–Cl(4)	98.55(7)
P–C(21)	1.793(6)	C(11)–P–C(21)	109.5(3)
P–C(31)	1.790(5)	C(11)–P–C(31)	109.7(3)
P–C(41)	1.798(7)	C(11)–P–C(41)	107.1(3)
C(11)–C(12)	1.507(11)	C(21)–P–C(31)	109.9(3)
		C(21)–P–C(41)	109.5(3)
		C(31)–P–C(41)	111.2(3)
		P–C(11)–C(12)	115.3(4)

C–C(aryl) 1.382 Å (average; individual e.s.d. 0.01—0.02 Å), C–C–C(aryl) 120 ± 1.5° (e.s.d. 1°). Primed atoms are related to the unprimed ones by the the centre of symmetry.

particular site in the crystal, the chlorine-contact envelope of the anion is virtually identical. Thus, the interionic forces give no discrimination between the alternative position, and the anion is completely disordered in both the complexes examined. The crude bond lengths and angles are given in Table 3, but these are affected by the averaged positions of the chlorine atoms. Consequently, only the Sn–Pt, Sn–Cl(3), and

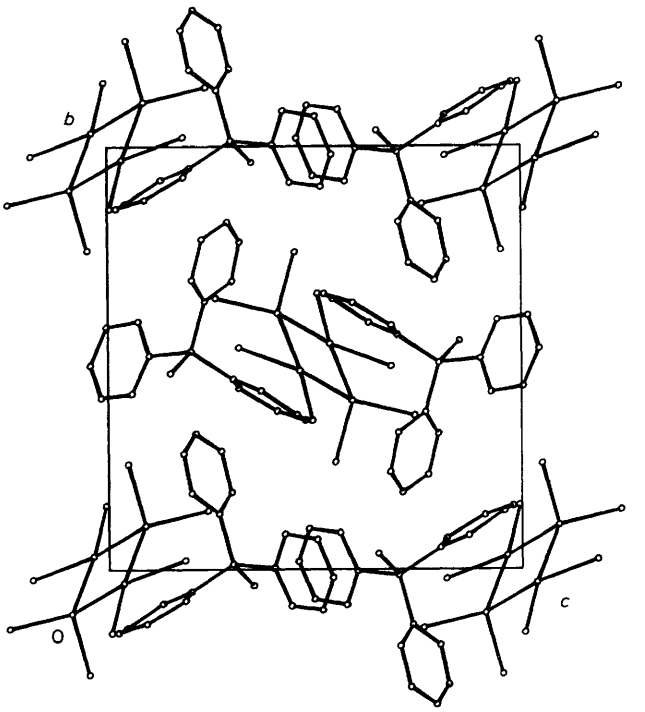

Figure 2. Packing diagram for (1), viewed down *a*. Both positions of the anion are shown

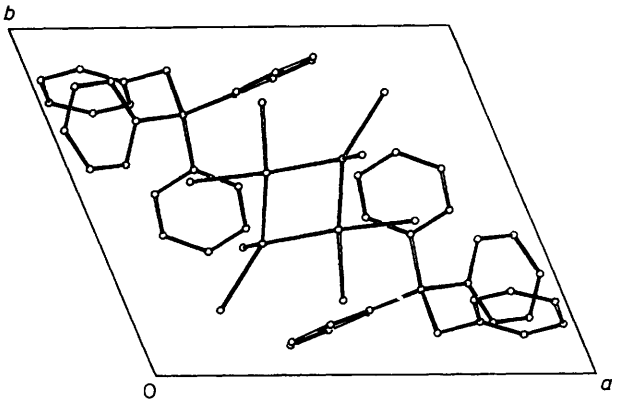

Figure 3. Packing diagram for (2), viewed down *c*

Sn–Cl(4) distances are likely to be reliable estimates, together with the Sn–Pt–Sn angle, and possibly the Cl(3)–Sn–Cl(4) angle (as the alternative positions for these chlorine atoms are probably not much separated). The Sn–Pt distance (average 2.3556 Å) is short, compared to those previously observed (tabulated in ref. 8), although there are no closely similar examples. The Sn–Cl(3) and –Cl(4) distances (average 2.352 Å) are similar to those found in $[Pt(SnCl_3)_5]^{3-}$.[8] The dimensions of the cation are unremarkable.

Figures 2 and 3 show the packing diagrams for (1) and (2). In both cases it can be seen that there are no strong directed cation–anion interactions. The principal interionic forces must be due to CH · · · Cl contacts, which do not discriminate between the two orientations of the anion.

Because of the disorder found in the crystal we have compared the far-i.r. spectrum of $[PPh_3(CH_2Ph)]_2[PtCl_2(SnCl_3)_2]$ with that of $[PMePh_3]_3[Pt(SnCl_3)_5]$ (Table 4). The spectra are fully consistent with the structures as determined by crystallo-

Table 4. Far-i.r. spectral data * (cm^{-1}) as Polythene discs

	$[PMePh_3]_3[Pt(SnCl_3)_5]$	$[PPh_3(CH_2Ph)]_2[PtCl_2(SnCl_3)_2]$
$\nu_{asym}(SnCl_3)$	375.5w	371.8w
$\nu_{sym}(SnCl_3)$	338vs	335w
$\delta_{asym}(SnCl_3)$	134w (sh)	132.5m
$\delta_{sym}(SnCl_3)$	117.5s	122m
ν(PtSn)	210.5w, 230w	198.4s, 224w
ν(PtCl)		302vs, 315.5vs

* Assignments for ν(PtSn) were made consistent with those of D. M. Adams and P. J. Chandler, *Chem. Ind.* (*London*), 1965, 269; J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079; for ν(PtCl), M. C. Baird, *J. Inorg. Nucl. Chem.*, 1967, **29**, 367; and for ν(SnCl), P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, 1964, **2**, 1043.

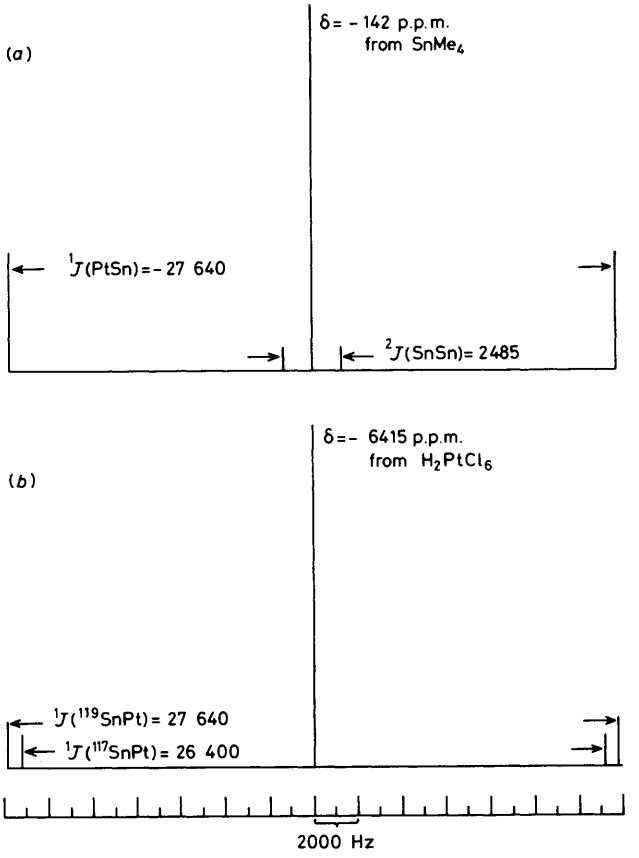

Figure 4. 37.10-MHz ^{119}Sn-{^1H} (*a*) and 21.28-MHz ^{195}Pt-{^1H} (*b*) n.m.r. spectra of [$^2H_6$]acetone solutions of $[PMePh_3]_2[PtCl_2(SnCl_3)_2]$; 20 000-Hz sweep widths taken at 303 K

graphy and exhibit no additional vibrations which could be attributed to this disorder. It is interesting that the Pt–Sn stretching frequencies occur at lower energy for the $[PtCl_2(SnCl_3)_2]^{2-}$ ion than for the $[Pt(SnCl_3)_5]^{3-}$ ion, even though the Pt–Sn bond is significantly shorter in the former (average 2.3556 *vs.* 2.5530 Å).

The difference in the platinum–tin bond strengths of these two compounds is, however, clearly evidenced by the ^{119}Sn and ^{195}Pt n.m.r. data shown in Figure 4. These spectra which remain unchanged over a period of 2 weeks at 25 °C indicate that the *cis* geometry of $[PtCl_2(SnCl_3)_2]^{2-}$ is probably the thermodynamically stable form. For this species one would expect to see a single ^{119}Sn resonance (relative intensity 1) flanked by satellites due to coupling with ^{195}Pt ($I = \frac{1}{2}$, 34% natural abundance) with relative intensities of 0.25. Because ^{119}Sn ($I = \frac{1}{2}$, 8.58% natural abundance) and ^{117}Sn ($I = \frac{1}{2}$, 7.61% natural abundance) will both be present in this complex, there will also be satellites due to ^{117}Sn–^{119}Sn coupling with relative intensities of 0.16. Similarly, the ^{195}Pt spectrum should show a central resonance (relative intensity 1) flanked by ^{119}Sn satellites (relative intensity 0.1) and ^{117}Sn satellites (relative intensity 0.09). In this spectrum, the ratio of $J(^{119}Sn^{195}Pt)$ to $J(^{117}Sn^{195}Pt)$ should be equal to the ratio of the ^{119}Sn to ^{117}Sn gyromagnetic ratios which is 1.046. The platinum–tin coupling constant in *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ (27 640 Hz) is considerably greater than that observed [1,8] for $[Pt(SnCl_3)_5]^{3-}$ (16 030 Hz) and in concert with the *X*-ray data suggests that the Pt–Sn bond is stronger and contains more *s* character in the former.

It is now reasonably well established that the $SnCl_3^-$ group is a good π-acceptor [8] and the *X*-ray and n.m.r. data support this contention in the following way. The n.m.r. data suggest a strong Pt–Sn bond with considerable *s* character which *should* give rise to a large *trans* influence and therefore a weak and long Pt–Cl bond. Although the Pt–Cl bonds (average 2.296 Å) are not very accurately determined because of the disorder problem, they are among the shortest yet observed by *X*-ray crystallography [Pt–Cl 2.291(2)—2.454(4) Å].[9] The unexpectedly short Pt–Cl bond lengths can be rationalised by the presence of a strong π-acceptor component in the Pt–Sn bonds inducing a π-donor component in the *trans*-Cl–Pt bonds and thereby strengthening these bonds.

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