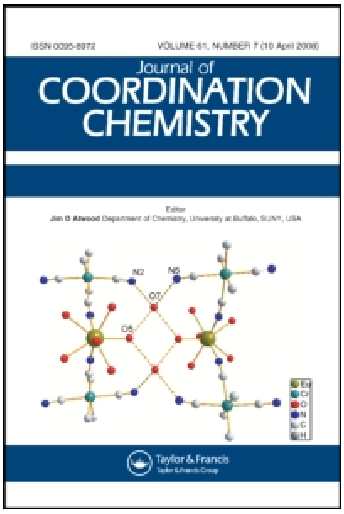

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Insertion of $SnCl_2$ into Pt-Cl bonds: synthesis and characterization of four- and five-coordinate trichlorostannylplatinum(II) complexes

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Insertion of $SnCl_2$ into Pt–Cl bonds: synthesis and characterization of four- and five-coordinate trichlorostannylplatinum(II) complexes

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Reaction of platinum(IV) chloride with $SnCl_2 \cdot 2H_2O$ in the presence of $[NHR_3]_3Cl$ (R = Me, Et) in 3M hydrochloric acid affords the anionic five-coordinate platinum(II) complexes $[NHR_3]_3[Pt(SnCl_3)_5]$, R = Me (**1**), Et (**2**), respectively. Moreover, platinum(IV) chloride reacts with $SnCl_2 \cdot 2H_2O$ in the presence of bis(triphenylphosphoranylidene)ammonium chloride in acetone/dichloromethane to form $[N(PPh_3)_2]_3[Pt(SnCl_3)_5]$ (**3**). In contrast, reaction of an acetone solution of platinum(IV) chloride with $SnCl_2 \cdot 2H_2O$ in the presence of bis(triphenylphosphoranylidene) ammonium chloride resulted in the formation of *cis*-$[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2]$ (**4**). The same products are obtained by using a platinum(II) salt as starting material. Similarly, *cis* and *trans*- dichlorobis(diethyl sulfide)platinum(II) reacts with $SnCl_2 \cdot 2H_2O$ in 5M hydrochloric acid to give $[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]$ (**5**) by facile insertion of $SnCl_2$ into the Pt–Cl bond. However, treatment of an acetone solution of *cis*- and *trans*-$[PtCl_2(SEt_2)_2]$ with $SnCl_2 \cdot 2H_2O$ in the presence of a small amount of HCl resulted in the formation of **5**, which dissociates in solution to give $[PtCl_2(SEt_2)_2]$. The complexes have been fully characterized by elemental analysis and multinuclear NMR (^1H, ^{13}C, ^{195}Pt, ^{119}Sn) spectroscopy. A structure determination of crystals grown from a solution of **2** by X-ray diffraction methods shows that platinum adopts a regular trigonal bipyramidal geometry.

Keywords: Platinum; Insertion; Dissociation; Spectroscopy; Crystal structure

1. Introduction

The insertion reaction of tin(II) chloride into the Pt–Cl bond is well established and provides an easy synthesis of trichlorostannylplatinum complexes [1–4]. The equilibrium reaction between platinum(II) complexes and tin(II) salts results in the formation of a wide variety of complexes in which structures depend upon mole ratios of platinum to tin and upon solvent [5, 6]. For instance, for the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with $SnCl_2$, it has been shown that simple insertion of $SnCl_2$ into Pt–Cl bonds occurs in chloroform but ligand rearrangement occurs in coordinating

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solvents such as acetone and acetonitrile to generate ionic complexes [6]. It is known, however, that the $SnCl_3$ moiety is a weakly coordinating ligand and is displaced by other ligands or dissociates in solution to give the starting platinum complex and solvated $SnCl_2$ [4, 7, 8]. Moreover, binary mixtures of platinum(II) complexes and tin(II) chloride have been extensively used in many catalytic processes such as olefin hydrogenation, isomerization and hydroformylation reactions [9–13]. Tin(II) chloride acts as a unique "co-catalyst", although its role is not fully understood [11, 14]. It is known that tin(II) chloride can act as a counter ion as $SnCl_3^-$, a Lewis acid and a trichlorostannato ligand bonded to platinum [14]. Proposed mechanisms for the role of $SnCl_2$ as "co-catalyst" are based on three-coordinate, square planar or five-coordinate intermediates involving the $SnCl_3^-$ ligand [5, 11, 15, 16].

While numerous studies of reactions of platinum(II) complexes with $SnCl_2$ have been reported, very few studies have been carried out to identify the structure of the catalyst precursor and so to elucidate the role of tin(II) chloride in the catalyst cycle. We have previously reported the first example of a platinum complex with the simultaneous presence of five- and four-coordinate platinum(II) species in the solid state, $[PtCl(SMe_2)_3]_3[Pt(SnCl_3)_5]$, prepared by insertion of $SnCl_2$ into the Pt–Cl bond of dichlorobis(dimethyl sulfide)platinum(II) [17]. In order to gain further insight into these species, we have investigated the reaction of $SnCl_2$ with several platinum complexes in which $SnCl_2$ has been inserted into Pt–Cl bonds resulting in the formation of anionic four- or five-coordinate trichlorostannylplatinum(II) complexes. Results of this study are reported below.

2. Experimental

2.1. *Materials and methods*

All solvents and chemicals were of reagent grade and used without further purification. Elemental analyses were performed on a Heraus CHN Rapid system and a Vista-pro CCD ICP-OES. NMR data were recorded using Bruker Avance DRX 500 and AQS 300 MHz spectrometers. Spectra are referenced to TMS (^{1}H, ^{13}C), Na_2PtCl_6 in D_2O (^{195}Pt) or $SnMe_4$ (^{119}Sn). The starting complex *cis*, *trans*-$[PtCl_2(SEt_2)_2]$ was prepared according to a literature procedure [18].

2.2. $[NHMe_3]_3[Pt(SnCl_3)_5]$ *(1)*

$SnCl_2 \cdot 2H_2O$ (0.17 g, 0.75 mmol) was added to a 3 M HCl solution (5 cm^3) containing $PtCl_4$ (0.05 g, 0.15 mmol) and $[NHMe_3]Cl$ (0.04 g, 0.42 mmol). The solution colour changed rapidly to red and a pink solid formed. The product was filtered off and air dried; m.p. 345°C. Anal. Calcd for $C_9H_{30}Cl_{15}N_3PtSn_5$ (%): C, 7.2; H, 2.0; N, 2.8; Pt, 13.0; Sn, 39.6. Found: C, 7.7; H, 2.5; N, 2.4; Pt, 12.7; Sn, 39.2. NMR data: $\delta(^{195}Pt)$ in acetone-d$_6$ −968 [s, $^1J(^{195}Pt–^{119}Sn) = 16067$ Hz, $^1J(^{195}Pt–^{117}Sn) = 15309$ Hz]; $\delta(^{119}Sn)$ in acetone/methanol (1 : 1) −129 [s, $^1J(^{195}Pt–^{119}Sn) = 16017$ Hz; $^2J(^{119}Sn–^{117}Sn)$ was not observed].

2.3. *[NHEt$_3$]$_3$[Pt(SnCl$_3$)$_5$] (2)*

Following the same procedure as for the preparation of **1**, $SnCl_2 \cdot 2H_2O$ (0.17 g, 0.75 mmol) was reacted with 6 cm^3 of a 3M HCl solution containing $PtCl_4$ (0.05 g, 0.15 mmol) and [NHEt$_3$]Cl (0.06 g, 0.44 mmol) to give an orange solid; m.p. 280°C. Anal. Calcd for $C_{18}H_{48}Cl_{15}N_3PtSn_5$ (%): C, 13.3; H, 3.0; N, 2.6; Pt, 12.0; Sn, 36.5. Found: C, 13.2; H, 3.2; N, 2.5; Pt, 11.9; Sn, 35.8. NMR: $\delta(^1H)$ in acetone-d$_6$ 1.43 [t, 27H, $^3J(HH) = 7.3$ Hz]; 3.48 [dq, 18H, $^3J(HH) = 7.3$ Hz, $^3J(HNCH_2) = 5.3$ Hz]; 7.92 [t, 3H, $^1J(NH) = 47$ Hz]; δ (^{13}C) 9.29 [s, 9C of methyl groups]; 47.8 [s, 9C of methylene groups]; $\delta(^{195}Pt)$ in acetone/ethanol (1 : 1) −969 [s, $^1J(^{195}Pt–^{119}Sn) =$ 16042 Hz, $^1J(^{195}Pt–^{117}Sn) = 15363$ Hz]; $\delta(^{119}Sn)$ −130 [s, $^1J(^{195}Pt–^{119}Sn) = 16039$ Hz, $^2J(^{119}Sn\text{-}^{117}Sn) = 6238$ Hz]. Stable crystals suitable for X-ray crystallographic study were grown from CH_2Cl_2/*n*-pentane at −5°C.

2.4. *[N(PPh$_3$)$_2$]$_3$[Pt(SnCl$_3$)$_5$] (3)*

To an acetone solution (10 cm^3) of $PtCl_4$ (0.05 g, 0.15 mmol) and $SnCl_2 \cdot 2H_2O$ (0.17 g, 0.75 mmol) was added a dichloromethane solution (5 cm^3) of bis(triphenylphosphoranylidene)ammonium chloride (0.26 g, 0.45 mmol). After a few minutes, solvent was removed and the residue solidified with diethylether. The resulting red solid was air dried; m.p. 220°C. Anal. Calcd for $C_{108}H_{90}Cl_{15}N_3P_6PtSn_5$ (%): C, 44.2; H, 3.1; N, 1.4; Pt, 6.6; Sn, 20.2. Found: C, 44.7; H, 3.2; N, 0.8; Pt, 5.7; Sn, 19.9. NMR data in CD_2Cl_2: $\delta(^{195}Pt)$ −976 [s, ^1J ($^{195}Pt–^{119}Sn) = 16002$ Hz, ^1J ($^{195}Pt–^{117}Sn) = 15275$ Hz]; $\delta(^{119}Sn)$ −126 [s, $^1J(^{195}Pt–^{119}Sn) = 15978$ Hz, $^2J(^{119}Sn–^{117}Sn) = 6149$ Hz]. Attempts at growing single crystals suitable for X-ray structure determination have been unsuccessful.

2.5. cis-*[N(PPh$_3$)$_2$]$_2$[PtCl$_2$(SnCl$_3$)$_2$] (4)*

To a stirred solution of $PtCl_4$ (0.05 g, 0.15mmol) and $SnCl_2 \cdot 2H_2O$ (0.07 g, 0.31 mmol) in acetone (10 cm^3) was added a solution of bis(triphenylphosphoranylidene)ammonium chloride (0.17 g, 0.3 mmol) in acetone (3 cm^3). After a few minutes, the solution colour changed from red to yellow and the solution was then stored at 0°C. After several days, yellow crystals formed; m.p. 250°C. Anal. Calcd for $C_{72}H_{60}Cl_8N_2P_4PtSn_2$ (%): C, 48.2; H, 3.3; N, 1.6; Pt, 10.9; Sn, 13.2. Found: C, 48.6; H, 3.6; N, 1.0; Pt, 10.4; Sn, 12.6. NMR data in CD_2Cl_2: $\delta(^{195}Pt)$ −4293 [s, $^1J(^{195}Pt–^{119}Sn) = 27892$ Hz; $^1J(^{195}Pt–^{117}Sn)$ was not observed]; $\delta(^{119}Sn)$ −379 [s, $^1J(^{195}Pt–^{119}Sn) = 27938$ Hz; $^2J(^{119}Sn–^{117}Sn)$ was not observed].

2.6. *[PtCl(SEt$_2$)$_3$]$_3$[Pt(SnCl$_3$)$_5$] (5)*

To a 5M HCl solution (10 cm^3) containing *cis*, *trans*-[PtCl$_2$(SEt$_2$)$_2$] (0.06 g, 0.13 mmol) was added $SnCl_2 \cdot 2H_2O$ (0.10 g, 0.44 mmol). The solution colour changed from yellow to red and a red-orange solid formed rapidly. The product was filtered off and air dried; m.p. 115–120°C. Anal. Calcd for $C_{36}H_{90}Cl_{18}Pt_4S_9Sn_5$ (%): C, 15.3; H, 3.2; Pt, 27.6; Sn, 21.0. Found: C, 14.8; H, 3.3; Pt, 27.0; Sn, 20.6. NMR data in CD_2Cl_2: $\delta(^1H)$ 1.45 [t, 6H, $^3J(HH) = 7.6$ Hz, methyl groups in Pt–SEt$_2$ *trans* to Cl];

Table 1. Experimental details, crystal data and refinement parameters for complex **2**.

Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	31.244(4)
b (Å)	24.701(3)
c (Å)	19.955(3)
β (°)	128.937(2)
V (Å^3)	11978(3)
D_{Calcd} (g cm^{-3})	1.61
Z	8
Absorption coefficient (mm^{-1})	5.34
θ Range (°)	1.3–17.2
Crystal size (mm^3)	0.06 × 0.03 × 0.10
Crystal colour	Orange-red
$T_{\min}/T_{\max}$	0.62/0.86
Collected reflections	12 569
Independent reflections	3566 ($R(\text{int}) = 0.0704$)
Observed reflections	2996 ($I > 2\sigma(I)$)
Refinement method	Full-matrix least-squares on F^2
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	3566/173/256
Index ranges	$25 \geq h \geq -26$, $20 \geq k \geq -20$, $16 \geq l \geq -16$
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.124$, $wR_2 = 0.298$
Goodness-of fit on F^2	1.17
Largest diff. peak and hole (e Å^{-3})	2.16 and −1.46

1.47 [t, 12H, ^{3}J(HH) = 7.4 Hz, methyl groups in Pt–SEt$_2$ *cis* to Cl]; 3.1 [m, 12H, ^{3}J(HH) = 7.4 Hz, all methylene groups in Pt–SEt$_2$]; δ(^{13}C) 12.2, 12.3 [s, 6C of methyl groups]; 31.0, 31.6 [s, 6C of methylene groups; δ(^{195}Pt) −4389 [s, Pt(SnCl$_3$)$_5^{3-}$; ^{1}J(^{195}Pt–^{119}Sn) could not be observed]; −4150 [s, PtCl(SEt$_2$)$_3$]$^+$; δ(^{119}Sn) −124 [s, ^{1}J(^{195}Pt–^{119}Sn) = 16037 Hz, ^{2}J(^{119}Sn–^{117}Sn) =6143 Hz]. Attempts to grow crystals for X-ray structure determination were unsuccessful.

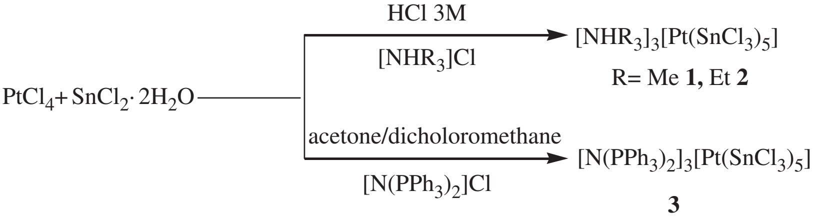
2.7. *X-ray crystallography*

Measurements were performed on a Bruker APEX CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) covering a whole sphere in reciprocal space. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on Laue symmetry [19]. The structure was solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL software package [20]. Due to the very high electron density of the complex anions it was not possible to model the light atoms of the cations successfully. Their presence is only indicated by residual electron density in apparently empty regions of the crystal. Experimental details, crystal data and refinement parameters are presented in table 1.

3. Results and discussion

3.1. *Solution studies*

Platinum(II)–tin complexes **1–5** have been obtained by insertion of $SnCl_2$ into Pt–Cl bonds, yielding anionic trichlorostannylplatinum(II) complexes. All reactions proceed under mild conditions with good yield and they are almost immediate. Products have been characterized by elemental analysis and multinuclear NMR (^{1}H, ^{13}C, ^{195}Pt, ^{119}Sn) spectroscopy and in the case of **2** by an X-ray structure determination. Reaction of a dilute hydrochloric acid solution of platinum(IV) chloride with stannous chloride dihydrate in a 1 : 5 mole ratio (Pt : Sn) in the presence of trimethylammonium chloride or triethylammonium chloride resulted in the formation of **1** and **2**, respectively. Similarly, **3** was prepared in acetone/dichloromethane in the presence of bis(triphenylphosphoranylidene)ammonium chloride as an ion pair, as shown in equation (1).



(1)

The ^{195}Pt NMR spectrum of **1** in acetone reveals a central resonance at $\delta = -968$ flanked by $^{119/117}Sn$ satellites with ^{1}J (^{195}Pt–^{119}Sn) = 16067 Hz and ^{1}J (^{195}Pt–^{117}Sn) = 15309 Hz. Moreover, the ^{119}Sn NMR spectrum shows a signal at $\delta = -129$ with $^{1}J(^{195}Pt$–$^{119}Sn) = 16017$ Hz. The observation of tin and platinum satellites in the ^{195}Pt and ^{119}Sn spectra, respectively, shows that the covalent Pt–Sn bond in the anion is maintained in solution. We expected to see two different tin environments in the absence of tin site exchange. The observation of a single ^{119}Sn resonance indicates facile exchange process on the NMR scale. Similar sets of ^{195}Pt and ^{119}Sn spectra are obtained for solutions of **2** and **3**. These data demonstrate again that Pt–Sn bonds persist in solution. However, reaction of an acetone solution of platinum(IV) chloride with tin(II) chloride in the presence of bis(triphenylphosphoranylidene)ammonium chloride in acetone at mole ratios of 1 : 2 or 1 : 3 (Pt : Sn) gives yellow crystals of *cis*-$[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2]$ (**4**), equation (2).

$$PtCl_4 + SnCl_2 \cdot 2H_2O \xrightarrow[\text{[N(PPh}_3)_2\text{]Cl}]{\text{acetone}} cis\text{-}[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2] \quad (2)$$

4

There is no evidence for the formation of **4** when the reaction is carried out at a 1 : 1 or a 1 : 4 mole ratio (Pt : Sn). The ^{195}Pt NMR of **4** in CD_2Cl_2 reveals a signal at $\delta = -4293$ with $^{1}J(^{195}Pt$–$^{119}Sn) = 27892$ Hz. In addition, the ^{119}Sn NMR of complex **4** shows a signal at $\delta = -379$ with $^{1}J(^{195}Pt$–$^{119}Sn) = 27938$, very close to the reported value for *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ ($\delta = -375$) with $^{1}J(^{195}Pt$–$^{119}Sn) = 27627$ Hz and $^{1}J(^{195}Pt$–$^{117}Sn) = 26392$ Hz [21]. The reported ^{195}Pt–^{117}Sn coupling constants for *trans*-$[PtCl(SnCl_3)(PEt_3)_2]$ and *trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$ are 28954 and 20410 Hz, respectively [8]. Thus, the *cis* stereochemistry for complex **4** can be suggested. Significant shielding of the tin resonance in *cis*-$[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2]$ relative to the $[Pt(SnCl_3)_5]^{3-}$ anions is consistent with the greater platinum(II)–tin π-back donation in the former [21]. In addition, platinum–tin coupling constants are considerably larger for *cis*-$[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2]$ than for $[Pt(SnCl_3)_5]^{3-}$ anions in complexes **1**–**3** and **5**, indicating that the stronger Pt–Sn bond in *cis*-$[N(PPh_3)_2]_2[PtCl_2(SnCl_3)_2]$ provides further support for the above. It should be mentioned that the same products have been obtained by using potassium tetrachloroplatinate(II) as starting material. Therefore, it appears that tin(II) chloride acts as a reducing agent as well as a ligand. Such a reducing role for tin(II) chloride has been reported previously [22].

Similarly, treatment of an acidic solution of *cis*, *trans*-$[PtCl_2(SEt_2)_2]$ with tin(II) chloride leads to diethylsulfide migration to generate an ionic species, $[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]$ (**5**) as shown in equation (3). A similar reaction of the dimethyl sulfide analogue has been reported [17].

$$\textit{cis,trans}\text{-}[PtCl_2(SEt_2)_2] + SnCl_2 \cdot 2H_2O \xrightarrow{\text{HCl 5M}} \underset{\mathbf{5}}{[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]} \qquad (3)$$

The ^{195}Pt NMR spectrum shows that there are two platinum resonances at $\delta = -4150$ and -4389, assigned tentatively to $[PtCl(SEt_2)_3]^+$ and $[Pt(SnCl_3)_5]^{3-}$, respectively. The observation of two platinum resonances indicates that no dissociation of the complex occurs in dichloromethane solution. It is surprising that the platinum chemical shifts in the $[Pt(SnCl_3)_5]^{3-}$ anions are cation dependent. For example, platinum chemical shifts in $[NHMe_3]_3[Pt(SnCl_3)_5]$ (**1**) ($\delta = -968$ in acetone), $[NHEt_3]_3[Pt(SnCl_3)_5]$ (**2**) ($\delta = -969$ in acetone/ethanol) and $[N(PPh_3)_2]_3[Pt(SnCl_3)_5]$ (**3**) ($\delta = -976$ in dichloromethane) differ significantly from those observed in $[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]$ (**5**) ($\delta = -4389$ in dichloromethane) and $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$ ($\delta = -4701$ in acetone) [21].

Furthermore, an acetone solution of *cis*, *trans*-$[PtCl_2(SEt_2)_2]$ containing a small amount of HCl in the presence of tin(II) chloride (Pt : Sn = 1 : 4) gave a red solution of **5**. The solution turned yellow immediately and yellow crystals of *cis*, *trans*-$[PtCl_2(SEt_2)_2]$ were recovered from solution. Thus, an equilibrium as shown in equation (4) was observed.

$$\textit{cis, trans}\text{-}[PtCl_2(SEt_2)_2] + SnCl_2 \cdot 2H_2O \xrightleftharpoons{\text{acetone/HCl 5M}} \underset{\mathbf{5}}{[PtCl(SEt_2)_3]_3[Pt(SnCl_3)_5]} \qquad (4)$$

In conclusion, the equilibrium reactions of Pt(II)/(IV) complexes with stannous chloride led to the formation of various four- or five-coordinate platinum complexes containing trichlorostannato ligands in which the equilibrium strongly depends on the nature of starting platinum species, mole ratio of reactants, solvents and the ion pair. It may be stated that the equilibrium characteristic of a Pt/Sn system under catalytic conditions, e.g., hydrogenation, hydroformylation or isomerization, can be related to the stability of four- or five-coordinate platinum precursors. These complexes can extend their coordination numbers to five or six (e.g., by formation of platinum–hydride or platinum–alkyl complexes) [10, 14, 23], resulting in various degrees of catalytic activity and selectivity.

Table 2. Selected bond distances [Å] and bond angles (°) for complex **2**.

Pt1–Sn5	2.540(5)
Pt1–Sn4	2.543(5)
Pt1–Sn3	2.553(4)
Pt1–Sn1	2.553(5)
Pt1–Sn2	2.568(4)
Sn1–Cl12	2.346(17)
Sn1–Cl11	2.35(2)
Sn1–Cl13	2.40(2)
Sn5–Pt1–Sn4	178.92(18)
Sn5–Pt1–Sn3	89.9(2)
Sn4–Pt1–Sn3	90.5(2)
Sn5–Pt1–Sn1	90.44(18)
Sn4–Pt1–Sn1	90.30(18)
Sn3–Pt1–Sn1	120.29(17)
Sn5–Pt1–Sn2	89.64(16)
Sn4–Pt1–Sn2	89.30(16)
Sn3–Pt1–Sn2	120.12(16)
Sn1–Pt1–Sn2	119.59(15)
Cl12–Sn1–Cl11	96.4(9)
Cl12–Sn1–Cl13	93.1(8)
Cl11–Sn1–Cl13	97.6(12)
Cl12–Sn1–Pt1	119.3(5)
Cl11–Sn1–Pt1	122.6(7)
Cl13–Sn1–Pt1	121.2(7)

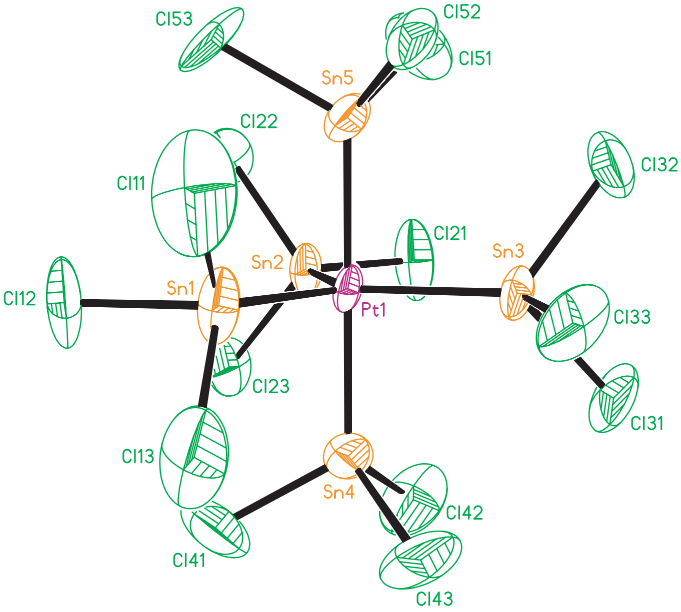


Figure 1. ORTEP diagram of $[Pt(SnCl_3)_5]^{3-}$ anion in complex **2** showing the atom numbering scheme.

3.2. *Crystal structure analysis*

Crystals suitable for an X-ray structure analysis were grown from a solution of **2** but the quality of the data was poor and the obtained structure is not complete (see experimental part); only the complex anion $[Pt(SnCl_3)_5]^{3-}$ could be clearly characterized. Selected bond lengths and angles are given in table 2. An ORTEP diagram with the numbering scheme for $[Pt(SnCl_3)_5]^{3-}$ is given in figure 1. The structure of $[Pt(SnCl_3)_5]^{3-}$ is a trigonal bipyramid in which the Sn_{ax}–Pt–Sn_{ax} unit is almost linear and the Sn_{ax}–Pt–Sn_{eq} angles are almost 90°. The average equatorial Pt–Sn lengths (2.553(7) Å) and the average axial Pt–Sn lengths (2.542(5) Å) are consistent with the theory for trigonal bipyramidal d^8 transition metals in which axial bonds should be shorter than equatorial bonds [24]. Moreover, the platinum and tin atoms which form the triangular plane are almost coplanar. The geometry around the Sn centers is distorted tetrahedral with Pt–Sn–Cl bond angles ranging from 116 to 123° and Cl–Sn–Cl bond angles from 93 to 101°, as expected from Bent's rules [25].

Supplementary material

CCDC 276140 contains supplementary crystallographic data for this structure. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retreiving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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