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Synthesis, spectroscopic and structural characterization of diphenyltin(IV) complexes of acetone Schiff bases of *S*-alkyldithiocarbazates

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Abstract

New diphenyltin(IV) complexes of empirical formula, $[Sn(C_6H_5)_2(NS)Cl]$ (NS = anionic forms of the acetone Schiff bases of *S*-methyl or *S*-benzyldithiocarbazate) have been prepared and characterized by IR, NMR and Mössbauer spectroscopic techniques. The crystal and molecular structures of the acetone Schiff bases of *S*-methyldithiocarbazate (Hacsme) and *S*-benzyldithiocarbazate (Hacsbz) and their tin(IV) complexes have been determined by X-ray diffraction. In the solid state, both the Schiff bases exist in their thioketo tautomeric forms with the azomethine nitrogen atom *trans* to the thione sulfur atom but in the tin(IV) complexes they are present in their deprotonated ene-thiolate forms being coordinated to the tin atom as bidentate chelating agents *via* the azomethine nitrogen and thiolate sulfur atoms. The tin atom adopts a five-coordinate, approximately trigonal bipyramidal geometry, with the thiolate sulfur atom of the Schiff base and the two phenyl groups occupying the equatorial positions. The azomethine nitrogen atom and the chlorine ligand occupy axial positions. The distortion from a regular trigonal bipyramidal or a square-pyramidal geometry is attributed to the restricted bite sizes of the five-membered chelate rings.

Keywords: Acetone Schiff bases of *S*-methyl- and *S*-benzyldithiocarbazate; Diphenyltin(IV) complexes; Oganotin complexes of dithiocarbazates

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1. Introduction

Schiff bases derived from *S*-alkyl esters of dithiocarbazic acid comprise an important class of sulfur–nitrogen chelating agents containing both soft sulfur and intermediate nitrogen donor atoms in their structural backbones by virtue of which they are capable of reacting with both transition and some main group metal ions [1–10] forming stable complexes some of which have been shown to exhibit interesting physico-chemical properties [11] and potentially useful pharmacological activities [1,10,12]. As an example, the palladium(II) complex of the acetone Schiff base of *S*-methyldithiocarbazate (Hacsme) has been shown to exhibit cytotoxic activity in the 9KB test system – a human epidermoid carcinoma of the nasopharynx [13]. The palladium(II) complex has also been found to display cytotoxic activity against T-lymphoblastic leukemia cancer cells [14]. There are also several other examples where Schiff bases derived from *S*-alkyl esters of dithiocarbazic acid and some of their metal complexes have been shown to display antifungal and antibacterial properties [15].

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Although a large amount of work on the synthesis and characterization of transition metal complexes of Schiff bases of *S*-alkyl esters of dithiocarbazic acid have been reported [1–15] very little work has been reported on organometallic complexes of these ligands. In view of very little information available on organotin(IV) complexes of dithiocarbazates and as part of our ongoing work on metal complexes of dithiocarbazic acid and its derivatives, we report here the synthesis, characterization and X-ray crystal and molecular structures of the acetone Schiff bases of *S*-methyl- and *S*-benzyldithiocarbazate together with the structures of their chlorodiphenyltin(IV) complexes.

2. Experimental

2.1. Reagents

Chemicals and solvents used were of analytical reagent grade and used without any further purification. Dichlorodiphenyltin(IV) was purchased from the Aldrich Chemical Company.

2.2. Physical measurements

Microanalyses for C, H & N were performed by the Elemental Analysis Laboratory, National University of Singapore, Singapore. Molar conductivity of *ca.* 10^{-3} M solutions of the complexes in DMSO were measured by means of a Jenway 4310 conductivity meter. The IR spectra were measured as KBr discs on a Perkin–Elmer 2000 FT-IR spectrometer and the electronic spectra were measured as Nujol mulls on a Shimadzu MPC-3100 spectrophotometer. The ^{1}H NMR spectra of the tin(IV) complexes were run in $CDCl_3$ on a Bruker DPX 300 MHz spectrometer using TMS as an internal standard. The Mössbauer spectra were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with moving source geometry. A 5-mCi $Ca^{119m}SnO_3$ source was used. The spectra were measured at 80 K using a liquid–nitrogen cryostat (CYRO Industries of America Inc.). The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed by a least-square fit to Lorentzian shaped lines.

2.3. Preparation of the ligands

The Schiff bases were prepared by following procedures reported previously [14,16]. The compounds as isolated from the reaction were suitable for X-ray crystallography.

2.4. General method of preparation of the complexes

To a solution of $SnPh_2Cl_2$ (1 mmol) in boiling abs. ethanol (70 ml) was added a solution of the appropriate Schiff base (1 mmol) in the same solvent (70 ml) and the mixture heated under reflux for 48 h and then left to stand overnight. The product that had formed was filtered off, washed with abs. ethanol and dried in a vacuum desiccator over anhydrous silica gel. These compounds as isolated were suitable for X-ray work. Yield: 50–60%. *Compound* **3** Sn(acsme)Ph_2Cl: *Anal.* Calc. for $C_{17}H_{19}N_2S_2ClSn$: C, 43.48; H, 4.08; N, 5.96. Found: C, 43.40; H, 4.03; N, 5.85%. *Compound* **4** Sn(acsbz)Ph_2Cl: *Anal.* Calc. for $C_{23}H_{23}N_2S_2ClSn$: C, 50.62; H, 4.25; N, 5.13. Found: C, 50.52; H, 4.15; N, 5.46%.

2.5. Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD 4 four-circle diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the $\omega - 2\theta$ mode within the range $2 < 2\theta < 50°$. Empirical absorption correction (ψ scans) and data reduction were performed with the WINGX [17] suite of programmes. The structures were solved by direct methods with SHELX86 and refined by full-matrix least-squares analysis with SHELXL97 [18]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were included at estimated positions using a riding model. Drawings of each molecule were produced with ORTEP3 [19]. A summary of the crystal data, structure solution and refinement parameters are given in Table 1 and selected bond lengths appear in Table 6.

3. Results and discussion

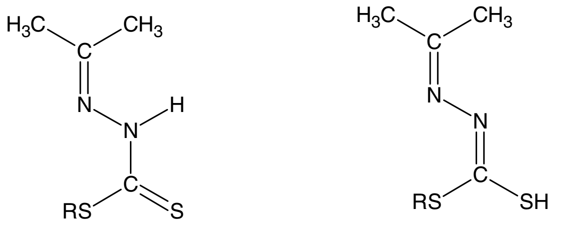
The acetone Schiff bases of *S*-methyldithiocarbazate and *S*-benzyldithiocarbazate have a thioamide (–NH–CS–) functional group and consequently, in principle, they are capable of existing either as the thione form (1a) or the thiol form (1b) or as a mixture of both thione and thiol tautomeric forms (Fig. 1). In the solid state it has been shown that they exist in their thione forms since their IR spectra exhibit the νNH band at *ca.* 3300 cm^{-1} and no νSH band at *ca.* 2600 cm^{-1} [14]. However, in solution they might exist as an equilibrium mixture of both the thione and thiol tautomeric forms. The ^{1}H NMR spectra of the Schiff bases in $CDCl_3$ exhibit a signal at *ca.* 10.15 ppm which is characteristic of an NH as opposed to an SH resonance. No signal at *ca.* 4.00 ppm attributable to the SH proton was detected indicating that even in solution they remain predominantly as the thione tautomer.

3.1. Characterization of the Sn(IV) complexes

In a boiling ethanolic solution the Schiff bases react with $SnPh_2Cl_2$ in their thiol tautomeric forms, deprotonate and coordinate to the tin(IV)ion forming charge neutral complexes of formula, $SnPh_2(NS)Cl$ (*NS* = deprotonated form of the Schiff bases). The analogous acetone thiosemicarbazone which exhibits a structural backbone very similar to the present compounds, has been shown to react with

Table 1
Crystallographic data

	Hacsme (**1**)	Hacsbz (**2**)	Sn(acsme)Ph$_2$Cl (**3**)	Sn(acsbz)Ph$_2$Cl (**4**)
Empirical formula	$C_5H_{10}N_2S_2$	$C_{11}H_{14}N_2S_2$	$C_{17}H_{19}N_2S_2ClSn$	$C_{23}H_{23}N_2S_2ClSn$
Formula weight	162.27	238.36	469.60	545.69
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/a$	$P2_1/c$	$P2_1cn$	$P2_1/n$
a (Å)	14.58(1)	11.942(1)	9.535(2)	8.2242(9)
b (Å)	11.653(4)	6.163(7)	12.848(2)	13.445(1)
c (Å)	19.41(1)	16.942(3)	16.493(2)	22.187(3)
β (°)	98.58(6)	94.77(1)		92.81(2)
V (Å^3)	3261(3)	1242.2(3)	2020.5(6)	2450.4(5)
D_{calc} (Mg/m^3)	1.322	1.274	1.544	1.479
Z	16	4	4	4
μ (mm^{-1})	0.573	0.399	1.603	1.334
$F(000)$	1376	504	936	1096
Independent reflections [R_{int}]	5702 [0.0523]	2173 [0.0323]	2121 [0]	4309 [0.0155]
Observed reflections ($I > 2\sigma(I)$)	2538	1040	1452	3175
Data/restraint/parameters	5702/0/337	2173/0/138	2121/1/198	4309/0/265
Goodness-of-fit on F^2	1.015	0.997	0.993	1.020
R_1 (observed data) and wR_2 (all data)	0.0539 and 0.1668	0.0430 and 0.1188	0.0830 and 0.2503	0.0273 and 0.0722



(1a; thione form; R = CH_3, CH_2Ph) (1b; thiol form)

Fig. 1. The thione and thiol tautomeric forms of the Schiff base (R = CH_3, Hacsme; R = CH_2Ph, Hacsbz).

$SnPh_2Cl_2$ yielding a diphenyltin(IV) complex containing the neutral form of the ligand [20]. This example illustrates the diversity of reactivity found in these Schiff base ligands in their coordination chemistry with Sn(IV).

The complexes are stable at room temperature and may be kept in a desiccator over anhydrous silica gel for extended periods without any sign of decomposition. The molar conductivities of Sn(acsme)Ph$_2$Cl and Sn(acsbz)Ph$_2$Cl in DMF are 11.7 and 11.8 Ω^{-1} cm^2 mol^{-1}, respectively, indicating that even in a polar coordinating solvent like DMF, they behave essentially as non-electrolytes. The conductance data confirm that the Schiff bases coordinate to the tin atom in their monodeprotonated forms.

The IR spectra of the SnPh$_2$(*NS*)Cl complexes when compared with those of the free Schiff bases (Table 2) show that the νNH bands of the free ligands at *ca.* 3300 cm^{-1} are absent in the spectra of the complexes indicating that the ligands are coordinated to the tin atom in their deprotonated mercaptide forms. The shift of the azomethine $\nu_{C=N}$ band in the IR spectra of the free ligands (1634–1628 cm^{-1}) to lower wavenumber (1612–1608 cm^{-1}) in the spectra of complexes support coordination of the azomethine nitrogen atom to the tin atom. This is further supported by the shift of the $\nu_{N–N}$ band of the free ligands to higher wavenumbers in the spectra of the complexes.The electronic spectra of the complexes show the intraligand n → π* and π → π* transitions in the ranges 363 and 311–258 nm, respectively. The n → π* band of the free ligands is not affected in the electronic spectra of the complexes but there is a hypsochromic shift of the π → π* band upon coordination to Sn(IV).

The ^{1}H NMR spectra of the complexes do not contain the signal due to the NH proton of the free ligands at 10.15 ppm supporting further the IR evidence presented earlier that the ligands are coordinated to the tin atom in

Table 2
IR and electronic spectra for the ligands and their diphenyltin(IV) chloride complexes

Compound	IR bands				Electronic spectra[b] λ_{max} (nm)
	νNH	νCN	νNN	νCSS	
Hacsme[a]	~3300sh	1634	1064s	998s	364, 293
Hacsbz[a]	~3300sh	1628s	1069	998s	340, 298
[Sn(acsme)(C_6H_5)$_2$Cl]		1608s	1068m	1024, 997m	363sh, 311
[Sn(acsbz)(C_6H_5)$_2$Cl]		1612s	1074m	1011, 996m	362sh, 325sh, 258

[a] Data taken from Ref. [14].
[b] Solid state (Nujol mull).

their deprotonated thiolate forms. The ^{1}H NMR spectra of $SnPh_2(NS)Cl$ show two signals due to two acetone-derived methyl groups due to restricted rotation about the C=N bond. The methyl group, *syn* to the N–N bond resonates at a higher field than the *anti* methyl group [21] (see Table 3).

The Mössbauer spectra of the $Sn(NS)Ph_2Cl$ complexes are shown in Figs. 2 and 3 and the isomer shift (δ), quadrupole splitting (Δ) and ρ values are given in Table 4. The parameters (δ and Δ) are within the range found with Sn (IV) and organotin compounds [22]. The Mössbauer spectra of the tin complexes exhibit identical δ indicating that the substituents (methyl or phenyl) on one of the sulfur atoms of the dithiocarbazate moiety do not have any effect at all on the s-electron density at the tin nucleus. The spectra of the two compounds also exhibit the same values of Δ indicating that they have the same structure. X-ray crystallographic structure determination (see later) confirms this fact. The Mössbauer spectra of the present tin(IV) complexes have lower δ values than the starting tin compound, $SnPh_2Cl_2$ ($1.34\ mm\ s^{-1}$) [23]. A re-hybridization in the $[Sn(NS)Ph_2Cl]$ complexes (due to higher coordination number of the tin atom in the complexes relative to that in $SnPh_2Cl_2$) accounts for the smaller isomer shift δ value. A greater involvement of the d orbitals in the tin complexes, which take part in the re-hybridization scheme causes a reduction in the s-electron contribution in the complexes relative to that of the starting tin compound [23], thus decreasing the value of the isomer shift. The ρ values, which are used to predict coordination numbers of tin complexes, are found to be 2.02, supporting a coordination number greater than four for the tin ion in the tin complexes [24].

The angle, θ between the axial carbon atoms and tin atom can be obtained from the Mössbauer spectrum using the relationship, $|\Delta| = -4[R](1–0.75\sin^2\theta)^{1/2}$ where Δ is the observed quadrupole splitting, θ is the R–Sn–R angle in the complex and $[R]$ is the partial quadrupole splitting (PQS) of the axial groups [25]. The calculated angle for $Sn(acsme)Ph_2Cl$ is 122.9° using $[R]$ of −0.94 [26] and for $Sn(acsbz)Ph_2Cl$, 127.3° using $[R]$ of −0.89 [26]. This compares favorably with the values of the angles found by X-ray crystallography; 122.9° and 127.1°, respectively.

3.2. Crystal structures of the free ligands

The structures of Hacsme and Hacsbz are shown in Figs. 4 and 5, respectively, and relevant bond lengths and bond angles are given in Table 5. The asymmetric unit of Hacsme has four crystallographically independent molecules (referred to here as molecules A, B, C and D) which have very similar bond lengths and bond angles. Molecule

Table 3
^{1}H and ^{13}C NMR spectroscopic data

Compound	^{1}H NMR assignments					^{13}C NMR assignments					
	CH_3(*syn*)	CH_3(*anti*)	SCH_3/SCH_2^-	NH	Ar	CH_3(syn)	CH_3(anti)	SCH_3/SCH_2^-	CN	CS	ArC
Hacsme	[1.96][a] 1.95 (s, 3H)	[2.04][a] 2.08 (s, 3H)	[2.57][a] 2.62 (s, 3H)	9.78 (1H)		16.68	17.74	25.28	152.73	200.62	
Hacsbz	1.95 (s, 3H)	2.04 (s, 3H)	4.52 (s, 2H)	9.68 (1H)	7.28–7.32 (m, 2H) 7.40 (d, $J = 8$ Hz, 2H)	16.79	25.24	39.48	152.81	198.93	127.43 128.57 129.44 136.04
$[Sn(acsme)(C_6H_5)_2Cl]$	1.55 (s, 3H)	2.28 (s, 3H)	2.52 (s, 3H)		7.26 (m, 4H), 7.45 (m, 4H), 7.49 (m,2H)	14.92	22.92	25.65	143.67	174.31	129.09 130.02 134.51 134.90
$[Sn(acsbz)(C_6H_5)_2Cl]$	1.54 (s, 3H)	2.28 (s, 3H)	4.42 (s, 2H)		7.25–7.77 (m, 15H)	23.01	25.67	36.34	143.67	174.54	127.59 128.69 128.54 129.68 128.99 129.10 130.03 134.88

[a] Data reported by [29].

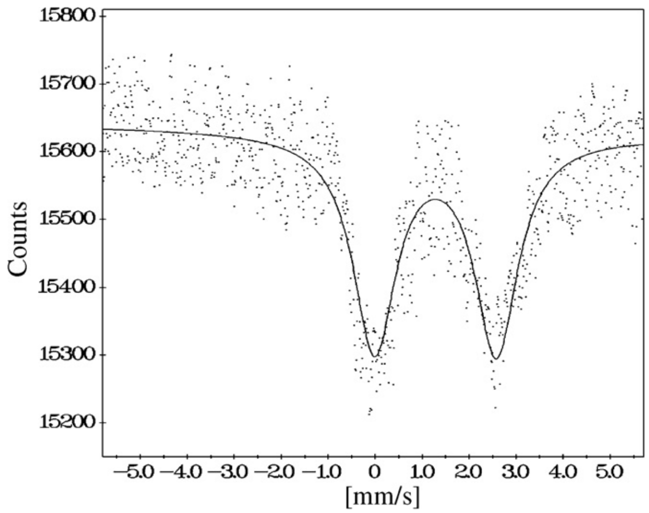


Fig. 2. The Mössbauer spectrum of Sn(acsme)Ph_2Cl.

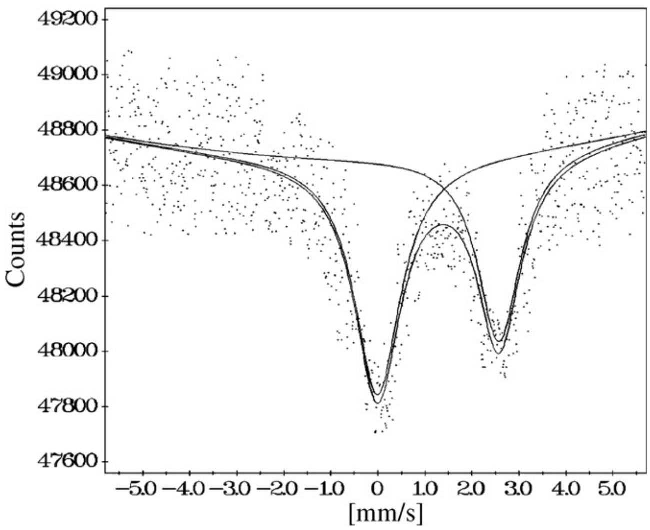


Fig. 3. The Mössbauer spectrum of Sn(acsbz)Ph_2Cl.

Table 4
Mössbauer spectroscopic data for the diphenyltin(IV) complexes

Compound	δ (mms^{-1})	Δ (mms^{-1})	ρ
Sn(acsme)$(C_6H_5)_2Cl$	1.28	2.58	2.02
Sn(acsbz)$(C_6H_5)_2Cl$	1.28	2.59	2.02

‘A’ is shown in Fig. 4. H-bonding in the structure finds that molecules A and D forms centrosymmetric H-bonded dimers while molecules B and C pair up in a pseudocentrosymmetric arrangement involving N1*n*-H···S2*n* pairs (data not shown).

However, the asymmetric unit of Hacsbz contains only one molecule which too is H-bonded to a centrosymmetri-

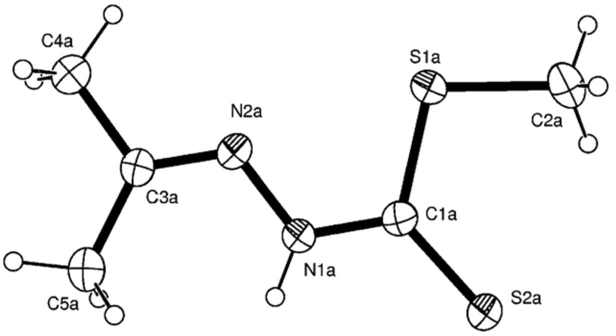


Fig. 4. ORTEP3 view of **1** Hacsme (only one of the four molecules (A) in the asymmetric is shown with 30% probability ellipsoids).

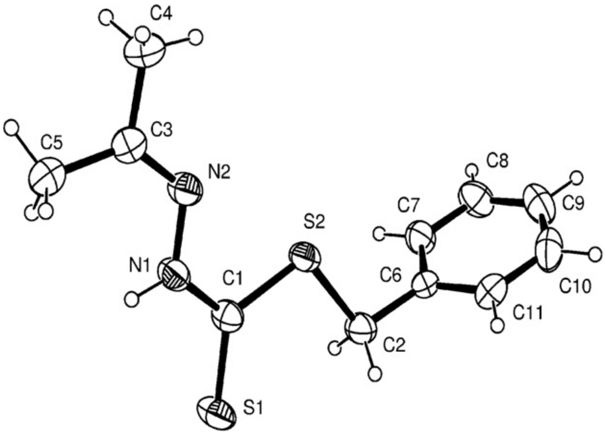


Fig. 5. ORTEP3 view of **2** Hacsbz (30% probability ellipsoids).

Table 5
Selected bond lengths

Bond	1	2	3	4
Sn1–Cl1			2.461(7)	2.465(1)
Sn1–S1			2.431(5)	2.418(1)
Sn1–C6			2.14(2)	2.121(3)
Sn1–C12			2.09(2)	2.122(3)
Sn1–N2			2.35(2)	2.399(3)
C1–S1	1.662(5),1.649(5), 1.663(5),1.652(5)	1.655(4)	1.74(3)	1.752(3)
C1–N1	1.346(6),1.337(6), 1.344(6),1.344(6)	1.332(4) 1.393(4)	1.29(3)	1.272(4)
N1–N2	1.387(5),1.393(5), 1.395(5),1.384(5)	1.393(4)	1.43(3)	1.412(3)

Angles (°)	3	4
C(6)–Sn1– C(12)	129.3(7)	127.1(1)
C(6)–Sn1–N(2)	88.2(7)	88.92(11)
C(12)–Sn1–N(2)	94.2(9)	94.66(11)
C(6)–Sn1–S(1)	115.7(7)	118.29(10)
C(12)–Sn1–S(1)	114.4(4)	113.78(11)
N(2)–Sn1–S(1)	76.8(5)	76.38(7)
C(6)–Sn1–Cl(1)	94.6(6)	94.11(9)
C(12)–Sn1-Cl(1)	96.4(6)	96.02(10)
N(2)–Sn1–Cl(1)	162.3(5)	163.97(7)
S(1)–Sn(1)–Cl(1)	86.2(2)	88.37(4)

cally related molecule in the same manner as molecules A and D in the structure of Hacsme. The crystal structures of the Schiff bases also confirm that both ligands crystallize in their thione tautomeric forms as previously predicted by spectroscopic techniques with the thione sulfur atom *trans* to the azomethine nitrogen atoms. In this conformation these ligands are unable to bind the tin atom as bidentate *NS* chelating ligands but, in solution, a 180° rotation about the C1–N1 bond enables them to act as bidentate chelating agents. The C1–S1 bond lengths (~1.65 Å) indicate that they are essentially double bonds but the length of the C3–N2 bond is intermediate of a single and double bond indicating electron delocalization in the –N–C–S (thioamide) group.

3.3. Crystal structures of the Sn(IV) complexes

The crystal structures of the two Sn complexes are shown in Figs. 6 and 7 and important bond lengths and bond angles are given in Table 5.

The structures show that the tin atom in each compound is five-coordinated with the deprotonated Schiff base chelates the metal ion *via* the azomethine nitrogen atom and the thiolate sulfur atom. The phenyl and chloro ligands occupy the remaining three coordination positions of the coordination polyhedron. The stereochemistry adopted by the metal is intermediate between a trigonal-bipyramid (TBPY) and a square-pyramid (SPY). This may be illustrated by considering distortion from an ideal TBPY geometry. Thus, taking the azomethine nitrogen atom (N2) and the chloro ligand as the axial donor atoms, angles of 163.2(6)° and 163.97(7) are subtended in **3** and **4**, respectively, which are much smaller than the ideal value of 180°. The coordinate angles between the equatorial donors (C6, C12 and S1) also show marked differences from their ideal 120° values. A similar comparison can also be made for an ideal SPY geometry taking S1 as the apical donor and Cl(1), C(6), C(12) and N(2) as donors defining the basal plane.

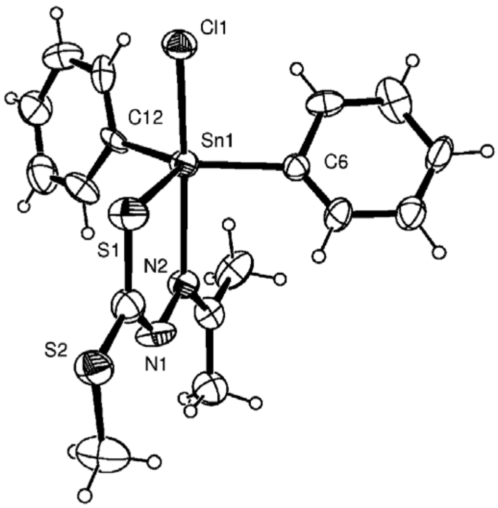


Fig. 6. ORTEP3 view of **3** Sn(acsme)Ph_2Cl (30% probability ellipsoids).

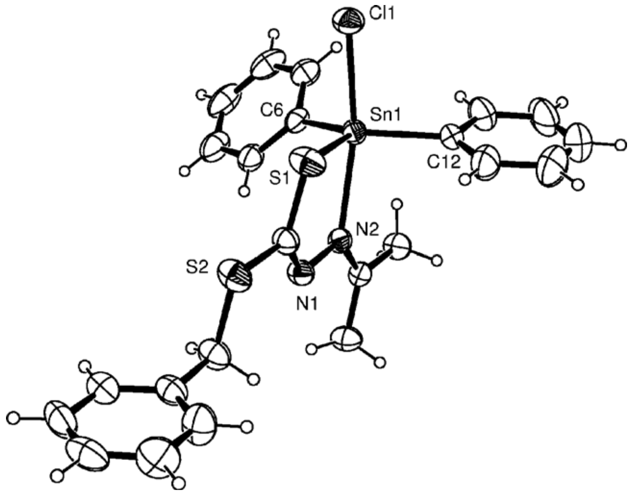


Fig. 7. ORTEP3 view of **4** Sn(acsbz)Ph_2Cl (30% probability ellipsoids).

An angular structural parameter, τ (index of trigonality) has been proposed previously [27] for distinguishing, quantitatively, between a distorted trigonal-bipyramid and a distorted square-pyramid in five-coordinate complexes. The parameter $\tau = \beta - \alpha/60^\circ$ where α and β are the two largest angles; $\tau = 0$ for an ideal SPY geometry (α and $\beta = 180^\circ$) and $\tau = 1$ for an ideal TBPY geometry. Using this criteria the τ values of the present complexes are found to be 0.6 indicating distortion that is somewhere between both extrema, but tending slightly toward TBPY. The largest deviations from ideal geometry are attributable to the restricted bite size of the chelating Schiff base.

The Sn–S distances in both complexes are close to the sum of the covalent radii (2.42 Å) but much shorter than the sum of their van der Waal's radii [4.0 Å] indicating the formation of a genuine Sn–S bond. The Sn–N distances in **3** and **4** are only slightly larger than the sum of the non-polar covalent radius (2.15 Å) again indicating strong Sn–N interactions. A comparison of Sn-donor atom distances in the present diphenyltin(IV) complexes with those of related tin(IV) complexes is presented in Table 6 where the influence of coordination number and ligands is illustrated.

The five-membered chelate ring in **4** adopts an envelope conformation with the atoms C1 and N1 each lying *ca.* 0.3 Å out of the plane defined by Sn1, N2 and S1, while the same chelate ring in **3** is essentially planar within experimental uncertainty. A comparison of the bond distances in the dithiocarbazate chain shows that in both tin complexes the C–S bonds are longer than observed in the respective free ligands but intermediate between those characteristic of single C–S (~1.85 Å) and double bonds (~1.56 Å). Coordination of the ligands to the tin atom in their iminothiolate forms raises the C1–N1 bond order at the expense of the C1–S1 bonds.

Table 6
Comparison of Sn-donor atom distances in some organotin(IV) complexes

	Sn–S	Sn–C	Sn–Cl	Sn–N_{azo}	Ref.
$Sn(actsc)_2Ph_2Cl_2$	2.72	2.142(3)	2.569(1)		[20]
$Sn(acsme)_2Cl_2$	2.457(4)		2.4000(5)	2.313(11)	[29]
$Sn(acsme)Ph_2Cl$	2.431(5)	2.14(2) 2.09(2)	2.461(7)	2.35(2)	This work
$Sn(acsbz)Ph_2Cl$	2.418(1)	2.121(3) 2.122(3)	2.465(1)	2.399(3)	This work
$[Sn(CH_3)_2(Pytsc)Cl]\cdot 0.5H_2O$	2.478(2)	2.105(7)			[28]
		2.108(7)	2.672(1)	2.359(4)	

3.4. Conclusions

In the solid state, the acetone Schiff bases of *S*-methyl and *S*-benzyldithiocarbazate, like all other Schiff bases derived from *S*-alkyl esters of dithiocarbazic acid, remain in their thione tautomeric forms with the thione sulfur atom *trans* to the azomethine nitrogen atom but in solution they convert to the thiol form accompanied by an inversion of N2 with the concomitant formation of diphenyltin(IV)chloride complexes of the deprotonated Schiff bases. Spectroscopic and X-ray diffraction studies show that the substituents on one of the sulfur atoms of the dithiocarbazate moiety virtually have no effect on the s-electron density at the tin nucleus and on the stereochemistry adopted by the tin complexes.

4. Supplementary material

CCDC 653521, 653522, 653523 and 653524 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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