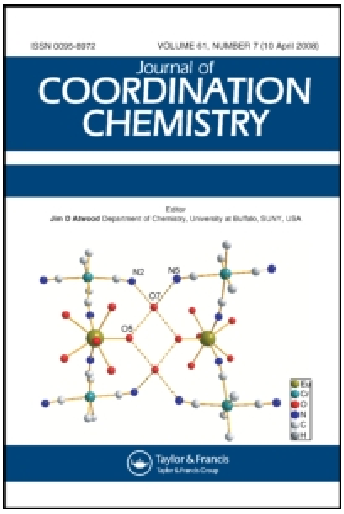

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Synthesis and characterization of pentagonal bipyramidal organotin(IV) complexes of 2,6-diacetylpyridine Schiff bases of S-alkyl- and aryldithiocarbazates

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Synthesis and characterization of pentagonal bipyramidal organotin(IV) complexes of 2,6-diacetylpyridine Schiff bases of S-alkyl- and aryldithiocarbazates

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New organotin(IV) complexes with empirical formula Sn(*SNNNS*)R_2, where *SNNNS* is the dianionic form of 2,6-diacetylpyridine Schiff bases of S-methyldithiocarbazate (H_2dapsme) or S-benzyldithiocarbazate (H_2dapsbz) and R = Ph or Me, have been prepared and characterized by IR, UV-Vis, NMR and Mössbauer spectroscopic techniques and conductance measurements. The molecular structures of the Sn(dapsme)R_2 (R = Ph and Me) have been determined by single crystal X-ray diffraction techniques. Both complexes have a distorted pentagonal-bipyramidal geometry in which the tin is coordinated by a dinegatively charged pentadentate chelating agent *via* pyridine nitrogen, two azomethine nitrogens, and two thiolate sulfurs. The five donors (N_3S_2) provided by the Schiff base occupy the equatorial plane close to a pentagonal planar array while the carbanion ligands occupy axial sites.

Keywords: Organotin(IV) complexes; Dithiocarbazates; 2,6-Diacetylpyridine Schiff bases of S-alkyldithiocarbazates; Seven-coordinate organotin(IV) complexes

1. Introduction

Coordination chemistry of pentadentate thiosemicarbazones derived from 2,6-diacetylpyridine has received considerable attention [1–17] due to their ability to form stable metal complexes with both transition and main group metals having interesting structural features and potential application as chemotherapeutic agents [3b]. Although a large number of pentagonal-bipyramidal complexes of Sn(IV) [9, 10], Sn(II) [2], Zn(II) [1, 6], Cd(II) [1], In(III) [14], and Mn(II) [12, 13] with pentadentate

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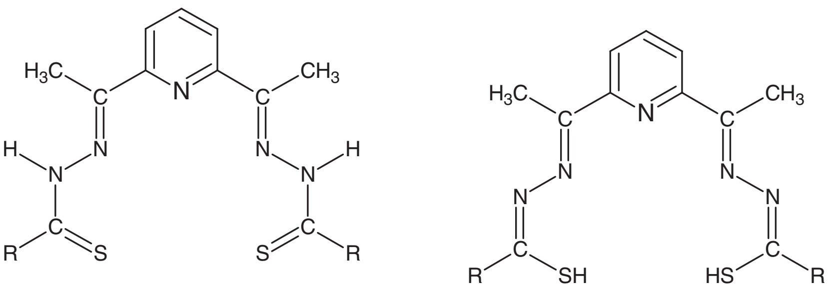

Figure 1. The thione (left) and thiol (right) tautomeric forms of H_2dapsme (R = Me) and H_2dapsbz (R = bz).

thiosemicarbazones have been structurally characterized, less work has been reported on the related 2,6-diacetylpyridine Schiff bases of S-alkyldithiocarbazates (figure 1), which have a backbone similar to that of 2,6-diacetylbis(thiosemicarbazones) but exhibit significantly different coordination chemistry. For example, the 2,6-diacetylpyridine Schiff base of S-benzyldithiocarbazate (H_2dapsbz; figure 1; $R = CH_2C_6H_5$) reacts with a nickel(II) salt producing a dinuclear nickel(II) complex containing an unusual bridging pyridine N-donor [18]. With zinc(II), it forms a very different dimeric zinc(II) complex where each ligand binds to one Zn(II) as a tridentate complex and as a bidentate complex to the other Zn(II) [19]. With tin(IV) iodide and chloride, these ligands have been shown to yield pentagonal-bipyramidal tin(IV) complexes [20].

In view of the potential applications of organotin complexes of sulfur–nitrogen chelating agents in industry and chemotherapy and as part of our ongoing study of metal complexes of dithiocarbazate ligands, we report here the synthesis and characterization of some seven-coordinate organotin(IV) complexes of two pentadenate dithiocarbazate ligands together with the X-ray crystal structures of [Sn(dapsme)R_2] ($R = C_6H_5$, CH_3).

2. Experimental

2.1. *Chemicals*

All chemicals were of analytical reagent grade and used without purification. Dichlorodiphenyltin(IV) and dichlorodimethyltin(IV) were purchased from Aldrich Chemical Company. The ligands were prepared as described in our previous papers [18, 21]. All physical measurements and analytical procedures used in this work were similar to those described previously [1].

2.2. *Preparation of the complexes*

A general method of preparation for all Sn(*SNNNS*)R_2 (L = dapsme or dapsbz, R = Ph or Me) complexes was employed. To a solution of the ligand (1.5 mmol) in a boiling mixture of dichloromethane (300 mL) and abs. ethanol (30 mL) was added a solution of $SnPh_2Cl_2$ (1.5 mmol). The mixture was then refluxed for 6 h. On standing overnight the complexes crystallized from the reaction mixture and were filtered off, washed with ethanol and dried in a desiccator over anhydrous silica gel. Yield: 46–60%; Sn(dapsme)Me_2 required refluxing for 72 h. Crystals of Sn(dapsme)Ph_2 and Sn(dapsme)Me_2 suitable for X-ray analysis were obtained during the preparation of the complexes.

Found (%): C, 46.80; H, 3.89; N, 10.97. Calcd for Sn(dapsme)Ph_2 ($C_{25}H_{25}N_5S_4Sn$) (%): C, 46.73; H, 3.92; N, 10.92. Found (%): C, 54.29; H, 4.04; N, 9.65. Calcd for [Sn(dapsbz)Ph_2]$\cdot H_2O$ ($C_{37}H_{35}N_5OS_4Sn$) (%): C, 54.68; H, 4.34; N, 9.62. Found (%): C, 35.01; H, 4.20; N, 13.41. Calcd for Sn(dapsme)Me_2 ($C_{15}H_{21}N_5S_4Sn$) (%): C, 34.76; H, 4.08; N, 13.51.

2.3. *Crystallography*

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD4 four-circle diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å) and operating in the ω–2θ mode within the range $2 < 2\theta < 50°$. Empirical absorption correction (Ψ scans) and data reduction were performed with the WINGX [22] suite of programs. The structures were solved by direct methods using SHELX86 and refined by a full-matrix least-squares analysis using SHELXL97 [23]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas hydrogens were included at estimated positions. The drawing of the molecule (figure 2) was produced with ORTEP3 [24]. A summary of crystal data, structure solution and refinement parameters are given in table 1 and selected bond lengths appear in table 2. The structure of Sn(dapsme)Me_2 was disordered about a crystallographic mirror plane but refinement could be carried out without the need for any restraints on the bond lengths or angles. Due to the close proximity of the different components of this disorder, only partial anisotropic refinement could be carried out on the non-H atoms.

2.4. *Spectral and conductance measurements*

The IR, electronic, NMR, and conductance measurements were performed as described previously [19]. 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-*m*Ci $Ca^{119m}SnO_3$ 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-squares fit to Lorentzian shaped lines.

3. Results and discussion

3.1. *Spectral measurements*

In the solid state, the 2,6-diacetylpyridine Schiff bases of S-methyl- and S-benzyldithiocarbazate (figure 1 (left); R = $-CH_3$, $-CH_2C_6H_5$) remain solely as the

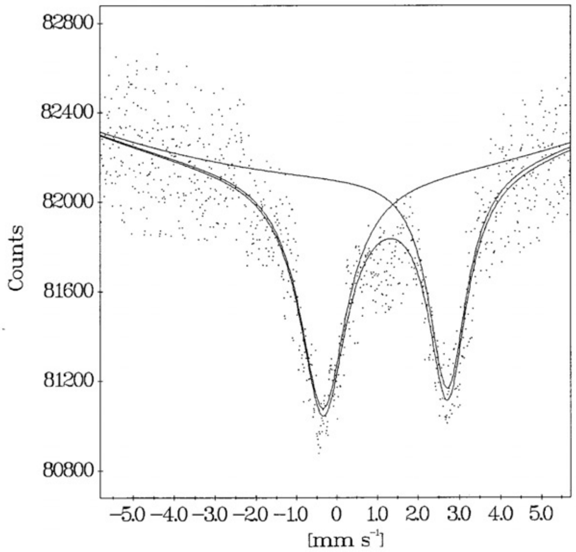

Figure 2. Mössbauer spectrum of [Sn(dapsme)Ph_2].

Table 1. Crystal data for dimethyl and diphenyl Sn(dapsme).

	Sn(dapsme)Ph_2	Sn(dapsme)Me_2
Empirical formula	$C_{25}H_{25}N_5S_4Sn$	$C_{15}H_{21}N_5S_4Sn$
Formula weight	642.43	518.30
Temperature (K)	293	293
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pcmn*
Unit cell dimensions (Å, °)		
a	9.683(1)	10.032(1)
b	14.3492(7)	14.245(5)
c	19.133(2)	14.355(2)
β	102.005(8)	
Volume (Å^3), *Z*	2600.3(4), 4	2051.4(8), 4
Calculated density (g cm^{-3})	1.641	1.678
Absorption coefficient (mm^{-1})	1.329	1.662
F(000)	1296	1040
Independent reflection	2283 [*R*(int) = 0.0295]	1874 [*R*(int) = 0.0186]
Observed reflection ($I > 2\sigma$)	1879	1585
R indices (all data)	$R_1 = 0.0898$, $wR_2 = 0.3187$	$R_1 = 0.0352$, $wR_2 = 0.0989$

thione tautomer [18, 21] although in principle, they are capable of exhibiting thione-thiol tautomerism since they possess the thioamide –NH–C=S functional group. In solution they can, however, exist as an equilibrium mixture of both the thione and thiol tautomers. We have previously shown that in DMSO-d_6 the ligands exhibit a broad ^{1}H NMR signal at *ca* 12.65 ppm, attributable to the resonance of the *sec* NH proton. The appearance of the –NH– signal at *ca* 13 ppm and the absence of any SH signal at *ca* 4.00 ppm indicate that in DMSO both Schiff bases also remain in their thione forms, with the *sec* NH protons being intermolecularly hydrogen bonded to a

Table 2. Selected bond lengths (Å) and angles (°) of dimethyl and diphenyl Sn(dapsme).

	Sn(dapsme)Ph_2	Sn(dapsme)Me_2
Sn1–S1/Sn1–S3	2.645(5)	2.579(4)/2.704(3)
Sn1–N2/Sn1–N4	2.42(1)	2.31(3)/2.52(3)
Sn1–N3	2.43(2)	2.371(5)
Sn1–C_{axial} (Ph or Me)	2.16(2)	2.246(4), 2.194(6)
S1–Sn1–S1′/S1–Sn1–S3	80.6(2)	80.3(2)
S1–Sn1–N2/S3–Sn1–N4	72.5(3)	74.9(5)/70.4(6)
N3–Sn1–N2/N3–Sn1–N4	67.2(3)	68.0(5)/66.3(6)
C_{axial}–Sn1–C_{axial}	171.2(9)	171.6(2)
C_{axial}–Sn1–S1/C_{axial}–Sn1–S1′ (or S3)	92.8(4)/93.9(5)	93.5(1)/93.5(2)
C_{axial}–Sn1–N3	85.6(4)	85.8(1)/85.8(2)

thione sulfur of another molecule or the NH protons participate in hydrogen bonding with DMSO. In the solid state, the Schiff base remains as the thione tautomer. In an ethanol-dichloromethane mixture and in the presence of organotin(IV) dichloride they rearrange to the thiol tautomeric forms forming organotin(IV) complexes of their deprotonated thiolate forms. The related thiosemicarbazones, however, do not always deprotonate in neutral media and as a result, complexes of both protonated [25, 26] and deprotonated [27] thiosemicarbazones have been synthesized. Examples of metal complexes in which both protonated and deprotonated forms of a thiosemicarbazone exist in the same complex have also been reported [28]. In contrast to thiosemicarbazones, Schiff bases derived from S-alkyl/aryl esters of dithiocarbazic acid almost invariably deprotonate in the presence of metal salts and coordinate in their mercaptide forms even in the presence of mineral acids.

Reaction of the Schiff bases with SnR_2Cl_2 (R = Ph, Me) in a refluxing mixture of ethanol and dichloromethane yields bright orange crystalline organotin(IV) complexes with empirical formula Sn(*SNNNS*)R_2, where *SNNNS* = dapsme or dapsbz. The complexes were sparingly soluble in acetonitrile, chloroform and dichloromethane and slightly more soluble in DMSO in which conductivity measurements were made. The molar conductances of the complexes in DMSO (1.6–2.0 $Ohm^{-1}\,cm^2\,mol^{-1}$) indicate that they are non-electrolytes in this solvent. The conductance data further indicate that the ligands are coordinated to tin(IV) in their doubly deprotonated forms and that the alkyl groups are also coordinated to tin(IV).

A comparison of IR spectra of the ligands with those of the tin complexes (table 3) shows that the *sec* ν_{NH} bands of the free ligands at 3154–3176 cm^{-1} are absent in spectra of the complexes, indicating that the ligands deprotonate at this position upon coordination to tin. The shift of the azomethine $\nu_{C=N}$ of the free H_2dapsme and H_2dapsbz ligands from 1600–1617 cm^{-1} to 1573–1595 cm^{-1} in the complexes also supports coordination of the ligands to tin *via* the azomethine nitrogens. This is further supported by the shift of the $\nu_{N\text{–}N}$ bands of the free ligand to higher wavenumber in spectra of the tin complex [29]. The splitting of the ν_aCSS band of the ligand at *ca* 959 cm^{-1} in IR spectra of the complexes indicates coordination of the ligands to tin *via* one sulfur [30].

The electronic spectral data of the complexes (table 3) show that in addition to intraligand bands in the range 345–358 nm and 256–264 nm assignable to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, the $S \rightarrow Sn^{IV}$ charge-transfer band appears as a shoulder at 428–457 nm in spectra of the complexes, giving them their characteristically

Table 3. IR and electronic spectral data of dimethyl and diphenyl Sn(dapsme).[a]

Compound	ν_{NH}	$\nu_{C=N}$	$\nu_{N\text{–}N}$	ν_{CSS}	λ_{max} (nm)
H_2dapsme[b]	3176 s,br	1617 m	1065 s	959 s	345(4.2), 256(4.5)
H_2dapsbz[c]	3157 br,w	1600 m	1102 m	845 w	358, 263
Sn(dapsme)Ph_2	–	1595 m	1138 m	844 s 968 sh	*ca* 457 sh, *ca* 398, 298
Sn(dapsbz)Ph_2	–	1573 m	1112 w	948 s 930 sh	*ca* 428 sh, *ca* 348, 281
Sn(dapsme)Me_2	–	1590 m	1136 m	950 sh 940 s	*ca* 440 sh, 343, 241

Notes: [a]IR bands (cm^{-1}) UV spectra in Nujol.
[b]In CH_2Cl_2 from Ref. [6].
[c]Ref. [12].

brilliant orange/yellow color. Similar charge transfer bands have also been observed in metal complexes of thiosemicarbazones [31, 32].

Table 4 lists ^1H and ^{13}C NMR spectral data of the ligands and their organotin(IV) complexes. [Sn(dapsme)$(CH_3)_2$] had limited solubility in DMSO-d_6 in which it also showed signs of decomposition and, therefore, meaningful NMR spectral data for this compound could not be obtained. However, changes in spectra of the present ligands upon complexation with tin(IV) follow the same pattern as observed for related tin(IV) complexes of other pentadentate ligands [5, 9]. These may be summarized as follows: (i) the N (H) signal at *ca* 12.65 ppm of the free ligands are absent in spectra of the complexes because of deprotonation of the ligands during coordination with tin; (ii) the pyridine ring protons are deshielded on coordination *via* the pyridine nitrogen but the $-N{=}C(CH_3)$ protons are not affected even though coordination *via* azomethine nitrogen occurs. The ^{13}C NMR spectrum of Sn(dapsme)Ph_2 could not be recorded because of insufficient solubility in DMSO-d_6. However, in the ^{13}C NMR spectrum of Sn(dapsbz)Ph_2, the carbon of the thiocarbonyl group undergoes significant shielding on coordination to tin(IV), in contrast with the ^{13}C NMR spectra of the seven-coordinate tin(IV) complex of the related 2,6-diacetylpyridine thiosemicarbazone where only a small shift of this signal was observed [9]. The carbons of the methyl groups attached to the carbon of azomethine are deshielded on coordination with tin, similar to that found in related tin complexes [9].

Mössbauer spectra of the present organotin(IV) complexes exhibit a single quadrupole-split doublet, the two peaks being slightly asymmetric. A representative spectrum is shown in figure 2 and the isomer shift and quadrupole splitting values are given in table 5.

The isomer shifts and quadrupole splittings are comparable to the data reported for Sn(dapsme)(n-Bu)$_2$ [17], dapsme and other pentagonal bipyramidal diphenyltin(IV) complexes of the related dibutylpentadentate 2,6-diacetylbis(thiosemicarbazone) ligands [8, 16] and dithiocarbazate [16]. As expected, the isomer shift value of the Sn(dapsme)Ph_2 complex is lower than that of Sn(dapsme)$(CH_3)_2$ and Sn(dapsme)(n-Bu)$_2$ because of the lower electron donating ability of phenyl compared to alkyl. Furthermore, the isomer shift of Sn(dapsme)Ph_2 [1.19 mm s^{-1}] is lower than that of the parent acid, Ph_2SnCl_2 [1.34 mm s^{-1}] [33], probably because of re-hybridization to higher coordination for Sn^{IV} in the complex relative to the parent acid. This can be attributed to involvement of the *d* orbitals which now take part in the

Table 4. ^1H and ^{13}C NMR spectral data for the Schiff bases and their tin(IV) complexes in DMSO-d_6.

	H_2dapsme	H_2dapsbz	Sn(dapsme)$(C_6H_5)_2$	[Sn(dapsbz)$(C_6H_5)_2$] · H_2O
^1H NMR assignments				
–NH	12.45(s,br,1H)	12.70(s,br,1H)	–	–
py–H	7.90–7.93(m) 7.74–7.79(m) 7.60(t,2H)	8.05(d,2H) 7.90(t,1H)	8.30(s,H)	8.40(s,1H) 8.74(d,2H)
Ar–H	–	7.22–7.30, 7.33–7.39(m,5H)	7.10–7.25(m)	7.28–7.47(m,5H) 6.90–7.00(m) 7.07–7.28(m) 7.36–7.85(m)
–N=C–CH_3	2.30(s,6H)	2.50(s,6H)	2.30(s,6H)	2.42(s)
–SCH_2/SCH_3	3.12(s,6H)	4.48(s,4H)	2.78(s,6H)	4.51(s,4H)
^{13}C NMR assignments				
CS	201.6	199.8	–	185.1
–C=N	154.5	154.3		158.9
C_{py}	152.2 138.3 121.7	152.2 138.4 121.8		143.4 132.0 129.7
C_{Ar}	–	137.6 130.1 129.4 129.4 127.5	–	157.5 148.0 138.3 128.0
SCH_2/SCH_3	18.0	39.0		36.8
–CH_3	13.7	13.8		16.1

Table 5. Mössbauer spectral data of some pentagonal bipyramidal organotin(IV) complexes.

Compound	δ (mm s^{-1})	Δ (mm s^{-1})	ρ	Reference
Sn(dapsme)$(C_6H_5)_2$[a]	1.19	3.05	2.56	This work
Sn(dapsme)$(CH_3)_2$	1.51	3.16	2.09	This work
Sn(dapsme)(n-Bu)$_2$	1.46	3.53	2.41	[17]
[Sn(dapsbz)$(C_6H_5)_2$][b] · H_2O	1.67	3.64	2.98	This work
[Sn(daptsc)$(C_6H_5)_2$] · 2DMF[c]	1.22	2.84	2.32	[9]
[Sn(Hdaptsc)$(C_6H_5)_2$]Cl[d]	1.21	3.13	2.59	[8]

[a] dapsme = doubly deprotonated form of the 2,6-diacetylbis(S-methyldithiocarbazate).
[b] dapsbz = doubly deprotonated anion of the 2,6-diacetylbis(S-benzyldithiocarbazate).
[c] daptsc = dianionic form of the 2,6-diacetylbis(thiosemicarbazone).
[d] Hdaptsc = singly negatively charged 2,6-2,6-diacetylbis(thiosemicarbazone).

Sn^{IV} hybridization scheme, thus reducing the contribution of the s orbitals in the overall hybridization of the tin electrons [34]. However, similar values of the isomer shifts of [Sn(dapsme)$(CH_3)_2$] [1.51 mm s^{-1}] and the parent acid $Sn(CH_3)_2Cl_2$ [1.52 mm s^{-1}] [35] show that hybridization is not the only contributing factor to the isomer shift.

The quadrupole splittings are comparable to the data reported for other seven-coordinate pentagonal bipyramidal complexes with sulfur-containing ligands ($\Delta = 2.84$–4.36 mm s^{-1}) [16]. As the distribution of ligands around tin become more symmetrical, Δ becomes smaller. In comparing the axial ligands in the Sn(dapsme) complexes, the diphenyl complex is more symmetrical than the dimethyl complex. The Δ increases and the symmetry of the ligands around tin decreases as the axial ligand changes from methyl to butyl and when the methyl in the other ligand is replaced by a phenyl group. The Δ for [Sn(dapsbz)$(C_6H_5)_2$]$\cdot H_2O$ is larger than the Δ's for other complexes suggesting that the waters are coordinated to tin, decreasing the symmetry of the ligands around tin leading to an increase in Δ.

The ρ-values have been used to deduce the coordination number of tin in various organotin compounds. Values less than 2.1 have been identified with compounds in which tin is less than four-coordinate, while five- and higher coordination have been assigned to values greater than 2.1 [36]. In all spectra (table 5), ρ is greater than 2.1 so the coordination of the tin is greater than 4.

The semiquantitative relationship $|\Delta| = -4[R](1-0.75\ \sin^2\theta)^{1/2}$ [16], where Δ is the experimentally observed Mössbauer quadrupole splitting, θ is the R–Sn–R angle in the complex and [R] is the partial quadrupole splitting (PQS) of an alkyl group, has recently been used to calculate the PQS of alkyl and aryl groups in a fairly large number of seven-coordinate pentagonal-bipyramidal organotin complexes. Using this relationship we find the PQS values for the Ph and Me groups in Sn(dapsme) as −0.77 and −0.80, respectively, which agree well with those reported for analogous organotin(IV) complexes recently reported by de Sousa *et al.* [16]. It, therefore, seems that the semi-empirical relationship shown above can be reasonably used to predict the R–Sn–R angle in pentagonal bipyramidal organotin(IV) complexes whose X-ray crystal structures are not available. The calculated angle, θ, for [Sn(dapsbz)$(C_6H_5)_2$] is 180° using the average PQS value of −0.80.

3.2. *The crystal structure of Sn(dapsme)Ph_2*

The molecular structure of Sn(dapsme)Ph_2 is illustrated in figure 3 together with the adopted numbering scheme. The complex has crystallographic two-fold symmetry with the axis passing through Sn, N3, and C4. The coordination geometry approximates a

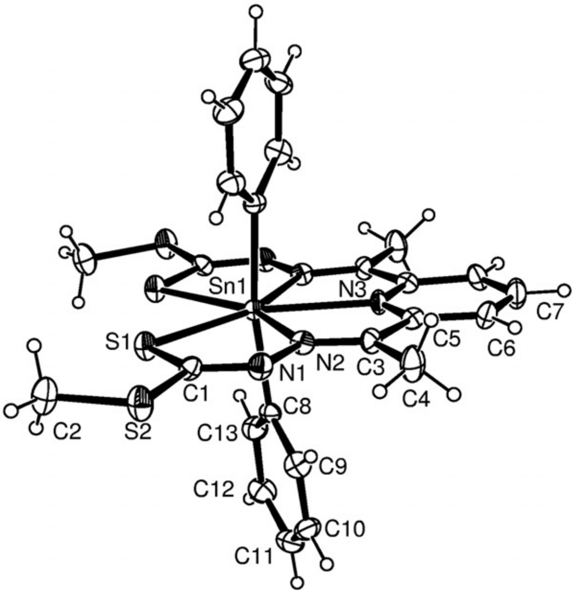

Figure 3. Molecular structure of Sn(dapsme)Ph_2 (30% probability ellipsoids).

pentagonal bipyramid with all equatorial coordinate angles involving adjacent donor atoms within 8° of their ideal value (72°). The axially coordinated phenyl ligands are within 5° of orthogonal with respect to the equatorial donor atoms. The planar pentadentate *SNNNS* Schiff base in its deprotonated thiolate form is coordinated to tin at the equatorial position through the thiolate sulfurs, the two azomethine nitrogens and the pyridine nitrogen. The two unique Sn–N distances are slightly higher than the sum of the non-polar covalent radii 2.15 Å. Both S-methyl groups point in the same direction in a roughly parallel disposition.

The equatorial Sn–S and Sn–N bond distances are similar to those observed for other tin(IV) complexes having similar geometries (table 6). In contrast with other tin(IV) complexes of related pentadentate thiosemicarbazone ligands [5, 19], the Sn–N$_{py}$ bond distance in the present complex is close to the Sn–N$_{azomethine}$ distance. The higher basicity of the azomethine nitrogens relative to the pyridine nitrogen should lead to shorter Sn–N$_{azomethine}$ distances. This has in fact been observed in most four-, five-, and six-coordinate metal complexes of thiosemicarbazones [37]. The similarity of the Sn–N$_{py}$ and Sn–N$_{azomethine}$ distances in the present complex may be ascribed to the geometric requirement of the structure in which tin(IV) bonds with the pyridine nitrogen in such a way that it prevents the closer approach of the two imine nitrogens, although the precision of the structure is rather low, so this may be obscuring genuine differences between the sets of coordinate bonds. The Sn–S distance is typical of complexes of this type (table 6). Irrespective of the oxidation state of tin, all these complexes have comparable tin-donor atom distances. An examination of bond distances in the dithiocarbazate chain shows that the C1–S1 bond is longer than that observed in the free S-benzyldithiocarbazate [38] and other Schiff bases derived from related dithiocarbazates [39] present in their thione form as opposed to the ene-thiolate form of the coordinated anion. The N1–C1 bond (1.309(7) Å) also shortens in the anion

Table 6. Comparison of bond tin-donor atom distances (Å) in related seven-coordinate tin complexes.

Compound	Sn–S/O	Sn–N$_{azom.}$	Sn–N$_{py}$	Sn–C	Sn–X	Reference
Sn(dapsme)Ph$_2$	2.645(5)	2.419(13)	2.428(19)	2.161(15)	–	This work
Sn(dapsme)Me$_2$	2.705(3) 2.575(4)	2.52(3) 2.31(3)	2.371(10)	2.245(4) 2.193(6)	–	This work
[Sn(Hadaptsc)Ph$_2$]Cl	2.592(1) 2.703(1)	2.353(4) 2.491(4)	2.348(4)	2.163(4) 2.170(4)	–	8
[Sn(daptsc)Ph$_2$] · 2DMF	2.593(1) 2.603(1)	2.427(4) 2.421(4)	2.368(3)	2.178(4) 2.179(4)	–	9
[Sn(H$_2$dapsc)Cl$_2$] · 2H$_2$O	2.123(6) 2.127(5)	2.259(6)	2.272(7)	–		5
[Sn(CH$_3$)(Cl)Hdaptsc]Cl · CH$_3$OH	2.527(2) 2.633(6)	2.288(6) 2.430(6)	2.238(6)	2.166(8)	2.476(2)	5
[CH$_3$Sn(H$_2$dapsc)Cl]Cl$_2$ · 2H$_2$O	2.177(6) 2.180(6)	2.284(7) 2.252(7)	2.262(2)	2.122(9)	2.386(2)	5
Sn(dapsme)I$_2$ work	2.5629(15)	2.354(5)	2.280(6)	–	2.28128(5)	18
[Sn(H$_2$daptsz-Me)(CH$_3$OH)$_2$] · CH$_3$OH	2.554(5) 2.567(6)	2.349(17) 2.317(15)	2.24(2)	–	1.971(14) 1.979(5)	2
Sn(dapcheximtsc)Bu$_2$	2.6924(6) 2.6924(6)	2.437(5) 2.437(5)	2.415(6)	2.148(10) 2.170(8)	–	10

Hadaptsc = monodeprotonated form of the 2,6-diacetylpyridinebis(thiosemicarbazone); H$_2$dapsc = neutral form of the 2,6-diacetylpyridinebis(semicarbazone); dapsme = doubly deprotonated form of the 2,6-diacetylpyridine Schiff base of S-methyldithiocarbazate; dapchemximtsc = doubly deprotonated form of 2,6-diacetylpyridinebis(3-hexamethyleneiminyl thiosemicarbazone).

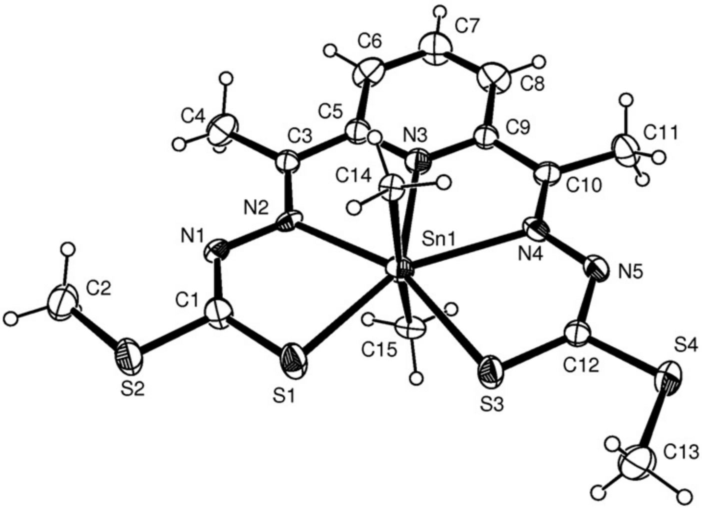

Figure 4. The molecular structure of Sn(dapsme)Me$_2$ (30% probability ellipsoids).

relative to that seen in the charged neutral analog due to the increasing C–N bond order going from –NH–C=S to –N=C–S$^-$.

3.3. *The crystal structure of Sn(dapsme)Me$_2$*

The complex is disordered about a crystallographic mirror plane with only Sn residing on this plane. A view of the molecular structure is shown in figure 4 while the disorder is portrayed in figure 5. The lack of H–bonding may be attributed to the complex being able to pack in two orientations that are each rotated by ~4° from the mirror plane. The two S-methyl groups adopt different orientations, further violating the crystallographic symmetry. This leads to significantly different Sn1–S1 and Sn1–S3 bond lengths (table 2). Notwithstanding the disorder of the structure, the coordinate angles again are close to that of a pentagonal bipyramid (table 2).

The Sn–S and Sn–N distances are comparable to those of other pentagonal bipyramidal organotin(IV) complexes of related ligands (table 6). As found in most tin(IV) complexes of pentadentate bis(thiosemicarbazones), the Sn–N$_{py}$ distance in this complex is shorter than the Sn–N$_{azomethine}$ distance, although the azomethine nitrogen has higher basicity than the pyridine nitrogen atom. The geometric requirement of the doubly deprotonated pentadentate *SNNNS* ligand is probably responsible for this behavior. Bond distances in the dithiocarbazate side chains of the two arms of the ligand are intermediate between single and double bonds, indicating delocalization of electrons in the N–C–N–C– chains.

4. Conclusions

The 2,6-diacetylpyridine Schiff bases of S-methyl- and S-benzyldithiocarbazates, like most Schiff bases derived from S-alkyl esters of dithiocarbazic acid, remain as the

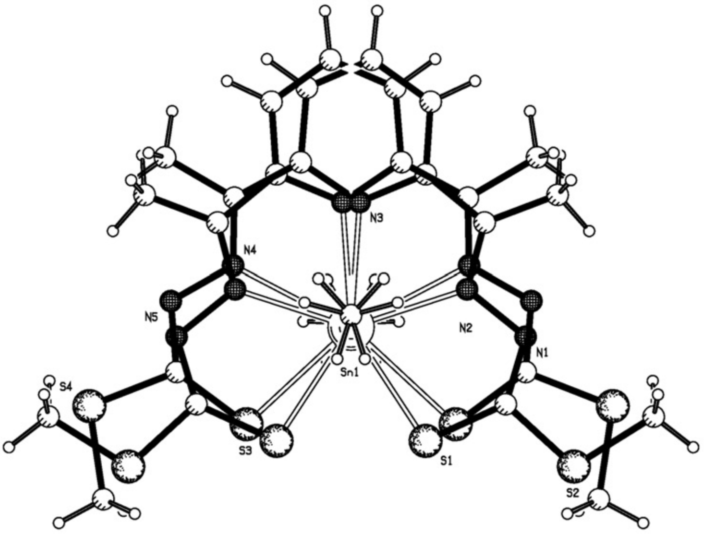

Figure 5. Disorder in the structure of Sn(dapsme)Me_2. The crystallographic mirror plane is perpendicular to the equatorial plane and runs vertically along the page bisecting the Sn and the two axial methyl ligands.

thione tautomer in both the solid state and solution. However, in the presence of organotin(IV) dichlorides they are converted to the iminothiol form, deprotonate and coordinate to tin(IV) as dinegative pentadentate *SNNNS* chelating agents. The tendency of the ligands to deprotonate even in a neutral solution may be attributed to the extra stability gained through π-electron delocalization along the –C–N–N–C–S– chains in the two arms of these ligands. Formation of stable 1 : 1 metal–ligand complexes with organotin(IV) dichlorides with elimination of HCl indicates that these ligands are capable of coordinating with non-transition metals, such as tin, even though they have both soft sulfur donors in their backbones. The ligands approximate a pentagonal array of donors, and the structures approach a pentagonal bipyramidal configuration despite the significantly different coordinate bonds made with Sn(IV). These results are an extension of our previous studies of the 2,6-diacetylpyridine Schiff bases of S-alkyl- and aryldithiocarbazate metal complexes [18–20]. In addition to interesting structural aspects, organotin complexes have been shown to possess various biocidal properties [39–44].

Supplementary material

Full crystallographic data in CIF format, CCDC Nos 655635 and 655636 for Sn(dapsme)Ph_2 and Sn(dapsme)Me_2, respectively, have been deposited at the Cambridge Crystallographic Data Centre and are available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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