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Synthesis and Structural Studies for a Series of Aromatic Schiff Base Complexes with Triphenyltin Chloride and Triphenyltin Isothiocyanate

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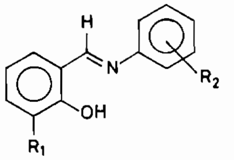
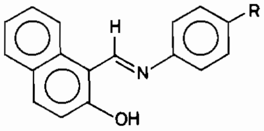
Abstract

A series of complexes of formula $(C_6H_5)_3SnX{\cdot}L$ (X = Cl, NCS) for a range of ligands L, where L = o-$HOC_6H_4CH{=}NC_6H_4R$; o-$HOC_6H_3(OMe)CH{=}NC_6H_5$ or 2-$HOC_{10}H_6CH{=}NC_6H_4R$ (R = CH_3, OCH_3) have been synthesised by the reactions of triphenyltin chloride or isothiocyanate with *N*-aryl-salicylideneimines and *N*-aryl-2-hydroxynaphthylideneimines. Infrared, PMR, conductivity and Mössbauer data are presented. The crystal structure of one complex, isothiocyanatotriphenyl(1-[(4′-methylphenylimino)-methyl]-2-naphthol)tin(IV), is reported. The crystals are monoclinic, space group $P2_1/c$, $a = 12.409(1)$, $b = 15.229(3)$, $c = 17.242(2)$ Å, $\beta = 99.828(9)°$, $V = 3210.5$ Å^3, $Z = 4$, $D_{calc} = 1.385$ Mg m^{-3}, $\mu = 0.89$ mm^{-1}, $F(000) = 1336$, $T = 295$ K, final $R = 4.0\%$ for 2898 unique observed reflections. The complex has a five coordinate distorted trigonal bipyramidal structure, with the phenyl groups taking up the equatorial positions around the tin atom. The ligand, which exists in the form of a zwitterion in the complex, binds to the tin via the phenolic oxygen atom. The other complexes are believed to have similar structures to this.

Introduction

Several reports have appeared during the last decade concerning the Schiff base complexes of organotin(IV) halides and pseudo halides, and involving the coordination of the ligands in either their deprotonated or neutral forms [1–3]. We now wish to report the synthesis and characterisation of a series of hitherto unknown complexes of general formula Ph_3SnX (X = Cl, NCS) with a range of aromatic Schiff bases in their neutral forms, and the results of an X-ray structural investigation for one of the complexes, $Ph_3SnNCS{\cdot}L$ (L = L_8). The various ligands used are shown below





	R_1	R_2
L_1	H	H
L_2	H	4-OCH_3
L_3	H	2-OCH_3
L_4	H	4-CH_3
L_5	OCH_5	4-OCH_3

L_6 R = H
L_7 R = OCH_3
L_8 R = CH_3

Experimental

Triphenyltin chloride was purchased from Alpha Inorganics and used without further purification. Triphenyltin isothiocyanate (melting point (m.p.) 168–170 °C) was prepared by the literature method [4] and recrystallised from benzene before use.

The Schiff bases were prepared by the condensation of salicylaldehyde, 3-methoxy-salicylaldehyde or 2-hydroxy-naphthaldehyde with the appropriate primary amine in refluxing benzene, the water formed being removed azeotropically. The ligands were purified by recrystallisation from 95% ethanol or methanol.

The complexes were prepared by refluxing the calculated amount (for 1:1 complex formation) of ligand and either triphenyltin chloride or triphenyltin isothiocyanate, in 95% ethanol for thirty minutes. The complexes crystallised when the solutions were

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cooled in the freezer overnight. They were filtered off and recrystallised from ethanol.

Conductance measurements in nitrobenzene were made at room temperature using a Phillips PW 9501 conductivity bridge with a cell constant of 0.71 cm^{-1}.

PMR spectra were obtained with a Perkin-Elmer R12B spectrometer with deuterochloroform as solvent.

The IR spectra of the ligands and complexes were recorded in the region 4000–600 cm^{-1} with a Beckmann Acculab '4' instrument, with samples between NaCl plates, either as neat liquid films, or as Nujol mulls. For the 600–200 cm^{-1} region, the Beckmann IR 4250 spectrophotometer was used with the samples as KBr discs.

Mössbauer data were recorded at the International Tin Research Institute, Greenford, U.K.

Tin was determined gravimetrically as SnO_2. Microanalyses were performed at the Chemistry Department, National University of Singapore, Singapore.

Crystal Data

Complex: isothiocyanatotriphenyl(1-[(4'-methylphenylimino)-methyl]-2-naphthol)tin(IV).

Monoclinic. Space group $P2_1/c$, $a = 12.409(1)$, $b = 15.229(3)$, $c = 17.242(2)$ Å, $\beta = 99.828(9)°$, $V = 3210.5$ Å^3, $Z = 4$, $D_{calc} = 1.385$ Mg m^{-3}, $\mu = 0.89$ mm^{-1}.

Intensity Data

Intensity data were collected from a 0.1 × 0.1 × 0.3 mm yellow rod-shaped crystal using graphite monochromatised Mo Kα radiation. A total of 5849 reflections were measured on a Picker diffractometer using the $\theta/2\theta$ scanning mode with profile analysis [5] to $2\theta_{max} = 50°$. Of the reflections measured, 5689 were unique, of which 2898 were considered significant, with $I_{net} \geqslant 2.5\sigma(I_{net})$. The intensities were corrected for measured direct beam polarisation [6], but absorption correction was not applied ($\mu = 0.89$ mm^{-1}). The cell parameters were obtained by least squares refinement of the setting angles of 54 reflections with $40.0° \leqslant 2\theta \leqslant 44.0°$. [$\lambda_{(Mo\ K\alpha_1)} = 0.70392$ Å].

Structure Solution and Refinement

The structure was solved using Fourier and direct methods. The Sn and S atoms were found from an *E* map based on phases derived by MULTAN [7] for the 204 largest *E* values. A heavy-atom-phased difference map revealed all the other non-H atoms. All non-H atoms were refined anisotropically. The H atoms were then located on a difference map and their positional parameters were refined together with isotropic thermal parameters, while the other atoms were refined anisotropically by full-matrix least squares. The final residuals are $R_f = 0.040$ and $R_w = 0.021$ for the significant reflections and $R_f = 0.114$ and $R_w = 0.024$ for all reflections. Weights based on counting statistics were used throughout. All calculations were performed with the NRCVAX system of programs [8]. Literature values [9] were used for the scattering factors.

Results and Discussion

Melting points, molar conductance values and mircroanalytical data for the complexes are recorded in Table I. In almost every instance, the complexes crystallised with 1:1 stoichiometry, regardless of the proportions of ligand and triphenyltin compound used. The complexes were all yellow to red in colour, thermally stable with sharply defined melting points

TABLE I. Analytical, Melting Point and Conductivity Data for the Complexes

Complex Ligand:Ph_3SnX		Elemental analysis, found (calc.) (%)				Melting point (°C)	Molar conductance (ohm^{-1} cm^{-1} mol^{-1})
L	X	C	H	N	Sn		
L_1	Cl	63.88(63.89)	4.53(4.51)	2.41(2.40)	20.37(20.37)	70–72	2.18
L_1	NCS	63.15(63.49)	4.30(4.34)	4.25(4.63)	20.48(19.61)	144–145	1.75
L_2	Cl	62.42(62.72)	4.61(4.62)	2.36(2.29)	19.14(19.57)	109–110	1.19
L_2	NCS	61.95(62.38)	4.44(4.45)	3.97(4.41)	19.25(18.68)	136–138	1.42
L_3	Cl	62.19(62.79)	4.67(4.62)	2.18(2.29)	19.14(19.57)	69–71	1.22
L_4	Cl	64.85(64.29)	4.87(4.73)	2.46(2.34)	20.94(19.86)	80–82	0.69
L_4	NCS	64.45(63.90)	4.54(4.57)	4.65(4.52)	19.54(19.16)	136–138	1.15
L_5	Cl	61.68(61.66)	4.61(4.71)	2.35(2.18)	19.26(18.47)	77–79	2.93
L_5	NCS	61.92(61.37)	4.56(4.55)	4.25(4.21)	17.48(17.84)	153–154	2.91
L_6	NCS	66.93(65.97)	4.36(4.31)	4.38(4.28)	18.10(18.11)	146–147	2.50
L_7	Cl	66.09(65.23)	4.60(4.57)	2.18(2.11)	17.27(17.91)	130–132	1.54
L_7	NCS	65.79(64.83)	4.41(4.42)	4.24(4.09)	17.91(18.39)	180–181	3.11
L_8	NCS	66.38(66.38)	4.50(4.53)	4.23(4.19)	17.16(17.73)	170–171	3.04

TABLE II. PMR Data for the Complexes

Complex Ligand:Ph_3SnX		Azomethine proton CH=NR	Phenolic proton OH	$-CH_3/OCH_3$ proton
L	X	(δ ppm)	(δ ppm)^a	(δ ppm)
L_1	Cl	8.60	12.20	
L_1	NCS	8.65	13.30	
L_2	Cl	8.65	13.45	3.80
L_2	NCS	8.55	13.50	3.80
L_3	Cl	8.70	13.90	3.85
L_4	Cl	8.40	13.60	2.30
L_4	NCS	8.30	13.45	2.30
L_5	Cl	8.60	13.85	3.80; 3.90
L_5	NCS	8.55	12.25	3.50; 3.75
L_6	NCS	9.05(7)^b	14.60	
L_7	Cl	9.17^a	14.05	3.75
L_7	NCS	9.20^a	14.20	3.80
L_8	NCS	9.15(6)^b	14.80	2.45

^{a}Broad peak. ^{b}J(c/s) in parentheses.

and were found to be soluble in the common organic solvents. The observed molar conductances in nitrobenzene were in the range 0.69–3.40 ohm^{-1} cm^2 mol^{-1}, indicating that the compounds were non-electrolytes in this solvent, and that in each instance, the chloride or isothiocyanate group is bound to the tin atom. (Molar conductances expected for 1:1 and 2:1 electrolytes in nitrobenzene are 25–35 and 44–60 ohm^{-1} cm^2 mol^{-1} respectively [10].)

Confirmation of the 1:1 stoichiometry of the complexes comes from a comparison of the integrated intensities of the methyl or methoxy protons of the ligands and the organotin phenyl protons, in the PMR spectra (Table II). The sharp singlet assigned to the azomethine proton [11] of the salicylidene (δ = 8.50 ppm) and the 2-hydroxynaphthylidene (δ = 9.20 ppm) ligands was found to be unchanged on coordination, indicating that the N-atom is not coordinated to the metal. On the other hand, the peak due to the phenolic proton for each ligand molecule (δ = 13–15 ppm) was significantly broadened on complex formation. Coordination through oxygen is expected to result in a wakening of the O–H bond, and a strengthening of the C=N•••H hydrogen bond, which in turn leads to the observed broadening of the peak due to the phenolic proton. Similar observations have been reported for *N*,*N*′-bis(salicylaldehyde)ethylenediimine [12] and the dialkyltin dichloride complexes of the *N*-arylsalicylideneimines [13].

The infrared evidence (Table III) also suggests that the ligands are behaving as monodentates via the phenolic oxygen atoms. A strong band assigned to the C=N stretching vibration is observed at 1610–1630 cm^{-1} for the ligands [3]. However, in the complexes, this band shifts towards higher frequency (1620–1660 cm^{-1}). Similar shifts in C=N stretching frequency for ligands of this type have been found to indicate coordination to the tin atom by oxygen [14, 15]. This has been confirmed by the X-ray structural analysis of the complex of dimethyltin dichloride with 2-(*p*-methoxyphenyliminomethyl)-phenol [16].

Due to the strong intramolecular hydrogen bonding present, the stretching vibration of the phenolic O–H is lowered and broadened, and the weak, broad bands observed in the spectra of the uncoordinated ligands in the 2600–3000 cm^{-1} range are attributed to these restricted vibrations [17]. For the complexes, these bands are shifted towards higher energies by about 200 cm^{-1}, suggesting that the ring formed by intramolecular hydrogen bond for-

TABLE III. IR Data for the Complexes

Complex Ligand:Ph_3SnX		ν(CN) (cm^{-1})	ν(Sn–Ph)		ν(NCS)^a (cm^{-1})	ν(Sn–Cl) (cm^{-1})
L	X		(cm^{-1})	(cm^{-1})		
L_1	Cl	1635	270	235		220
L_1	NCS	1635	270	240	2050	
L_2	Cl	1645	270	230		220
L_2	NCS	1645	270	235	2060	
L_3	Cl	1640	270	240		220
L_4	Cl	1635	270	235		230
L_4	NCS	1650	275	240	2040	
L_5	Cl	1630	270	230		220
L_5	NCS	1640	270	240	2040	
L_6	NCS	1630	280	230	2035	
L_7	Cl	1630	270	240		220
L_7	NCS	1640	275	235	2030	
L_8	NCS	1620	280	240	2040	

^{a}ν(CN) for NCS group in Ph_3SnNCS.

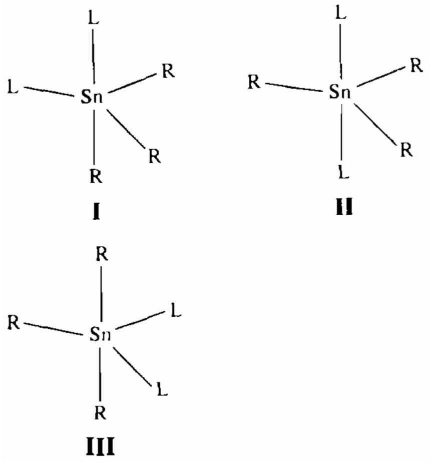

Fig. 1. Possible isomers of trigonal bipyramidal R_3SnL_2.

TABLE IV. Mössbauer Data[a] for the Complexes

Complex	Isomer shift[b] (mm s^{-1})	Quadrupole splitting (ΔE_Q) (mm s^{-1})
$Ph_3SnCl \cdot L_1$	1.27	3.22
$Ph_3SnCl \cdot L_2$	1.24	3.14
$Ph_3SnCl \cdot L_3$	1.29	3.28
$Ph_3SnNCS \cdot L_6$	1.26	3.32
$Ph_3SnNCS \cdot L_8$	1.22	3.38

[a] The accuracy for all these parameters is ±0.05 mm s^{-1}.
[b] Relative to $BaSnO_3$.

mation is still present after coordination has occurred [12].

In the low frequency infrared region, bands observed at ~230 and ~280 cm^{-1} in all the complexes are assigned to the tin–phenyl stretching vibrations. The frequencies of these vibrations are largely unaffected by changes in the coordination number of the tin atom, and occur at almost the same frequencies as in the parent triphenyltin compound [18]. Each of the triphenyltin chloride complexes displayed a band in the region 220–230 cm^{-1}. These are assigned to the Sn–Cl stretching mode, which is sensitive to an increase in the coordination around the tin atom, and in each case is shifted downfield by some 100 cm^{-1} from its value in triphenyltin chloride [18]. The strong absorptions observed at ~2040 cm^{-1} for all the thiocyanate groups indicate N-bonding to the tin atom in each instance [19].

The results so far discussed suggest that the ligands are all behaving as unidentates, the Cl or NCS groups are coordinated, and so the complexes are five-coordinate, most probably trigonal bipyramidal. The three possible isomers are shown in Fig. 1. Each of these possible isomeric forms would be expected to show a different quadrupole splitting value in the Mössbauer spectrum [20, 21]. For isomers of type **I**, the range of ΔE_Q is 1.7–2.3 mm s^{-1}; for type **II**, 3.0–3.9 mm s^{-1} and for type **III**, 3.5–4.1 mm s^{-1}. The ΔE_Q values (Table IV) obtained for the complexes all fall in the range 3.14–3.38 mm s^{-1}, and thus clearly belong to type **II**, supporting the assignment, for all the complexes of trigonal bipyramidal structures, with the three phenyl groups in the equatorial plane in each case.

This conclusion has been confirmed by the completion of a full X-ray structural determination for one of the complexes: isothiocyanatotriphenyl(1-

TABLE V. Atomic Parameters x, y, z and B_{iso}. Estimated Standard Deviations Refer to the Last Digit Printed

	x	y	z	B_{iso}
Sn	0.89887(3)	0.21436(3)	0.604041(23)	4.308(21)
S	1.27014(12)	0.27046(11)	0.55186(9)	5.89(9)
O(2)	0.7388(3)	0.16047(23)	0.63280(20)	4.53(20)
N(1)	0.5627(4)	0.1221(3)	0.5351(3)	3.8(3)
N(2)	1.0558(4)	0.2628(4)	0.5733(3)	6.2(3)
C(1)	0.5666(4)	0.1492(3)	0.6740(3)	3.3(3)
C(2)	0.6806(5)	0.1666(4)	0.6889(3)	4.1(3)
C(3)	0.7277(5)	0.1917(4)	0.7667(4)	5.5(4)
C(4)	0.6677(5)	0.1945(4)	0.8253(3)	5.3(4)
C(5)	0.4957(7)	0.1770(4)	0.8754(4)	5.5(4)
C(6)	0.3874(7)	0.1581(5)	0.8633(4)	6.6(5)
C(7)	0.3352(7)	0.1369(5)	0.7887(5)	6.9(5)
C(8)	0.3912(6)	0.1334(5)	0.7268(4)	5.5(4)
C(9)	0.5031(5)	0.1524(4)	0.7370(3)	3.7(3)
C(10)	0.5548(5)	0.1746(3)	0.8124(3)	3.9(3)
C(11)	0.8207(6)	0.3351(4)	0.5716(4)	5.0(4)
C(12)	0.8566(8)	0.3873(5)	0.5152(5)	6.4(5)
C(13)	0.7989(10)	0.4605(6)	0.4847(5)	8.4(7)
C(14)	0.7071(10)	0.4849(7)	0.5102(6)	8.8(7)
C(15)	0.6707(10)	0.4373(7)	0.5676(8)	9.8(8)
C(16)	0.7250(8)	0.3624(6)	0.5965(5)	7.6(6)
C(17)	0.5158(5)	0.1292(4)	0.5978(4)	3.7(3)
C(18)	1.1456(5)	0.2662(4)	0.5657(3)	4.3(3)
C(21)	0.9806(5)	0.1793(5)	0.7179(3)	4.6(4)
C(22)	0.9736(6)	0.0969(6)	0.7474(5)	6.1(5)
C(23)	1.0227(7)	0.0724(7)	0.8238(5)	7.6(6)
C(24)	1.0792(7)	0.1361(9)	0.8697(5)	7.7(7)
C(25)	1.0889(6)	0.2199(8)	0.8437(5)	7.4(6)
C(26)	1.0399(6)	0.2410(6)	0.7667(5)	6.1(5)
C(31)	0.8793(4)	0.1201(4)	0.5125(3)	4.0(3)
C(32)	0.8528(5)	0.0332(5)	0.5237(5)	5.0(4)
C(33)	0.8434(6)	−0.0277(5)	0.4634(6)	6.0(5)
C(34)	0.8564(6)	−0.0013(6)	0.3903(5)	6.7(5)
C(35)	0.8807(6)	0.0837(7)	0.3759(5)	6.8(5)
C(36)	0.8940(5)	0.1453(5)	0.4368(4)	5.2(4)
C(41)	0.5142(5)	0.1054(4)	0.4559(3)	3.9(3)
C(42)	0.5832(6)	0.0964(4)	0.4027(4)	4.7(4)
C(43)	0.5387(7)	0.0833(5)	0.3234(4)	5.7(4)
C(44)	0.4299(7)	0.0787(4)	0.2985(4)	5.6(4)
C(45)	0.3623(6)	0.0893(5)	0.3531(5)	6.2(4)
C(46)	0.4036(6)	0.1021(5)	0.4319(4)	5.1(4)
C(47)	0.3816(11)	0.0658(9)	0.2110(6)	9.4(7)
H(1)	0.641(4)	0.126(3)	0.553(3)	4.2(14)

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

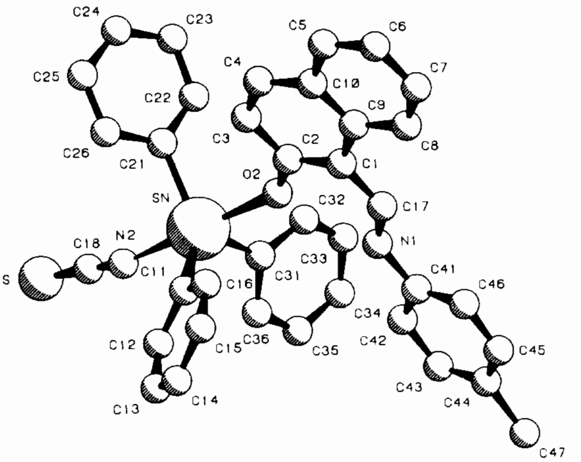

Fig. 2. Molecular configuration and atomic numbering scheme.

[4′-methylphenylimino)-methyl]-2-naphthol)tin(IV) (or $Ph_3SnNCS \cdot L_8$).

This complex has a trigonal bipyramidal structure, with the three phenyl groups occupying the equatorial positions around the Sn atom, while the O atom of the ligand and the N of the NCS group occupy the axial positions.

The final atomic positional parameters and the equivalent isotropic temperature factors are given in Table V. The structure of the complex and the atomic numbering scheme are shown in Fig. 2, while Table VI, lists the bond distances and angles. A stereoscopic view of the molecule is given in Fig. 3.

The Sn atom is slightly displaced from the equatorial plane defined by the three bonding C atoms of the phenyl groups (0.050(4) Å), and the O–Sn–N angle is 177.94(14)°. The average Sn–C(Ph) distance of 2.115(6) Å is within the range of Sn–C(Ph) distances (2.105–2.16 Å) reported in the literature [22]. The C–C bond lengths in the phenyl groups are all normal.

The NCS group is almost linear, the NCS angle being 178.1(5)°. The Sn–N distance of 2.230(5) Å seems to fall in the middle of a range of Sn–N bond lengths reported for other organotin compounds. It is longer than the average Sn–N distance of 2.10(2) Å in diisothiocyanatodimethyltin(IV) [23] and 2.168(6) Å (2,2′-bipyridyl)diisothiocyanatodiphenyltin(IV) [24]. But it is shorter than the Sn–N bond lengths of 2.28 Å found in both diisothiocyanatodimethyl(terpyridyl)tin(IV) [25] and isothiocyanatotriphenyl(pyridinium-2-carboxylato)tin(IV) monohydrate [26]. The N–C and C–S distances, 1.144(6) and 1.605(6) Å, respectively, are similar to those found in other metal isothiocyanato complexes [27, 28].

A striking feature of the structure is that the phenolic proton of the ligand has moved to the imine nitrogen. The Schiff base is thus coordinated in the form of a zwitterion. Similar proton transfers from

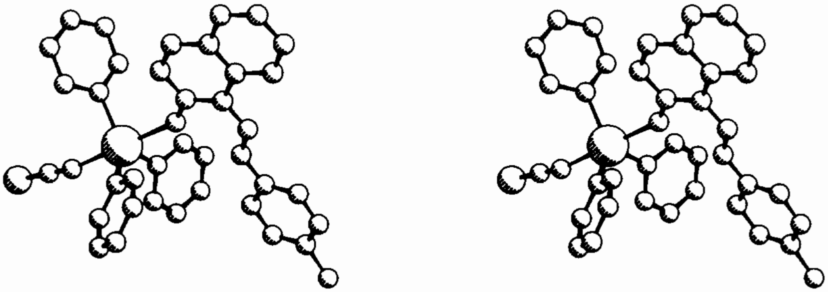

Fig. 3. Stereoview of the complex.

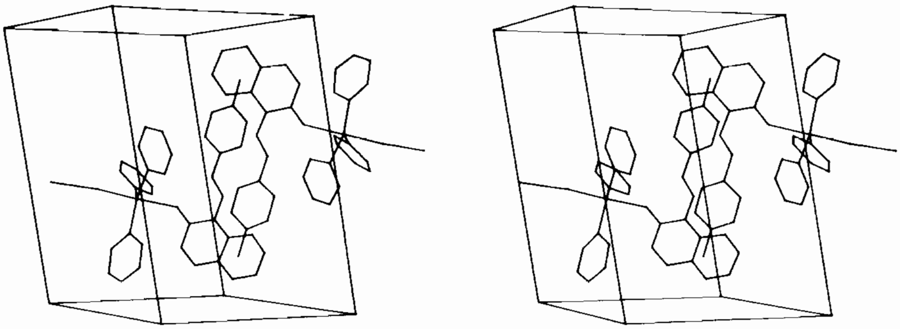

Fig. 4. Stereoview of packing arrangement.

TABLE VI. Bond Lengths (Å) and Angles (°)

Sn–O(2)	2.280(4)	C(12)–C(13)	1.380(14)
Sn–N(2)	2.230(5)	C(13)–C(14)	1.342(18)
Sn–C(11)	2.110(6)	C(14)–C(15)	1.364(19)
Sn–C(21)	2.118(6)	C(15)–C(16)	1.375(15)
Sn–C(31)	2.117(6)	C(21)–C(22)	1.362(11)
S–C(18)	1.605(6)	C(21)–C(26)	1.385(11)
O(2)–C(2)	1.306(6)	C(22)–C(23)	1.404(12)
N(1)–C(17)	1.316(8)	C(23)–C(24)	1.368(16)
N(1)–C(41)	1.418(7)	C(24)–C(25)	1.364(18)
N(2)–C(18)	1.144(8)	C(25)–C(26)	1.400(12)
C(1)–C(2)	1.420(8)	C(31)–C(32)	1.386(10)
C(1)–C(9)	1.447(7)	C(31)–C(36)	1.402(9)
C(1)–C(17)	1.391(8)	C(32)–C(33)	1.383(12)
C(2)–C(3)	1.421(8)	C(33)–C(34)	1.359(14)
C(3)–C(4)	1.355(9)	C(34)–C(35)	1.361(14)
C(4)–C(10)	1.413(9)	C(35)–C(36)	1.396(11)
C(5)–C(6)	1.356(12)	C(41)–C(42)	1.365(9)
C(5)–C(10)	1.411(9)	C(41)–C(46)	1.364(10)
C(6)–C(7)	1.376(12)	C(42)–C(43)	1.400(11)
C(7)–C(8)	1.371(10)	C(43)–C(44)	1.347(12)
C(8)–C(9)	1.400(10)	C(44)–C(45)	1.374(12)
C(9)–C(10)	1.390(8)	C(44)–C(47)	1.538(11)
C(11)–C(12)	1.386(12)	C(45)–C(46)	1.382(11)
C(11)–C(16)	1.393(12)	N(1)–H(1)	0.97(5)
O(2)–Sn–N(2)	177.94(15)	C(11)–C(12)–C(13)	121.5(9)
O(2)–Sn–C(11)	89.63(21)	C(12)–C(13)–C(14)	120.8(10)
O(2)–Sn–C(21)	90.29(18)	C(13)–C(14)–C(15)	119.7(10)
O(2)–Sn–C(31)	85.70(16)	C(14)–C(15)–C(16)	120.0(11)
N(2)–Sn–C(11)	91.66(25)	C(11)–C(16)–C(15)	121.8(9)
N(2)–Sn–C(21)	90.23(21)	N(1)–C(17)–C(1)	127.0(6)
N(2)–Sn–C(31)	92.32(20)	S–C(18)–N(2)	178.1(5)
C(11)–Sn–C(21)	126.24(24)	Sn–C(21)–C(22)	121.8(5)
C(11)–Sn–C(31)	113.85(23)	Sn–C(21)–C(26)	120.9(5)
C(21)–Sn–C(31)	119.75(25)	C(22)–C(21)–C(26)	117.3(6)
Sn–O(2)–C(2)	138.4(3)	C(21)–C(22)–C(23)	123.4(8)
C(17)–N(1)–C(41)	129.1(5)	C(22)–C(23)–C(24)	116.9(9)
Sn–N(2)–C(18)	161.6(5)	C(23)–C(24)–C(25)	122.6(8)
C(2)–C(1)–C(9)	120.7(5)	C(24)–C(25)–C(26)	118.6(9)
C(2)–C(1)–C(17)	119.3(5)	C(21)–C(26)–C(25)	121.3(9)
C(9)–C(1)–C(17)	120.0(5)	Sn–C(31)–C(32)	122.9(5)
O(2)–C(2)–C(1)	120.8(5)	Sn–C(31)–C(36)	119.5(5)
O(2)–C(2)–C(3)	121.9(5)	C(32)–C(31)–C(36)	117.6(6)
C(1)–C(2)–C(3)	117.3(5)	C(31)–C(32)–C(33)	121.9(7)
C(2)–C(3)–C(4)	121.5(6)	C(32)–C(33)–C(34)	119.3(8)
C(3)–C(4)–C(10)	122.2(6)	C(33)–C(34)–C(35)	121.1(7)
C(6)–C(5)–C(10)	120.5(7)	C(34)–C(35)–C(36)	120.2(8)
C(5)–C(6)–C(7)	119.4(7)	C(31)–C(36)–C(35)	119.9(7)
C(6)–C(7)–C(8)	121.1(7)	N(1)–C(41)–C(42)	116.9(6)
C(7)–C(8)–C(9)	121.2(7)	N(1)–C(41)–C(46)	122.5(6)
C(1)–C(9)–C(8)	123.6(5)	C(42)–C(41)–C(46)	120.5(6)
C(1)–C(9)–C(10)	119.2(5)	C(41)–C(42)–C(43)	118.8(7)
C(8)–C(9)–C(10)	117.2(5)	C(42)–C(43)–C(44)	121.7(7)
C(4)–C(10)–C(5)	120.3(6)	C(43)–C(44)–C(45)	118.1(7)
C(4)–C(10)–C(9)	119.0(5)	C(43)–C(44)–C(47)	121.4(8)
C(5)–C(10)–C(9)	120.6(6)	C(45)–C(44)–C(47)	120.4(8)
Sn–C(11)–C(12)	119.8(6)	C(44)–C(45)–C(46)	121.5(7)
Sn–C(11)–C(16)	123.8(6)	C(41)–C(46)–C(45)	119.2(7)
C(12)–C(11)–C(16)	115.9(7)	C(17)–N(1)–H(1)	107(3)
		C(41)–N(1)–H(1)	123(3)

oxygen to nitrogen have been reported recently for some organotin complexes of picolinic [26] and quinaldic [29] acids, which also coordinate to tin(IV) atoms in the form of zwitterions. For these two acids, a five-membered ring is formed by the intramolecular hydrogen bonding, whereas in the present instance a six-membered ring must be involved. However, the protonation of the nitrogen effectively blocks that atom from any coordinative interaction with the tin in all these examples.

The complexes pack together in the crystal in pairs of centrosymmetrically-related dimers, with the Schiff bases lying flat, one above the other, and head-to-tail relative to each other. Figure 4 is a stereoview illustrating this fascinating packing arrangement. See also 'Supplementary Material'.

We believe that all the complexes described above have five coordinate, trigonal bipyramidal structures, essentially similar to that of $Ph_3SnNCS{\cdot}L_8$. The data in Tables I–IV support this belief.

But, microanalytical data for the triphenyltin chloride complexes of L_6 and L_8 suggest a ligand: organotin ratio of 3:2, indicating that these complexes may have different structures. Further investigations into the structures of these two interesting compounds are proceeding.

Supplementary Material

The anisotropic thermal parameters, final structure factors and some additional structural information are available from the Editor-in-Chief.

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