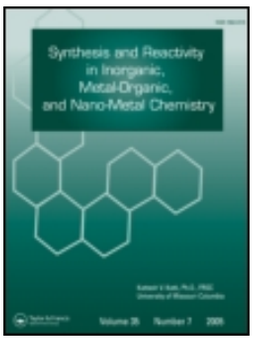

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SYNTHESIS AND CHARACTERIZATION OF ORGANOTIN(IV) COMPLEXES OF N-(2-MERCAPTOPHENYL)-SALICYLALDIMINE

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ABSTRACT

The organotin(IV) complexes of N-(2-mercaptophenyl)salicylaldimine, $ROCOCH_2CH_2SnClL$ ($L = OC_6H_4CH{=}NC_6H_4S$, R = alkyl), were synthesized by the reaction of 2-alkoxycarbonylethyltin trichlorides with N-(2-mercaptophenyl)salicylaldimine (H_2L) in the presence of triethylamine and were characterized by elemental analyses, IR, ^1H NMR spectra and X-ray single crystal diffraction. The structural features of these compounds are discussed.

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INTRODUCTION

Since Hutton *et al.*[1] reported the syntheses of 2-alkoxycarbonylethyltin trichlorides, $ROCOCH_2CH_2SnCl_3$, the structure and coordination chemistry of these systems have attracted considerable attention.[2–11] The crystal structure determinations[2,3,7–10] and spectral data[1,4–7,11] of $ROCOCH_2CH_2SnCl_3$ and their 1:1 adducts with monodentate donors showed that the carbonyl oxygen is coordinated intramolecularly to tin leading to the formation of a five-membered cheating ring. However, the intramolecular coordination can be broken in the 1:2 adducts with monodentate donors and 1:1 adducts with bidentate donors.[3–5,11] To our knowledge, little attention has been devoted to the complexes of $ROCOCH_2CH_2SnCl_3$ with Schiff bases, particularly with tridentate Schiff base ligands.[11] In this paper, we report the synthesis and structural characterization of the complexes of 2-alkoxycarbonylethyltin trichlorides with N-(2-mercapto-phenyl)salicylaldimine.

RESULTS AND DISCUSSION

The synthesis of β-alkoxycarbonylethyltin trichloride complexes with N-(2-mercaptophenyl)salicylaldimine (H_2L) may be represented by the following equations:

$$ROCOCH_2CH_2SnCl_3 + H_2L + Et_3N \rightarrow ROCOCH_2CH_2SnClL + 2Et_3N{\cdot}HCl$$

R = CH_3(**1**); CH_3CH_2(**2**); $CH_3CH_2CH_2$ (**3**);
$CH_2{=}CHCH_2$ (**4**); $CH_3(CH_2)_2CH_2$ (**5**); $(CH_3)_2CHCH_2$ (**6**);
cyclo-C_6H_{11} (**7**).

The analytical and physical data of these complexes are listed in Table I. They are orange-yellow crystals, which are air-stable and soluble in benzene and in common polar organic solvents, such as ethanol, chloroform, acetone and nitrobenzene, but insoluble in saturated hydrocarbons such as hexane and petroleum ether. The molar conductance values (4.0–6.2 $S\,cm^2\,mol^{-1}$) of the complexes in nitrobenzene at room temperature suggest that they are non-electrolytes.[12]

Table I. Physical and Analysis Data for the Complexes

Complex No.	Empirical Formula (Formula Weight)	Yield (%)	M.p. (°C)	Λ_m ($S\,cm^2\,mol^{-1}$)	Analysis %, Found (Calculated)				
					C	H	N	S	Sn
(1)	$C_{17}H_{16}ClNO_3SSn$ (468.52)	80.3	196	5.4	43.54 (43.58)	3.23 (3.44)	2.94 (2.99)	6.78 (6.84)	25.08 (25.34)
(2)	$C_{18}H_{18}ClNO_3SSn$ (482.54)	84.6	178	4.8	44.82 (44.80)	3.52 (3.76)	2.91 (2.90)	6.62 (6.64)	24.71 (24.60)
(3)	$C_{19}H_{20}ClNO_3SSn$ (496.57)	78.4	184	4.0	45.84 (45.95)	3.98 (4.06)	2.76 (2.82)	6.44 (6.46)	23.89 (23.90)
(4)	$C_{19}H_{18}ClNO_3SSn$ (494.55)	82.6	162	6.2	45.96 (46.14)	3.61 (3.67)	2.82 (2.83)	6.37 (6.48)	24.12 (24.00)
(5)	$C_{20}H_{22}ClNO_3SSn$ (510.60)	80.5	154	5.4	47.09 (47.04)	4.17 (4.34)	2.77 (2.74)	6.23 (6.28)	23.08 (23.23)
(6)	$C_{20}H_{22}ClNO_3SSn$ (510.60)	68.5	192	5.9	46.89 (47.04)	4.25 (4.34)	2.62 (2.74)	6.28 (6.28)	23.20 (23.23)
(7)	$C_{22}H_{24}ClNO_3SSn$ (536.63)	74.6	201	5.4	49.22 (49.24)	4.37 (4.51)	2.58 (2.61)	5.84 (5.97)	22.24 (22.12)

Infrared Spectra

The characteristic IR bands of the complexes in KBr pellets are listed in Table II. The stretching frequencies of C=O and C-O bonds of the ester groups in the complexes lie in the ranges 1648–1660 and 1262–1271 cm^{-1}, respectively. Compared with ν(C=O) (~1740 cm^{-1}) and ν(C-O) (~1200 cm^{-1}) of the corresponding free fatty acid esters, the former shifts to lower frequency and the latter to higher frequency in the complexes. This indicates that the carbonyl group is coordinated intramolecularly to the tin atom and a five-membered chelate ring is formed in these molecules.[1,5] Remarkable changes in the frequencies of the following stretching vibrations in the bound ligand, compared with the free ligand, occur: the C=N vibration bands undergo a shift to lower frequency by 20–28 cm^{-1}, the phenolic C-O stretching vibrations, ν(Ar-O), increase by 28–35 cm^{-1}, the OH (3140 cm^{-1}) and SH (2520 cm^{-1}) stretching vibrations are not observed. These changes clearly show that metal-chelate complexes are formed *via* the O, N, and S atoms of the ligand.[11,13] The medium-strong absorption band at 540 cm^{-1}, which is absent in the spectra of the ligand and parent organotins, may be assigned to the Sn-O vibration.[14,15] The Sn-S stretching vibration is expected[16] in the region below 400 cm^{-1} and cannot be obtained using KBr disks. Thus, it may be seen that all the complexes are hexa-coordinated with respect to tin. Their suggested structures are shown in Fig. 1.

^{1}H NMR Spectra

^{1}H NMR data of the complexes in $CDCl_3$ solution are presented in Table III. The protons of CH_2Sn (~1.80 ppm) and $COCH_2$ (~2.90 ppm) in the complexes resonate at higher magnetic field than those in the parent

Table II. IR Spectral Data (cm^{-1}, KBr) of the Compounds[a]

Compd.	ν(C=O)	ν(C-O)	ν(Ar-O)	ν(C=N)	ν(Sn-O)
(1)	1657 vs	1268 s	1310 s	1605 s	540 m
(2)	1654 vs	1266 s	1308 s	1610 s	538 m
(3)	1648 vs	1268 s	1305 s	1606 s	542 m
(4)	1656 vs	1264 s	1312 s	1602 s	540 m
(5)	1658 vs	1262 s	1305 s	1610 s	538 m
(6)	1652 vs	1271 s	1310 s	1606 s	542 m
(7)	1660 vs	1264 s	1308 s	1610 s	545 m

[a]vs = very strong, s = strong, m = medium.

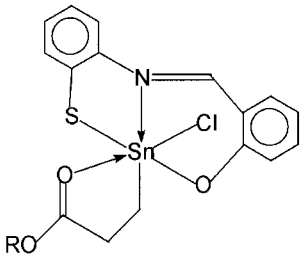

Figure 1. Suggested structures of the complexes.

organotin compounds,[1,10,11] which is in agreement with the increased electron density on the tin atom through ligand donation. The OH and SH proton signals of the ligand are absent in the complexes indicating the deprotonation of OH and SH groups and bonding of tin with oxygen and sulfur atoms. Compared with the free ligand, the proton of the azomethine (CH=N) group in the complexes shows a marked downfield shift ($\Delta\delta = \sim 0.20$ ppm) due to coordination of CH=N with the tin atom and thus decreasing the electron shielding of the CH=N proton. The protons of the aromatic ring appear in the range of 6.56–7.59 ppm.

Crystal Structure of (1)

The molecular structure and unit cell constants for **(1)** are shown in Figs. 2 and 3. The selected bond lengths and bond angles are given in Table IV. The complex exists as a discrete molecule which contains a five-membered chelate ring, formed *via* carbonyl oxygen to tin coordination, and a five-membered and a six-membered chelate ring from the negatively

Table III. ^{1}H NMR (δ, $CDCl_3$) Spectral Data of the Compounds[a]

Compd.	CH_nO (n = 1–3)	$COCH_2$	CH_2Sn	CH=N
(1)	3.79 s	2.94 t	1.82 t	8.66 s
(2)	4.12 q	2.90 t	1.82 t	8.67 s
(3)	4.03 t	2.94 t	1.80 t	8.66 s
(4)	4.56 d	2.89 t	1.85 t	8.65 s
(5)	4.14 t	2.90 t	1.80 t	8.66 s
(6)	3.99 d	2.89 t	1.82 t	8.67 s
(7)	5.00 m	2.87 t	1.78 t	8.67 s

[a]d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet.

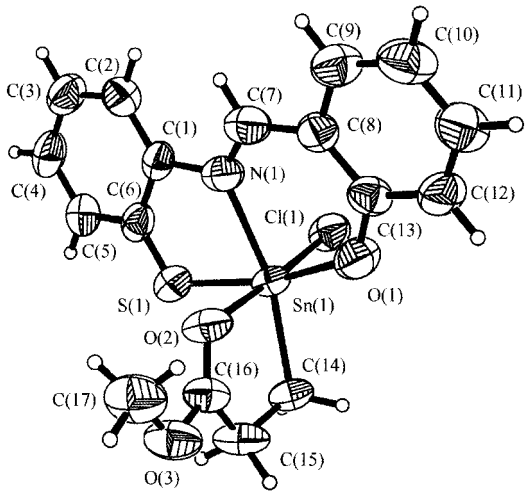

Figure 2. Molecular structure of $CH_3OCOCH_2CH_2SnClL$ **(1)**.

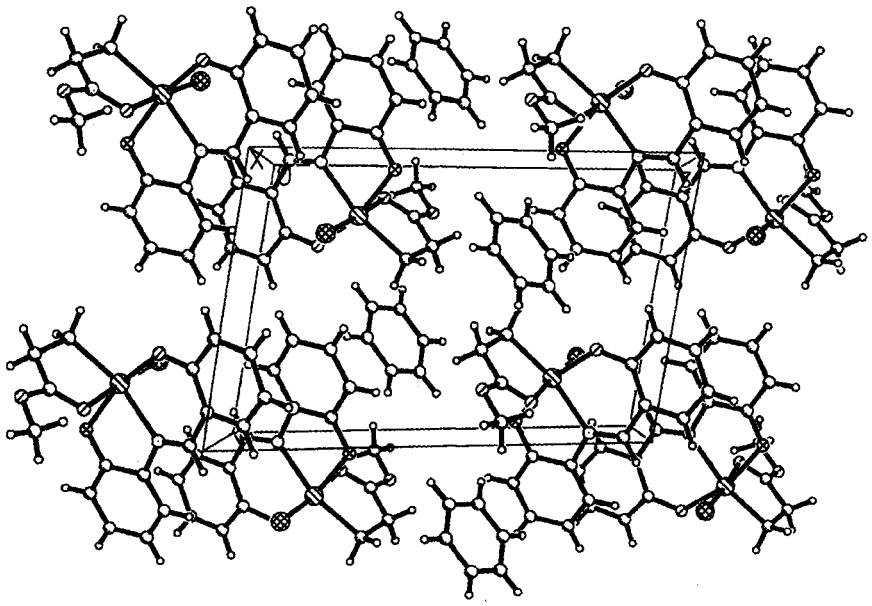

Figure 3. Molecular packing arrangement in the unit cell.

Table IV. Selected Bond Lengths (Å) and Angles (°) for **(1)**

Bond Lengths			
Sn(1)-O(1)	2.031(3)	C(1)-C(6)	1.396(6)
Sn(1)-O(2)	2.396(3)	C(2)-C(3)	1.372(7)
Sn(1)-S(1)	2.458(3)	C(3)-C(4)	1.385(8)
Sn(1)-N(1)	2.187(4)	C(4)-C(5)	1.368(7)
Sn(1)-C(14)	2.138(4)	C(5)-C(6)	1.386(6)
Sn(1)-Cl(1)	2.401(1)	C(7)-C(8)	1.445(7)
S(1)-C(6)	1.748(5)	C(8)-C(9)	1.396(7)
O(1)-C(13)	1.335(3)	C(8)-C(13)	1.406(6)
O(2)-C(16)	1.216(5)	C(9)-C(10)	1.356(7)
O(3)-C(16)	1.312(5)	C(10)-C(11)	1.379(8)
O(3)-C(17)	1.457(6)	C(11)-C(12)	1.369(8)
N(1)-C(1)	1.461(6)	C(12)-C(13)	1.395(7)
N(1)-C(7)	1.262(6)	C(14)-C(15)	1.503(7)
C(1)-C(2)	1.387(7)	C(15)-C(16)	1.499(7)
Bond Angles			
S(1)-Sn(1)-O(1)	162.93(3)	C(7)-N(1)-C(1)	121.4(4)
O(1)-Sn(1)-C(14)	95.7(2)	C(6)-C(1)-N(1)	112.2(4)
S(1)-Sn(1)-C(14)	95.6(2)	C(3)-C(2)-C(1)	120.2(4)
O(1)-Sn(1)-N(1)	88.09(14)	C(2)-C(3)-C(4)	119.3(5)
S(1)-Sn(1)-N(1)	77.52(14)	C(5)-C(4)-C(3)	121.0(4)
C(14)-Sn(1)-N(1)	161.1(2)	C(4)-C(5)-C(6)	121.0(4)
O(1)-Sn(1)-O(2)	83.01(14)	S(1)-C(6)-C(5)	121.4(4)
S(1)-Sn(1)-O(2)	86.31(13)	S(1)-C(6)-C(1)	120.8(4)
C(14)-Sn(1)-O(2)	77.81(12)	C(5)-C(6)-C(1)	117.8(4)
N(1)-Sn(1)-O(2)	83.13(12)	N(1)-C(7)-C(8)	125.3(5)
O(1)-Sn(1)-Cl(1)	94.64(11)	C(9)-C(8)-C(13)	119.3(5)
S(1)-Sn(1)-Cl(1)	95.15(10)	C(9)-C(8)-C(7)	114.7(4)
C(14)-Sn(1)-Cl(1)	105.53(3)	C(13)-C(8)-C(7)	126.1(4)
N(1)-Sn(1)-Cl(1)	93.45(11)	C(10)-C(9)-C(8)	121.2(5)
O(2)-Sn(1)-Cl(1)	176.03(5)	C(9)-C(10)-C(11)	119.5(5)
C(7)-N(1)-Sn(1)	126.3(4)	C(12)-C(11)-C(10)	121.1(4)
C(1)-N(1)-Sn(1)	111.9(3)	C(11)-C(12)-C(13)	120.8(4)
C(6)-S(1)-Sn(1)	115.7(3)	O(1)-C(13)-C(12)	117.7(4)
C(16)-O(2)-Sn(1)	110.2(3)	O(1)-C(13)-C(8)	124.2(4)
C(13)-O(1)-Sn(1)	130.0(3)	C(12)-C(13)-C(8)	118.1(4)
C(15)-C(14)-Sn(1)	110.8(3)	C(14)-C(15)-C(16)	114.5(4)
C(16)-O(3)-C(17)	116.5(3)	O(3)-C(16)-O(2)	122.9(4)
C(2)-C(1)-C(6)	120.7(4)	O(2)-C(16)-C(15)	123.7(4)
C(2)-C(1)-N(1)	127.1(4)	O(3)-C(16)-C(15)	113.4(4)

bivalent tridentate ligand L. The tin atom is hexa-coordinated with the coordinating atoms C(14), Cl(1), N(1), O(1), O(2), and S(1) defining a distorted octahedral arrangement. The bond angles of S(1)-Sn(1)-O(1), O(2)-Sn(1)-Cl(1) and C(14)-Sn(1)-N(1) are 162.93(3), 176.03(5) and 161.1(2)°, respectively. The evidence of the distortion can be rationalized by the strain imposed on the bidentate (C, O) and tridentate (O, N, S) ligands. The crystal contains C_6H_6 as solvent of crystallization in a 1:1 ratio. The Sn-O(2) distance (2.396(3) Å) in compound **(1)** is comparable to the intramolecular Sn-O distances in other $ROCOCH_2CH_2Sn$ compounds (Sn-O, 2.337—2.436 Å).[2,3,7—10,17]

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were of reagent grade and were used without further purification. 2-Alkoxycarbonylpropyltin trichlorides and N-(2-mercaptophenyl)salicylaldimine were prepared according to literature procedures,[1,18] respectively. Carbon, hydrogen, nitrogen and sulfur analyses were determined using a Perkin Elmer 2400 Series II elemental analyzer, and tin was determined titrimetrically as Sn^{2+}. Melting points were measured on a TX4-100A microscopic melting point apparatus. IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrophotometer using KBr discs in the range 4000—400 cm^{-1}. NMR spectral data were collected using a Bruker AC-80 FT-NMR spectrometer with $CDCl_3$ as solvent and TMS as internal standard.

Synthesis of the Complexes

A solution of H_2L (1.15 g, 5 mmol) dissolved in 60 mL of benzene was added dropwise with stirring to an equimolar solution of $CH_3OCOCH_2CH_2SnCl_3$ (1.56 g, 5 mmol) in 40 mL of benzene, and then triethylamine (1.11 g, 11 mmol) was added. The reaction mixture was refluxed for 2 h. The precipitate ($Et_3N{\cdot}HCl$) formed was removed by filtration, and the yellow filtrate containing the product was concentrated to *ca.* 20 mL and cooled to room temperature. The orange-yellow crystals obtained were recrystallized from benzene-petroleum ether (b.p. 60–90 °C) (1:1, v/v) and dried *in vacuo*. The yield is 1.90 g.

All other organotin(IV) derivatives of H_2L were synthesized following the same above method. The yields, melting points and analyses of all complexes were listed in Table I.

Crystal Structure Determination of (1)

All X-ray crystallographic data were obtained on a Bruker P4 four-circle diffractometer with graphite monochromated Mo-K_α (0.71073 Å). The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on scans was applied. The calculations were performed using the Bruker XSCANS[19] program package. The structure was solved by direct methods which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedure using the Bruker SHELXTL program.[20] Anisotropic displacement parameters were employed for non-H atoms and H-atoms were included in the model at their calculated positions and refined isotropically. Molecular

Table V. Crystal Data and Structure Refinements Details

Empirical formula	$C_{17}H_{16}ClNO_3SSn{\cdot}C_6H_6$
Formula weight	546.63
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	8.734(2)
b (Å)	9.425(3)
c (Å)	14.561(3)
α (°)	98.02(3)
β (°)	103.98(3)
γ (°)	98.66(3)
Volume ($Å^3$)	1130.4(7)
Z	2
Dc ($g\,cm^{-3}$)	1.606
μ (mm^{-1})	1.305
F (000)	532
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$
θ Range (°)	2.25 to 25.00
Index range	$0 \le h \le 10,\ -10 \le k \le 10,\ -17 \le l \le 17$
Reflections collected	3804
Independent collections	3516 [R(int) = 0.027]
Absorption correction	Psi-scan
Refine method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.115
Final R indices [$I > 2\sigma(I)$]	R = 0.034, Rw = 0.084
R indices (all data)	R = 0.043, Rw = 0.089
Largest peak and hole (e A^{-3})	0.722 and −0.548

graphics were drawn with the program package Bruker SHELXTL.[20] A summary of crystal data, data collection and refinements are contained in Table V.

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