

Tin(IV) Complexes of Tridentate Schiff Bases having ONS Donor Systems

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Four new tin(IV) complexes of tridentate dithiocarbamate Schiff bases have been synthesized and characterized by their elemental analyses and UV, IR, ^1H NMR, and Mössbauer spectroscopies and X-ray powder diffraction. Complexes having the general formulae, $\text{Sn}(\text{OCOCH}_3)_2\text{L}$, where L = dianion of *S*-benzyl- β -N-(2-hydroxyphenyl)methylene and methyl dithiocarbamate, are five-coordinated in distorted trigonal bipyramidal geometry, whereas complexes of the type SnL_2 show hexa-coordination about the tin atom which is arranged in a distorted octahedral geometry with an orthorhombic lattice.

Introduction

The pronounced biological activity [1, 2] of the metal complexes of ligands derived from dithiocarbamic acids has led to interest in their coordination

chemistry. However, studies made so far deal exclusively with the stereochemistry of transition metal complexes [3, 4] and the coordination behavior of these ligands with organometallic moieties [5]. Our continuing interest in chelated tin compounds [6] has led us to synthesize the corresponding inorganic tin(IV) derivatives and to study their stereochemistry along with their biological activity.

Experimental

Chemicals and solvents used were dried and purified by standard methods, and moisture was excluded from the glass apparatus using CaCl_2 drying tubes. The ligands [4] and tin tetraacetate [7] were prepared by the literature methods. All the manipulations were carried out in dry conditions. The complexes were prepared by methods similar to those reported in our earlier communication [6].

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TABLE I. Analyses and Physical Characteristics of Tin(IV) Complexes.

Compound	Yield %	M.P. °C	Color	Analysis %			
				Sn Found (Calcd)	S Found (Calcd)	C Found (Calcd)	H Found (Calcd)
1. $\text{Sn}(\text{OCOCH}_3)_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{S}_2\text{O})$	88	175	Yellow	22.08 (22.15)	11.25 (11.91)	41.38 (42.45)	4.15 (3.35)
2. $\text{Sn}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{S}_2\text{O})_2$	90	251	Yellow	16.54 (17.10)	17.35 (17.80)	51.82 (50.08)	4.01 (3.33)
3. $\text{Sn}(\text{OCOCH}_3)_2(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O})$	87	245	Yellow	20.87 (21.58)	11.08 (11.61)	42.05 (43.55)	2.09 (3.62)
4. $\text{Sn}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}_2\text{O})_2$	91	224	Yellow	16.19 (15.92)	16.58 (17.13)	51.59 (51.73)	4.56 (3.75)

TABLE II. $^{119\text{m}}\text{Sn}$ Mössbauer Parameters (mm s^{-1}) and Characteristic IR bands (cm^{-1}) of the Tin(IV) Complexes.

Compound	IS ^a	QS ^b	$\rho(=QS/IS)$	Γ_+	Γ_-	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{Sn}-\text{N})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{S})$	$\nu(\text{C}=\text{O})$
1. $\text{Sn}(\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}_2)_2$	0.26	0.66	2.5	1.48	1.29	1585	430	562	320	1700
2. $\text{Sn}(\text{OCOCH}_3)_2(\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}_2)$	0.30	0.87	2.9	1.11	1.30	1580	425	570	330	—
3. $\text{Sn}(\text{OCOCH}_3)_2(\text{C}_{16}\text{H}_{14}\text{ON}_2\text{S}_2)$	0.22	0.86	3.9	1.36	1.31	1585	422	558	332	1697
4. $\text{Sn}(\text{C}_{16}\text{H}_{14}\text{ON}_2\text{S}_2)_2$	0.23 ^c	0.68 ^d	2.9	—	—	1590	425	565	325	—

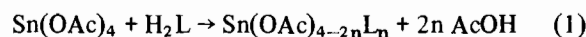
^a $\pm 0.03 \text{ mm s}^{-1}$, ^b $\pm 0.06 \text{ mm s}^{-1}$, ^c $\pm 0.04 \text{ mm s}^{-1}$, ^d $\pm 0.07 \text{ mm s}^{-1}$.

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The electronic spectra were recorded in methanol on a Pye-Unicam SP-8-100 spectrophotometer. Infra-red spectra were obtained on a Perkin-Elmer 577 grating spectrophotometer, either as Nujol mulls or in benzene or chloroform solution. Nmr spectra were recorded on a Perkin-Elmer RB-12 spectrometer in DMSO-d_6 using TMS as an internal standard at 90 MHz. $^{119\text{m}}\text{Sn}$ Mössbauer spectra were recorded at 77 K on a Ranger Engineering, constant-acceleration spectrometer equipped with a NaI scintillation counter using $\text{Ca}^{119\text{m}}\text{SnO}_3$ as the source. The zero velocity was based upon $\text{Ca}^{119\text{m}}\text{SnO}_3$, and velocity calibrations were based upon β -tin and natural iron foils. Standard non-linear least-squares techniques were used to fit the data to Lorentzian curves. The powder diffraction pattern was recorded on a Philips Model PM diffractometer fitted with FeK_α target and Mn filter. The unit cell dimensions and indexed 'd' values were obtained using Hesse-Lipson's method [8].

Results and Discussion

The reactions of tin tetraacetate with the ligands proceed smoothly but slowly with the elimination of acetic acid, which was removed azeotropically with toluene:




($n = 1$ or 2)

The derivatives so isolated are high melting solids, sparingly soluble in organic solvents. However, the 1:1 mixed ligand complexes are hydrolyzed in the atmosphere, presumably owing to the presence of the cleavable acetoxy groups (Tables I and II).

In the electronic spectra of the ligands [9], a band at *ca.* 216 nm is observed, which may be assigned to the 1B band of the phenyl ring. This shifts to higher wavelengths on complexation and is observed at *ca.* 222 nm in the complexes. Also the ligand chromophore, C=N, which absorbs at *ca.* 290 nm, shifts to a higher wavelength and is observed at *ca.* 298 nm in the complexes. The band observed in the spectrum of the ligand at *ca.* 340 nm is likely to be the secondary band of the benzene red shifted owing to the chromophore $-\text{C}=\text{N}-\text{N}=\text{C}-$, and this shifts to *ca.* 370 nm in the complexes, possibly owing to the polarization of C=N bonds caused by the metal-ligand interaction. Three sharp bands in the region 250–265 nm assigned as charge transfer bands are observed, suggesting the formation of σ -bonds [10] and ($p \rightarrow d$) bonds [11] between p-orbitals of O and S and vacant 5d-orbitals of tin.

The infra-red spectra of the ligands [12] show a broad and strong band in the region 3300–2850 cm^{-1} , attributable to $\nu(\text{CH})$ and $\nu(\text{NH})$ modes, while no peak is observed at *ca.* 2570 cm^{-1} , showing the

TABLE III. ^1H N.m.r. Data (δ , ppm) of Ligands and Sn(IV) Complexes.

Ligands and Compounds	$-\text{OH}$	$-\text{C}_6\text{H}_3^{\text{a}}$ & $-\text{C}_6\text{H}_4$	$-\text{C}-\text{R}$ $\text{R} = -\text{H}$ $= -\text{CH}_3$	$-\text{NH}$	$-\text{CH}_2$	$-\text{OC}-\text{CH}_3$ 
$\text{C}_6\text{H}_4\text{OHCHNNHCS}_2\text{CH}_2\text{C}_6\text{H}_5$	13.10	7.20	8.43	10.10	4.50	—
1. $\text{Sn}(\text{OCOCH}_3)_2(\text{C}_6\text{H}_4\text{OCHNNCS}_2\text{CH}_2\text{C}_6\text{H}_5)$	—	7.15	8.68	—	4.45	2.08
2. $\text{Sn}(\text{C}_6\text{H}_4\text{OCHNNCS}_2\text{CH}_2\text{C}_6\text{H}_5)_2$	—	7.12	8.72	—	4.42	—
$\text{C}_6\text{H}_4\text{OHC}(\text{CH}_3)\text{NNHCS}_2\text{CH}_2\text{C}_6\text{H}_5$	11.42	7.29	2.40	10.15	4.68	—
3. $\text{Sn}(\text{OCOCH}_3)_2\text{C}_6\text{H}_4\text{OC}(\text{CH}_3)\text{NNCS}_2\text{CH}_2\text{C}_6\text{H}_5$	—	7.28	2.56	—	4.48	1.95
4. $\text{Sn}[\text{C}_6\text{H}_4\text{OC}(\text{CH}_3)\text{NNCS}_2\text{CH}_2\text{C}_6\text{H}_5]_2$	—	7.20	2.75	—	4.55	—

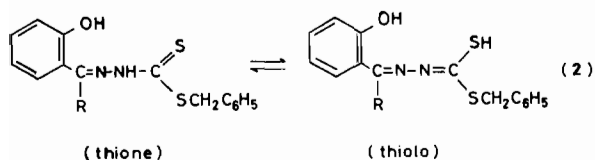
^aCentre of two multiplets.

TABLE IV. X-ray Powder Diffraction Data for $\text{Sn}(\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}_2)_2$.

hkl	d calcd.	d obsd.	I obsd.	hkl	d calcd.	d obsd.	I obsd.
011	11.95	11.95	95	170	3.18	3.19	26
030	8.05	7.98	47	114	3.14	3.16	20
110	7.72	7.70	27	129	3.06	3.05	14
101	7.02	7.09	44	080	3.02	3.02	24
012	6.62	6.63	53	223	2.95	2.96	40
040	6.03	6.03	36	081	2.94	2.93	36
132	4.40	4.34	35	300	2.71	2.71	21
131	5.29	5.32	36	311	2.65	2.66	17
130	5.73	5.80	28	091	2.63	2.64	20
050	4.83	4.84	28	253	2.58	2.58	20
013	4.50	4.46	15	331	2.53	2.53	20
140	4.85	4.89	100	191	2.51	2.52	17
150	4.16	4.19	17	332	2.40	2.41	18
210	4.02	4.02	37	244	2.40	2.39	16
113	3.94	3.93	23	313	2.33	2.35	14
211	3.86	3.88	22	254, 006	2.30	2.30	13
123	3.79	3.73	19	225	2.24	2.23	14
161	3.49	3.50	63	264	2.20	2.21	16
004, 070	3.46	3.47	35	235	2.19	2.19	17
011	3.33	3.30	19	126	2.17	2.17	19
232	3.22	3.22	16	283	2.14	2.14	19
				314	2.12	2.12	10

absence of $\nu(\text{SH})$. However, the latter band appears in the solution spectra with the disappearance of $\nu(\text{NH})$ and $\nu(\text{C}=\text{S})$ bands. This spectral evidence suggests the existence of a tautomeric equilibrium [13] between the two forms of ligand, as shown below (2).

In the IR spectra of the complexes all $\nu(\text{E}-\text{H})$ ($\text{E} = \text{O}, \text{S}$) bands are absent, showing the bonding of oxygen and sulfur to the metal by the loss of thiolic and enolic protons of the ligands. A band



of medium intensity at *ca.* 1585 cm^{-1} in the complexes may be assigned to the $\nu(\text{C}=\text{N})$ frequency, which originally appears in the ligand at *ca.* 1605 cm^{-1} in both the solution and solid state. The shift of this band to lower energy indicates the coordination of an azomethine nitrogen to the tin atom [14].

A strong band is observed at *ca.* 1690 cm^{-1} in the complexes $\text{Sn}(\text{OAc})_2\text{L}$, and may be assigned to the $\nu(\text{C}=\text{O})$ of the acetoxy group. This is found at quite high frequency and must be a free $\nu(\text{C}=\text{O})$. Clearly then this group plays no part in the coordination to tin. Bands of medium intensity at *ca.* 660 and *ca.* 615 cm^{-1} are assigned to scissoring and out of plane bending vibrations of the acetoxy group.

Besides this, in all the compounds synthesized several new bands observed at *ca.* 565 cm^{-1} , *ca.* 425 cm^{-1} , and *ca.* 325 cm^{-1} may be assigned to $\nu(\text{Sn}-\text{O})$ [6], $\nu(\text{Sn}-\text{N})$ [6] and $\nu(\text{Sn}-\text{S})$ [15] respectively, thus lending support to the proposed coordination in the complexes.

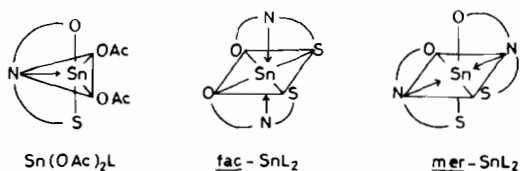
In the nmr spectra a broad signal at δ 7.28 ppm is observed in all the complexes, owing to the phenyl protons of both salicylaldehyde residue and benzyl group. A further sharp signal is observed at δ 4.45 ppm, attributable to the $-\text{CH}_2$ protons of the benzyl group. In the complexes the disappearance of the signals at δ 1.45, 4.35 and 10.09 ppm (assigned to OH, SH and NH protons respectively) in the spectra of the ligands clearly indicates deprotonation [9]. Signals at δ 8.65 ppm in complexes 1 and 2 and at δ 2.56 ppm in complexes 3 and 4 occur owing to the $-\text{CH}$ and $-\text{CH}_3$ protons, respectively. These are shifted downfield from their positions in the ligands owing to the coordination of C=N group with the metal atom. The complexes $[\text{Sn}(\text{OCOCH}_3)_2\text{L}]$ show additional signals at δ 1.95 ppm owing to the $-\text{CH}_3$ protons of the acetoxy group [7] (Table III).

The Mössbauer isomer shift (IS) values confirm the presence of tin in its +4 oxidation state [16], and the relatively low values indicate the coordination number to be more than four. This is supported by the quadrupole splitting (QS) and ρ (QS/IS) values compared with those for tin derivatives having coordination number four [16, 17]. Though a decrease in IS is generally observed on the interaction of octahedral tin(IV) with donors having two $\text{N} \rightarrow \text{Sn}$ bonds, the IS values in our case are affected by the presence of $\text{Sn}-\text{S}$ bonds, where the sulfur atoms afford a greater electron releasing tendency than do the nitrogen donors [18]. The greater QS values in those complexes containing the acetate groups reflect a greater imbalance in the electric field gradient about the tin atom, produced by a combination of strong and weak electron withdrawing groups.

The X-ray powder diffraction study of compound 1, $\text{Sn}(\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}_2)_2$, shows an orthorhombic lattice with unit cell dimensions (Table IV):

$$\begin{aligned} a &= 8.13 \text{ \AA} & Z &= 4 \\ b &= 24.15 \text{ \AA} & V &= 2709.48 \text{ \AA}^3 \\ c &= 23.8 \text{ \AA} & \rho &= 1.707 \text{ g cm}^{-3} \end{aligned}$$

On the basis of the observed spectral evidence, the following tentative structures with (probably distorted) trigonal bipyramidal and octahedral geometries can be proposed:



The compound SnL_2 may adopt either of the two geometries or even both, but at this stage an unambiguous assignment is impossible. The compound $\text{Sn}(\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}_2)_2$ was also tested for its antitumor activity in the P 388 lymphocyto-leukemia system, and has not been found to show significant activity ($\text{TC} = 109$) [19].

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