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Synthesis and Spectroscopic Investigations of Some Binuclear Organotin(IV) Complexes of Malonobis(salicylidenehydrazide) and Crystal Structure Study of $[(C_2H_5)_2Sn]_2[OC_6H_4CH{=}NNCO]_2CH_2$

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The Schiff base, $[HOC_6H_4CH{=}NNHCO]_2CH_2$ $[H_4L]$, derived from the condensation of salicylaldehyde and malonodihydrazide, reacted with organotin chlorides to yield binuclear complexes of the type $R_2Sn[L]SnR_2$, where R=CH_3–, C_2H_5–, C_4H_9–, C_6H_5–, $CH_3CO_2CH_2CH_2$–, and $C_6H_5CH_2$–. The complexes were characterized and the structure assigned on the basis of their elemental analysis, IR, ^1H, ^{13}C, ^{119}Sn NMR spectral, and X-ray crystallographic data. In these complexes, the ligand functions as a flexibly bridging tetrabasic hexadentate moiety binding two tin atoms through ONO donor atoms and both tin atoms are in trigonal bipyramidal environment.

A single crystal diffraction study of the complex, $[(C_2H_5)_2Sn]_2(OC_6H_4CH{=}NNCO)_2CH_2$, confirms the structure to be binuclear. The crystals are monoclinic, space group $I2/a$ with $a=12.312(2)$, $b=11.526(2)$, $c=18.858(2)$ Å, $\beta=94.69(2)^\circ$, volume=2667.1(7) Å^3, $Z=4$, $D_c=1.718$ g cm^{-3}. The final discrepancy factors are $R=0.042$, $R_w=0.055$ for 1698 observed reflections. Half of the molecule is bridged to the other half by two fold symmetry via C(13) atom. The tin atom has distorted trigonal bipyramidal coordination with two oxygens occupying axial positions while two ethyl groups and azomethine nitrogen occupy the equatorial positions. The two ethyl groups coordinated to tin are cis to each other.

The dihydrazones derived from condensation of *o*-hydroxyaromatic aldehydes or ketones and acyl dihydrazides are similar to monohydrazones in all respects except that they possess two hydrazone groupings separated from each other by methylene, phenylene or sulfur chains of varying length.

Buuttoi et al.[1] have reported monohydrazides such as salicylhydrazide, 5-chloro- and 5-bromo-salicylhydrazide and 2-hydroxy-3-naphthohydrazide etc. and their hydrazones obtained by the condensation with various aldehydes and ketones, and studied their biological applications. It was found that the tuberculostatic activity of these hydrazones was highly dependent on the molecular structure.

Ma et al.[2] have studied antitubercular activity of salicylohydrazide and its hydrazone derivatives and found that hydrazones derived from phenolic aldehydes are more active against M. tuberculosis.

Binuclear dioxomolybdenum(VI) complexes of dihydrazones, $[OC_6H_3RCH{=}NNCO]_2(CH_2)_n[MoO_2]_2(py)_2$, where n=0, 1, 2, 4, 8; R=H or OCH_3, have been synthesized and characterized by Havanur and Mahale,[3] in which the ligand coordinates to molybdenum in the enol form forming an octahedral structures containing two *cis*-dioxomolybdenum groups.

Mahale et al.[4] have treated titanium oxide perchlorate and tin tetrachloride with dihydrazones (H_4L) derived from dihydrazides of dicarboxylic acids and salicylaldehyde or 3-methoxy salicylaldehyde, in alcoholic medium and in presence of pyridine, to form the complexes $[(TiO)_2(L)(py)_2]$ and $[SnCl_2(LH_2)(py)_2]$, respectively. However, Ti(IV) and Sn(IV) react in a different manner with the ligands. Thermal stabilities of complexes are also discussed. A hexacoordinated polymeric structure is assigned to the titanium complexes, whereas the tin complexes are also hexacoordinated but linked through two oxygens, two nitrogens of pyridine and two chlorine atoms.

There are some reports on the study of Co(II), Ni(II), Cu(II), Zn(II), Mn(II), Fe(II), Cd(II), Hg(II), U(II), and lanthanide complexes of dihydrazones.[5—12] However, there is no report in the literature on organotin complexes of dihydrazones.

In continuation of our work,[13—19] on the syntheses and study of group 14 metal complexes of Schiff bases, we herein report the synthesis and characterization of binuclear organotin(IV) complexes of the ligand, malonobis(salicylidenehydrazide) $[H_4L]$, and X-ray crystal structure analysis of the compound, $[(C_2H_5)_2Sn]_2[OC_6H_4CH{=}NNCO]_2CH_2$.

Experimental

Materials. The starting chemicals were of reagent or analytical grade. The solvents were dried and distilled before use. Infrared spectra were recorded in Nujol mull, KBr pellets or as CH_2Cl_2 solution on a Perkin–Elmer Model 1620 FT-IR spectrophotometer. The proton NMR spectra were recorded, using a Varian FT-80 A spectrometer and WH-90 spectrometer, in $CDCl_3$ solution. The ^{119}Sn NMR spectra were recorded on a Bruker MSL 300 spectrometer at 111.89 MHz. The ^{119}Sn NMR spectra with complete proton noise decoupling were recorded in CH_2Cl_2 solution at ambient temperature. The chemical shifts were determined relative to tetramethyltin (negative signs indicate upfield shifts from Me_4Sn (δ=0 ppm).

The ligand, malonobis(salicylidenehydrazide), $[HOC_6H_4CH{=}NNHCO]_2CH_2$ $[H_4L]$[12] and the diestertin dichloride,

Table 1. Analytical Data for Organotin(IV) Complexes of Malonobis(salicylidenehydrazide)

	Compound	Color	Mp	Elemental analysis (%) Found (Calcd)			
			°C	Sn	C	H	N
1	$[(CH_3)_2Sn]_2(L)$	Yellow	168	37.29	39.81	3.68	8.90
	$Sn_2C_{21}H_{24}N_4O_4$			(37.45)	(39.79)	(3.82)	(8.84)
2	$[(C_2H_5)_2Sn]_2(L)$	Yellow	165	34.25	43.41	4.70	8.01
	$Sn_2C_{25}H_{32}N_4O_4$			(34.41)	(43.52)	(4.68)	(8.12)
3	$[(C_4H_9)_2Sn]_2(L)$	Yellow	98	29.45	49.33	5.87	7.00
	$Sn_2C_{33}H_{48}N_4O_4$			(29.59)	(49.41)	(6.03)	(6.98)
4	$[(C_6H_5)_2Sn]_2(L)$	Yellow	160	26.75	55.66	3.71	6.21
	$Sn_2C_{41}H_{32}N_4O_4$			(26.91)	(55.82)	(3.66)	(6.35)
5	$[(C_6H_5CH_2)_2Sn]_2(L)$	Yellow	150	25.25	57.44	3.41	5.89
	$Sn_2C_{45}H_{40}N_4O_4$			(25.30)	(57.61)	(4.30)	(5.97)
6	$[(CH_2CH_2CO_2CH_3)_2Sn]_2(L)$	Yellow	102	25.66	42.85	4.27	5.89
	$Sn_2C_{33}H_{40}N_4O_{12}$			(25.74)	(42.98)	(4.37)	(6.08)

$Cl_2Sn(CH_2CH_2CO_2CH_3)_2$, were prepared according to methods reported in the literature.[20)]

X-Ray Data Collection. Yellow needle shaped crystals of the complex, $[(C_2H_5)_2Sn]_2[OC_6H_4CH{=}NNCO]_2CH_2$, were grown from benzene. Crystal dimensions $0.08 \times 0.12 \times 0.80$ mm; cell parameters from 24 reflections ($28° < 2\theta < 36°$); monoclinic $I2/a$, $a=12.312(2)$, $b=11.526(2)$, $c=18.858(2)$ Å, $\beta=94.69(2)°$, $V=2667.1(7)$ Å^3, $Z=4$, $D_c=1.718$ g cm^{-3}. Intensity data collected on Enraf–Monius CAD-4F/11M single crystal X-ray diffractometer; graphite monochromatic Mo $K\alpha$ radiation (0.7107 Å); $\omega/2\theta$ scan mode, average scan speed 1° min^{-1}; $\theta < 23.5°$; of 1975 reflections collected ($h=0$ to 13, $k=0$ to 12 and $l=\pm 21$) 1698 were judged significant ($|F_o| \geqslant 3\sigma|F_o|$). The structure solution by direct methods using MULTAN. A full matrix refinement of scale factor, positional and anisotropic thermal parameters for non H atoms (H atoms geometrically fixed confirmed by difference Fourier held fixed during refinement) converged to $R=0.042$ and $R_w=0.055$. Weights based on counting statistics. All the calculations were carried out using P.C. versions of NRCVAX programs.[21)]

Figure 1 gives the perspective view of the molecule along with the crystallographic numbering of atoms. The atomic parameters along with their esd's and equivalent isotropic thermal parameters for non hydrogen atoms are given in Table 4. Table 5 gives the bond lengths and angles.

Synthesis of $[(C_2H_5)_2Sn]_2(L)$. A solution of the ligand, LH_4 (0.34 g; 1 mmol) in benzene (20 cm^3) and $(C_2H_5)_2SnCl_2$ (0.50 g; 2 mmol) were mixed together in presence of $(C_2H_5)_3N$ (0.41 g; 4 mmol) and refluxed for 5 h. The precipitate, $(C_2H_5)_3N{\cdot}HCl$, formed during the reaction was removed by filtration. The filtrate was concentrated to a small volume and cooled in ice-salt mixture. The precipitation of the product was effected by layering hexane over the cooled solution. The yellow crystalline solid separated was collected by filtration, washed with hexane and dried in vacuo. Yield 0.50 g (72%), mp 165 °C. Found: Sn, 34.25; C, 43.41; H, 4.70; N, 8.01%. Calcd for $Sn_2C_{25}H_{32}N_4O_4$: Sn, 34.41; C, 43.52; H, 4.68; N, 8.12%. The atomic parameters along with their esd's and equivalent isotropic thermal parameter for H-atms and non-H atoms are deposited as Document No. 67037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The following complexes $[(CH_3)_2Sn]_2(L)$, $[(C_4H_9)_2Sn]_2(L)$, $[(C_6H_5)_2Sn]_2(L)$, $[(C_6H_5CH_2)_2Sn]_2(L)$, and $[(CH_2CH_2CO_2CH_3)_2Sn](L)$ were prepared adopting the above procedure.

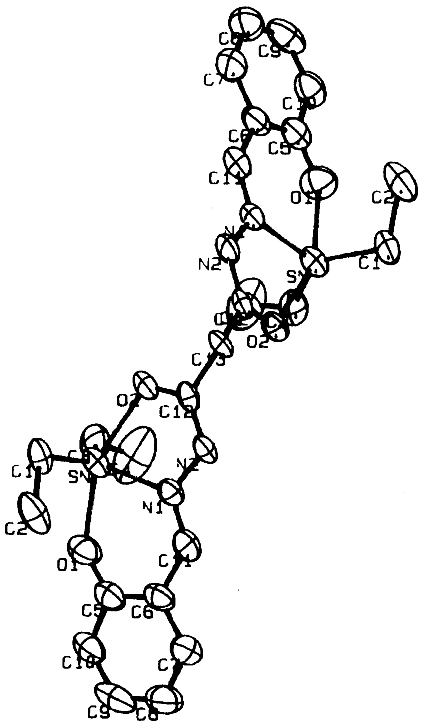

Fig. 1. Molecular structure with atom numbering-scheme. Thermal ellipsoids are shown at the 50% probability level.

Results and Discussion

The Schiff base, malonobis(salicylidenehydrazide) (H_4L), is a hexadentate ligand which functions as dibasic in the keto form and tetrabasic moiety in the enol form under suitable experimental conditions. The ligand forms binuclear diorganotin complexes by utilizing all the four hydroxyl groups during the complex formation. In the present study, the reaction of organotin chlorides with H_4L in 2 : 1 molar ratio in benzene medium using triethylamine as HCl acceptor, re-

Table 2. IR Spectral Bands of Malonobis(salicylidenehydrazide) and Its Organotin(IV) Complexes (cm^{-1})[a]

No.[b]	(C=N)	Amide II+ (C–O)(L)	(C–O)(L)	(N–N)
H_4L	1608	1569	1263	959, 971
1	1613, 1542	1532	1308	980, 998
2	1611, 1538	1526	1312	975, 997
3	1607, 1541	1524	1297	963, 984, 1001
4	1608, 1543	1530	1298	970, 996
5	1609, 1542	1523	1297	970, 1000
6	1608, 1538	1526	1300	970, 1006

a) NH of H_4L=3279s, 3189w. (C=O) amide-I of H_4L=1673. Ester C=O of complex 6=1731, 1714. Ester C–O of complex 6=1260, 1213. b) Nos. are same as in Table 1.

Table 3. ^1H and ^{119}Sn NMR Spectral Data for Malonobis(salicylildenehydrazide) and Its Organotin(IV) Complexes (δ/ppm)[a]

Ligand/ Complex[b]	Aliphatic	CH	CH_2	Aromatic protons	$\delta(^{119}Sn)$
H_4L	—	8.19—8.33	3.23	6.53—7.58	—
1	0.78	8.57	3.30	6.60—7.37	−152.40
2	0.92—2.03	8.52	3.28	6.52—7.32	−160.51
3	0.87—1.61	8.56	3.31	6.57—7.36	−189.44
4	—	8.45	3.30	6.66—8.02	−324.72
5	—	8.51	3.38	6.73—7.62	−336.30
6	—	8.53	3.35	6.65—7.40	−246.30

a) H_4L; NH=9.9, 10.95. OH=11.33, 11.70.
Complex 1; $^2J\,(^{117}Sn, {}^1H)=74$ Hz; $^2J\,(^{119}Sn, {}^1H)=79$ Hz; $^3J\,(^{117}Sn, {}^1H)(CH_2)=66$ Hz; $^3J\,(^{119}Sn, {}^1H)(CH)=46$ Hz.
Complex 6; α-CH_2=1.69 ppm. β-CH_2=2.77 ppm. OCH_3 (ester)=3.68 ppm. b) Nos. are same as in Table 1.

Table 4. Atomic Parameters x, y, z and B_{iso} for Non-H Atoms esd's. refer to the last digit printed.

Atom	x	y	z	B_{iso}(Å^2)
SN	.51054(4)	.02213(5)	.37602(3)	3.83(3)
O 1	.4790 (5)	.0772 (5)	.2703 (3)	5.5 (3)
O 2	.6141 (4)	−.0529 (5)	.4645 (3)	4.1 (3)
N 1	.6464 (5)	−.0703 (5)	.3315 (3)	3.6 (3)
N 2	.7128 (4)	−.1380 (5)	.3789 (3)	3.6 (3)
C 1	.3869 (6)	−.1059 (5)	.3746 (4)	3.9 (4)
C 2	.3626 (7)	−.1595 (8)	.3022 (5)	5.7 (5)
C 3	.5283 (7)	.1933 (8)	.4136 (5)	5.3 (4)
C 4	.6177 (10)	.2590 (10)	.4011 (7)	10.8 (9)
C 5	.5216 (7)	.0556 (7)	.2118 (4)	4.2 (4)
C 6	.6145 (7)	−.0146 (7)	.2066 (4)	4.1 (4)
C 7	.6591 (7)	−.0294 (9)	.1402 (4)	5.6 (5)
C 8	.6139 (9)	.0225 (10)	.0804 (5)	6.3 (5)
C 9	.5216 (9)	.0901 (9)	.0844 (5)	6.1 (5)
C10	.4763 (7)	.1068 (8)	.1483 (5)	5.0 (4)
C11	.6705 (6)	−.0742 (7)	.2666 (4)	4.2 (4)
C12	.6883 (5)	−.1223 (7)	.4438 (4)	3.4 (3)
C13	.7500 (0)	−.1954 (9)	.5000 (0)	3.4 (5)

sulted in the formation of binuclear complexes of the type $R_2Sn[L]SnR_2$, where R=CH_3, C_2H_5, C_4H_9, C_6H_5, $C_6H_5CH_2$, or $CH_3COOCH_2CH_2$, with the replacement of all the four protons from the ligand.

$$2R_2SnCl_2 + H_4L \xrightarrow[C_6H_6,\ 80^\circ]{Et_3N,\ -HCl} 2R_2Sn[L]SnR_2$$

The color, melting point and elemental analyses are summarized in Table 1. The complexes are yellow solids

Table 5. Bond Distances (Å) and Bond Angles (°) with esd's in Parenthesis

SN–O1	2.098(6)		
SN–O2	2.193(6)		
SN–N1	2.206(6)		
SN–C1	2.119(8)		
SN–C3	2.102(9)		
		O1–SN–O2	153.3(2)
		O1–SN–N1	82.6(2)
		O1–SN–C1	97.0(3)
		O1–SN–C3	92.4(3)
		O2–SN–N1	71.8(2)
		O2–SN–C1	96.2(3)
		O2–SN–C3	94.3(3)
		N1–SN–C1	103.0(3)
		N1–SN–C3	121.1(3)
		C1–SN–C3	135.5(3)
O1–C5	1.284(10)		
		SN–O1–C5	134.5(5)
O2–C12	1.298(9)		
		SN–O2–C12	113.2(5)
N1–N2	1.399(8)		
N1–C11	1.283(9)		
		SN–N1–N2	116.6(4)
		SN–N1–C11	128.4(5)
		N2–N1–C11	114.9(6)
N2–C12	1.297(9)		
		N1–N2–C12	110.9(6)
C1–C2	1.506(12)		
		SN–C1–C2	112.7(5)
C3–C4	1.372(15)		
		SN–C3–C4	121.5(8)
C5–C6	1.411(12)		
C5–C10	1.409(12)		
		O1–C5–C6	124.1(7)
		O1–C5–C10	119.2(7)
		C6–C5–C10	116.6(7)
C6–C7	1.418(11)		
C6–C11	1.449(11)		
		C5–C6–C7	120.3(7)
		C5–C6–C11	123.7(7)
		C7–C6–C11	116.0(7)
C7–C8	1.355(13)		
		C6–C7–C8	121.3(9)
C8–C9	1.385(16)		
		C7–C8–C9	119.1(10)
C9–C10	1.382(13)		
		C8–C9–C10	121.1(9)
		C5–C10–C9	121.5(8)
		N1–C11–C6	126.6(7)
C12–C13	1.509(9)		
		O2–C12–N2	126.4(7)
		O2–C12–C13	117.3(6)
		N2–C12–C13	116.2(6)

and soluble in benzene and chloroform but insoluble in hexane. The results of the elemental analyses are consistent with the suggested formulae for the complexes.

IR Studies. The IR spectral data of the Schiff base and the complexes are given in Table 2.

^{1}H NMR Studies. The ^{1}H NMR spectral data of the Schiff base and the complexes are given in Table 3. Due to poor solubility of the ligand in $CDCl_3$, its NMR spectrum was recorded in DMSO-d_6. The doublets due to CH(azomethine), NH, and OH may suggest the nonequivalence of the two halves of the Schiff base.

The ^{1}H NMR spectra of the complexes are recorded in $CDCl_3$.

^{119}Sn NMR Studies. The tin chemical shift, (^{119}Sn), of the complexes $[(CH_3)_2Sn]_2(L)$, $[(C_2H_5)_2Sn]_2(L)$, $[(C_4H_9)_2Sn]_2(L)$, and $[(C_6H_5CH_2)_2Sn]_2(L)$ observed are at −152.40, −160.51, −189.44, and −336.30 ppm respectively. These $\delta(^{119}Sn)$ values fall in the range of five-coordinate tin(IV)compounds.[22] As the carbon number of the alkyl group attached to tin increases an upfield shift of ^{119}Sn resonances has been noticed. Otera[22] has observed similar upfield shift for tin resonances for pentacoordinated and hexacoordinated organotin(IV) complexes containing different alkyl groups. The $\delta(^{119}Sn)$ value observed for $[(CH_3)_2Sn]_2(L)$ at −152.40 ppm is consistent with the reported $\delta(^{119}Sn)$ value for the well characterized pentacoordinated complex $Me_2Sn(SAB)$.[22]

The ester complex, $[(CH_2CH_2CO_2CH_3)_2Sn]_2(L)$, shows the chemical shift value at −246.30 ppm. The observed large shielding has been attributed to the increased coordination number of tin as a result of ester carbonyl coordination.

The (^{119}Sn) resonance for the complex, $[(C_6H_5)_2Sn]_2(L)$, is at −324.72 ppm. Replacement of methyl groups by phenyl groups, in general, results in an upfield shift of $\delta(^{119}Sn)$ which is comparable with the shift observed between Me_2SnCl_2 and Ph_2SnCl_2.[23]

The Crystal Structure of $[(C_2H_5)_2Sn]_2[OC_6H_4CH{=}NNCO]_2CH_2$. Half of the molecule is bridged to the other half by two fold symmetry via C(13) atom which lies on the two fold axis. The tin atom has distorted trigonal bipyramidal coordination with two oxygen atoms occupying axial positions. The tin atom is displaced by 0.053(5) Å from the equatorial plane defined by two carbon atoms of ethyl groups and azomethine nitrogen while O(1) [2.041(7) Å] and O(2) [2.121(8) Å] are displaced on either side of the plane. Similar distorted trigonal bipyramidal coordination has been observed in different organotin(IV) complexes.[24—29] The phenyl ring and six membered and five membered chelate rings are forming a good plane except atoms C(12) and O(2). The dihedral angle between this plane and the equatorial plane is 86.7(2)°. The two halves of the molecules are inclined to each other at an angle of 105.4(1)°. In the present study Sn–N=2.206(6); Sn–O(1)=2.098(6); Sn–C(1)=2.102(9) and Sn–C(3)=2.119(8) Å are short while Sn–O(2)=2.193(6) Å fall in the middle range.[26—28,30]

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