

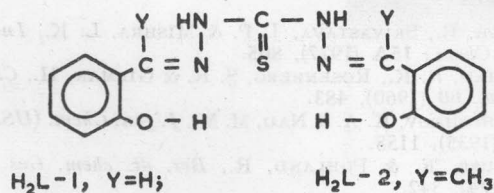
Complexes of Tin(IV) & Organotin(IV) Chlorides with Schiff Bases Derived from Thiocarbohydrazide

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Tin(IV) and organotin(IV) complexes of quadridentate Schiff bases [derived from salicylaldehyde or *o*-hydroxyacetophenone and thiocarbohydrazide having ONSO donor system have been synthesized and characterized through elemental analysis, conductance measurement, molecular weight determination, infrared and NMR spectroscopy. They are represented by the general formulae Cl_2SnL , $RClSnL$ and R'_2SnL (where $R=Ph$, $R'=Ph, Bu, C_6H_5CH_2, p-CH_3C_6H_4$ or C_6H_{11} and L^{2-} = dianion of the Schiff base). Coordination of ligands to tin involves both the deprotonated phenolic (OH) oxygens, thioamide (C=S) sulphur and one of the hydrazone (C=N) nitrogens.

RECENTLY Singh *et al.*¹ have synthesized the mononuclear and dinuclear complexes of 1,5-bis-(salicylidene)thiocarbohydrazone (H_2 -bstcz) with Mn(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and Pb(II) and concluded that the ligand could act as pentadentate, quadridentate or terdentate. The present investigation reports for the first time the synthesis and structure of the complexes of tin(IV) and organotin(IV) chlorides with dianionic tetradentate Schiff bases (H_2L-1 and H_2L-2) of the type (I).



Diphenyltin dichloride, di-*p*-tolyltin dichloride and dicyclohexyltin dichloride were prepared by the reported methods²⁻⁴. Tin tetrachloride, phenyltin trichloride, dibutyltin dichloride, dibenzyltin dichloride (Alfa Inorganics), *o*-hydroxyacetophenone (Aldrich) were used as such. Salicylaldehyde (BDH) was distilled before use. The amine thiocarbohydrazone and its Schiff bases 1,5-bis(salicylidene)thiocarbohydrazone (m.p. 190°d) and 1,5-bis(*o*-hydroxyacetophenone)thiocarbohydrazone (m.p. 200°d) were prepared by reported methods⁵⁻⁸.

The complexes were prepared by the direct interaction of the Schiff bases with tin(IV) or organotin(IV) chlorides.

In a typical experiment a solution of Schiff base (0.9 g, 3 mmol) in absolute methanol (25 ml) was added dropwise under stirring to sodium methoxide prepared from sodium (0.10 g, 4.4 mmol) and

methanol (10 ml). The mixture was stirred for 2 hr. Tin(IV)- or organotin(IV) chloride (3 mmol) in absolute methanol was then added dropwise to the above solution and the stirring continued for another 2 hr. The resulting solid product was filtered, washed with the same solvent and dried *in vacuo*. In a few cases, the desired product was obtained after distilling off the excess solvent under reduced pressure and subsequent cooling. The complexes were purified by recrystallization from benzene-pet. ether mixture, yield 67-90%.

The complexes are yellow coloured solid with sharp melting points, thermally stable and unaffected by atmospheric oxygen and moisture (Table 1). They are soluble in common organic solvents. Molecular weight determination (cryoscopically in benzene at 32°) indicates their monomeric nature and molar conductance data in methyl cyanide at 32° obtained using a Phillips conductivity bridge (model PR 9500) suggest their non-electrolytic character in solution.

The ligands H_2L-1 and H_2L-2 show almost identical IR active absorptions (ν_{max} in cm^{-1}). The characteristic changes observed in the spectra of the complexes are those originating from (C=S), (C=N) and phenolic (OH) groups of the ligand.

The strong and broad bands at 3190 and 3410 in the spectra of the ligands H_2L-1 and H_2L-2 respectively due to H-bonded νOH disappear in the spectra of the complexes indicating deprotonation of phenolic (OH) groups during complexation^{9,10}. The two medium intensity bands observed near 3150 ± 10 and 3040 ± 10 may be assigned to asymmetric and symmetric $\nu N-H$ respectively¹⁰. The band around 1260 in H_2L-1 and H_2L-2 attributed to phenolic (C-O) mode¹¹ is significantly shifted to higher frequency side suggesting bonding from the oxygen atom of the hydroxy group to the tin atom^{12,13}.

The $\nu C=N$ absorption at 1600 (ref. 14) in the spectra of the ligands appears as a split band on complexation with one band located almost at the original position, 1595 ± 5 due to uncoordinated $\nu(C=N)$ and the other shifted to lower frequency at 1565 ± 5 arising from the coordinated (C=N) mode. The splitting of the $\nu(C=N)$ absorption suggests that only one of the nitrogens is involved in coordination and other is free and uncoordinated¹⁵.

The $\nu C=S$ appearing at 790 and 785 in the spectra of the ligands H_2L-1 and H_2L-2 respectively^{16,17} is observed as a band of medium intensity at 740 ± 10 in the spectra of the complexes. This shift to lower wave number suggests that the thioamide sulphur is one of the bonding sites in the complexes.

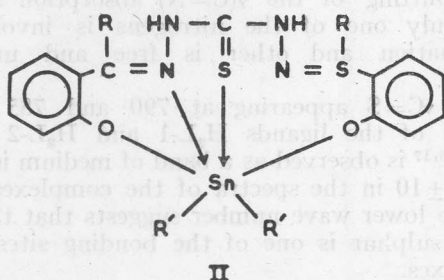
NMR spectra of two representative complexes $Ph_2Sn[(OC_6H_4CH:N.NH)_2C:S]$ and $Bu_2Sn[(OC_6H_4CCH_3:N.NH)_2C:S]$ were recorded at room temperature on a Varian A90D instrument in $CDCl_3$ with TMS internal reference (chemical shift in δ -scale). A multiplet in the region 7.30-8.00 is due to phenyl ring protons¹⁸. A singlet observed in the range 8.30-8.50 in the spectrum of the complex $Ph_2Sn[(OC_6H_4CH:N.NH)_2C:S]$ is assigned to $-CH=N$ proton¹⁹. The spectrum of Bu_2Sn

TABLE 1 — CHARACTERIZATION DATA OF TIN(IV) AND ORGANOTIN(IV) COMPLEXES OF SCHIFF BASE H₂L-1

Compound	m.p. (°C)	Found (%) (Calc.)				Mol. wt obs. (Calc.)
		Sn	C	H	N	
SCHIFF BASE H ₂ L-1						
Ph ₂ SnL-1	>250	20.65 (20.34)	55.30 (55.43)	3.64 (3.79)	9.40 (9.57)	572 (585)
Bu ₂ SnL-1	135	21.69 (21.83)	50.52 (50.68)	5.40 (5.54)	9.89 (10.28)	532 (545)
(C ₆ H ₅ CH ₂) ₂ SnL-1	>250	19.60 (19.41)	56.70 (56.82)	4.20 (4.27)	9.28 (9.14)	590 (613)
(p-CH ₃ C ₆ H ₄) ₂ SnL-1	175	19.55 (19.41)	56.80 (56.82)	4.10 (4.27)	9.12 (9.14)	598 (613)
(C ₅ H ₁₁) ₂ SnL-1	>250	19.74 (19.93)	54.12 (54.32)	5.80 (5.74)	9.28 (9.38)	588 (597)
Cl ₂ SnL-1	>250	23.64 (23.70)	35.80 (35.89)	2.34 (2.40)	11.04 (11.16)	*
PhClSnL-1	>250	22.06 (21.89)	46.28 (46.40)	3.10 (3.15)	10.25 (10.30)	*
SCHIFF BASE H ₂ L-2						
Ph ₂ SnL-2	215	19.50 (19.41)	56.90 (56.82)	4.18 (4.27)	9.13 (9.14)	625 (613)
Bu ₂ SnL-2	113	20.58 (20.76)	52.44 (52.40)	5.85 (5.98)	9.80 (9.77)	560 (573)
(C ₆ H ₅ CH ₂) ₂ SnL-2	92	18.94 (18.56)	58.30 (58.08)	4.60 (4.71)	8.82 (8.74)	623 (641)
(p-CH ₃ C ₆ H ₄) ₂ SnL-2	185	18.51 (18.56)	58.00 (58.08)	4.82 (4.71)	8.70 (8.74)	622 (641)
Cl ₂ SnL-2	>250	21.90 (22.45)	38.68 (38.52)	3.10 (4.03)	10.66 (10.57)	*
PhClSnL-2	>250	20.72 (20.82)	48.42 (48.33)	3.74 (3.70)	9.76 (9.80)	*

*Insufficient solubility.

[(OC₆H₄CCH₃: N.NH)₂C: S] shows a multiplet around 0.7-1.7 due to Sn-C₄H₉ protons¹⁸ and a doublet in the region 2.30-2.50 attributed to C-CH₃ protons. Spectra and their integration correspond to the proposed stoichiometry of the compounds. On the basis of the analytical and spectral data, structure (II) may be suggested for the complexes.



II, R = H or CH₃; R' = C₆H₅, C₄H₉, C₆H₅CH₂, p-CH₃C₆H₄, C₆H₁₁ or Cl

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Organotellurium Tetrahalides

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Dialkyltellurium diiodides do not undergo oxidation on reaction with inter-halogens (IX, X = Cl, Br or I) to give the corresponding Te(VI) derivatives. Instead solid adducts, $R_2Te_2 \cdot IX$ are formed. The compounds have been characterized by elemental analysis and spectral data.

DIALKYLTELLURIUM tetraiodides, R_2TeI_4 have been known¹⁻⁵ for a long time as loose adducts between R_2TeI_2 and I_2 . Attempts to prepare similar adducts with dihalogens other than iodine failed⁶. We recently reported⁷ the oxidation of $Ar_2Te(II)$ by interhalogens (IX, X = Cl, Br); pseudo-interhalogens (CNX', X' = Br, I) and (SCN)₂ to the corresponding Te(IV) derivatives. Our attempts to oxidize dialkyltellurium(IV) diiodides by IX (X = Cl, Br or I) to corresponding Te(VI) derivatives have however resulted in the formation of some new dialkyltellurium tetrahalides which may best be described as solid adducts, $R_2TeI_2 \cdot IX$. Reaction did not occur between IX and a dialkyltellurium dichlorides (or bromides).

Telluracyclopentane⁸, telluracyclohexane⁹, dimethyltellurium diiodides¹⁰, and iodine monobromide¹¹ were prepared by reported methods. Iodine monochloride was a BDH product.

Some typical experiments are given below; data for other reactions are summarized in Table 1. All the compounds were obtained in yields >90%.

Reaction of telluracyclopentane diiodide with iodine monochloride — To a chloroform solution (50 ml) of telluracyclopentane diiodide (1.3 g, 3 mmol) was added a solution of ICl (0.487 g, 3 mmol) in the same solvent (10 ml). The mixture was stirred for 1 hr and then refluxed for a few minutes. The reaction mixture on concentration and cooling gave reddish black needles of $C_4H_8TeI_2 \cdot ICl$.

$C_4H_8TeI_2 \cdot I_2$, $C_4H_8TeI_2 \cdot IBr$, $C_5H_{10}TeI_2 \cdot ICl$, $C_5H_{10}TeI_2 \cdot IBr$, $(CH_3)_2TeI_2 \cdot ICl$, $(CH_3)_2TeI_2 \cdot IBr$ were similarly prepared.

Reaction of $C_4H_8TeI_2 \cdot I_2$ with silver chloride — The adduct (1.20 g; 2 mmol) in chloroform (50 ml) was stirred with freshly prepared silver chloride (1.48 g; 8 mmol). Silver iodide (along with excess AgCl)

TABLE 1 — CHARACTERIZATION DATA OF DIALKYLTELLURIUM TETRAHALIDES

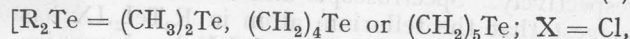
Compound	m.p. (°C)	Found (%) (Calc.)	
		Te	(I+X)
$(CH_3)_2TeI_2 \cdot ICl$	108	22.28 (22.23)	73.84 (72.52)
$(CH_3)_2TeI_2 \cdot IBr$	115	20.68 (20.60)	74.89 (74.37)
$C_4H_8TeI_2 \cdot I_2$	118	19.00 (18.45)	73.00 (73.44)
$C_4H_8TeI_2 \cdot ICl$	110	22.72 (21.27)	68.20 (69.37)
$C_4H_8TeI_2 \cdot IBr$	94	20.20 (19.75)	70.80 (71.55)
$C_5H_{10}TeI_2 \cdot ICl$	102	20.38 (20.78)	66.84 (67.79)
$C_5H_{10}TeI_2 \cdot IBr$	104	18.34 (19.38)	70.38 (69.96)
$C_4H_8TeBr_2^*$	130 (128-31) ⁸	38.08 (37.15)	46.78 (46.53)
$C_4H_8TeCl_2^*$	112-13 (112-13) ⁸	50.49 (50.13)	28.88 (27.88)
$(CH_3)_2TeCl_2^*$	90(92-97) ⁹	55.98 (55.58)	31.32 (31.32)
$C_5H_{10}TeCl_2^*$	103(105) ⁹	35.79 (35.68)	43.23 (44.70)

*The product obtained in Eq. (2).

was filtered off and the filtrate on concentration afforded $C_4H_8TeCl_2$ (0.50 g; 100%); m.p. 112° (lit.⁸

m.p. 112-13°).

Tetrahalides were prepared by treating dialkyltellurium diiodides with ICl, IBr or I_2 in chloroform (Eq. 1).

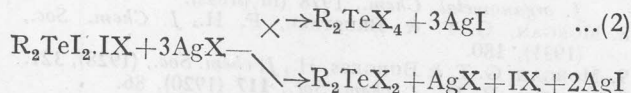


Br or I]

All the tetrahalides are sharp melting coloured solid and nonconducting in methyl cyanide. In aqueous solution they behave as 1:1 binary electrolytes ($\approx 500 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) corresponding to $[R_2Te(OH)]^+I_3^-$ in agreement with the reported⁵ behaviour of $C_5H_{10}TeI_4$. The adducts lose IX

when allowed to stand under vacuum.

The reaction of R_2TeI_2 with ICN and of R_2TeCl_2 or R_2TeBr_2 with ICl or IBr did not yield adducts under similar conditions. The tetrahalides on reaction with excess of AgCl or AgBr yielded R_2TeCl_2 or R_2TeBr_2 respectively (Eq. 2) indicating the presence of loose molecular adducts of Te(IV) rather than Te(VI) derivatives.



The UV and NMR spectra of the diiodides and the corresponding tetrahalides (Tables 2 and 3) are virtually identical. The visible spectra however do differ. Unlike the diiodides the tetrahalides show a strong peak at 510 nm (X = I); 499 (X = Cl);