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Reactions of Tin Tetraacetate with Sulphur Ligands

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Reactions of tin tetraacetate with thiols (n-C_4H_9-SH and n-$C_6H_{13}SH$), dithiols [$HS(CH_2)_nSH$; n = 2,3,4 and 6], thioglycol [$HS(CH_2)_2OH$], thiocarboxylic acids (CH_3COSH, C_2H_5COSH, C_6H_5COSH) and mercapto carboxylic acids ($HSCH_2COOH$, HS-(CH_2)$_2$COOH, and HSC_6H_4-o-COOH) have been carried out in chloroform or toluene (with the azeotropic removal of the liberated acetic acid) in various molar ratios. These reactions are very facile, yielding various types of compounds, containing Sn–S linkages. The new compounds, which are generally crystalline with sharp melting points, have been characterized by elemental analysis and IR as well as PMR spectral study.

Introduction

Reactions of thiocarboxylic acids [1], mercaptocarboxylic acids [2] and esters [3] with organotin(IV) and Sn(IV) [4] moieties have been studied recently. Following a facile route to the synthesis of tin tetraacetate, its reactions with mono- and dicarboxylic acids [5] and with β-diketones [6] have also been recently reported. In view of the easy accessibility of tin tetraacetate in good yield and the high reactivity of Sn–O linkage towards sulphur ligands, it was thought worthwhile to explore the possibility of utilizing this compound for the synthesis of various types of organic derivatives of tin(IV). The present paper deals with the reactions of tin tetraacetate with different sulphur ligands, such as mono- and dithiols, thiocarboxylic acids and mercaptocarboxylic acids.

TABLE I. PMR Data in CCl_4.

S. No.	Compound	τ, ppm
1	$Sn(S\overset{O}{\overset{\|}{C}}CH_2CH_3)_4$	7.20q (CH_2) 8.70t (CH_3)
2	$CH_3CH_2\overset{O}{\overset{\|}{C}}SH$	7.45q (CH_2) 8.99t (CH_3) 2.85s (SH)
3	$CH_3CH_2\overset{O}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}CH_2CH_3$	7.15q (CH_2) 8.70t (CH_3)

Results and Discussion

Tin tetraacetate reacts readily with butane- and hexane-thiol to yield the corresponding tetrathiolatotin derivatives:

$$Sn(OAc)_4 + 4RSH \rightarrow Sn(SR)_4 + 4AcOH\uparrow$$

$$(R = C_4H_9, C_6H_{13})$$

The facile conversion of Sn–O bond into Sn–S bond has been noted by a number of workers [7–9]. However, it may be relevant to mention that triethyltin isopropylthiolate has been reported to give triethyltin acetate on reaction with acetic acid [10].

Tin tetraacetate also reacts with thioacetic and thiopropionic acids in 1:4 molar ratios at room temperature in benzene or chloroform to yield the expected tin tetrathioacetate and thiopropionate. The reaction proceeds readily and the products are fine crystalline solids in quantitative yields:

$$Sn(OAc)_4 + 4R\overset{O}{\overset{\|}{C}}SH \xrightarrow[\text{temp.}]{\text{room}} Sn(S\overset{O}{\overset{\|}{C}}R)_4 + 4AcOH\uparrow$$

$$(R = CH_3, CH_3CH_2–)$$

These products are soluble in common organic solvents. The above reactions, when carried out in refluxing toluene benzene or even in excess thioacetic acid give an insoluble solid in low yield with high tin content. Even on keeping the compounds for some time at room temperature, the tetrathiocarboxylates initially formed, eliminate thiocarboxylic

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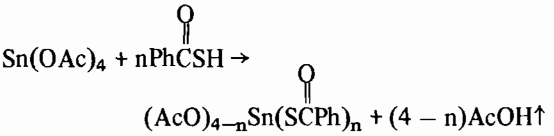
anhydride (liquid) by intra or intermolecular condensation to yield a polymeric solid. Tin tetrathiopropionate tends to disproportionate during attempted distillation to give thiopropionic anhydride.

The IR spectrum shows carbonyl absorptions of the tetrathiocarboxylates at 1660, 1550 and 1450 cm^{-1} indicating both free as well as bridging carboxyl groups in the moiety. Molecular weight in refluxing chloroform of a freshly prepared sample of tin tetrathiopropionate indicates its monomeric nature. The PMR values of these compounds are given in Table I.

Stepwise substitution of acetate moiety in tin tetraacetate by thiobenzoate moiety could be achieved by carrying out the reaction in toluene with an appropriate molar ratio. The liberated acetic acid could be removed azeotropically with toluene and estimated to check the progress of the reaction:



$$Sn(OAc)_4 + nPh\overset{O}{\overset{\|}{C}}SH \rightarrow (AcO)_{4-n}Sn(S\overset{O}{\overset{\|}{C}}Ph)_n + (4-n)AcOH\uparrow$$

(n = 1, 2, 3 and 4)

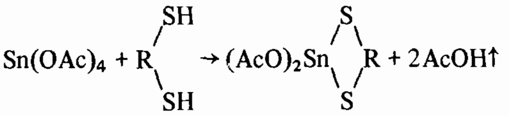
These products, which are white crystalline solids, are precipitated from the reaction medium as acetic acid is removed. When the above reactions are carried out in refluxing chloroform, a clear solution is obtained, which gives the desired product on removing the volatile portion under reduced pressure.

The thiobenzoate derivatives are crystalline solids with sharp melting points. These are soluble in chloroform and pyridine and show monomeric behaviour in refluxing chloroform. The PMR spectra of these mixed acetate thiobenzoate derivatives in $CDCl_3$ show a multiplet at 1.45–2.35τ, due to aromatic protons and only one sharp singlet at 7.77τ for the acetate protons.

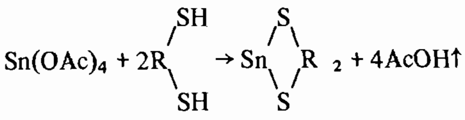
The IR spectrum of $Sn(SCOC_6H_5)_4$ shows three strong absorptions in the carbonyl region at 1630, 1590 and 1570 cm^{-1}, which indicates that probably both free as well as bridging thiobenzoate groups are present. In mixed acetate thiobenzoate derivatives, in addition to the above peaks, a sharp peak of medium intensity is present at 1700 ± 10 cm^{-1}. It may, therefore, be assumed that carbonyl oxygens of the acetate moieties are free. In case of tin tetraacetate, the peak due to the free carboxyl group appears at 1704 cm^{-1}.

The IR spectra of all these thiobenzoate derivatives show absorptions of medium intensity at 360 cm^{-1}, which may be assigned to Sn–S stretching vibrations.

Reactions of tin tetraacetate with dithiols in refluxing toluene proceed as follows:



(II)

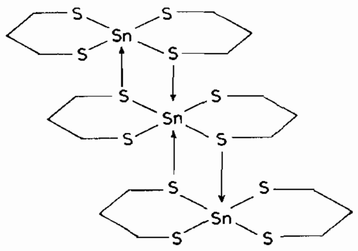


(III)

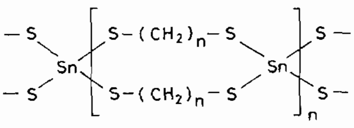
R = $-(CH_2)_2-$, $-(CH_2)_3-$, CH_3-CHCH_2-, $-(CH_2)_4-$, $(CH_2)_6-$

All the compounds of the type (II) and (III) are obtained as insoluble white solids, except the compound(II) with ethane-1,2-dithiol, and (III) with ethane-1,2-, and propane-1,2-dithiols, which are soluble in hot chloroform and pyridine.

A few examples of *spiro* chelates of the type (III) (with ethane-1,2-, propane-1,2- and propane-1,3-dithiols) have been synthesized previously by Poller *et al.* [11]. According to these workers, the first two compounds are monomeric but propane-1,3-dithiol derivative is a coordination polymer as shown below:

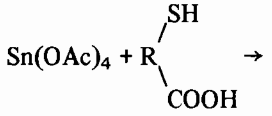


The above three compounds obtained here are identical with those described by Poller *et al.* [11]. Compounds (III) with butane-1,4- and hexane-1,6-dithiol are insoluble in simple organic solvents as well as coordinating solvents like pyridine. In view of the long chain length of these dithiols, it is possible that their products are not *spiro* chelates, but cross-linked chain polymers.



Among the dithiolatotin diacetate derivatives (II) ethane-1,2-dithiol derivative is sparingly soluble in $CHCl_3$, propane-1,2-dithiol derivative is insoluble in organic solvents, but soluble in pyridine and other dithiol derivatives are insoluble even in pyridine. Probably, the latter derivatives are chain polymers having acetate bridges. The IR spectra show a sharp peak at ~1700 cm^{-1} indicating the presence of acetate moiety with free carbonyl group. In addition, ethane-1,2- and propane-1,2-dithiol derivatives show a medium intensity peak at 1530 cm^{-1}, whereas other compounds show a rather broad absorption in the region 1530–1610 cm^{-1}. These data indicate that the former two compounds have only bridging acetate groups, whereas the others have chelating as well as bridging acetate groups, in addition to the free acetate groups. The absorptions due to Sn–S stretching vibrations in compounds of the type (II) and (III) are observed at 430 ± 15 and 320 ± 10 cm^{-1}.

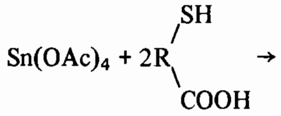
Reactions of tin tetraacetate with mercaptoacetic, 3-mercaptopropionic and *o*-mercaptobenzoic acids in 1:1 and 1:2 molar ratios occur readily in refluxing toluene with the liberation of acetic acid:



$$Sn(OAc)_4 + R\begin{smallmatrix} SH \\ COOH \end{smallmatrix} \rightarrow$$

$$(AcO)_2Sn(S{-}R{-}COO) + 2ACOH\uparrow$$

(IV)



$$Sn(OAc)_4 + 2R\begin{smallmatrix} SH \\ COOH \end{smallmatrix} \rightarrow$$

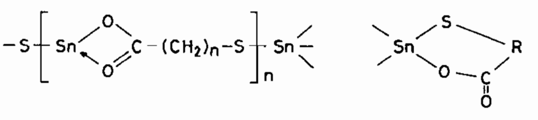
$$Sn(S{-}R{-}COO)_2 + 4AcOH\uparrow$$

(V)

[R = $-CH_2-$, $-CH_2-CH_2-$ and C_6H_4-*o*–]

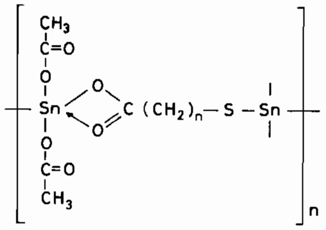
All the above six compounds are insoluble in organic solvents as well as in donor solvents, and are presumably polymeric in nature. The bifunctional mercaptocarboxylate moieties, ($-S(CH_2)_nCOO-$) may give either cyclic compounds [COO- and $-S-(CH_2)_n-$ being attached to the same tin atom] or they may form linear polymeric chains (the carbocyclic and mercapto groups being attached to different tin atoms). Stapfer and Herber [2] suggested a linear polymeric chain structure for diorganotin derivative of mercaptocarboxylic acids on the basis of IR and Mössbauer spectral data.

Compounds of the type (IV) and (V) are probably polymers [2, 12], with a skeleton similar to the one given below (a) and not of chelated derivative (b).

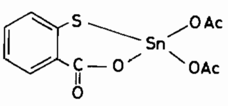


(a) (b)

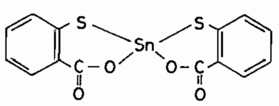
It is rather difficult to derive any fruitful conclusions only from the IR data. The compounds (V) (R = CH_2- and $-CH_2-CH_2-$) show a broad absorption in the region 1500–1580 cm^{-1} indicating the presence of both chelating and bridging carboxyl groups. On the other hand, compounds (IV) (R = $-CH_2-$ and $-CH_2-CH_2-$) show a sharp peak at 1700 cm^{-1} in addition to the broad absorption at 1520–1570 cm^{-1}. These compounds can be assumed, therefore, to have acetate moieties with only free carbonyl groups.



In *o*-mercaptobenzoic acid derivatives, the ligand moiety cannot act as a bridging group between two tin atoms, similar to mercaptoacetate or mercapto propionate moieties due to steric reasons. These are, probably cyclic compounds of the type:



VII



VIII

However, physical properties of these compounds indicate that they are also polymeric in nature (*via* intermolecular coordination). Due to the insolubility of these products in all common solvents, further investigations were precluded.

Experimental

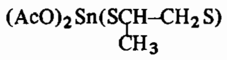
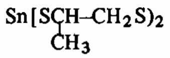
Special precautions were taken to carry out the reactions under strictly anhydrous conditions. All reagents and solvents were carefully dried and purified before use.

$Sn(OAc)_4$ was prepared as previously reported [5]. Estimation of tin, acetate and sulphur were carried out as described earlier [5]. Molecular weights were determined ebulliometrically in boiling $CHCl_3$. IR and PMR spectra were taken on Perkin-Elmer 522 and R-12B spectrometers, respectively.

Reaction of Tin Tetraacetate with Thioacetic Acid in C_6H_6

A mixture of $Sn(OAc)_4$ (1.2 g, 3.38 mmol) and thioacetic acid (1.04 g, 13.69 mmol) in benzene (25 ml) was kept overnight. A clear solution, without any

TABLE II. Reactions of $Sn(OAc)_4$ with Dithiols, Thiocarboxylic Acids, Mercaptocarboxylic Acids and Thiols in Refluxing Toluene.

S. No.	$Sn(OAc)_4$ (g)	Reactants (g)	Molar ratio	Yield (g) Found (Calcd.)	Compound and Nature	AcOH in Azeotrope (g) Found (Calcd.)	Analysis			M.P. or B.P. (°C)	Mol. Wt. Found (Calcd.)
							Sn % Found (Calcd.)	S % Found (Calcd.)	AcOH % Found (Calcd.)		
Ethane-1,2-dithiol											
1.	2.31	0.61	1:1	1.65 (2.14)	$(AcO)_2Sn[S(CH_2)_2S]$ White solid	0.78 (0.78)	35.88 (36.13)	19.33 (19.47)	30.25 (35.89)	155	
2.	2.12	1.12	1:2	1.64 (1.80)	$Sn[S(CH_2)_2S]_2$ White solid	1.43 (1.44)	39.18 (39.22)	42.46 (42.36)		185	
Propane-1,2-dithiol											
3.	2.50	0.75	1:1	2.46 (2.47)	 $(AcO)_2Sn(S\underset{CH_3}{C}H–CH_2S)$ White solid	0.85 (0.84)	34.75 (34.64)	18.72 (18.71)	34.12 (34.43)	135	
4.	2.19	1.33	1:2	1.99 (2.04)	 $Sn[S\underset{CH_3}{C}H–CH_2S)_2$ White solid	1.49 (1.48)	35.74 (35.85)	38.92 (38.73)		115	
Propane-1,3-dithiol											
5.	2.31	0.70	1:1	1.96 (2.23)	$(AcO)_2Sn[S(CH_2)_3S]$ White solid	0.78 (0.78)	34.54 (34.64)	18.71 (18.71)	33.21 (34.43)	258	
6.	2.18	1.33	1:2	1.98 (2.03)	$Sn[S(CH_2)_3S]_2$ White solid	1.46 (1.48)	35.86 (35.85)	38.85 (38.73)		158	
Butane-1,4-dithiol											
7.	3.87	1.15	1:1	3.32 (3.39)	$(AcO)_2Sn[S(CH_2)_4S]$ White solid	1.16 (1.14)	33.54 (33.25)	17.82 (17.96)	33.15 (33.09)	148	
8.	2.04	1.40	1:2	2.06 (2.04)	$Sn[S(CH_2)_4S]_2$ White solid	1.36 (1.38)	33.01 (33.05)	35.90 (35.71)	–	216d.	
Hexane-1,6-dithiol											
9.	2.20	0.93	1:1	2.23 (2.39)	$(AcO)_2Sn[S\text{-}(CH_2)_6S]$ White solid	0.75 (0.74)	30.79 (30.84)	16.76 (16.66)	30.29 (30.66)	340d.	
10.	2.21	1.87	1:2	2.42 (2.59)	$Sn[S–CH_2)_6S]_2$ Viscous greenish solid	1.46 (1.50)	28.71 (28.60)	30.91 (30.89)	–	–	
Thioglycol											
11.	1.65	0.36	1:1	1.40 (1.46)	$(AcO)_2Sn[S(CH_2)_2O]$ Viscous solid	0.54 (0.56)	38.18 (37.96)	10.48 (10.23)	36.89 (37.72)	–	

12.	2.01	0.89	1:2	1.59	$Sn[O(CH_2)_2S]_2$	1.32	43.69	23.69	–	210	
				(1.54)	White powdered solid	(1.36)	(43.81)	(23.66)			
Thiobenzoic acid											
13.	1.76	0.69	1:1	2.12	$(AcO)_3Sn(SCOC_6H_5)$	0.29	26.83	7.12	40.62	118	418
				(2.15)	Light yellow solid	(0.30)	(27.44)	(7.41)	(40.89)		(433)
14.	1.89	1.47	1:2	2.51	$(AcO)_2Sn(SCOC_6H_5)_2$	0.68	23.19	12.89	23.36	125	541
				(2.72)	Light yellow solid	(0.64)	(23.22)	(12.55)	(23.09)		(511)
15.	2.01	2.34	1:3	3.36	$(AcO)Sn(SCOC_6H_5)_3$	1.00	19.85	16.05	9.92	129	533
				(3.33)	Light yellow solid	(1.02)	(20.14)	(16.32)	(10.03)		(589)
16.	1.70	2.65	1:4	3.25	$Sn(SCOC_6H_5)_4$	1.12	17.71	18.86	–	135	634
				(3.35)	Light yellow solid	(1.15)	(17.80)	(19.21)			(667)
Thiosalicylic acid											
17.	2.05	0.89	1:1	2.16	$(AcO)_2Sn(OOCC_6H_4S)$	0.66	30.57	8.41	30.62	320	–
				(2.25)	Light yellow solid	(0.69)	(30.53)	(8.24)	(30.34)		
18.	1.82	1.58	1:2	2.20	$Sn(OOCC_6H_4S)_2$	1.15	28.22	15.42	–	did not melt till	
				(2.19)	Light yellow solid	(1.23)	(28.07)	(15.15)		355	
Mercaptoacetic acid											
19.	1.44	0.36	1:1	1.22	$(AcO)_2Sn(SCH_2COO)$	0.49	36.12	9.83	36.25	310d.	
				(1.32)	White solid	(0.49)	(36.33)	(9.81)	(36.10)		
20.	1.53	0.79	1:2	1.30	$Sn(SCH_2COO)_2$	0.92	39.61	21.41	–	156	
				(1.30)	White solid	(1.04)	(39.73)	(21.45)			
Mercaptopropionic acid											
21.	2.14	0.64	1:1	2.06	$(AcO)_2Sn(S(CH_2)_2COO)$	0.73	34.88	9.34	34.56	132	
				(2.06)	White solid	(0.73)	(34.83)	(9.40)	(34.62)		
22.	2.07	1.24	1:2	1.81	$Sn(S(CH_2)_2COO)_2$	1.37	36.25	19.78	–	154	
				(1.90)	White solid	(1.40)	(36.33)	(19.61)			
n-Butane-thiol											
								$(-SC_4H_9)$			
23.	2.30	2.33	1:4	3.09	$Sn(SC_4^nH_9)_4$	1.54	25.99	74.89	–	156/0.1 mm	–
				(3.08)	Colourless liquid	(1.55)	(25.01)	(75.00)			
n-Hexane-thiol											
								$-S(CH_2)_5CH_3$			
24.	2.17	2.88	1:4	3.51	$Sn[S(CH_2)_5CH_3]_4$	1.45	20.33	79.83	–	186/0.1 mm	–
				(3.60)	Colourless liquid	(1.47)	(20.23)	(79.76)			

exothermic reaction, was obtained. On removing the volatiles under reduced pressure, a white powder was obtained (1.33 g; 96%). *Anal.* Found: Sn, 27.71; S, 30.57. Calcd. for $C_8H_{12}O_4S_4Sn$: Sn, 28.35; S, 30.84%.

Reaction of Tin Tetraacetate with Propane-1,3-dithiol in CHCl$_3$

$Sn(OAc)_4$ (1.54 g, 4.34 mmol) and 1,3-propane dithiol (0.48 g, 4.44 mmol) were mixed in chloroform (30 ml) and the solution was refluxed for 6 h (~56–60 °C). The volatile portions were removed *in vacuo* obtaining a white solid (1.7 g, 92%). *Anal.* Found: Sn, 34.56; S, 18.89; acetoxy,33.71%. Calcd. for $C_7H_{12}O_4S_2Sn$: Sn, 34.64; acetoxy, 34.41; S, 18.71%.

Reaction of Tin Tetraacetate with Thiobenzoic Acid in Equimolar Ratio in CHCl$_3$

A mixture of $Sn(OAc)_4$ (1.36 g, 3.83 mmol) and thiobenzoic acid (0.52 g, 3.77 mmol) in chloroform (20 ml) was refluxed for 4 h at 60 °C. The light yellow coloured solution was evaporated under vacuum to remove the excess solvent. A light yellow solid (1.51 g, 92%) was obtained as the final product. *Anal.* Found: Sn, 27.12; S, 7.22; acetoxy, 40.83%. Calcd. for $C_{13}H_{14}O_7SSn$: Sn, 27.44; S, 7.41; acetoxy, 40.95%.

Reaction between Sn(OAc)$_4$ and Thiopropionic Acid in 1:4 Molar Ratio in CHCl$_3$

$Sn(OAc)_4$ (3.77 g; 10.62 mmol) and thiopropionic acid (3.83 g, 42.56 mmol) were mixed in chloroform (20 ml). A clear solution was obtained, which was left aside for 1 h. The solvent was then removed under vacuum to yield a white solid (4.96 g, 97%), corresponding to $Sn(SCOCH_2CH_3)_4$. *Anal.* Found: Sn, 24.65; S, 26.80%. Calcd. for $C_{12}H_{20}O_4S_4Sn$: Sn, 24.98; S, 27.01%. Similar reactions of tin tetraacetate with thiols, dithiols and mercaptocarboxylic acids were carried out in toluene in different molar ratios and the relevant data are listed in Table II.

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