Inorganica Chimica Acta, 57 (1982) 223–226

Synthesis and Characterization of Dialkyltin Complexes Containing Sulfur Donor Atoms

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Received May 14, 1981

Dimethyltin(IV) complexes incorporating thiocarboxylic acids have been synthesized and characterized. Elemental analyses, proton, tin, carbon NMR, infrared spectra and mass spectra suggest that the tin binds two thio groups, two alkyl groups, and water, resulting in a pentacoordinate tin ion.

Introduction

In support of studies in this laboratory on the environmental fate of organotin compounds, we have investigated some reactions of dimethyltin oxide with thio-containing ligands having the goal of synthesizing water-soluble organotin compounds. Previously a large number of dialkyltin complexes with esters of thioglycolic and thiopropionic acids [1] have been synthesized for use as plasticizers. Synthesis of several water-soluble triorganotins has been reported [2]. These compounds are attractive for such uses as wood preservation, where water-solubility would facilitate the impregnation process. In this report we present the synthesis and characterization of water-soluble dimethyltin complexes of thioglycolic acid, thiopropionic acid and thiolactic acid.

Experimental

Materials

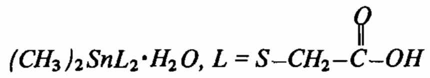
Dimethyltin oxide was obtained from Alfa Ventron Inorganics; sodium thioglycolate, 2-mercaptopropionic acid, thiolactic acid and 2-mercaptobenzoic acid were obtained from Sigma Chemical Co.

Physical Measurements

^{119}Sn and ^{13}C NMR spectra were obtained in the pulse Fourier transform (PFT) mode with proton noise decoupling using a Varian Model FT80A spectrometer equipped with the Varian Broadband accessory. Proton spectra were obtained on the Varian Switchable (^{1}H/^{13}C) Probe. The normal operating temperature was 30 °C. For proton and carbon spectra $(CH_3)_4Si$ contained in a coaxial inner capillary was used as a standard. For ^{119}Sn spectra $(CH_3)_4Sn$ in the same configuration was used as standard. D_2O served as internal lock.

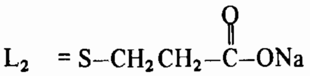
Elemental analyses were performed by the Microchemical Analysis Lab, Department of Chemistry, University of California, Berkeley. Mass spectra were obtained from the Mass Spectrum Laboratory, Department of Chemistry, University of California, Berkeley. The exciting voltage was 70. Infrared spectra were obtained on a Beckman IR-5A as Nujol mulls.

Preparation of the complexes



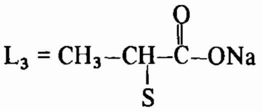
$(CH_3)_2SnL_2\cdot H_2O$, $L = S{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH$

Solid $H{-}S{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}ONa$ (0.02 mol) was added to 15 ml of O_2-free deionized H_2O. A concentrated solution (O_2-free) of NaOH was added until the solution was basic to litmus. The 0.01 mol $(CH_3)_2SnO$ was added as a solid, all the while N_2 was bubbling through the solution. After 4 hr the $(CH_3)_2SnO$ had dissolved leaving a pink colored solution. This solution was filtered and then concentrated HCl was added dropwise producing a voluminous white precipitate. Stirring was continued under N_2 for 1 hr. The material was then isolated, washed with deionized water twice and dried at 100 °C in a vacuum overnight. This exact procedure was followed for the preparation of other complexes of dimethyl tin oxide with the ligands



$L_2 = S{-}CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}ONa$

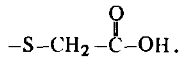
and

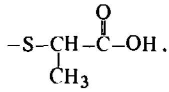


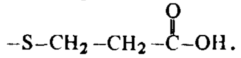
$L_3 = CH_3{-}\underset{\underset{S}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}ONa$

TABLE I. Elemental Analyses and Physical Properties.

Empirical Formula	H/C Found	Calc for M/L = ½	Color	M.P. °C
$Me_2SnL^1_2(H_2O)$	2.09	2.00	white powder	>250
$Me_2SnL^2_2(H_2O)$	2.04	2.00	white powder	>250
$Me_2SnL^3_2(H_2O)$	2.00	2.00	white powder	>250

L^1 =

$-S-CH_2-\overset{O}{\overset{\|}{C}}-OH.$

L^2 =

$-S-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH.$

L^3 =

$-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH.$

Results and Discussion

Complexes of the empirical formula $(CH_3)_2Sn(L)_2(H_2O)$, where $L = S-CH_2-\overset{O}{\overset{\|}{C}}-OH$, $S-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$, or $CH_3-\underset{S}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-OH$ have been synthesized and had to be stored over P_2O_5 to prevent them from absorbing H_2O from the atmosphere and becoming very tacky.

Elemental analyses (H/C ratios) establish a M/L ratio of ½, Table I. Mass spectra were obtained on the complexes in an effort to obtain parent ion peaks attributable to the empirical formula $(CH_3)_2Sn(L)_2(H_2O)$. The distinct relative abundance distribution for tin (^{116}Sn, 14.24%; ^{118}Sn, 24.01%, and ^{120}Sn, 32.97%) help in establishing the fragmentation patterns for the complexes. All of the complexes, in addition to parent ions [% relative intensity, 5.10], display peaks in their spectra at 180 [23,16], 182 [27.58], 184 [30.01] mass units corresponding to the fragment SnS_2, thereby helping to confirm the M/L ratio of ½ (percent relative intensities are in brackets).

Infrared spectra were obtained on the complexes as Nujol mulls. The free ligands contained a strong sharp S–H absorption at 2525 cm^{-1} which was not present in the spectrum of the complex [3]. This suggests that: 1) the sulfur has been deprotonated and 2) the sulfur is coordinated to the tin atom. The position of the C=O absorption (1575 cm^{-1}) is the same in both the free ligand and the complex indicating that it is not involved in complexation with the tin atom. The intensity of the band is strong and broad in both cases. The complexes also displayed broad IR bands at 3350 cm^{-1} indicating a coordinated water molecule.

With the above information it seems evident that in the solid state the complexes are $(CH_3)_2Sn(L)_2(H_2O)$. To obtain information on the characteristics of the complex in basic solution (pH 8–10) we employed ^1H, ^{119}Sn and ^{13}C NMR techniques.

Commercial $(CH_3)_2SnO$ by itself possesses limited solubility in water even under basic conditions. The presence of a chelating ligand in the form of thioglycolate, or any other H–S–R type ligand, increases the solubility of $(CH_3)_2SnO$ under basic conditions, pH $\geqslant$ 8. Successive experiments were undertaken wherein the M/L ratio was varied from 1/10 to ½ and the ^1H and ^{13}C NMR were measured, Fig. 1. Assignments are based on known chemical shift data [4–6]. Table II lists the chemical shifts obtained when $(CH_3)_2SnO$ was titrated with $H-S-CH_2-\overset{O}{\overset{\|}{C}}-ONa$. The same trends are observed with the other ligands.

It is evident from the data in Table II that the alkyl carbon ($-CH_2-$) of thioglycolate is deshielded as a function of tin (M) concentration. This trend is consistent with sulfur coordination and is evident on alpha carbons of other systems when a proton is removed leaving an anion behind [5]. In addition, the ^{13}C for the carboxylate group does not vary too much as a function of metal (M) concentration, indicating that it does not coordinate with Sn. This result is consistent with the IR data which also suggested that the carboxylate group does not coordinate. The ^{13}C chemical shift of the methyl groups on the tin at first glance do not appear to be consistent with (M/L ratio of ½) earlier reports [7–9] on the $\delta^{13}C$ chemical shifts of methyl tin complexes as a function of the number of sulfur atoms attached to the tin. The $\delta^{13}C$ chemical shifts for the methyl groups of the complexes $(CH_3)_2Sn(S-C_2H_5)_2$ were found to be –0.8 ppm whereas the chemical shift for the methyl groups found in our case is 2.68 ppm.

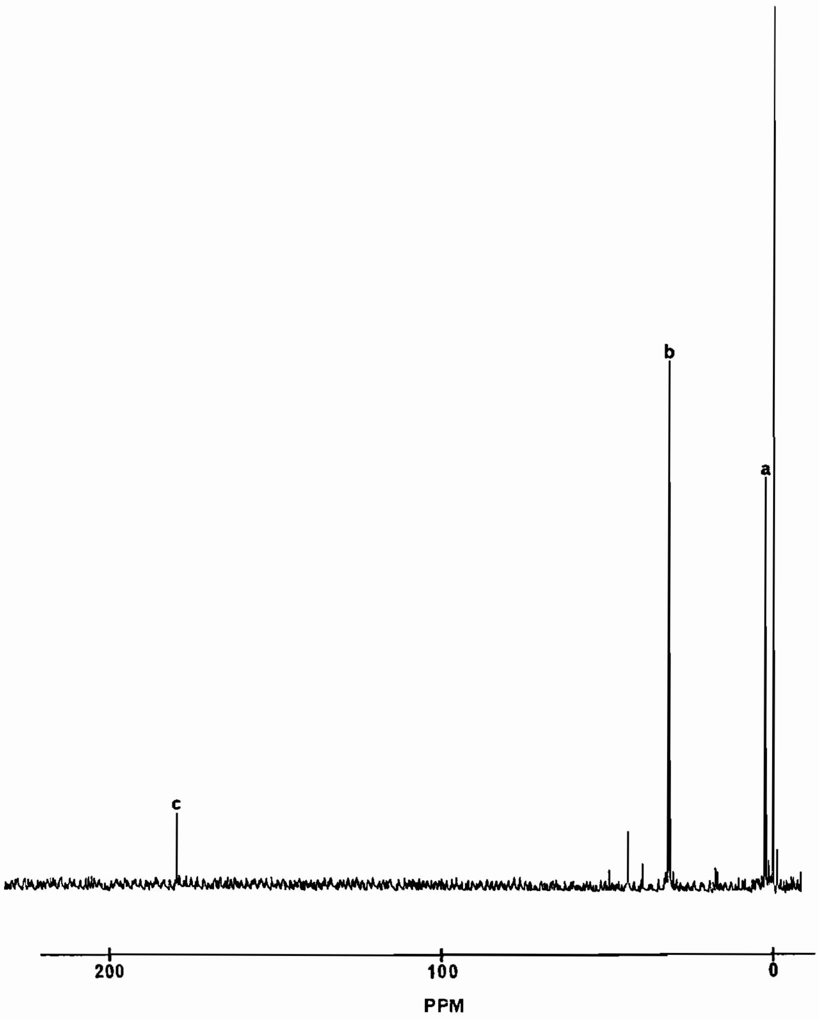


Fig. 1. Carbon-13 NMR of $(H_3C)_2Sn(OH_2)(L)_2$ in D_2O at pH 9. TMS coaxial. 10,000 transients. $(\underset{a}{H_3C})_2Sn(S-\underset{b}{CH_2}-\underset{c}{\overset{O}{\overset{\|}{C}}}-OH)_2$-$(H_2O)$. M/L ratio is ½.

TABLE II. ^1H and ^{13}C Chemical Shifts as a Function of Metal to Ligand Ratio (M/L) ppm downfield from TMS.

M/L Ratio	H–S	$-CH_2-$		$-\overset{O}{\overset{\|}{C}}-ONa$	$Sn-(CH_3)_2$	
	δ^1H	δ^1H	$\delta^{13}C$	$\delta^{13}C$	δ^1H	$\delta^{13}C$
Ligand only[a]	3.32	4.84	29.46	180.59	–	–
1/10	3.34	4.85	30.02	180.67	0.96	2.79
1/5	3.41	4.85	30.73	180.90	0.98	2.83
1/2	3.56	4.95	31.65	180.75	1.00	2.41

[a] Ligand = $H-S-CH_2-\overset{O}{\overset{\|}{C}}-ONa$.

Mitchell [10] also reported the ^{13}C chemical of methyl carbons attached to tin as a function of the coordination number of the tin atom. He found that the carbons became more deshielded as the coordination number increased from 4 to 5. This phenomenon was not observed in the ^{13}C chemical shifts of the methyl groups of $(CH_3)_2O$ when titrated with the ligands.

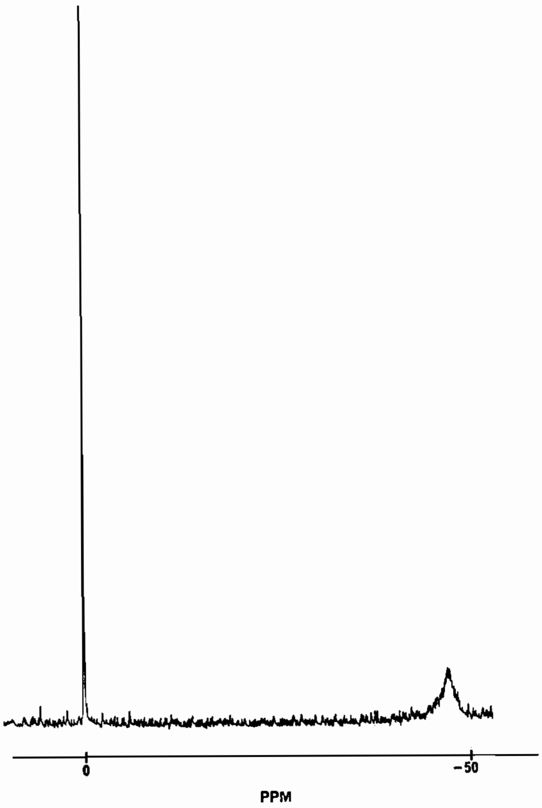


Fig. 2. Tin-119 NMR of $(H_3C)_2Sn(OH_2)(L)_2$ in D_2O at pH 9. $(CH_3)_4Sn$ coaxial. 40,000 transients. M/L ratio is ½.

In addition to the use of alkyl thiocarboxylic acids we employed 2-mercaptobenzoic acid and found that it would also solubilize $(CH_3)_2SnO$. The same phenomena with regard to NMR parameters were observed. The $^{13}CH_3$ of the methyl groups attached to the tin was found to be 2.54 ppm and the $^{13}COOH$ did not change as a function of M/L ratio.

To complement the ^1H and ^{13}C NMR investigations mentioned above, ^{119}Sn NMR spectra were obtained on the complexes in D_2O at pH 9. The $\delta^{119}Sn$ for the complexes were found to be upfield from tetramethyl tin (Fig. 2). The chemical shifts indicate a very shielded tin atom and are in marked contrast to the ^{119}Sn chemical shifts reported for complexes of the type $(CH_3)_2Sn(S{-}R)_2$ whose $\delta^{119}Sn$ chemical shifts are around 100 ppm downfield from $(CH_3)_4Sn$. The $\delta^{119}Sn$ chemical shifts for the complexes Ph_2SnS (−19.5 ppm) and $(CH_3)_2SnS$ (−125.6 ppm) are more closely related to those observed here. However, in both examples the tin environment is four-coordinate. Kennedy, *et al.* [11], also reported the ^{119}Sn chemical shifts of a series of compounds with tin–sulfur bonds. In that report they observed a ^{119}Sn chemical shift at −80.5 ± 5 ppm for the mixture $Sn(NEt_3)_4{-}(CH_3S)_4Sn$, in CH_2Cl_2. While the four-coordinated complex had a ^{119}Sn chemical shift of +93 ± 5 ppm, the peak at −80.5 ± 5 ppm was ascribed to a five-coordinated species. Smith, *et al.* [12] and Mitchell and Walter [13] had also reported earlier the high field shift observed when the tin atom increases its coordination number. Consequently, the high field tin chemical shifts that were observed in these complexes can be attributed to a pentacoordinate tin atom and is in agreement with the $\delta^{13}C$ chemical shifts of the methyl groups.

Stapfer and Herber [1] have reported on the structure of similar organotin complexes containing mercaptoesters. For the complex of dimethyltin and isoctyl thioglycolate, prepared in water, a trigonal bipyramidal geometry was postulated with a *cis*-configuration of the methyl groups. Their infrared and Mössbauer data indicated that one isoctyl thioglycolate ligand was monodentate and the other was bidentate. The results on our complexes indicate that the carbonate ion does not participate in coordination and that our fifth ligand is water.

In summary, ^1H, ^{13}C, ^{119}Sn NMR results indicate that $(CH_3)_2SnO$ chelates to thioglycolate type ligands, through the sulfur, to form a complex with a M/L ratio of ½ whose coordination number is 5. Infrared and NMR results suggest that the carboxylate entity does not coordinate to the metal ion.

Acknowledgement

The support of the Office of Naval Research is acknowledged.

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