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The Synthesis of Some *N*,*N*-Dialkylselenocarbamate Complexes of Tin(IV), and Their Infrared and PMR Spectra

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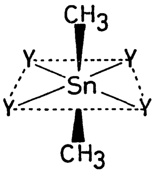
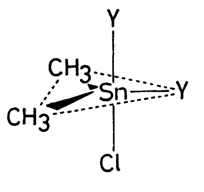
Several *N*,*N*-dialkylselenocarbamate complexes of tin(IV), $(CH_3)_2Sn[OSeCNR_2]_2$ (**1**), $(CH_3)_2ClSn[OSeCNR_2]$ (**2**) ($R=CH_3$ and C_2H_5) and $(CH_3)_3Sn[OSeCN(CH_3)_2]$ (**3**), have been prepared, and their infrared and proton magnetic resonance spectra have been examined. The results indicate that in **1** and **2** the selenocarbamate ligands are coordinated to the tin atom in a bidentate manner, although the coordination of the oxygen atom is weak. On the other hand, **3** has a tetra-coordinate tin with a free carbonyl bond. The configurations of these complexes are discussed and compared with those of the corresponding thio-, dithio-, diseleno-, and thioselenocarbamate complexes of tin(IV).

In previous papers, one of the present authors has demonstrated that dimethyltin(IV) bis(*N*,*N*-dimethyldithio-¹⁾ and -diselenocarbamates,²⁾ $(CH_3)_2Sn[Y_2CN(CH_3)_2]_2$ ($Y=S$ and Se), have a distorted octahedral *trans*-configuration (I), and that dimethylchlorotin(IV) *N*,*N*-dimethyldithio-¹⁾ and -diselenocarbamates,²⁾ $(CH_3)_2ClSn[Y_2CN(CH_3)_2]$, form a trigonal bipyramid, with the $(Sn-)CH_3$ groups being located in equatorial positions (II); we reached these conclusions on the basis of the infrared and proton magnetic resonance spectra. These structures have been confirmed by the X-ray crystallographic analysis of $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$³⁾ and $(CH_3)_2ClSn[S_2CN(CH_3)_2]$.⁴⁾ Similar configurations have been suggested for the *N*,*N*-dimethylthioselenocarbamate complexes of tin(IV), $(CH_3)_2Sn[SSeCN(CH_3)_2]_2$ and $(CH_3)_2ClSn[SSeCN(CH_3)_2]$, in which the Sn–Se bond is more ionic than the Sn–S bond, judging from the benzene-induced solvent shifts of the $N-CH_3$ proton signals in the PMR spectra.⁵⁾



(I)



(II)

(Y= S and Se)

It seems to be of interest at this stage to prepare other types of tin(IV)-carbamates, such as thio- and selenocarbamates, and to compare their spectroscopic properties with those of the complexes described above. Concerning the thiocarbamates, only the trimethyltin(IV) derivative has been reported on thus far,⁶⁾⁷⁾

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1) M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).

2) T. Kamitani, H. Yamamoto, and T. Tanaka, *ibid.*, **32**, 2621 (1970).

3) T. Kimura, N. Yasuoka, and N. Kasai, This Bulletin, **45**, 1649 (1972).

4) K. Furue, T. Kimura, N. Yasuoka, N. Kasai, and M. Kakudo, *ibid.*, **43**, 1661 (1970).

5) T. Kamitani and T. Tanaka, *Inorg. Nucl. Chem. Lett.*, **6**, 91 (1970).

6) R. F. Dalton and K. Jones, *J. Chem. Soc.*, **A**, **1970**, 590.

7) C. H. Yoder, A. Komiyama, J. E. Kochanowski, and F. H. Saydam, *J. Amer. Chem. Soc.*, **93**, 6515 (1971).

although a few transition metal complexes have been characterized.[8]

The present paper was undertaken to prepare some *N,N*-dialkylselenocarbamate complexes of tin(IV), $(CH_3)_2Sn[OSeCNR_2]_2$, $(CH_3)_2ClSn[OSeCNR_2]$ (R= CH_3 and C_2H_5), and $(CH_3)_3Sn[OSeCN(CH_3)_2]$, which are the first metal-selenocarbamates, and to elucidate their configurations and the bonding between the ligand anions and the tin(IV) on the basis of the infrared and PMR spectra.

Experimental

Dimethylammonium N,N-*Dimethylselenocarbamate,* $[(CH_3)_2NH_2](dmsc)$ *(dmsc:* $OSeCN(CH_3)_2$*), and Diethylammonium* N,N-*Diethylselenocarbamate,* $[(C_2H_5)_2NH_2](desc)$ *(desc:* $OSeCN(C_2H_5)_2$*).* These starting substances were synthesized by the reaction of dimethyl- or diethylamine, selenium powder, and carbon monoxide in tetrahydrofuran according to a procedure described elsewhere.[9]

*Dimethyltin Bis(*N,N*-dimethylselenocarbamate),* $(CH_3)_2Sn(dmsc)_2$*.* A solution of $(CH_3)_2SnCl_2$ (2.54 g, 11.5 mmol) in dry benzene (25 ml) was stirred, drop by drop, into a solution of $[(CH_3)_2NH_2](dmsc)$ (4.53 g, 23.0 mmol) in tetrahydrofuran (25 ml) at room temperature; the mixture was then stirred further for 2 hr. Then the precipitate which appeared, $(CH_3)_2NH_2Cl$, was filtered off, and the filtrate was evaporated under reduced pressure. The resulting product was recrystallized from carbon tetrachloride to give pale yellow crystals (4.93 g, 10.9 mmol); mp 166 °C.

Found: C, 21.06; H, 3.96; N, 6.07%; mol wt, 458. Calcd for $C_8H_{18}N_2O_2Se_2Sn$: C, 21.31; H, 4.02; N, 6.21%; mol wt, 458.

*Dimethyltin Bis(*N,N*-diethylselenocarbamate),* $(CH_3)_2Sn(desc)_2$*.* This compound was similarly prepared by the reaction of $(CH_3)_2SnCl_2$ (1.87 g, 8.50 mmol) with $[(C_2H_5)_2NH_2](desc)$ (4.31 g, 17.0 mmol) in benzene. Recrystallization from petroleum ether gave yellow crystals (4.08 g, 8.05 mmol); mp 81—83 °C.

Found: C, 28.62; H, 5.47; N, 5.31%; mol wt, 528. Calcd for $C_{12}H_{26}N_2O_2Se_2Sn$: C, 28.43; H, 5.17; N, 5.53%; mol wt, 507.

Dimethylchlorotin N,N*-Dimethylselenocarbamate,* $(CH_3)_2ClSn(dmsc)$*.* A mixture of $(CH_3)_2Sn(dmsc)_2$ (4.73 g, 10.5 mmol) and $(CH_3)_2SnCl_2$ (2.32 g, 10.5 mmol) in dry benzene was stirred for 2 hr at room temperature. Then the solution was evaporated under reduced pressure, and the resulting product was recrystallized from carbon tetrachloride to give pale yellow crystals (6.34 g, 18.9 mmol); mp 75 °C.

Found: C, 17.96; H, 3.86; N, 4.06%; mol wt, 352. Calcd for $C_5H_{12}NClOSeSn$: C, 17.91; H, 3.61; N, 4.18%; mol wt, 355.

Dimethylchlorotin N,N*-Diethylselenocarbamate,* $(CH_3)_2ClSn(desc)$*.* A mixture of $(CH_3)_2Sn(desc)_2$ (3.25 g, 6.41 mmol) and $(CH_3)_2SnCl_2$ (1.41 g, 6.41 mmol) in carbon tetrachloride was treated as in the case of $(CH_3)_2ClSn(dmsc)$. The resulting oily product was dissolved in an ether–petroleum ether mixture, and then the solution was cooled to −78 °C to give pale yellow crystals (4.07 g, 11.2 mmol); mp 31 °C.

Found: C, 22.85; H, 4.74; N, 3.99%; mol wt, 373. Calcd for $C_7H_{16}NClOSeSn$: C, 23.12; H, 4.44; N, 3.86%; mol wt, 363.

Trimethyltin N,N*-Dimethylselenocarbamate,* $(CH_3)_3Sn(dmsc)$*.* A solution of $(CH_3)_3SnCl$ (1.34 g, 6.72 mmol) in benzene was added to a solution of $[(CH_3)_2NH_2](dmsc)$ (1.32 g, 6.72 mmol) in tetrahydrofuran, after which the mixture was stirred for 3 hr at room temperature. After the precipitate of $(CH_3)_2NH_2Cl$ had been filtered off, the filtrate was evaporated under reduced pressure; the resulting product was recrystallized from tetrahydrofuran to give brownish yellow crystals (1.27 g, 4.03 mmol); mp 32 °C.

Found: C, 22.76; H, 5.05; N, 4.54%; mol wt, 325. Calcd for $C_6H_{15}NOSeSn$: C, 22.89; H, 4.80; N, 4.45%; mol wt, 325.

Physical Measurements. The molecular-weight determinations were carried out by the use of Mechrolab vapor pressure osmometer in the 0.018—0.034 M range in chloroform. The infrared spectra were recorded in Nujol and in hexachlorobutadiene mulls on a Hitachi-Perkin 225 Spectrophotometer, while the proton magnetic resonance spectra were measured at 100 MHz on a Japan Electron Optics PS-100 Spectrometer, equipped with a variable-temperature probe and controller. The chemical shifts were measured against tetramethylsilane as the internal standard.

Results and Discussion

Properties. All the complexes are soluble in common organic solvents, except for $(CH_3)_2Sn(dmsc)_2$ and $(CH_3)_2ClSn(dmsc)$, which are less soluble in petroleum ether. They are stable to air and moisture, in contrast with the very hygroscopic property of $[(CH_3)_2NH_2](dmsc)$ and $[(C_2H_5)_2NH_2](desc)$, but somewhat sensitive to the light in the solid state and in solution. The molecular-weight determination indicates that the selenocarbamate complexes are all monomeric in chloroform.

Configurations. The relevant infrared frequencies of the present complexes are listed in Table 1. All the complexes exhibit an intense band about 1600 cm^{-1};

TABLE 1. RELEVANT INFRARED FREQUENCIES (cm^{-1} IN Nujol) OF SELENOCARBAMATE-TIN(IV) COMPLEXES[a)]

Compound	ν(C=O)	ν_{as}(Sn–C)	ν_s(Sn–C)	ν(Sn–Se)	ν(Sn–Cl)
$(CH_3)_2Sn(dmsc)_2$	1592 s	557 s	519 s	337 m	
$(CH_3)_2Sn(desc)_2$	1586 s	552 s	517 s	322 m	
$(CH_3)_2ClSn(dmsc)$	1590 s	563 s	524 s	343 m	290 s
$(CH_3)_2ClSn(desc)$	1587 s	558 s	524 s	325 m	288 s
$(CH_3)_3Sn(dmsc)$	1620 s	534 s	511 s	328 m	

a) The abbreviations used in this table are as follows: s, strong; m, medium.

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[8] B. J. McCormick and B. P. Stormer, *Inorg. Chem.*, **11**, 729 (1972), and the references cited therein.

[9] N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **93**, 6344 (1971); K. Kondo, N. Sonoda, Y. Yoshida, M. Koishi, and S. Tsutsumi, *Chem. Lett.*, **1972**, 401.

Table 2. PMR spectra of selenocarbamate-tin (IV) complexes

Compound		τ ppm, in CCl$_4$	τ ppm, in C$_6$H$_6$	$\Delta^{a)}$ ppm	$J(^{119}$Sn–CH$_3)^{b)}$ Hz
$(CH_3)_2Sn(dmsc)_2$	N–CH$_3$	6.89	7.54	+0.65	
		7.06	7.60	+0.54	
	Sn–CH$_3$	8.90	8.48	−0.42	76
$(CH_3)_2Sn(desc)_2$	N–CH$_2$	6.59	6.98	+0.39	
		6.70	7.00	+0.30	
	C–CH$_3$	8.77	9.14	+0.37	
		8.87	9.16	+0.29	
	Sn–CH$_3$	8.91	8.47	−0.44	77
$(CH_3)_2ClSn(dmsc)$	N–CH$_3$	6.91	7.85	+0.94	
		7.08	7.88	+0.80	
	Sn–CH$_3$	8.92	8.95	+0.03	73
$(CH_3)_2ClSn(desc)$	N–CH$_2$	6.64	7.23	+0.59	
		6.75	7.29	+0.54	
	C–CH$_3$	8.70	9.31	+0.61	
		8.77	9.35	+0.58	
	Sn–CH$_3$	8.90	8.94	+0.04	73
$(CH_3)_3Sn(dmsc)$	N–CH$_3$	6.72	7.41	+0.69	
		6.91	7.52	+0.61	
	Sn–CH$_3$	9.28	9.42	+0.14	55

a) $\Delta = \tau(C_6H_6) - \tau(CCl_4)$.
b) The values in CCl$_4$.

this band can tentatively be assigned to the ν(C=O).[11] In the $(CH_3)_3Sn(dmsc)$ complex, the ν(C=O) frequency is in agreement with those of the desc anion (1620 cm^{-1})[12] and of $(CH_3)_3Sn[OSCN(CH_3)_2]$ (1621 cm^{-1}), the latter of which has a tetracoordinate tin with the tin-sulfur bond.[6] It may, therefore, be assumed that in $(CH_3)_3Sn(dmsc)$ only the selenium atom, not the oxygen, attaches to the tin. The similar tetra-coordinate tin was also reported on in recent X-ray structure determinations for the two modifications (orthorhombic and monoclinic) of trimethyltin *N*,*N*-dimethyldithiocarbamate, $(CH_3)_3Sn[S_2CN(CH_3)_2]$.[13]

On the other hand, the dimethyltin(IV) complexes exhibit the ν(C=O) band at a frequency lower by about 30 cm^{-1} than $(CH_3)_3Sn(dmsc)$. In addition, all the complexes, including $(CH_3)_3Sn(dmsc)$, commonly show an medium intense band due to the ν(Sn–Se) in the 322—343 cm^{-1} range. There seems to be no band ascribable to the ν(Sn–O) vibration down to 200 cm^{-1}. In view of these results, the selenocarbamate anions can be said to act as bidentate ligands in the dimethyltin(IV) complexes, but the coordination of the oxygen to the tin atom is weak.

The weak coordination of the oxygen atom brings about a stereochemical characteristic of the selenocarbamate complexes of tin(IV), which may be examined by comparing the intensities of the ν_{asym}(Sn–C) and ν_{sym}(Sn–C) bands in the infrared spectra. The intensity ratio of $I\nu_{sym}$(Sn–C)/$I\nu_{asym}$(Sn–C) (abbreviated as I_s/I_a) of $(CH_3)_2Sn(dmsc)_2$ (0.61) is appreciably larger than those of the corresponding dithio-,[1] diseleno-,[2] and thioselenocarbamate[5] complexes (0.21, 0.23, and 0.19 respectively). In the PMR spectra of both $(CH_3)_2Sn(dmsc)_2$ and $(CH_3)_2Sn(desc)_2$, the J-(^{119}Sn–CH$_3$) values (Table 2) are considerably smaller than those (83—84 Hz) of the analogous dithio-,[1] diseleno-,[2] and thioselenocarbamates.[5] These infrared and PMR results may be interpreted as much more a distortion of the $(CH_3)_2Sn$ moiety in $(CH_3)_2Sn(dmsc)_2$ and $(CH_3)_2Sn(desc)_2$ from the *trans*-octahedron(I) configuration, which may result in a configuration like a *cis*-one, although a detailed structure has to await the X-ray structure determination.

The I_s/I_a value of $(CH_3)_2ClSn(dmsc)$ (0.95) is close to those of the corresponding dithio-,[1] diseleno-,[2] and thioselenocarbamates[5] (0.97, 0.93, and 0.91 respectively). Furthermore, the $J(^{119}$Sn–CH$_3)$ values are virtually invariant (73—75 Hz; Table 2 and Refs. 1, 2, and 5) among all of these complexes, including $(CH_3)_2ClSn(desc)$. Thus, the present dimethylchlorotin(IV) complexes may be concluded to have the configuration shown by II.

Description of the PMR Spectra. The dmsc complexes in solution exhibit a doublet for the N–CH$_3$ proton signals at room temperature (Table 2), as expected from the restricted rotation around the carbamate C$\overset{...}{=}$N bond. The down-field signal is smaller in height and broader than the up-field one both in carbon tetrachloride and in benzene. These appearances are quite similar to the case of $(CH_3)_2ClSn[SSeCN(CH_3)_2]$ in carbon tetrachloride;[5] therefore, the former signal may be assigned to the CH$_3$$^{(A)}$ protons *trans* to the selenium atom with respect to the

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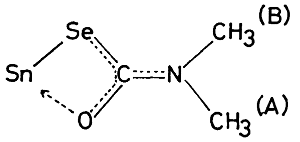
[11] The dithio-,[1] diseleno-,[2] and thioselenocarbamate[5] complexes of tin(IV) exhibit an intense band due to ν(C$\overset{...}{=}$N) in the 1490—1550 cm^{-1} range. It may, therefore, be more reasonable to identify the band at about 1600 cm^{-1} as the ν(N$\overset{...}{=}$C$\overset{...}{=}$O). However, the ν(C$\overset{...}{=}$N) dose not very largely contribute to this frequency, since the partial double-bond character is not large, as will be described below.

[12] The wave number of $[(C_2H_5)_2NH_2]$ (desc); the spectrum of $[(CH_3)_2NH_2]$ (dmsc) has not been recorded because of its extremely hygroscopic property.

[13] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc.*, **A**, **1970**, 490.



C=N bond in the planar selenocarbamate. The desc complexes in benzene[14] show doublets of a quartet and of a triplet for the $N-CH_2$ and $C-CH_3$ proton signals respectively at room temperature. By the analogy with the dmsc complexes, the down-field signals of each pair may be ascribed to the $N-CH_2$ or $C-CH_3$ protons *trans* to the selenium atom with respect to the C=N bond.

The $N-CH_3$ proton chemical shifts of $(CH_3)_2Sn(dmsc)_2$ in varying volume ratios of carbon tetrachloride to benzene are depicted in Fig. 1, which indicates that the solvent effect in benzene is a little larger with the $CH_3^{(A)}$ than with the $CH_3^{(B)}$. This is also the case with the remaining dmsc and desc complexes (Table 2). It may further be noticed in Table 2 that the *N*-alkyl protons of $(CH_3)_2ClSn(dmsc)$ and $(CH_3)_2ClSn(desc)$ undergo profound benzene shifts compared with those of $(CH_3)_2Sn(dmsc)_2$ and $(CH_3)_2Sn(desc)_2$ respectively. This may be responsible for decreasing the electron density of the nitrogen atom of the former complexes relative to the latter; this idea is supported by the fact that the coalescence temperatures of the $N-CH_3$ proton signals of $(CH_3)_2ClSn(dmsc)$ are a little higher than those of $(CH_3)_2Sn(dmsc)_2$, 55 and 50 °C in nitrobenzene respectively. These temperatures are considerably lower than that of $(CH_3)_2ClSn[SSeCN(CH_3)_2]$ (110 °C in 1,1,2,2-tetrachloroethane),[15] indicating, although only qualitatively, that the C=N double bond character of the selenocarbamate complexes of tin(IV) is not very large. This conclusion is in accordance with the weak coordination of the carbonyl oxygen of the selenocarbamates to the tin atom.

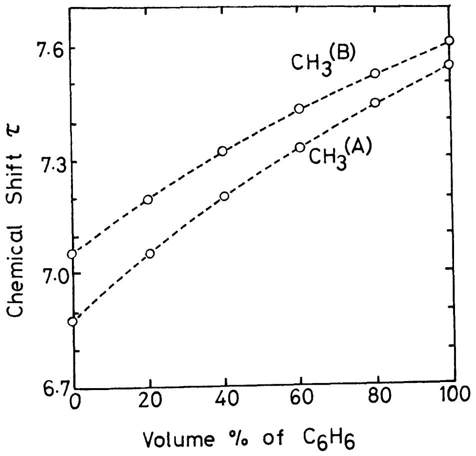


Fig. 1. Chemical shifts of the $N-CH_3$ protons of $(CH_3)_2Sn(dmsc)_2$ in $CCl_4-C_6H_6$ mixtures.

The authors wish to express their hearty thanks to Professor Noboru Sonoda and Mr. Kiyoshi Kondo of this University for giving them guidance in preparing the starting materials, $[(CH_3)_2NH_2](dmsc)$ and $[(C_2H_5)_2NH_2](desc)$; they are also grateful to the Shinko Chemical Co., Ltd., Osaka, for supplying the elemental selenium.

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[14] In carbon tetrachloride, the $N-CH_2$ proton signals occur as a quintet (1: 4: 6: 4: 1), a superposition of two quartets.

[15] T. Tanaka and T. Kamitani, unpublished work.