

## Synthesis of Mixed Carbamate Complexes of Dimethyltin(IV) and Their Properties in Solution

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*Mixed carbamate complexes of dimethyltin(IV) with the formula  $Me_2SnLL'$  ( $LL'$  = all combinations of  $SC(O)NMe_2$ ,  $SeC(O)NMe_2$ ,  $S_2CNMe_2$ ,  $SSeCNMe_2$  and  $Se_2CNMe_2$ , except for that of  $S_2CNMe_2-Se_2CNMe_2$  reported previously) were prepared and characterized by their melting points and X-ray powdered patterns as well as elemental analyses. Infrared spectra of the complexes in Nujol mulls reveal that all carbamate ligands act in bidentate manners.  $^1H$  NMR spectra indicate that (i) the mixed-carbamate complex partly disproportionates to the corresponding bis-carbamate complexes, and they exist as an equilibrium mixture with statistical ratios (about 1:2:1) in solution, and (ii) the  $XYCNMe_2$  ligands ( $XY = SS, SSe, SeSe$ ) coordinated to the tin(IV) are more labile than the  $XC(O)NMe_2$  ( $X = S, Se$ ). The assignments of each proton signal are also described.*

### Introduction

In spite of some efforts to prepare organotin(IV) complexes with two different chelate ligands, so called mixed-chelate complexes of tin(IV), only a few following compounds were isolated so far:  $Ph_2Sn(Ox)-(PhCOCHCOPh)$  ( $Ox = 8$ -oxyquinolate)<sup>1</sup> and  $Me_XSn(Ox)(T)$  ( $X = Me$  and  $Cl$ ;  $T = tropolonate$ ).<sup>2</sup> One of the difficulties to prepare mixed-chelate complexes of tin(IV) may result from the lability of chelate ligands coordinated to the tin atom in solution. In addition, whether the mixed-chelate complexes can be isolated or not seems to be highly dependent on the solubility difference between the mixed- and bis-chelate complexes, of which the latter is usually produced by the disproportionation of the former in solution,<sup>2</sup> that is, the mixed-chelate complex may be easily isolated when it is less soluble than the corresponding bis-chelates.

Some time ago, one of the authors reported the preparation and spectroscopic characterization of dimethyltin(IV) N,N-dimethyldithiocarbamate–N,N-dimethyldiselenocarbamate,  $Me_2Sn(S_2CNMe_2)(Se_2CNMe_2)$

(1).<sup>3</sup> The isolation of this complex leads us to the assumption that the similarity of coordination ability between the two types of ligands would favor the isolation of mixed-chelate complexes. In this viewpoint, we attempted to prepare mixed-chelate complexes of dimethyltin(IV) with all combinations of five sorts of carbamate ligands: N,N-dimethylmonothio-, -monoseleno-, -dithio-, -thioseleno- and -diselenocarbamates. This paper reports the synthesis and spectroscopic characterization of nine complexes, except 1 reported previously.<sup>3</sup>

### Experimental

#### Starting Materials

Dimethylammonium N,N-dimethylmonothio- and -monoselenocarbamates,  $Me_2NH_2(mtc)$ <sup>4</sup> and  $Me_2NH_2(msc)$ <sup>5</sup> ( $mtc = SC(O)NMe_2$ ;  $msc = SeC(O)NMe_2$ ), were obtained by the literature methods. Dimethylchlorotin (IV) N,N-dimethyldithio-, -thioseleno-, and -diselenocarbamates,  $Me_2ClSn(dtc)$ ,<sup>6</sup>  $Me_2ClSn(tsc)$ ,<sup>7</sup> and  $Me_2ClSn(dsc)$ <sup>3</sup> ( $dtc = S_2CNMe_2$ ,  $tsc = SSeCNMe_2$ ,  $dsc = Se_2CNMe_2$ ) were synthesized as described previously. Dimethyltin(IV) bis(N,N-dimethyldichalcogenocarbamates),  $Me_2SnL_2$  ( $L = mtc$ ,<sup>8</sup>  $msc$ ,<sup>9</sup>  $dtc$ ,<sup>6</sup>  $tsc$ <sup>7</sup> and  $dsc$ <sup>3</sup>) were prepared by the methods described previously.

#### Mixed-carbamate Complexes

To a benzene solution (20 ml) of  $Me_2NH_2 \cdot L$  (2.1 mmol,  $L = mtc$  or  $msc$ ) was added  $Me_2ClSnL'$  (2.1 mmol,  $L' = dtc$ ,  $tsc$ , or  $dsc$ ) in benzene (15 ml), and the mixture was stirred for about 2 hr at room temperature. The resulting precipitate of  $Me_2NH_2Cl$  was filtered off and the filtrate was evaporated to dryness under reduced pressure. The product was recrystallized from carbon tetrachloride to give colorless crystals of  $Me_2SnLL'$ .

Other complexes with combinations of  $mtc$ – $msc$ ,  $dtc$ – $tsc$ , and  $tsc$ – $dsc$  were prepared by ligand exchange reactions between the two appropriate bis-carbamate complexes in benzene by the similar procedure. The

former compound was recrystallized from ligroin, and the latter from carbon tetrachloride.

All the compounds were obtained in about 70% yields. Analytical data and properties of the complexes are summarized in Table I.

#### Physical Measurements

X-Ray powder patterns were obtained by the use of a Rigaku X-ray diffractometer. Infrared spectra were recorded in Nujol mulls on a Hitachi-Perkin Elmer 225 spectrophotometer.  $^1\text{H}$  NMR spectra were measured at 100 MHz on a Japan Electron Optics PS-100 spectrometer equipped with a variable temperature probe and a controller.  $^1\text{H}$  chemical shifts were measured against tetramethylsilane as the internal standard.

### Results and Discussion

#### Characterization and Properties

Only  $\text{Me}_2\text{Sn}(\text{mtc})(\text{dsc})$  seems to be somewhat impure, judging from its elemental analysis and a broad melting point (Table I). Repeated recrystallizations of this compound have been attempted from various organic solvents, such as carbon tetrachloride, ligroin and benzene. The analysis of the  $^1\text{H}$  NMR spectrum, however, indicates that the compound is contaminated by a small amount of  $\text{Me}_2\text{Sn}(\text{dsc})_2$ . This may be due to the little difference of solubility in these organic solvents between  $\text{Me}_2\text{Sn}(\text{mtc})(\text{dsc})$  and  $\text{Me}_2\text{Sn}(\text{dsc})_2$ . The remaining compounds have sharp melting points, and the elemental analyses are compatible with the

TABLE I. Melting Points and Analytical Data of  $\text{Me}_2\text{SnLL}'$ .

L	L' <sup>a</sup>	M.p. (°C)	%C <sup>b</sup>	%H <sup>b</sup>	%N <sup>b</sup>
mtc	msc	176–177	23.82 (23.79)	4.72 (4.49)	6.87 (6.93)
mtc	dtc	182–183	25.54 (25.75)	4.94 (4.86)	7.48 (7.50)
mtc	tsc	180	22.45 (22.88)	4.21 (4.32)	6.63 (7.50)
mtc	dsc	158–161	19.46 (20.58)	3.71 (3.89)	5.83 (6.00)
msc	dtc	178–179	23.06 (22.88)	4.57 (4.32)	6.72 (6.67)
msc	tsc	175–176	20.31 (20.58)	4.10 (3.89)	6.12 (6.00)
msc	dsc	167–168	18.30 (18.70)	3.67 (3.53)	5.33 (5.30)
dtc	tsc	192–193	21.75 (22.03)	4.15 (4.16)	6.42 (6.42)
tsc	dsc	177–178	17.98 (18.13)	3.27 (3.42)	5.33 (5.29)

<sup>a</sup> mtc =  $\text{SC}(\text{O})\text{NMe}_2$ , msc =  $\text{SeC}(\text{O})\text{NMe}_2$ , dtc =  $\text{S}_2\text{CNMe}_2$ , tsc =  $\text{SSeCNMe}_2$ , and dsc =  $\text{Se}_2\text{CNMe}_2$ . <sup>b</sup> Calculated values in parenthesis.

composition of the mixed-carbamate complexes. The X-ray powder pattern of  $\text{Me}_2\text{Sn}(\text{msc})(\text{dtc})$  is not superimposable with those of the corresponding bis-carbamate complexes,  $\text{Me}_2\text{Sn}(\text{msc})_2$  and  $\text{Me}_2\text{Sn}(\text{dtc})_2$ , as shown in Figure 1. Similar relations were obtained between other mixed-carbamates and the corresponding bis-carbamates. These results indicate that the complexes are mixed-carbamate ones, but not equimolar mixtures of the two kinds of bis-carbamates. The complexes are stable to air and moisture, and soluble in common organic solvents.

#### Infrared Spectra

Relevant infrared frequencies of the complexes are listed in Table II. It is well known that  $\text{Me}_2\text{SnL}'_2$  ( $L' = \text{dtc},^6 \text{tsc},^7 \text{dsc}^3$ ) exhibit the  $\nu(\text{C}=\text{N})$  band near  $1500 \text{ cm}^{-1}$ . On the other hand, the spectra of  $\text{Me}_2\text{SnL}_2$  ( $L = \text{mtc},^{10} \text{msc}^9$ ) show the  $\nu(\text{C}=\text{O})$  band which is more or less coupled with  $\nu(\text{C}=\text{N})$  at 1580 and  $1592 \text{ cm}^{-1}$  respectively. Thus, two absorptions due to  $\nu(\text{C}=\text{O})$  may be expected to occur in  $\text{Me}_2\text{Sn}(\text{mtc})(\text{msc})$ , and those

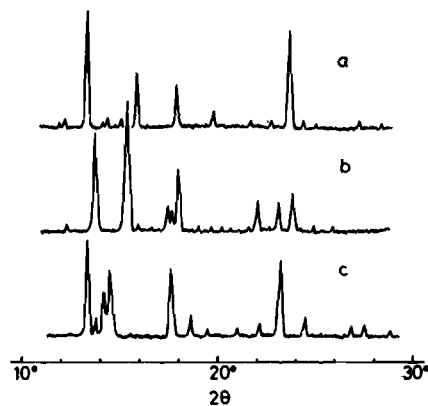


Figure 1. X-Ray powdered patterns of  $\text{Me}_2\text{Sn}(\text{msc})(\text{dtc})$  (a),  $\text{Me}_2\text{Sn}(\text{msc})_2$  (b), and  $\text{Me}_2\text{Sn}(\text{dtc})_2$  (c).

TABLE II. Relevant Infrared Frequency ( $\text{cm}^{-1}$  in Nujol) of  $\text{Me}_2\text{SnLL}'^a$ .

L	L'	$\nu(\text{C}=\text{O})$ , $\nu(\text{C}=\text{N})$	$\nu_{\text{as}}(\text{Sn}-\text{C})$	$\nu_{\text{s}}(\text{Sn}-\text{C})$	
mtc	msc	1594vs	1578vs	561s	520s
mtc	dtc	1592vs	1520vs	558s	525w
mtc	tsc	1590vs	1510vs	555s	522w
mtc	dsc	1592vs	1518vs	557s	517w
msc	dtc	1597vs	1508vs	554s	521w
msc	tsc	1592vs	1508vs	554s	515w
msc	dsc	1595vs	1515vs	551s	510w
dtc	tsc		1510vs	556s	517w
tsc	dsc		1506vs	551s	510w

<sup>a</sup> The abbreviations used in this table are as follows: vs, very strong; s, strong; m, medium; w, weak.

due to  $\nu(\text{C-N})$  both in  $\text{Me}_2\text{Sn}(\text{dtc})(\text{tsc})$  and  $\text{Me}_2\text{Sn}(\text{tsc})(\text{dsc})$ . In fact, in the former complex the  $\nu(\text{C=O})$  band was clearly resolved into two, but the latter exhibited only one broad  $\nu(\text{C=N})$  band, whose envelope seems to involve two absorptions arising from tsc and dtc or dsc ligands.

The  $\text{Me}_2\text{SnLL}'$  complexes ( $\text{L} = \text{mtc}, \text{msc}; \text{L}' = \text{dtc}, \text{tsc}, \text{dsc}$ ) display two strong bands around 1590 and 1510  $\text{cm}^{-1}$ , which are tentatively assigned to  $\nu(\text{C=O})$  and  $\nu(\text{C=N})$  respectively. These two frequencies of all the complexes are fairly close to those of the corresponding dimethyltin(IV) bis(carbamate), in which the carbamate ligands are known to act in a bidentate manner.<sup>3, 6-10</sup> It may therefore be reasonable to conclude that all the carbamate ligands of the present complexes act in a similar fashion.

### <sup>1</sup>H NMR Spectra

<sup>1</sup>H NMR data of the complexes are collected in Table III. The spectrum of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  shows three Sn-Me signals at  $\delta = 1.08, 1.30$  and 1.51 ppm in dichloromethane, and  $\delta = 1.50, 1.70$  and 1.92 ppm in benzene at room temperature; the intensity ratios were about 1:2:1, which is approximately the statistical distribution, in both solvents, as depicted in Figure 2. The fairly sharp signal at the highest and the broad one at the lowest magnetic field are almost identical in chemical shifts with the Sn-Me signals of  $\text{Me}_2\text{Sn}(\text{msc})_2$ <sup>9</sup> and  $\text{Me}_2\text{Sn}(\text{tsc})_2$ <sup>7</sup> respectively, not only in dichloromethane but also in benzene. This indicates that  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  partly disproportionates to  $\text{Me}_2\text{Sn}(\text{msc})_2$  and  $\text{Me}_2\text{Sn}(\text{tsc})_2$  in solution. Thus, the remaining signal at the intermediate field is unequivocally assigned

TABLE III. Chemical Shift ( $\delta$ ) and Coupling Constant (Hz) of  $\text{Me}_2\text{SnLL}'$ .

L	L'	Signal	In $\text{CH}_2\text{Cl}_2^a$	Assignment	In $\text{C}_6\text{H}_6^b$	Assignment	$J(^{119}\text{Sn-Me})^c$	
mtc	msc	N-Me	2.90	msc	2.41	msc	76	
			3.07	mtc	2.46	mtc		
			3.09	mtc msc	2.48	msc		
		2.57	mtc					
mtc	dtc	N-Me	1.04		1.46			
			2.93	mtc	2.40	mtc		
			3.12	mtc	2.52	mtc		
		3.44	dtc	2.68	dtc			
mtc	tsc	Sn-Me	1.25		1.61			80
			2.96	mtc	2.51	mtc		
		N-Me	3.14	mtc	2.63	mtc		
			3.46	tsc	2.70	tsc		
		3.50	tsc	2.73	tsc			
mtc	dsc	N-Me	1.30		1.66		80	
			2.92	mtc	2.50	mtc		
			3.09	mtc	2.62	mtc		
		3.40	dsc	2.66	dsc			
msc	dtc	N-Me	1.35		1.86		80	
			2.91	msc	2.44	msc		
			3.08	msc	2.54	msc		
		3.41	dtc	2.73	dtc			
msc	tsc	Sn-Me	1.28		1.57		80	
			2.88	msc	2.46	msc		
		N-Me	3.06	msc	2.55	msc		
			3.36	tsc	2.65	tsc		
		3.40	tsc	2.74	tsc			
msc	dsc	N-Me	1.30		1.70		80	
			2.88	msc	2.46	msc		
			3.05	msc	2.58	msc dsc		
		3.43	dsc					
dtc	tsc	N-Me	1.39		1.81		80	
			3.38	tsc	2.71	tsc		
			3.42	tsc dtc	2.81	tsc dtc		
tsc	dsc	N-Me	1.51		1.92		84	
			3.38	tsc	2.62	tsc dsc		
			3.42	tsc dsc	2.71	tsc		
		Sn-Me	1.64		2.03		84	

<sup>a</sup> 3.8 wt%. <sup>b</sup> 5.7 wt%. <sup>c</sup> Measured at  $-70^\circ\text{C}$  in dichloromethane.

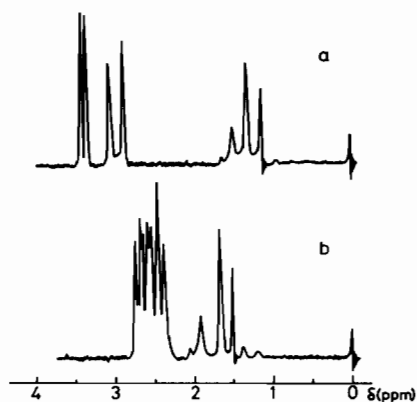


Figure 2.  $^1\text{H}$  NMR spectra of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  in dichloromethane (a) and in benzene (b) at room temperature.

to the Sn–Me protons of the mixed-carbamate complex.

Satellites due to spin–spin couplings between the Sn–Me protons and  $^{119}\text{Sn}$  ( $I = 1/2$ , 8.7%) or  $^{117}\text{Sn}$  ( $I = 1/2$ , 7.7%) were very broad at room temperature, because of intermolecular ligand exchanges. Both the satellites and main signals became sharp with decreasing temperature, and their line widths did not change below  $-50^\circ\text{C}$ . Limiting  $J(^{119}\text{Sn}\text{--Me})$  values are 76, 80, and 84 Hz in dichloromethane. The first and the last values are essentially the same as the  $J$  values of  $\text{Me}_2\text{Sn}(\text{msc})_2$ <sup>9</sup> and  $\text{Me}_2\text{Sn}(\text{tsc})_2$ <sup>7</sup> respectively. The value of 80 Hz is therefore associated with  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$ .

On the other hand, the Sn–Me signals became broad with increasing temperature. The lowest and the middle field signals almost coalesced at  $80^\circ\text{C}$  in chlorobenzene, while the highest one still remained without merging, as shown in Figure 3. Further heating, however, caused the complex to decompose. Taking into account that the three Sn–Me signals occurred with an almost identical space at low temperatures, this observation suggests that  $\text{Me}_2\text{Sn}(\text{tsc})_2$  and  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  are more easily

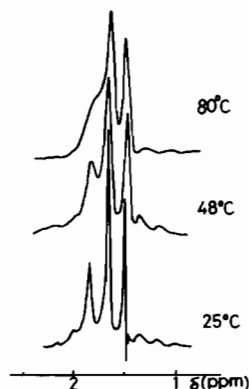


Figure 3. The Sn–Me signals of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$ .

subject to ligand exchanges than  $\text{Me}_2\text{Sn}(\text{msc})_2$ . This means that tsc is more labile than msc when they are coordinated to the tin(IV). Similar  $^1\text{H}$  NMR behavior of the Sn–Me protons was observed in other complexes of the  $\text{Me}_2\text{SnLL}'$  type ( $L = \text{mtc}$ ,  $\text{msc}$ ;  $L' = \text{dtc}$ ,  $\text{tsc}$ ,  $\text{dsc}$ ) in solution, and the dtc, tsc, or dsc ligand is suggested to be labile compared with mtc or msc.

We have previously reported that the  $J(^{119}\text{Sn}\text{--Me})$  values of  $\text{Me}_2\text{SnL}'_2$  ( $L' = \text{dtc}$ ,<sup>6</sup>  $\text{tsc}$ ,<sup>7</sup>  $\text{dsc}$ <sup>3</sup>) are 84–83 Hz, and those of  $\text{Me}_2\text{SnL}_2$  ( $L = \text{mtc}$ ,<sup>10</sup>  $\text{msc}$ <sup>9</sup>) are both 76 Hz. According to the relationship postulated by Holmes and Kaesz,<sup>11</sup> these values indicate that the  $s$  character of the tin atomic orbital directed to the Me group is larger in  $\text{Me}_2\text{SnL}'_2$  than in  $\text{Me}_2\text{SnL}_2$ . In other words, that directed to the carbamate ligand is smaller in the former complex than in the latter. This assumption can explain the greater lability of dtc, tsc, or dsc than mtc or msc.

The N–Me signals of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  in dichloromethane at room temperature appeared as two doublets due to the restricted rotation around the C=N bond of both carbamate ligands (Figure 2a). The chemical shifts of these signals are again very close to those of the N–Me protons of  $\text{Me}_2\text{Sn}(\text{msc})_2$ <sup>9</sup> or  $\text{Me}_2\text{Sn}(\text{tsc})_2$ <sup>7</sup> in the same solvent. This may imply that the N–Me proton chemical shifts of a given carbamate ligand are little influenced by another carbamate coordinated to the tin atom as the co-ligand. Thus, the doublet signals at the higher and the lower magnetic fields are assigned to the msc and tsc ligands respectively. In addition, down-field signals of each doublet would be ascribed to the N–Me group *trans* to the selenium atom with respect to the C=N bond of msc and tsc, by reference to assignments for the  $^1\text{H}$  NMR spectra of  $\text{Me}_2\text{Sn}(\text{msc})_2$ <sup>9</sup> and  $\text{Me}_2\text{Sn}(\text{tsc})_2$ <sup>7</sup> reported previously.

Figure 4 shows the variation of the N–Me chemical shifts of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  in dichloromethane/benzene mixtures in various volume ratios. Two doublet signals in dichloromethane are further split with increasing amounts of benzene, and finally four doublets\* occurred in pure benzene (Figure 2b). This phenomenon can be explained in terms of benzene induced solvent shifts,<sup>7,9</sup> whose magnitude operating on a given ligand is different between the mixed- and bis-carbamate complexes. Assignments of the signals in benzene are straightforward, because again two doublets among the signals are little altered in chemical shifts from those of  $\text{Me}_2\text{Sn}(\text{msc})_2$ <sup>9</sup> and  $\text{Me}_2\text{Sn}(\text{tsc})_2$ <sup>7</sup> in benzene, respectively.

Analogous benzene induced solvent shifts of the N–Me signals were observed in  $\text{Me}_2\text{SnLL}'$ , where  $L = \text{mtc}$  or  $\text{msc}$  and  $L' = \text{dtc}$ ,  $\text{tsc}$ , or  $\text{dsc}$ . In the three complexes with  $\text{LL}' = (\text{mtc})(\text{msc})$ ,  $(\text{dtc})(\text{tsc})$ , and  $(\text{tsc})(\text{msc})$ , however, the N–Me signals of a given ligand

\* The second highest field signal would be a superposition of two different N–Me groups.

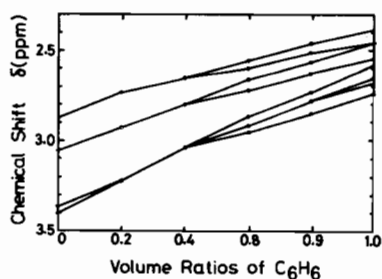


Figure 4. N-Me chemical shifts of  $\text{Me}_2\text{Sn}(\text{msc})(\text{tsc})$  in dichloromethane/benzene mixtures in various volume ratios at room temperature.

showed no separation from those of the corresponding bis-carbamate complexes even in benzene. This is due to the close similarity in coordinating ability toward the tin(IV) between mtc and msc, or among dtc, tsc, and dsc. The signals are assigned by the similar manner, and the results are given in Table III.

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