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cis—trans ISOMERISATION OF DIMETHYLTIN BIS(SALICYLALDEHYDE)-ETHYLENEDIIMINATE

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Summary

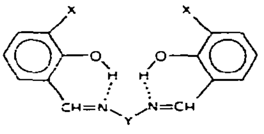
A series of diorganotin complexes of ONNO tetradentate Schiff bases derived from salicylaldehyde or its derivative and ethylene-, propylene-, or phenylene-diamine has been prepared. Two isomeric forms of the representative complex, dimethyltin bis(salicylaldehyde)ethylenediiminate, $(CH_3)_2Sn(BSED)$, are isolated in the solid state. This complex, when left to stand in open air in solution, is converted to an unusual complex, bis(dimethyltin)oxide bis(salicylaldehyde)ethylenediiminate, $[(CH_3)_2Sn]_2O(BSED)$, which is in turn decomposed into the ligand and dimethyltin oxide. It is suggested on the basis of infrared and 100 MHz PMR spectra that one isomer of $(CH_3)_2Sn(BSED)$ has a bent C—Sn—C moiety and a non-planar BSED ligand (*cis* form) and that the other has a nearly linear C—Sn—C moiety and a symmetric ligand (*trans* form). $(CH_3)_2Sn(BSED)$ undergoes *cis—trans* isomerization in solution and the equilibrium constants K ([*trans*]/[*cis*]) obtained indicate that the *cis* isomer is favored in non-coordinating solvents (CH_2Cl_2 and $C_6H_5NO_2$) and the *trans* in coordinating solvents ($CH_3CON(CH_3)_2$ and $[(CH_3)_2N]_3P{=}O$). Variable temperature PMR studies of the isomerization reaction have shown that the *trans* form is favored at high temperatures. Heats of isomerization have been obtained and free energies and entropies of isomerization calculated as follows: the ΔG (kcal/mol), ΔH (kcal/mol), and ΔS (eu) values in $C_6H_5NO_2$ and C_5H_5N at 25°C are 1.2, 5.0, and 12.8, and 0.2, 1.2, and 3.2, respectively.

Introduction

Complex formation between diorganotin moieties and tetradentate Schiff bases has attracted much attention in recent years [1]. One of the representative complexes is dimethyltin bis(salicylaldehyde)ethylenediiminate, $(CH_3)_2Sn(BSED)$, which has been prepared by four independent groups including ours [1—4]. The configurational conclusions put forward by each of these groups are unfortunately rather confusing. Thus, Barbieri and Herber have recently proposed the *trans* configuration for this complex on the basis of the Mössbauer and infrared studies. Randaccio and his coworkers [5] have confirmed the *trans* configuration of a sample donated by Barbieri by means of an X-ray crystallographic analysis. On the other hand, Murray et al. [2] have proposed the *cis* configuration based on the 60 MHz PMR spectrum of the complex in $CDCl_3$. Our 60 MHz PMR studies [3], however, have strongly suggested that there exist two isomers, at least, in solution.

Now it is found, owing to the increased sensitivity of 100 MHz PMR spectroscopy, that $(CH_3)_2Sn(BSED)$ actually can exist both as *cis* and *trans* isomers. Here we report the isolation of the two isomers in the solid state and their isomerization reactions in solution. This is the first example where both the *cis* and *trans* isomers of any diorganotin complex are isolated in the solid state. Also included are some studies of the related complexes. The abbreviations used for the ligands are as follows:

$BSED\cdot H_2$ = Bis(salicylaldehyde)ethylenediimine ($X = H$, $Y = (CH_2)_2$)
$BSPD\cdot H_2$ = Bis(salicylaldehyde)propylenediimine ($X = H$, $Y = (CH_2)_3$)
$BSPhD\cdot H_2$ = Bis(salicylaldehyde)phenylenediimine ($X = H$, $Y = 1,2\text{-}C_6H_4$)
$BVED\cdot H_2$ = Bis(*o*-vanillin)ethylenediimine ($X = OCH_3$, $Y = (CH_2)_2$).



Experimental

Preparation of complexes

trans-Dimethyltin N,N'-bis(salicylaldehyde)ethylenediiminate, trans-$(CH_3)_2$*-Sn(BSED).* Dimethyltin dichloride (2.80 g, 12.7 mmol) in anhydrous methanol (20 ml) was added dropwise to a stirred solution of sodium methoxide prepared from sodium (0.64 g, 28 mmol) and methanol (28 ml). The resulting mixture was stirred for 1 h, and followed by the addition of $BSED\cdot H_2$ (3.41 g, 12.7 mmol) suspended in methanol (50 ml). The mixture was refluxed for 2 h, concentrated by the partial distillation of the solvent, cooled, and then the crude product was filtered and recrystallized from methanol to afford yellow crystals of the *trans* isomer (2.52 g, 50%). $[(CH_3)_2Sn]_2O(BSED)$ (0.50 g) was obtained from the filtrate together with other unidentified products.

cis-Dimethyltin N,N'-bis(salicylaldehyde)ethylenediiminate, cis-$(CH_3)_2$*-Sn(BSED).* A dichloromethane solution of crude products obtained in a manner similar to that described above was filtered through a filter paper. The yellow crystals deposited on the filter paper were collected to give the desired *cis* isomer. Addition of ligroin (b.p. 70°) to the filtrate and concentration of the solution in vacuo also afforded the *cis* isomer. However, in some cases, the filtrate also gave a small amount of another product which was identified as $[(CH_3)_2Sn]_2$-$O(BSED)$.

Bis(dimethyltin)oxide N,N'-bis(salicylaldehyde)ethylenediiminate, [$(CH_3)_2Sn]_2O$(BSED). To a reagent grade benzene solution of crude $(CH_3)_2$-Sn(BSED) (1.00 g) was added n-heptane and the solution was cooled to deposit light yellow crystals (0.52 g), which were recrystallized from *N,N*-dimethylacetamide/methanol. The filtrate, upon concentration in vacuo, gave the ligand BSED$\cdot H_2$ (0.21 g). The whole procedure was repeated under an atmosphere of nitrogen by using the solvents dried over $LiAlH_4$, ending in similar results. Solvents saturated with heavy water also gave BSED$\cdot H_2$.

From reactions of dimethyl- or diphenyl-tin dichlorides, sodium methoxide, and appropriate ligands in a similar manner to that described for *trans*-$(CH_3)_2$Sn(BSED) the following compounds were prepared: diphenyltin *N,N'*-bis(salicylaldehyde)ethylenediiminate methanol solvate, $(C_6H_5)_2$Sn(BSED)$\cdot CH_3OH$ recrystallized from methanol several times to give the analytically pure sample; dimethyltin *N,N'*-bis(salicylaldehyde)propylenediiminate methanol solvate, $(CH_3)_2$Sn(BSPD)$\cdot CH_3OH$; diphenyltin *N,N'*-bis(salicylaldehyde)propylenediiminate methanol solvate, $(C_6H_5)_2$Sn(BSPD)$\cdot CH_3OH$ repeatedly recrystallized from methanol to give the analytically pure sample; dimethyltin *N,N'*-bis(*o*-vanillin)ethylenediiminate, $(CH_3)_2$Sn(BVED); diphenyltin *N,N'*-bis(*o*-vanillin)ethylenediiminate, $(C_6H_5)_2$Sn(BVED) repeatedly recrystallized from *N,N*-dimethylformamide/methanol to give the analytically pure sample.

Dimethyltin N,N'-bis(salicylaldehyde)phenylenediiminate methanol solvate, $(CH_3)_2$Sn(BSPhD)$\cdot CH_3OH$. This compound was prepared by adding BSPhD$\cdot H_2$ and then dimethyltin dichloride to sodium methoxide in methanol and recrystallized from the same solvent. Diphenyltin *N,N'*-bis(salicyladehyde)phenylenediiminate, $(C_6H_5)_2$Sn(BSPhD) was similarly prepared.

Melting points, analytical data, and molecular weights of the complexes are shown in Table 1.

X-ray powder patterns

The *d* spacings and visually estimated intensities of the stronger lines are listed. The abbreviations are as follows: vs, very strong; s, strong; m, medium; w, weak.

cis-$(CH_3)_2$Sn(BSED): 5.63 m, 4.75 m, 4.13 s, 3.90 m, 3.75 s, 3.45 m, 3.27 s, 3.09 m, 2.29 m, 2.26 m, 2.20 m, 1.63 m, 1.58 m.

trans-$(CH_3)_2$Sn(BSED): 5.03 vs, 3.26 vs, 3.02 s, 2.92 m, 2.55 m, 2.43 vs, 2.29 m, 2.19 w, 2.11 m, 1.83 m, 1.73 s.

[$(CH_3)_2Sn]_2O$(BSED): 5.71 m, 4.79 vs, 4.03 m, 3.89 s, 3.28 s, 2.78 w, 2.70 w, 2.58 s, 2.29 s, 2.25 m, 2.14 w, 1.60 w.

Variable temperature PMR studies

Variable temperature PMR studies of the equilibrium constant *K* (*[trans]/[cis]*) were attempted in many solvents. Difficulties were sometimes encountered mainly due to poor solubility and decomposition of $(CH_3)_2$Sn(BSED), even when the PMR tube was sealed under high vacuum. Among solvents which dissolve the complex sufficiently for the PMR measurements (more than 17 mg/0.7 ml), dibromomethane and 1,1,2,2-tetrachloroethane decomposed the complex and did not allow measurements at elevated temperatures. In dichloromethane at elevated temperatures where the amount of the *trans* isomer increases,

TABLE 1

SOME DIORGANOTIN COMPLEXES OF ONNO TETRADENTATE SCHIFF BASES

Compound	M.p. (°C)	Analysis found (calcd.) (%)			Mol. wt. [b] found (calcd.)
		C	H	N	
trans-$(CH_3)_2Sn(BSED)$	254-255 (dec.)	51.78	4.74	6.63	425 [c]
		(52.08)	(4.87)	(6.75)	(415)
cis-$(CH_3)_2Sn(BSED)$	250-252 (dec.)	51.89	5.10	6.75	446
		(52.08)	(4.87)	(6.75)	(415)
$(C_6H_5)_2Sn(BSED)\cdot CH_3OH$ [a]	246-248 (dec.)	60.76	4.71	5.05	
		(60.98)	(4.94)	(4.91)	
$(CH_3)_2Sn(BSPD)\cdot CH_3OH$ [a]	191-194	51.97	5.65	5.82	399 [d]
		(52.08)	(5.69)	(6.08)	(429) [e]
$(C_6H_5)_2Sn(BSPD)\cdot CH_3OH$ [a]	222-225 (dec.)	61.96	4.94	5.11	
		(61.57)	(5.17)	(4.79)	
$(CH_3)_2Sn(BSPhD)\cdot CH_3OH$ [a]	209-211	55.93	4.72	5.86	388 [d]
		(55.78)	(4.90)	(5.65)	(463) [e]
$(C_6H_5)_2Sn(BSPhD)$	228-230	65.18	4.18	4.92	539 [d]
		(65.45)	(4.12)	(4.77)	(587)
$(CH_3)_2Sn(BVED)$	254-256 (dec.)	50.25	5.05	5.99	415
		(50.55)	(5.10)	(5.92)	(475)
$(C_6H_5)_2Sn(BVED)$	257-259 (dec.)	59.50	4.94	4.81	
		(60.13)	(4.71)	(4.67)	
$[(CH_3)_2Sn]_2O(BSED)$	264-265 (dec.)	41.28	4.46	5.18	608
		(41.43)	(4.52)	(4.83)	(580)

[a] Presence of methanol was confirmed by PMR spectra. [b] Measured in chloroform at 25° C by a vapor pressure osmometer unless otherwise noted. [c] Measured in nitrobenzene by a cryoscopic method. [d] Some decomposition was observed. [e] Calculated value for the unsolvated monomer.

it took more than a few hours to arrive at equilibrium during which time a part of the *trans* isomer crystallized out, thus preventing accurate measurements of *K* values. Even in *o*-dichlorobenzene, *N*,*N*-dimethyl-formamide and -acetamide, partial crystallizaiton was observed at elevated temperatures. Only in nitrobenzene and pyridine could variable temperature PMR studies be performed successfully.

K values were obtained from the integrated intensity ratio of the Sn—CH_3 proton signals. Usually the higher field component of the *cis* isomer's signal and the *trans* isomer's signal overlapped in integration (integrated intensity *a*). Thus, the amount of the *cis* isomer was obtained by doubling the integrated intensity of the lower field component of its signal (*b*) and the amount of the *trans* isomer by subtracting *b* from *a*.

All samples for variable temperature PMR studies were allowed to stand for sufficient time to equilibrate before the spectra were recorded, with the spectrum followed until no further change occurred. Thus, measurements were made at least three times with the interval of about 15 min and at each time five integrated intensity ratios were averaged. Each study contained five different temperatures over a temperature range of 80°.

Instrumentation

Molecular weights were determined in chloroform at 25° by using a Mechrolab Vapor Pressure Osmometer or by a cryoscopic method in nitrobenzene. X-ray powder pattern data were collected on a Rigaku Refractometer. Infrared spectra were recorded on a Hitachi—Perkin—Elmer 225 (4000-400 cm^{-1}) and a Hitachi EPI-2G (700-200 cm^{-1}). PMR spectra were obtained on a JEOL JNM-PS-

100 spectrometer equipped with a JNM-VT-3B variable temperature controller. Sample tubes for variable temperature studies were sealed under high vacuum. The complex in solution was unchanged over a period of months. Tetramethylsilane was used as internal standard.

Results and discussion

Preparation

The complexes are yellow or orange (complexes of BSPhD) in color and stable in air in the solid state. The *trans* isomers were obtained by recrystallization usually from methanol. On the contrary, the *cis* isomer of $(CH_3)_2Sn(BSED)$ can be obtained easily by taking advantage of the isomerization reaction in dichloromethane, in which the complex exists as an equilibrium mixture of the both isomers, the *cis* isomer being predominant. The *cis* isomer is more soluble in common organic solvents than is the *trans*.

$(CH_3)_2Sn(BSED)$ is surprisingly converted to a novel compound $[(CH_3)_2Sn]_2O(BSED)$ and the ligand $BSED\cdot H_2$, when left to stand in air in less polar solvents such as benzene, dichloromethane, and 1,2-dichloroethane, but the complex is stable over an extended period of time (months) in dichloromethane in a PMR tube sealed under high vacuum.

Configuration of $(CH_3)_2Sn(BSED)$

The X-ray powder pattern data given in the experimental section clearly indicate that two isomeric forms of $(CH_3)_2Sn(BSED)$ exist in the solid state. Both the isomers are essentially monomeric in solution (Table 1).

Figure 1 shows the infrared spectra of *cis*- and *trans*-$(CH_3)_2Sn(BSED)$ as Nujol mulls in the skeletal stretching region [6]. The appearance of our spectrum of the *trans* isomer is similar to that reported [1], although there are some discrepancies in frequency. The bands around 600, 570 and 400 cm^{-1} have been

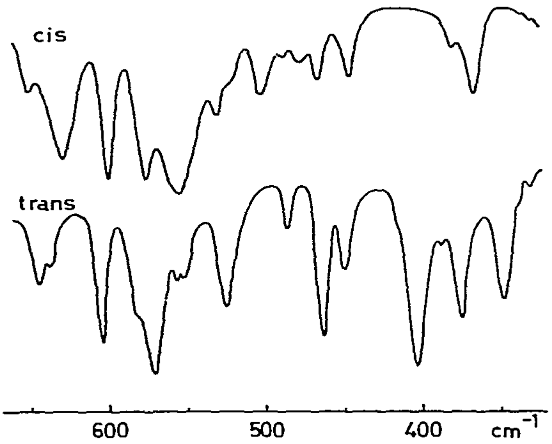


Fig. 1. Infrared spectra of *cis*- and *trans*-$(CH_3)_2Sn(BSED)$ as Nujol mulls.

tentatively assigned to ν(Sn—O), ν_{asym} (Sn—C), and ν(Sn—N), respectively [1]. However, it seems more likely to assign the band at 572 cm^{-1} to ν(Sn—O), since this is the strongest band in this region. Thus, we suggest that the shoulder at 580 cm^{-1} may be attributed to ν_{asym} (Sn—C). By a similar reasoning, the strongest and broad band at 556 cm^{-1} of the *cis* isomer is assigned to ν(Sn—O) and those at 576, 531, and 367 cm^{-1} to ν_{asym} (Sn—C), ν_{sym} (Sn—C), and ν(Sn—N), respectively. These assignments are consistent with a nearly linear C—Sn—C moiety for the *trans* isomer and a bent C—Sn—C skeleton for the *cis* isomer, although complicated mixings or overlap of several vibrational modes are possible for such complex molecules.

The clear-cut configurational assignments for the two isomers in solution have been greatly assisted by 100 MHz PMR spectroscopy. Figure 2 shows the PMR spectra of *cis* and *trans* isomers of $(CH_3)_2Sn(BSED)$ in dichloromethane and pyridine-d_5, respectively, and Table 2 summarizes the numerical data in a few solvents. Thus, the spectrum of *cis*-$(CH_3)_2Sn(BSED)$ shows doublets for each of the Sn—CH_3, =N—CH_2—, and —N=CH— protons in addition to a set of much weaker singlets for the *trans* isomer present to the extent of ca. 10% in dichloromethane. Although the —N=CH— proton apparently occurs as two signals, τ 1.87 and 1.52 in dichloromethane, the integrated intensity ratio shows that the former contains two signals. However, at high temperatures the signal at τ 1.87 is split into two components. It is noticed that the two Sn—CH_3 and —N=CH— signals have different coupling constants (Fig. 2 and Table 2), which could hardly be resolved by the use of 60 MHz spectrometers [2, 3]. On the other hand, the spectrum of the *trans* isomer shows a main set of singlets for each kind of proton together with faint signals for the *cis* isomer.

Based on a pseudooctahedron, two kinds of configurations, *cis* and *trans* shown in Fig. 3, may be envisaged for $(CH_3)_2Sn(BSED)$. Each of the two *cis* configurations has a non-superimposable mirror image and the number of the possible isomers is five altogether. The *trans* configuration is assumed to contain an almost linear C—Sn—C moiety and a symmetric BSED ligand, while the *cis* configurations have bent C—Sn—C skeletons and non-planar BSED ligands. Although X-ray crystallography shows the geometric non-equivalence of each

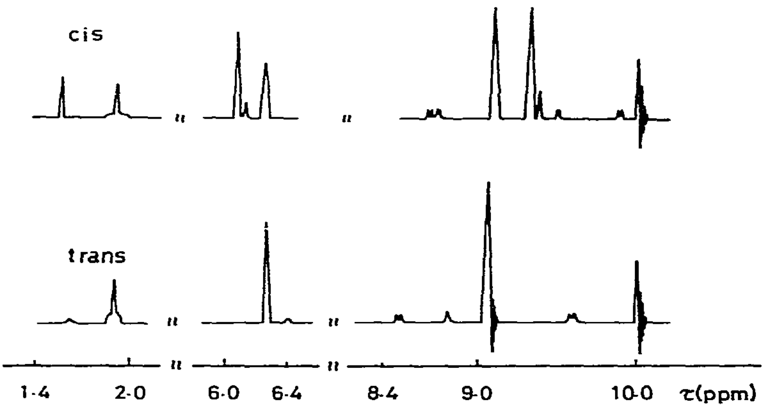


Fig. 2. PMR spectra of *cis*- and *trans*-$(CH_3)_2Sn(BSED)$ in dichloromethane and pyridine-d_5, respectively.

TABLE 2

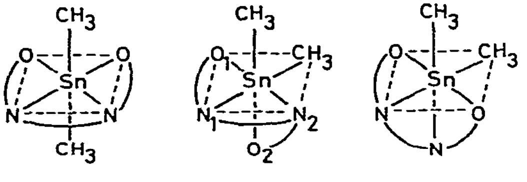
PMR PARAMETERS OF $(CH_3)_2Sn(BSED)$ IN VARIOUS SOLVENTS

Solvent	Isomer	τ(Sn—CH$_3$) (ppm)	τ(=N—CH$_2$—) (ppm)	τ(—N=CH—) (ppm)	$J(^{119}$Sn—CH$_3$) (Hz)	J(Sn←N=CH—) (Hz)
CH_2Cl_2	*trans*	9.34	6.08	1.87	111.0	8.4
	cis	9.30	6.23	1.87	116.4	15.0
		9.08	6.05	1.52	82.6	<4
$C_6D_5NO_2$	*trans*	9.20	5.95	1.80	110.7	8.6
	cis	9.22	6.21	1.88	116.3	[a]
		8.94	6.05	1.57	83.9	<4
C_5D_5N	*trans*	9.05	6.26	1.89	112.5	5.0
	cis	9.08	6.42	1.92	116.7	14.4
		8.78	6.27	1.63	83.3	<4
$CH_3CON(CH_3)_2$	*trans*	9.45	5.94	1.67	112.3	11.5
	cis	9.32	6.00	1.55	117.6	14.8
		9.11	6.13	1.28	84.7	<4

[a] Obscured by the undeuterated solvent.

kind of proton and the angle of 161° for the *trans* structure [5], it is not unreasonable to believe that the molecule might relax into a more symmetric structure in solution or undergo some rapid ring bending motion which would average the magnetic environments of each kind of proton on the NMR time scale. Thus, Sn—CH$_3$, =N—CH$_2$—, and —N=CH— protons of the *trans* configuration may be expected to occur as singlets with the $J(^{119}$Sn—CH$_3$) value of ca. 100 Hz or larger [7]. Therefore, one of the isomers, whose each kind of proton appears as a singlet with the $J(^{119}$Sn—CH$_3$) value of about 110 Hz, is assigned to have the *trans* configuration. Among the two *cis* configurations, B could have magnetically equivalent sets of each kind of proton and the $J(^{119}$Sn—CH$_3$) value would probably be much smaller than 100 Hz. Thus, the configuration B may be excluded, and the other isomer whose three kinds of proton all appear as doublets with two different $J(^{119}$Sn—CH$_3$) and J(Sn←N=CH—) values (Table 2) may be assigned to have the configuration A.

Recently a cobalt—BSED complex, Co(BSED)(acac) (acac = acetylacetonato), with a non-planar BSED has been prepared and its structure determined by an X-ray structural analysis [8]. The configuration of BSED in this complex is comparable to that of the configuration A. In addition, the X-ray structural analysis of $Co_2(BVED)_3$ has shown that the ligand configurations are similar to both the A and its mirror image [9]. Any complex with the ligand of the configuration B has never been known.



trans cis-A cis-B

Fig. 3. Possible configurations for $(CH_3)_2Sn(BSED)$.

According to the correlation given by Holmes and Kaesz [10] the $J(^{119}\mathrm{Sn{-}CH_3})$ value of 111.0 Hz will be reasonable for the *trans* isomer in dichloromethane (Table 2). However, the explanations for those values of the *cis* isomer in dichloromethane, 116.4 and 82.6 Hz, are not so straightforward. This is the first example of any dimethyltin complex that shows the existence of two different methyl groups in the molecule. An X-ray crystallographic analysis of a bis-type complex with ON bidentate ligands, dimethyltin bis(8-hydroxyquinolinate), has shown that the relative location of the coordinating atoms of the ligand is analogous to configuration B in Fig. 3, although this complex is a highly distorted octahedron [11]. Thus, both the $\mathrm{Sn{-}CH_3}$ groups may be assumed to be located *trans* to the N atoms, and the $J(^{119}\mathrm{Sn{-}CH_3})$ value is known to be 71.2 Hz in deuteriochloroform [12]. By analogy with these results, the CH_3 group of the *cis* isomer whose $J(^{119}\mathrm{Sn{-}CH_3})$ is 82.6 Hz, although somewhat larger than that of the quinolinate complex, may be assigned to be *trans* to the N_1 atom in configuration A in Fig. 3. The other CH_3 group with the $J(^{119}\mathrm{Sn{-}CH_3})$ value of 116.4 Hz is, therefore, assigned to be *trans* to the O_2 atom. Similarly, the N_2 atom of the —N=CH— group with the $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ of 15.0 Hz is *trans* to the O_1 atom and the N_1 atom, whose $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ value is smaller than 4 Hz, is *trans* to the CH_3 group.

The $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ values of $(CH_3)_2$Sn(BSED) are of the order of 10 Hz and considerably smaller than those (as large as 50 Hz in deuteriochloroform) of the dimethyltin complexes derived from ONO tridentate Schiff bases [13]. This result suggests that the Sn←N coordination in $(CH_3)_2$Sn(BSED) is much weaker than those of the latter complexes. Moreover, the coupling constants shown in Table 2 do not change so considerably as those of the latter [13], upon changing the solvents except for the $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ values of the *trans* isomer in pyridine-d_5 and *N,N*-dimethylacetamide, suggesting less interaction of the tin atom with the donor solvents and coordinative saturation in $(CH_3)_2$-Sn(BSED).

Isomerization reactions of $(CH_3)_2$Sn(BSED)

$(CH_3)_2$Sn(BSED) is found to undergo isomerization reactions in solution to form equilibrium mixtures of the *cis* and *trans* isomers, regardless of the starting isomer. Table 3 gives the equilibrium constants *K* of *cis—trans* isomerization of $(CH_3)_2$Sn(BSED) in some solvents. The *trans* to *cis* isomerization reaction takes place rather slowly (in hours) in dichloromethane and deuteriochloroform

TABLE 3

EQUILIBRIUM CONSTANT *K* [a] FOR THE *cis—trans* ISOMERIZATION OF $(CH_3)_2$Sn(BSED) AT 25°C

Starting isomer	Solvent	Concentration (10^{-2} mol/l)	*K* [a]
cis	CH_2Cl_2	8.8	0.12
cis	$C_6H_5NO_2$	6.0	0.13
trans	$C_6H_5NO_2$	6.0	0.12
cis	C_5H_5N	9.5	0.65
trans	C_5H_5N	9.5	0.67
trans	$CH_3CON(CH_3)_2$	7.5	1.3
trans	$[(CH_3)_2N]_3P{=}O$	9.5	3.5

[a] *K* = [*trans*]/[*cis*].

TABLE 4

TEMPERATURE EFFECT ON THE EQUILIBRIUM CONSTANT *K* [a] FOR THE *cis—trans* ISOMERIZATION OF $(CH_3)_2Sn(BSED)$

Solvent	$C_6H_5NO_2$		C_5H_5N	
Concn. (mol/l)	6.0×10^{-2}		9.5×10^{-2}	
	Temp. (*K*)	*K*	Temp. (*K*)	*K*
	298	0.13	298	0.67
	323	0.26	325	0.78
	343	0.35	343	0.89
	359	0.50	364	0.97
	380	0.87	383	1.08
ΔG (kcal/mol)	1.2		0.2	
ΔH (kcal/mol)	5.0		1.2	
ΔS (eu)	12.8		3.2	

[a] *K* = *[trans]*/*[cis]*.

at room temperature. This fact will account for the conclusion given by Murray et al. that $(CH_3)_2$ Sn(BSED) adopts the *cis* configuration [2]. In other words, it is likely that they measured the PMR spectrum of a deuteriochloroform solution of the *trans* isomer which had been transformed into the *cis* isomer while left to stand over a period of hours. It is certain that they originally obtained the *trans* isomer, because they recrystallized the compound from methanol. In methanol-d_4 the PMR spectrum of the complex shows the presence of the *trans* isomer only.

Although the data are rather scattered because of the limited solubility or instability of $(CH_3)_2$ Sn(BSED) in other solvents, they suggest that the *cis* isomer is favored in non-coordinating solvents (dichloromethane and nitrobenzene) and the *trans* isomer in coordinating solvents (*N*,*N*-dimethylacetamide and hexamethylphosphonamide).

Table 4 shows the temperature effect on the *K* values of $(CH_3)_2$ Sn(BSED) in two solvents. The data indicate that the *trans* isomer is favored at high temperatures in both solvents. A plot of ln *K* vs. the reciprocal of the absolute temperature is given in Figure 4 for the complex in pyridine. The data were treated

Fig. 4. A plot of ln *K* vs. the reciprocal absolute temperature for the pyridine solution of $(CH_3)_2Sn(BSED)$.

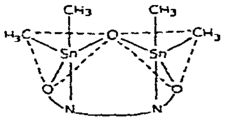
by a least squares analysis. Heats of isomerization were obtained from the plots and free energies and entropies of isomerization at 25° C were calculated. These data are also collected in Table 4. The data indicate that in both solvents the *cis* isomer is thermodynamically more stable than the corresponding *trans* form, and that heat is absorbed in the transformation of the *cis* into the *trans* form, although ΔH is rather small. ΔG^{298} is also small and ΔS is somewhat large for the nitrobenzene solution, suggesting that the isomerization process is entropy controlled. In other words, the increase in entropy upon isomerization may be attributed to the greater solvation of the more dipolar *cis* isomer so that isomerization to the *trans* form is accompanied by the release of the solvent.

In the isomerization process complete dissociation of the tetradentate ligand is unlikely, because the PMR spectrum of $(CH_3)_2Sn(BSED)$ in the presence of free ligand in dichloromethane shows both the signals due to the free and coordinated ligands. Pseudorotation through a twisting process may not be responsible for the mechanism, but probably a bond-rupture mechanism explains the isomerization process. Thus, the weak $Sn \leftarrow N$ coordination bond would be broken first, the C—Sn—C and the ligand configurations rearrange, and a new coordination formed.

Other complexes

$(CH_3)_2Sn(BSPD)\cdot CH_3OH$, $(CH_3)_2Sn(BSPhD)\cdot CH_3OH$, and $(CH_3)_2$-Sn(BVED) are essentially monomeric (Table 1), although some decompositions were observed with the former two during the measurements. The PMR spectra of these complexes in dichloromethane show a singlet for the $Sn—CH_3$ protons with the $J(^{119}Sn—CH_3)$ value of about 110 Hz and a single set of signals for other kinds of proton, suggesting the *trans* configurations. Minor signals which may be due to either the *cis* isomer or some decomposition products are observed. They do not seem to undergo the *trans* to *cis* isomerization reaction as easily as $(CH_3)_2Sn(BSED)$. Thus, several attempts to isolate their *cis* isomers turned out to be fruitless.

The PMR spectrum of the unusual complex $[(CH_3)_2Sn]_2O(BSED)$ in dichloromethane shows a doublet for the $Sn—CH_3$ protons, and singlets for the $=N—CH_2—$ and $—N=CH—$ protons. The integrated intensity ratio of these signals is 6/2/1. The absence of OH groups was confirmed by infrared and PMR spectra. Taking into consideration the formal oxidation state of four for the Sn atom, the following configuration is tentatively suggested for this complex. The molecular weight measured is in good agreement with this formula. In addition, an example of bridging BSED type ligand is already known [9].



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