Departmento of Applied Chemistry, Osaka University
Higashinoda, Miyakojima, Osaka, Japan

Far Infrared Spectra and Stereochemistry of Dimethylsulfoxide Complexes of Tin (IV),

Toshio Tanaka

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Assignments are given for the infrared spectra of bis-DMSO complexes of SnX_4 ($X=Cl$, Br and I), R_2SnCl_2 ($R=CH_3$, C_2H_5 and C_6H_5) and $(CH_3)_2SnBr_2$ in the region of 1200-100 cm^{-1}. In the first two series of complexes, the Sn-O stretching bands shift to higher frequencies with increasing electronegativity of substituents on the tin atom, indicating that the inductive effect of the substituents mainly affects the strength of the Sn-O coordination bond. The latter complex shows the Sn-O stretching band at a considerably higher frequency than would be expected from the inductive effect of the substituents. This is interpreted in terms of the difference in stereochemistry between $(CH_3)_2SnBr_2 \cdot 2DMSO$ and $R_2SnCl_2 \cdot 2DMSO$.

Introduction

It is well known that dimethylsulfoxide(DMSO) is a Lewis base which is able to coordinate to metal atoms or ions. For instance, it forms stable 2:1 adducts, with SnX_4($X=Cl$, Br and I), $RSnCl_3$ and R_2SnCl_2($R=CH_3$ and C_6H_5), and 1:1 adducts with R_3SnCl($R=CH_3$ and C_6H_5).[1-5] In the infrared studies of these adducts, the shift of S-O stretching frequency upon complex formation was pointed out.[1-3,5]

On the basis of infrared studies in the CsBr region, in which tin-halogen stretching bands may be expected, the bis-DMSO complexes of $SnCl_4$ and $SnBr_4$ were assumed to have *cis*-configuration. However, the infrared bands in this region have not yet been assigned unambiguously. Recently, Clark and Goel have suggested a *trans*-octahedral structure for $(CH_3)_2SnCl_2 \cdot 2DMSO$ from infrared study in the region of 4000-250 cm^{-1},[6] in which some absorption bands have been unassigned.

This paper reports the assignments for the infrared spectra of the series of bis-DMSO complexes of SnX_4($X=Cl$, Br and I), R_2SnCl_2($R=CH_3$, C_2H_5 and C_6H_5) and $(CH_3)_2SnBr_2$ in the region of 1200-100 cm^{-1}, and the assignments are correlated with their stereochemistry; for the $(CH_3)_2SnCl_2 \cdot 2DMSO$ partly different assignments from Clark and Goel's and an alternative stereochemistry are presented.

Experimental Section

Preparation of complexes. The bis-DMSO complexes of tin tetrahalides and diorganotin dihalides were prepared by the reaction of the corresponding tin(IV) compounds with DMSO (mole ratio of 1:2) in the following solvents; CCl_4 for $SnX_4 \cdot 2DMSO$($X=Cl$, Br and I) and $(CH_3)_2SnBr_2 \cdot 2DMSO$, and ether for $R_2SnCl_2 \cdot 2DMSO$($R=CH_3$, C_2H_5 and C_6H_5). Except for $SnI_4 \cdot 2DMSO$ which is a brownish orange powder, these complexes are white crystals. The melting points and the analytical data are shown in Table I.

Table I. Melting points and analytical data of bis-DMSO complexes of tin(IV)

Complexes	m. p. (°C)	C % Anal. (Calcd.)	H % Anal. (Calcd.)
$SnCl_4 \cdot 2DMSO$	Decomp. >270	11.73	3.05
	Decomp. 270-300[a]	(11.53)	(2.90)
	287[b]		
$SnBr_4 \cdot 2DMSO$	Decomp. >215	8.17	2.10
	Decomp. 198-204[a]	(8.08)	(2.03)
$SnI_4 \cdot 2DMSO$	Decomp. >80	7.01	2.17
	Decomp. 167-168[a]	(6.14)	(1.55)
$(C_6H_5)_2SnCl_2 \cdot 2DMSO$	134-135	38.36	4.46
	135[b]	(38.43)	(4.44)
$(CH_3)_2SnCl_2 \cdot 2DMSO$	110-110.5	19.04	4.85
	113[b]	(19.17)	(4.83)
$(C_2H_5)_2SnCl_2 \cdot 2DMSO$	64	24.30	5.57
		(23.78)	(5.49)
$(CH_3)_2SnBr_2 \cdot 2DMSO$	119-120	15.21	4.05
		(15.50)	(3.90)

[a] Ref. 3. [b] *Ref.* 5.

Infrared spectra. The infrared spectra were measured in nujol and in hexachlorobutadiene mulls by means of a Hitachi EPI-2G spectrophotometer(5000-400 cm^{-1}) and in solid paraffin of low melting point using a Hitachi FIS-1 spectrophotometer(500-80 cm^{-1}), both equipped with gratings. The former was calibrated by a polystyrene film(0.05 mm thickness), CO_2 gas and H_2O vapor, and the latter by H_2O vapor. The spectrum of a DMSO solution of $(CH_3)_2SnCl_2$ (about 7 wt. %) was also measured.

Nmr spectrum. The nmr spectrum of $(CH_3)_2SnBr_2$ in DMSO (about 2 wt. %) was measured at 60 Mc./sec. on a Japan Electron Optics JNM-3H-60 spectrometer at room temperature.

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(1) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, *82*, 2986 (1960).
(2) F. A. Cotton, R. Francis and W. D. Horrocks Jr., *J. Phys. Chem.*, *64*, 1534 (1960).
(3) M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 3224 (1961).
(4) I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964).
(5) H. G. Langer and A. H. Blut, *J. Organometal. Chem.*, *5*, 288 (1966).
(6) H. C. Clark and R. G. Goel, *J. Organometal. Chem.*, *7*, 263 (1967).

Table II. Infrared wave numbers and the modes of vibration for the bis-DMSO complexes of SnX_4(X=Cl, Br and I), R_2SnCl_2(R=C_6H_5, CH_3 and C_2H_5) and $(CH_3)_2SnBr_2$.

Modes of vibration	DMSO gas[a]	DMSO liquid	$SnCl_4$.2DMSO	$SnBr_4$.2DMSO	SnI_4.2DMSO	$(C_6H_5)_2SnCl_2$.2DMSO	$(CH_3)_2SnCl_2$.2DMSO	$(C_2H_5)_2SnCl_2$.2DMSO	$(CH_3)_2SnBr_2$.2DMSO[b]
R—branch ν(S—O) P—branch	1111 sh 1102 vs 1094 sh	1045 vs 1028 sh	923 vs 907 vs	911 vs	928 vs 908 sh	952 sh 946 vs	948 sh 942 s	956 m 941 vs	952 m 942 vs
CH_3 rocking	1016 m		1036 s	1034 s	1033 s	1021 m	1035 m	1038 m	1041 m
	1006 m	954 s	991 s	988 s	988 s	993 s	1000 s	997 s	990 s
	929 w	931 s	950 m	948 sh	943 sh	985 s	994 s		
	915 w	897 w				935 m	911 w	917 sh	918 w
ν_{asym}(C—S)	689 m	698 s	726 m	726 m	723 m	719 m	719 m 716 m	713 m	719 m
ν_{sym}(C—S)	672 m	667 m	685 m	683 vw	683 vw	?	680 vw	?	?
ν_{asym}(Sn—C)	—	—	—	—	—	264 m	575 m	532 m	575 m
ν_{sym}(Sn—C)	—	—	—	—	—	244 sh	507 vw	481 w	—
ν(Sn—O)	—	—	482 s	471 s, br	459 s, br	421 s, br	420 sh	413 m, br	430 s, br
	—	—	477 s		451 s, br	410 sh	414 s, br	406 m, br	419 sh
δ(C—S—O)		382 s	331 s	339 m	336 m	343 m	342 m	348 m	333 m
		333 s	302 m	314 w	310 w	314 w	312 m	318 w	315 m
ν(Sn—X)	—	—	339 s	236 s	194 s, br	229 s	244 s, br	238 s, br	
	—	—	321 s	226 s	146 m	201 m	187 sh(?)	?	
	—	—	279 sh			—	—	—	
	—	—	271 m	183 m	140 sh	—	—	—	
?	—	—	224 w, br	204 sh	209 sh	—	—	—	—
δ(octahedral)	—	—	193 w	157 w	111 w	164 m	168 m	154 m, br	
	—	—	177 w	139 w	89 sh	155 m	156 sh	130 sh	
	—	—	163 m	107 m	86 m	125 sh	125 w	120 m, br	
	—	—	155 sh	101 sh					
	—	—	148 m						
Inner vibrations of substituents on tin.	—	—	—	—	—	1028 w 1003 s 745 s 742 s 698 s 465 s 461 s 378 m 361 s 293 s	787 s, br	684 m, br 292 w	786 s, br

[a] Ref. 7. [b] Was not measured below 200 cm^{-1}.

Results and Discussion

Infrared spectra. Assignments of the infrared spectrum and a normal coordinate analysis of the DMSO molecule have been made by Horrocks and Cotton.[7] Using their results, the infrared spectra of tin(IV)-DMSO complexes in the present study can be assigned easily, except for the low frequency region. The observed frequencies for the series of tin(IV)-DMSO complexes and their probable assignments are given in Table II, together with those of DMSO molecule in the gas[7] and in the liquid states. Also the spectra in low frequency region are shownin Fig. 1-3.

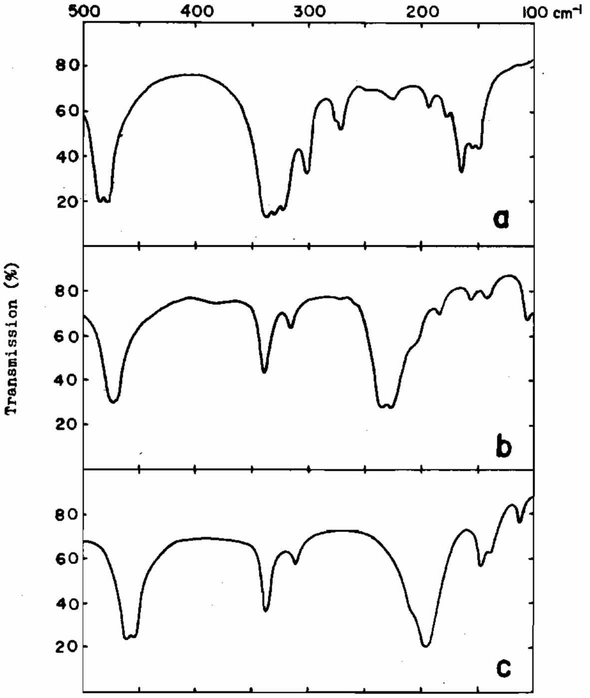

Figure 1. Far infrared spectra of $SnCl_4$.2DMSO (a), $SnBr_4$.2DMSO (b) and SnI_4.2DMSO (c).

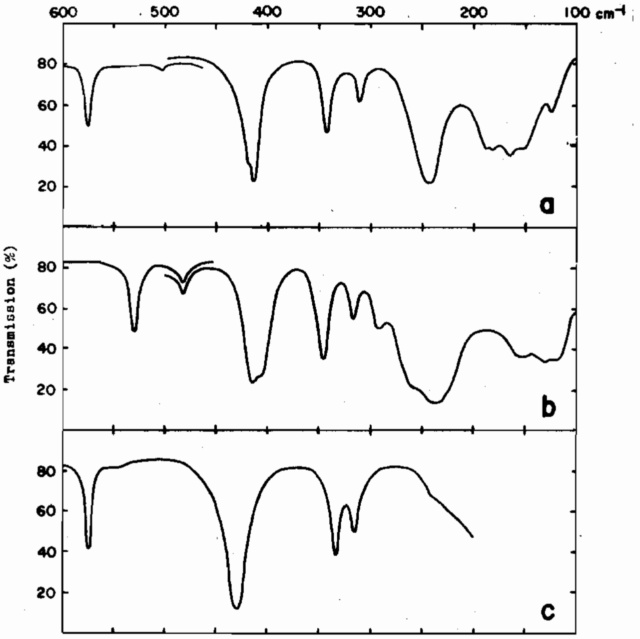

Figure 2. Far infrared spectra of $(CH_3)_2SnCl_2$.2DMSO (a), $(C_2H_5)_2SnCl_2$.2DMSO (b) and $(CH_3)_2SnBr_2$.2DMSO (c).

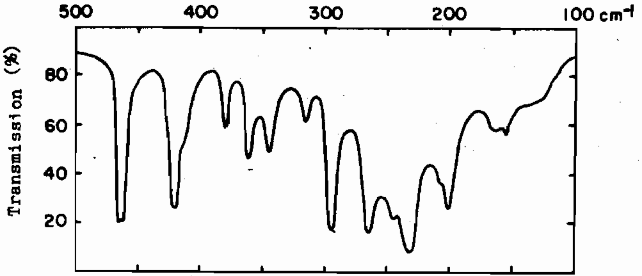

Figure 3. Far infrared spectra of $(C_6H_5)_2SnCl_2$.2DMSO.

Table II shows that complex formation causes the shifts of S-O stretching band to lower frequencies, indicating coordination through the oxygen atom of the DMSO, as already mentioned in the bis-DMSO complexes of tin(IV)[2,3,5] and of several transition metal ions.[2] In accordance with this, characteristic strong bands assigned to Sn-O stretching mode have been observed in the region of 490-410 cm^{-1}, which are notably high frequencies for a pure $O \rightarrow Sn$ coordination bond. This band shifts to higher wave numbers with increasing electronegativity of substituents on the tin atom. However, in the case of $(CH_3)_2SnBr_2 . 2DMSO$ the Sn-O stretching band occurs at an unexpected high frequency (Table II). Similar behaviour of the Sn-O stretching frequency was mentioned by us in reporting the infrared spectra of YZSn(acetylacetonate)$_2$ (Y, Z = Cl, Br, I, alkyl and aryl), and it was assumed that the inductive effect of substituents on the tin atom mainly affects the Sn-O coordination bond strength.[8]

For the solid complex $(CH_3)_2SnCl_2 . 2DMSO$ Clark and Goel reported an infrared band at 720 cm^{-1}. However the band has here been resolved into doublet at 719 and 716 cm^{-1}, which can be assigned to asymmetric C-S stretching mode. The reason for the splitting is not clear. The other complexes show the single peak. Although the asymmetric C-S stretching frequency is also sensitive to complex formation, the magnitude of the shifts are not so large as the S-O stretching one. The symmetric C-S stretching band has been recorded as a weak band in the bis-DMSO complexes of SnX_4(X = Cl, Br and I) and $(CH_3)_2SnCl_2$, but not the others. This is due to the lowering intensity with complex formation.

The solid $(CH_3)_2SnCl_2 . 2DMSO$ has given a weak band at 507 cm^{-1}, in agreement with Clark and Goel's observation.[6] The author assigns this band to symmetric Sn-C stretching vibration, though it is much less intense than the asymmetric Sn-C stretch at 575 cm^{-1} (Fig. 2a). Similarly, absorption bands of $(C_2H_5)_2SnCl_2 . 2DMSO$ at 532 and 481 cm^{-1} can be assigned to asymmetric and symmetric Sn-C stretching modes, respectively (Fig. 2b). On the contrary, the solid complex $(CH_3)_2SnBr_2 . 2DMSO$ gives only asymmetric Sn-C stretching band at 575 cm^{-1}, but not the symmetric one (Fig. 2c), suggesting that the configuration may differ from those of $R_2SnCl_2 . 2DMSO$ ($R = CH_3$ and C_2H_5).

The far infrared spectra of $SnX_4 . 2DMSO$ (X = Cl, Br and I) show single or split strong bands assigned to Sn-X stretching vibration, followed by some absorption bands with lower intensity, which may also be associated with the Sn-X stretch (Fig. 1). Although a band of $(CH_3)_2SnCl_2 . 2DMSO$ at 312 cm^{-1} was previously ascribed to Sn-Cl stretching mode,[6] all bis-DMSO complexes in the present work show two absorption bands around 310 and 340 cm^{-1}. Thus it is reasonable to assign these bands to symmetric and asymmetric C-S-O deformational modes, which are considered to shift to the lower frequencies with complex formation.

In the present work covering much lower infrared region the solid $(CH_3)_2SnCl_2 . 2DMSO$ has given a characteristic strong band at 244 cm^{-1}, but not 255 cm^{-1} reported by Clark and Goel.[6] The $(C_2H_5)_2SnCl_2 . 2DMSO$ shows the corresponding band at 238 cm^{-1}. There is no ambiguity for assigning these strong bands to Sn-Cl stretching vibration.

The solid complex $(C_6H_5)_2SnCl_2 . 2DMSO$ gives a complicated spectrum in the far infrared region (Fig. 3). In spite of this, the tentative assignments can be made easily by referring to the far infrared spectrum of diphenyltin dichloride.[9] Thus the bands at 421 and 229 cm^{-1} are associated with the Sn-O and the Sn-Cl stretching modes, respectively, because of their strong intensities. Both of these are followed by a shoulder at 410 cm^{-1} or a band of medium intensity at 201 cm^{-1}, which would be due to the Sn-O and the Sn-Cl stretching vibrations, respectively. Two other bands at 264 and 244 cm^{-1} would be associated with the Sn-C stretching modes.

One might expect to observe lattice vibrations of the tin(IV)-DMSO complexes in the low frequency region. From the present study, however, the absorption bands in this region can be associated with the deformational modes of the octahedral skeleton of tin (see Table II).

Stereochemistry. We shall assume the presence of discrete hexa-coordinated octahedral species for the solid complexes $SnX_4 . 2DMSO$ (X = Cl, Br and I), and disregard coupling between the Sn-X and the DMSO vibrations. Then for the *trans*-configuration only one infrared active fundamental Sn-X stretching vibration is predicted.[10] Although for the *cis*-configuration four infrared active fundamentals associated with Sn-X stretch are predicted,[11] these are not necessarily resolved. Thus it has been suggested for the *cis*-configuration that at least two fundamentals are expected to be observed.[10] Bipyridyl complex of $SnCl_4$, with the chlorine atoms necessarily in *cis*-positions, shows three bands possibly assigned to Sn-Cl vibration at 324 (s, br), 283 (m) and 251(w) cm^{-1};[12] the former two frequencies were already reported.[10] Similar complexity of the spectra is found for the $SnX_4 . 2DMSO$ (Fig. 1), clearly indicating a *cis*-stereochemistry for these complexes (Fig. 4), in agreement with the assumption by the previous workers (see ref. 4).

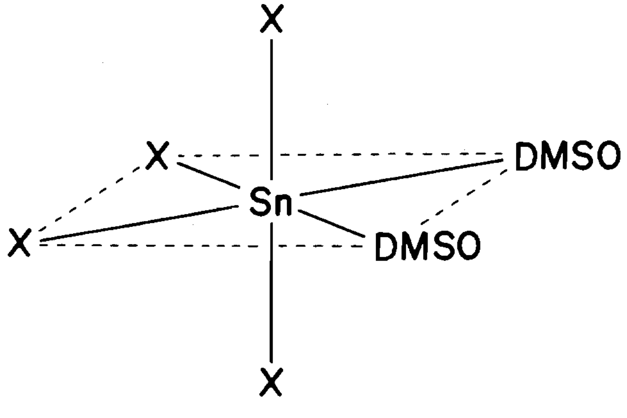

Figure 4. *Cis*-configuration of $SnX_4 . 2DMSO$ (X = Cl, Br and I).

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[7] W. D. Horrocks and F. A. Cotton, *Spectrochim. Acta*, *17*, 134 (1961).

[8] Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, *22*, 1571 (1966).

[9] R. C. Poller, *Spectrochim. Acta*, *22*, 935 (1966).

[10] I. R. Beattie, G. P. McQuillan, L. Rule and M. Webster, *J. Chem. Soc.*, 1514 (1963).

[11] I. R. Beattie, T. Gilson, M. Webster and G. P. McQuillan, *J. Chem. Soc.*, 238 (1964).

[12] T. Tanaka, to be published.

A comparison of infrared spectra in the region of 600-200 cm^{-1} between the solid complex $(CH_3)_2SnCl_2$. .2DMSO and a solution of $(CH_3)_2SnCl_2$ in DMSO is shown in Table III. The former spectrum closely resembles the latter, except for the region of 390-320 cm^{-1} obscured by the solvent. Only difference in these spectra is that the absorption bands of a DMSO solution of $(CH_3)_2SnCl_2$ are somewhat broad compared to those of the solid complex. Recently it has been suggested from nmr studies of $(CH_3)_2SnCl_2$ and its bis-DMSO complex in solution that the displacement of chloride from tin by DMSO molecule may be involved in the dissolution process:[13]

$$(CH_3)_2SnCl_2 + xDMSO \rightarrow (CH_3)_2Sn^{++}(DMSO)_x + 2Cl^-$$

However, if we assume the presence of discrete hexa-coordinated octahedral species for the solid $(CH_3)_2SnCl_2$.2DMSO, the present infrared observations suggest that the geometry around the tin atom is similar to that when $(CH_3)_2SnCl_2$ is dissolved in DMSO.

Table III. The comparison of the infrared spectra of $(CH_3)_2SnCl_2$. 2DMSO and a DMSO solution of $(CH_3)_2SnCl_2$ in the region of 600-200 cm^{-1}.

	$\nu_{asym}(Sn—C)$ cm^{-1}	$\nu_{sym}(Sn—C)$ cm^{-1}	$\nu(Sn—O)$ cm^{-1}		$\nu(Sn—Cl)$ cm^{-1}	$\frac{I_{\nu_{sym}}(Sn—C)}{I_{\nu_{asym}}(Sn—C)}$
$(CH_3)_2SnCl_2$. 2DMSO	575 m	507 w	421 sh	414 s, br	244 s, br	0.10
DMSO solution of $(CH_3)_2SnCl_2$	575 m	507 w	420 sh	413 s, br	247 s, br	0.11

The DMSO solution of $(CH_3)_2SnCl_2$ shows fairly large Sn-CH$_3$ proton spin interactions: $J_{^{119}Sn\text{-}CH_3} = 113$ cps. and $J_{^{117}Sn\text{-}CH_3} = 107$ cps.[13] Interpolation from the function[14] relating $J_{^{119}Sn\text{-}CH_3}$ to the apparent *s*-character of tin atomic orbital in the Sn-C bond indicates greater than 50% *s*-character, suggesting a linear geometry for the $(CH_3)_2Sn$ moiety.[13]

Bipyridyl complex of dimethyltin dichloride, $(CH_3)_2SnCl_2$.bipy, with the chlorine atoms necessarily in *cis*-positions,[15] shows three infrared bands in the Sn-Cl stretching region; 243(vs)*, 215(m) and 200(m) cm^{-1}. The former band and either of the latter two can be assigned to fundamental Sn-Cl stretching vibrations.[12] Recently, we have reported on the basis of infrared[8] and nmr spectra[16] that bis(acetylacetonato) tin dichloride, $Cl_2Sn(acac)_2$, has a octahedral *trans*-configuration in both solid and solution. This complex shows only one Sn-Cl stretching band at 345 cm^{-1},[17] which is fairly higher frequency than the corresponding bands observed for the $(CH_3)_2SnCl_2$.2DMSO and the $(CH_3)_2SnCl_2$.bipy. This would be associated with the difference in relative positions of the chlorine atoms among these complexes. Thus for the $(CH_3)_2SnCl_2$. .2DMSO it is reasonable to assign a *cis*-configuration with respect to the chlorine atoms (Fig. 5), though a *trans*-form has been assumed by Clark and Goel.[6]

From Fig. 5, two Sn-Cl stretching bands, asymmetric and symmetric, would be predicted. However, the band assigned to the asymmetric stretch is quite broad (Fig. 2a) and the band due to the symmetric vibration is probably obscured by it. While, the symmetric stretching vibration of colinear C-Sn-C linkage could be coupled with the Sn-O stretch to give a weak infrared band at 507 cm^{-1}, when the two DMSO molecules are in *cis*-positions with respect to each other.

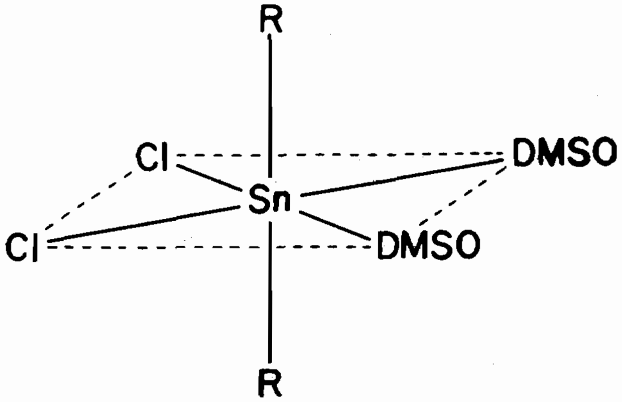

Figure 5. Configuration of R_2SnCl_2 . 2DMSO (R = CH_3, C_2H_5 and C_6H_5).

As already mentioned the solid complex $(CH_3)_2SnBr_2$. .2DMSO shows only one infrared band in the Sn-C stretching region (Fig. 2c). The proton spectrum of a DMSO solution of $(CH_3)_2SnBr_2$ also gives a large spin coupling constant between ^{119}Sn and CH$_3$ protons (110 cps.), indicating that the $(CH_3)_2Sn$ moiety of $(CH_3)_2SnBr_2$ in DMSO is substantially identical configuration with that of $(CH_3)_2SnCl_2$ in the same solvent. From these observations, the $(CH_3)_2SnBr_2$.2DMSO is most likely to have a *trans*-configuration, as is diagrammed in Fig. 6. This configuration would account for the unexpected high frequency of Sn-O stretching band in this complex as described above.

The bis-DMSO complexes of $(C_2H_5)_2SnCl_2$ and $(C_6H_5)_2SnCl_2$ are assumed to have the similar geometry around the tin atom to the corresponding dimethyltin dichloride complex, because their Sn-O stretching frequencies are those which would be expected from the inductive effect of the substituents. This configuration is supported by the occurrence of two Sn-Cl vibrations

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(13) W. Kitching, *Tetrahedron Letters*, 3689 (1966).
(14) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, *83*, 3903 (1961).
(15) J. P. Clark and C. J. Wilkins, *J. Chem. Soc.*, 871 (1966).
(*) Clark and Wilkins reported that the Sn-Cl absorption band is very broad, with evidence of four components; 255 (sh), 248 (sh), 240 (s) and 227 (sh) cm^{-1}, which were poorly resolved. Although the four components have also been observed in the present work, the three shoulders are not likely to be due to fundamental Sn-Cl stretching modes.
(16) Y. Kawasaki and T. Tanaka, *Inorg. Nucl. Chem. Letters*, 3, 13 (1967).
(17) Y. Kawasaki and T. Tanaka, to be published.

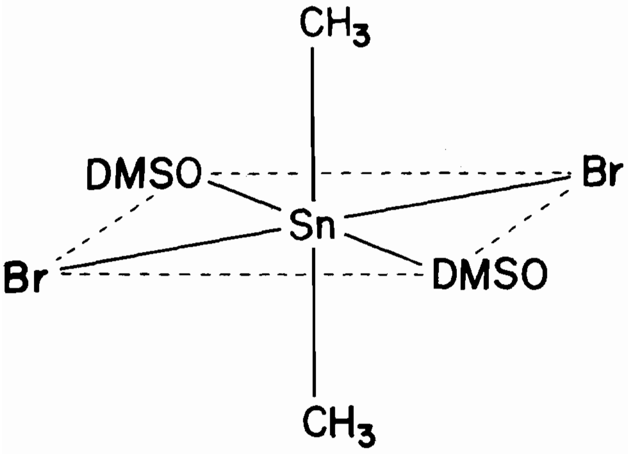

Figure 6. *Trans*-configuration of $(CH_3)_2SnBr_2 \cdot 2DMSO$.

in the diphenyltin dichloride complex. Considerable intensities of the symmetric Sn-C stretching band in these complexes may be due to coupling with the inner vibrations of ethyl or phenyl groups as well as the Sn-O vibration.

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