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Dimethylselenoxide Complexes of Tin(IV): Far Infrared Spectra and Stereochemistry

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Bis-dimethylselenoxide complexes of $SnCl_4$, R_2SnCl_2 ($R=CH_3$, C_2H_5 and C_6H_5) and $(CH_3)_2SnBr_2$ were prepared, and the infrared spectra in the region of 1000-80 cm^{-1} were tentatively assigned. The spectra indicate that dimethylselenoxide coordinates to the tin atom through oxygen, and that the coordinating power is comparable with that of dimethylsulfoxide. The far infrared spectra suggest a cis-*configuration for the $SnCl_4$ complex, and* trans-*alkyl and* cis-*halogen configurations for the dialkyltin dihalide complexes. The configuration of the 1 : 1 adduct of $(CH_3)_2SnCl_2$ with dimethylselenoxide is also proposed.*

Introduction

Although diorganoselenoxides are Lewis bases which are able to coordinate to metal compounds, their coordinating ability has not been studied as extensively as that of the corresponding sulfoxides. Recently, Paetzold and Vordank[1] reported the preparation and infrared spectra of diphenylselenoxide (DPSeO) complexes of several metal chlorides. Reflection spectra and magnetic moments of some of them were measured. Jensen and Krishnan,[2] in a paper which appeared during the course of the present work, reported infrared spectra of dimethylselenoxide (DMSeO) complexes of some transtiion metal chlorides. It was found in these studies that the Se–O stretching frequency was lowered for all the complexes studied, indicating the coordination of DPSeO and DMSeO through oxygen.

This paper reports the preparation of bis-DMSeO complexes of $SnCl_4$, R_2SnCl_2 ($R=CH_3$, C_2H_5 and C_6H_5) and $(CH_3)_2SnBr_2$, and their infrared spectra in the region of 1000-80 cm^{-1}. The spectra are tentatively assigned, and the stereochemistry (apart from that of the $(C_6H_5)_2SnCl_2$ complex) is suggested on the basis of the spectra. A 1: 1 adduct of $(CH_3)_2SnCl_2$ with DMSeO is also described.

Experimental Section

Dimethylselenoxide was prepared by the method described in the literature;[3] m.p. 84-86°C (lit. 86°C,[3] 94°C[4]). The bis-DMSeO complexes were synthesized under an atmosprere of nitrogen. When a dichloromethane solution of $SnCl_4$ was added to DMSeO in dichloromethane (mole ratio of about 1:2), the 1:2 adduct immediately precipitated. $(CH_3)_2SnCl_2$, $(C_2H_5)_2SnCl_2$, $(C_6H_5)_2SnCl_2$ and $(CH_3)_2SnBr_2$ reacted with DMSeO in a similar manner to give white crystals of the 1:2 adducts after the solutions had been standing for a day. These adducts were washed several times with dichloromethane and dried under reduced pressures. The melting points and analytical data are listed in Table I. The adducts are almost insoluble in common organic solvents and are decomposed by water.

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

Complexes	m.p. (°C)	C% Found (Calcd.)	H% Found (Calcd.)	Se% Found (Calcd.)
$SnCl_4.2DMSeO$	151-152 (decomp.)	9.36 (9.41)	2.39 (2.37)	
$(C_6H_5)_2SnCl_2.2DMSeO$	158-160	32.35 (32.36)	3.82 (3.73)	26.33 (26.59)
$(CH_3)_2SnCl_2.2DMSeO$	188-189	15.27 (15.43)	3.95 (3.86)	33.15 (33.62)
$(C_2H_5)_2SnCl_2.2DMSeO$	159-160	19.22 (19.30)	4.85 (4.45)	31.14 (31.72)
$(CH_3)_2SnBr_2.2DMSeO$	119-120	13.08 (12.90)	3.22 (3.25)	28.49 (28.27)

When a dichloromethane-carbon tetrachloride solution of DMSeO was added to an excess of $(CH_3)_2SnCl_2$ in carbon tetrachloride, a white precipitate was obtained. From the elemental analysis, this precipitate was found to be a mixture of the 1: 1 and 1:2 adducts, but the former has not been isolated.

Tin tetrabromide reacted with DMSeO in dichloromethane to give a precipitate of the 1:2 adduct (117-119°C, decomp.). This adduct is sensitive to moist air, and no analytically pure sample has been obtained. Similarly, adducts of SnI_4 and $(CH_3)_2SnI_2$ with DMSeO were obtained, but they liberated iodine quite rapidly in solution and were not isolated.

Infrared spectra. The spectra were recorded in nujol mulls on Hitachi EPI-2G (5000-400 cm^{-1}) and

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(1) R. Paetzold and P. Vordank, Z. *anorg. allgem. Chem.*, *347*, 294 (1966).

(2) K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, *21*, 1988 (1967).

(3) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962).

(4) R. Pactzold, U. Lindner, G. Bochman, and P. Reich, Z. *anorg. allgem. Chem.*, 352, 295 (1967).

EPI-L (700-200 cm^{-1}) grating spectrophotometers, and in solid paraffin of low melting point on a Hitachi FIS-1 vacuum grating spectrophotometer (500-80 cm^{-1}). These spectrophotometers were calibrated by a polystyrene film, CO_2 gas and H_2O vapor.

Results and Discussion

Infrared spectra. The spectra of bis-DMSeO complexes of tin(IV) have been assigned by comparison with those of the corresponding DMSO complexes (where DMSO = dimethylsulfoxide), which were previously reported by one of the authors.[5] The observed frequencies and their probable assignments are listed in Table II. Also, the far infrared spectra are shown in Figure 1.

Table II shows that the Se–O stretching band shifts 60-100 cm^{-1} to a lower frequency upon complex formation, indicating the coordination of DMSeO through oxygen atom. The magnitude of this shift is considerably smaller than that of the S–O stretching frequency of DMSO upon coordination, in which it was 150-200 cm^{-1}.[5] Apart from a band at 464 cm^{-1} in the diphenyltin dichloride complex, characteristic strong bands in the region of 480-380 cm^{-1} can be unambiguously assigned to the Sn–O stretching mode. These frequencies are somewhat lower than those of the corresponding bis-DMSO complexes.[5] When the mass difference between selenium and sulfur atoms is taken into account, these results would suggest that the coordinating power of DMSeO to the tin atom is comparable with that of DMSO.

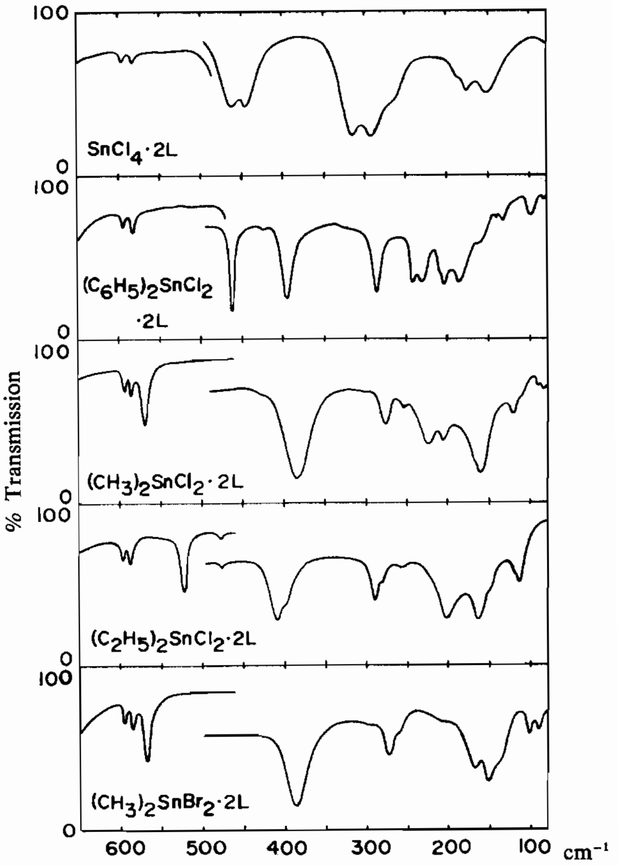

Figure 1. Far infrared spectra of bis-DMSeO complexes of tin(IV), L=DMSeO.

Table II. Infrared frequencies and the assignments for DMSeO complexes of tin(IV)[a]

Modes of vibration	DMSeO KBr disk[b]	nujol	$SnCl_4$. 2DMSeO	$(C_6H_5)_2SnCl_2$. 2DMSeO	$(CH_3)_2SnCl_2$. 2DMSeO	$(C_2H_5)_2SnCl_2$. 2DMSeO	$(CH_3)_2SnBr_2$. 2DMSeO	Mixture of $(CH_3)_2SnCl_2$ 1:1 and 1:2 adducts with DMSeO[c]
CH_3 rocking	978 s	942 s	971 s	964 m	982 s	981 m	978 m	982 m
	920 s	904 w	918 m	911 w	918 s	931 m	920 m	918 w
	893 m	884 m	903 w	897 w	899 w	913 w	900 w	900 sh
	865 m		876 w	862 w	881 m	880 m	879 m	882 w
ν(Se—O)	820 vs	813 vs	756 vs, br	761 vs, br	737 vs, br	744 vs, br	735 vs, br	739 vs, br
			740 s					
ν_{asym}(Se—C)	578 s	574 w	598 w	594 w	594 m	595 m	598 m	599 w
ν_{sym}(Se—C)		565 w	583 w	581 w	583 m	584 m	584 m	587 w
ν_{asym}(Sn—C)	—	—	—	287 s	569 m	521 m	569 m	578 m (570 sh)
ν_{sym}(Sn—C)	—	—	—	244 m		475 w		512 m
ν(Sn—O)	—	—	466 s, br	395 s, br	387 s, br	407 s, br	387 s, br	442 s, br
	—	—	445 s, br			400 sh		(388 m, br)
δ(DMSeO)	283[d]		265 sh[e]	?	277 m	282 sh	271 m	?
	249[d]				253 w	260 sh (?)	261 sh	?
ν(Sn—halogen)	—	—	319 vs, br	232 m	227 m	203 s, br	171 m	264 s, br
	—	—	293 vs, br	207 m	206 m		155 s	(226 m, br)
?			190 sh	185 m				
δ(octahedral)	—	—	179 m	160 w	159 s	163 s	155 s	
	—	—	165 sh	132 w	123 w	116 m	140 sh	
	—	—	152 m	100 m	93 m		104 m	
	—	—			86 m		89 m	
Inner vibrations of substituents on the tin atom				998 m	798 sh	677 s, br	798 sh	797 s
	—	—	—	742 s	777 s	291 m	774 s	765 sh
				701 s				
				464 s				

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. [b] Ref. 4. [c] Wave numbers in parenthesis are those of the 1:2 adduct. Also the spectrum below 200 cm^{-1} was not measured. [d] Raman lines of the 50% aqueous solution. [e] It might be more reasonable to assign to ν(Sn–Cl).

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(5) T. Tanaka, *Inorg. Chim. Acta, 1,* 217 (1967).

Less intense pairs of bands in the 600-580 cm^{-1} range are due to Se–C stretchings, and these frequencies are about 20 cm^{-1} higher than those of the free DMSeO molecule. A similar high frequency shift upon coordination was previously reported for S–C stretching frequencies of DMSO.[5]

The complexes $(CH_3)_2SnX_2 . 2DMSeO$ (where X=Cl and Br) showed the Sn–C asymmetric stretching band at 569 cm^{-1}, but not the symmetric one. In the diethyltin dichloride complex, however, both occured as infrared active bands, although the symmetric one is not intense. The diphenyltin dichloride complex exhibited four distinct absorptions from 300 to 200 cm^{-1}, in which region the Sn-phenyl stretching band is expected to be observed[6] as well as Sn–Cl stretching and DMSeO deformation bands. The highest two in this region, 287 and 244 cm^{-1}, are presumably due to the Sn-phenyl stretching vibrations.

The tin tetrachloride complex showed two fairly strong bands at 319 and 293 cm^{-1}, which can be assigned to Sn–Cl stretching modes. For the dialkyltin and diphenyltin dichloride complexes, medium intense bands in the 240-200 cm^{-1} range may also be associated with Sn–Cl stretching, since this vibrational mode of the corresponding bis-DMSO complexes was reported to occur in the same frequency region.* The dimethyltin dibromide complex showed two strong bands in the Sn–Br stretching region;** 171 and 155 cm^{-1}.

Recently, Jensen and Krishnan[2] reported three weak infrared bands near 385 cm^{-1} for the free DMSeO molecule, and these bands have been assumed to be due to C–Se–O bending. In the present study, however, these bands have not been observed. Skeletal bending vibrations of DMSeO molecule were previously reported to occur at 283 and 249 cm^{-1} in the Raman spectrum for the aqueous solution.[4] Bis-DMSeO complexes of tin(IV), except that of $(C_6H_5)_2SnCl_2$, showed one or two weak bands in this region, which may be assigned to C–Se–O or C–Se–C bending. In the diphenyltin dichloride complex these deformation bands would be obscured by more intense Sn-phenyl stretchings.

Table II also shows observed infrared frequencies for a mixture of 1:1 and 1:2 adducts of dimethyltin dichloride with DMSeO. The spectrum in the low frequency region is given in Figure 2, in which a shoulder at 570 cm^{-1} and bands at 388 and 226 cm^{-1} are assigned to Sn–C, Sn–O and Sn–Cl stretching vibrations of the 1:2 adduct, respectively, because these frequencies are very close to those of the analytically pure 1:2 adduct, $(CH_3)_2SnCl_2 . 2DMSeO$. The remaining bands below 580 cm^{-1} must therefore be ascribed to the 1:1 adduct. Thus, bands of 578 and 512 cm^{-1} can be assigned to asymmetric and symmetric Sn–C stretchings, and those of 442 and 264 cm^{-1} to Sn–O and Sn–Cl stretchings, respectively. In this case, DMSeO deformation bands may also be obscured by the strong Sn–Cl stretching band.

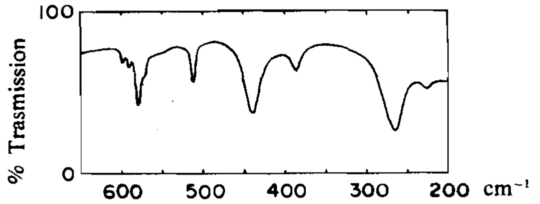
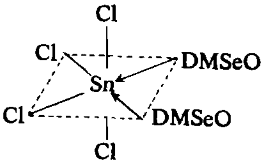


Figure 2. Far infrared spectrum of a mixture of 1:1 and 1:2 adducts of $(CH_3)_2SnCl_2$ with DMSeO.

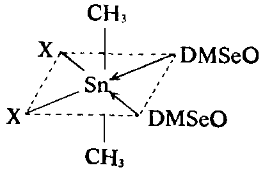
The adducts in the present study are believed to be non-ionic crystals, because of the appearance of Sn-halogen stretching bands as well as Sn–O and, in some adducts, Sn–C stretching band. In such cases, the lattice vibrations may be expected to occur in an extremely low frequency region; probably below 80 cm^{-1}. Therefore, infrared bands in the region of 185-80 cm^{-1} may substantially be associated with skeletal deformation vibrations around the tin atom, except the case of the dimethyltin dibromide complex, in which large vibrational couplings may exist between the Sn–Br stretching and the skeletal deformations.

Stereochemistry. We shall assume the presence of discrete hexa-coordinated octahedral species for the solid complex $SnCl_4 . 2DMSeO$ and disregard coupling between Sn–Cl and DMSeO vibrations. Then for the *trans*-configuration only one infrared active ν(Sn–Cl) and ν(Sn–O) fundamental is predicted, while for the *cis*-configuration, four infrared active ν(Sn–Cl) and two infrared active ν(Sn–O) fundamentals are predicted. However, these are not necessarily resolved but it has been suggested that for the ν(Sn–Cl), at least two fundamentals are expected to be observed.[7] In the present work, the tin tetrachloride complex showed two Sn–Cl and two Sn–O stretching bands, suggesting the *cis*-configuration (I).



(I)

The dimethyltin dichloride and dibromide 1:2 adducts exhibited only one Sn–C stretching in their infrared spectra. Also the Sn-halogen stretching bands were clearly resolved. On the similar assumption to the case of $SnCl_4 . 2DMSeO$, these results are suggestive of the *trans*-methyl and *cis*-halogen configuration (II), although the Sn–O stretching has not been resolved.



(II)

As already mentioned, the 1:1 adduct of $(CH_3)_2SnCl_2$ with DMSeO showed a symmetric Sn–C stretching

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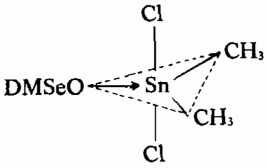
(6) R. C. Poller, *Spectrochim. Acta*, *22*, 935 (1966).

(*) ν(Sn-C) of $R_2SnCl_2 . 2DMSO$: $R=CH_3$, 244 cm^{-1}; $R=C_2H_5$, 238 cm^{-1}; $R=C_6H_5$, 229 and 201 cm^{-1}; ref. 5.

(**) It seems to be 200-150 cm^{-1} for the hexa-coordinated complexes of $(CH_3)_2SnBr_2$; T. Tanaka, Y. Matsumura, R. Okawara, Y. Musya, and S. Kinumaki, *Bull. Chem. Soc. Japan*, in press.

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

band which is as strong as the asymmetric one, and also only one Sn–Cl stretching band. These infrared observations suggest non-linear C–Sn–C and linear Cl–Sn–Cl moieties, respectively. Thus, if we assume a trigonal bipyramidal structure including penta-coordinated tin atom for the adduct, the configuration (III) is most probable.



(III)

It has been reported for $(CH_3)_3SnCl.D$ (where D = pyridine[8] and pyridine-N-oxide[9]), $[(CH_3)_2SnCl_3]^-$,[10,11] $(CH_3)_2SnX_2.D'$ (where X = Cl and Br, D' = dimethylformamide)[12] and $(CH_3)_nPF_{5-n}$ (n = 1 and 2)[13] that the less electronegative methyl groups occupy the equatorial positions in their trigonal bipyramidal structures. These results also support the configuration (III).

The octahedral complex $(C_2H_5)_2SnCl_2.2DMSeO$ exhibited a weak symmetric Sn–C stretching. This should be associated with a *trans*-ethyl configuration, because when the ethyl groups are located in *cis*-positions, symmetric Sn–C stretching band should be more intense, as was observed for 1:1 adduct of $(CH_3)_2SnCl_2$ with DMSeO, although the C–Sn–C bond angles are different from each other. The appearance of the weak band is presumably ascribed to mixing of Sn–C stretching with inner vibration of ethyl groups. However, the DMSeO donors are more likely to be in *cis*-positions, since this complex exhibited two Sn–O stretchings; one is strong and the other a shoulder. Thus, the diethyltin dichloride complex is assumed to have a similar configuration to the dimethyltin dichloride and dibromide 1:2 adducts (I).

For the diphenyltin dichloride complex two bands have been assigned to both the Sn–C and Sn–Cl stretching modes, and only one band to Sn–O stretching. The selection rule of infrared spectra might suggest a *trans*-DMSeO and *cis*-halogen (and also *cis*-phenyl) configuration. However, even if a *trans*-phenyl and *cis*-halogen configuration is assumed for this complex, the Sn–C symmetric stretching might be infrared active, since this vibration may be largely coupled with Sn–Cl symmetric stretching occuring at a frequency very close to it. Such a vibrational coupling is presumably effective in the diphenyltin dichloride complex, and therefore the actual configuration is not obvious from the present study.

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(8) R. Hulme, *J. Chem. Soc.*, 1524 (1963).
(9) Y. Kawasaki, M. Hori, and K. Uenaka, *Bull. Chem. Soc. Japan*, *40*, 2463 (1967).
(10) J. E. Fergusson, W. E. Roper, and C. J. Wilkins, *J. Chem. Soc.*, 3716 (1965).
(11) F. W. B. Einstein and B. R. Penford, *Chem. Commun.*, 780 (1966).
(12) G. Matsubayashi, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, in press.
(13) R. J. Gillespie, *Inorg. Chem.*, *5*, 1634 (1966).
in Chemistry Series", R. F. Gould, Ed., American Chemical Society,