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INFRARED SPECTRA OF ALKYLTIN ISOTHIOCYANATES

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INTRODUCTION

Recently many studies of the stereochemistry of organotin compounds have been reported[1,2]. Evidence has accumulated for the existence of penta-, hexa- and even hepta-coordinated tin atoms. This report deals with a study of the stereochemistry by means of infrared absorption spectra of several types of organotin isothiocyanates, including the compounds recently reported by the present authors[3,4].

Green *et al.*[5] first reported briefly an infrared spectroscopic investigation of $(n\text{-}C_4H_9)_3SnNCS$ and proposed the iso-form for the compound. Recently, Cummins and Dunn[6] have reported analogous results on the same compound from the measurement of the infrared absorption intensity of the NC stretching vibration and from the study of the molecular refraction data. Since this work was completed, the preparation of tetraethylammonium salts containing methyltin poly(iso)thiocyanate* anions[7], and the infrared study of trimethylmetal pseudohalides of the fourth group element[8] have been reported. Thayer and West have reviewed the chemistry of organometallic pseudohalides[9].

EXPERIMENTAL

The known compounds used in this investigation were prepared as described elsewhere[3,4,10]. The new compounds given in Table 1 were prepared according to the usual procedures[7,11].

The molecular weight of $(CH_3)_3SnNCS$ was determined cryoscopically in benzene [calcd. for $(CH_3)_3SnNCS$: 222; found: 230]. Oscillation photographs were taken with CuKα radiation for rotation about the needle axis of $(CH_3)_3SnNCS$.

The spectrum of each compound was recorded between 4000 and 400 cm^{-1} with a HITACHI EPI-2G spectrophotometer equipped with gratings. Each compound was mulled in nujol or hexachlorobutadiene, and in cases where the compound is considerably soluble, the spectra were also observed in the appropriate solvent.

RESULT AND DISCUSSION

Transition metal (iso)thiocyanate complexes have been extensively investigated in order to solve the interesting problem of whether the NCS group is bonded

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* These compounds were reported as thiocyanates[7].

TABLE 1

ANALYSES OF TRI- AND DIMETHYLTIN COMPLEX COMPOUNDS

	Compound	*M.p.* (°C)	*% Sn Found (Calcd.)*	*% NCS or % Cl Found (Calcd.)*	*% C Found (Calcd.)*	*% H Found (Calcd.)*	*% N Found (Calcd.)*	*% S Found (Calcd.)*
(I)	$(CH_3)_3SnNCS\cdot$pyridine	110–113	39.58 (39.43)	19.39 (19.30)				
(II)	$[(CH_3)_4N]^+[(CH_3)_3Sn(NCS)_2]^-$	157–158	33.47 (33.52)	32.87 (32.80)	31.15 (30.53)	5.96 (5.98)	11.62 (11.87)	18.38 (18.11)
(III)	$[(CH_3)_4N]_2^+[(CH_3)_2Sn(NCS)_4]^{2-}$	211–212	22.62 (22.42)	43.94 (43.89)	31.90 (31.77)	5.77 (5.71)	15.71 (15.88)	23.88 (24.23)

to the metal through the sulfur atom, M–SCN (thiocyanate), or through the nitrogen atom, M–NCS (isothiocyanate) (see *e.g.* ref. 12). The criterion adopted until now to establish the bond type is that the thiocyanato complexes exhibit very sharp, well-formed N–C stretching bands above 2100 cm^{-1}, whereas the isothiocyanato complexes exhibit relatively broad, more intense bands around or below 2100 cm^{-1}. The C–S stretching frequency of *ca.* 700 cm^{-1} is indicative of S-bonding, while a frequency of 860–780 cm^{-1} indicates N-bonding. In thiocyanato complexes a band due to the N–C–S bending is observed at 440–410 cm^{-1}, with weaker satellites at higher frequencies. In isothiocyanato complexes one band is found at 490–460 cm^{-1}.

As is seen from Tables 2–6, the infrared spectra of the alkyltin isothiocyanates investigated here show the strong N–C stretching absorption bands below 2100 cm^{-1} and one or two NCS bending bands at 490–460 cm^{-1}. The band due to the C–S stretching is often of low intensity and it is difficult to observe, especially when there is a stronger band due to the other vibration. However, the detailed comparison of the spectra of alkyltin isothiocyanates with those of the corresponding alkyltin halides can sometimes reveal the band at 850–800 cm^{-1}, as shown in the Tables 2–5. These observations indicate that the compounds investigated here are "isothiocyanates". The following discussion will be based on this result.

$(CH_3)_3SnNCS$ and $R_2Sn(NCS)_2$

The spectra of $(CH_3)_3SnNCS$ are shown in Fig. 1. The bands representing trimethyltin group vibrations and the inner vibrations of isothiocyanate group are easily assigned by comparing the spectra with those of trimethyltin halides[13], and the results are shown in Table 2.

The result is somewhat inconsistent with that proposed by Thayer and Strommen[8]. They assigned three bands appearing in the region 1070–1000 cm^{-1} to symmetric N–C–S stretching (C–S stretching mode). We observed no band in this region but a shoulder band at 829 cm^{-1}, which is comparable in frequency with the C–S stretching band observed in the spectra of many transition-metal isothiocyanates[12]. We further observed two bands* at 474 cm^{-1} and 467 cm^{-1} in the solid

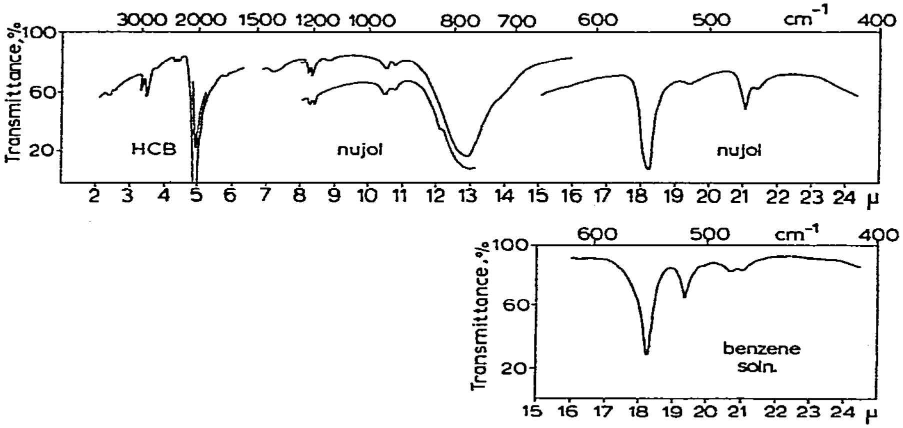

Fig. 1. Infrared absorption spectra of $(CH_3)_3SnNCS$.

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* Thayer and Strommen[8] observed one band at 478 cm^{-1}.

TABLE 2

INFRARED VIBRATIONAL FREQUENCIES OF $(CH_3)_3SnNCS$ (in cm^{-1})

Solid	*Solution*	*Assignments*
2098 sh	2050[a]; 2045[b] vs	N–C str.
2079 vs		
2046 sh		
1199 w	(not examined)	CH_3 sym. deform.
1189 w		
1186 sh		
950 w		overtone of NCS bend.
930 vw		
829 sh		
779 vs	781 s[c]	C–S str.
720 sh		CH_3 rock.
551 s	548 s[a]	SnC_3 asym. str.
515 w	517 m[a]	SnC_3 sym. str.
474 m	485 w[a]	NCS bend.
467 w	478 w[a]	

[a] In benzene. [b] In CCl_4. [c] In CS_2.

spectrum which shift on solution to slightly higher frequencies with a rather ambiguous shape as shown in Fig. 1. These bands might be associated with the N–C–S bending vibrations and the appearance of two bands would be explained by a hypothesis that the Sn–N–C bond is non-linear. However, the possibility of Fermi resonance is not invalid.

The noticeable feature of the spectra is the change of the relative intensity of the SnC_3 symmetric and asymmetric stretching vibrations near 515 cm^{-1} and 551 cm^{-1}. Apparently the SnC_3 symmetric stretching band intensity becomes greater on solution compared with that in the solid state. This change, as well as the lowering shift of N–C stretching band on solution, are interpreted as being due to a weak bridging through sulfur atom to the tin atom in the adjacent molecule, causing a slight unfolding of SnC_3 skeleton, which succeedingly weakens the symmetric SnC_3 stretching intensity. This weak bridge is destroyed on solution, as is observed in the molecular weight investigation in benzene, which gave a monomeric value.

The single crystal of this compound is a thin plate, but when it is cut in length, it breaks into fine needle pieces. This feature of fission follows the same trend observed for the crystals of trialkyltin carboxylates, which are considered to be polymeric in direction of the needle crystal by the bridging of the carboxylate group[2]. The identity period of $(CH_3)_3SnNCS$, 12.1 Å, in the direction of the needle may correspond to the length from the first tin atom to the third tin*. Since the Sn–Sn distance of 6.05 Å is too short to form a linear Sn–NCS–Sn linkage, it seems to support the hypothesis that the Sn–N–C bond is non-linear.

Unlike most of the other dialkyltin isothiocyanate derivatives which are investigated here, $R_2Sn(NCS)_2$ show marked high-frequency bands for N–C stretching vibration, as shown in Table 3. It might result from the bridging of NCS groups to adjacent tin atoms as interpreted for the spectra of $(CH_3)_3SnNCS$ in term of the

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* The Sn–Sn distance of linear Sn–CN–Sn chain in $(CH_3)_3SnCN$ is found to be 6.06 Å[14].

sulfur bridging. Other evidence suggesting a bridging structure for $R_2Sn(NCS)_2$ includes the relatively high melting point and the very low solubility in non-polar solvents, compared to corresponding dialkyltin dihalides[3].

TABLE 3

INFRARED VIBRATIONAL FREQUENCIES OF $R_2Sn(NCS)_2$

R	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	*Assignments*
	2088 vs	2079 vs	2075 vs	2081 vs	N–C str.
	2062 vs		2066 vs		
	965 w	961 m	962 w	962 w	overtone of NCS bend.
		930 sh	927 w	926 w	
	846 sh	835 w	840 w	842 w	C–S str.
	487 sh				NCS bend.
	483 m	483 m	483 m	483 m	
	459 m	465 m	463 m	462 m	

Configuration of the complexes

The relevant frequencies observed in the spectra of the four complexes, (I)–(IV), in the region 2–25 μ are given in Table 4, together with the result on $[(CH_3)_4N]^+NCS^-$, and the representative spectra are shown in Fig. 2.

The absence of an SnC_3 or SnC_2 symmetric stretching vibration band in the spectra of (I), (II) and (III) indicates planar or linear arrangement of SnC_3 and SnC_2 moieties in these compounds. As has been shown by the infrared spectra and an X-ray crystal study of $(CH_3)_3SnCl\cdot$pyridine[11,15], the molecule of (I) may also exist as an unsymmetric, bipyramidal structure with the pyridine and the NCS lying on either

TABLE 4

INFRARED VIBRATIONAL FREQUENCIES OF TRI- AND DIMETHYLTIN ISOTHIOCYANATE COMPLEXES (in cm^{-1})

(I) = $(CH_3)_3SnNCS\cdot$pyridine
(II) = $[(CH_3)_4N]^+[(CH_3)_3Sn(NCS)_2]^-$
(III) = $[(CH_3)_4N]_2^+[(CH_3)_2Sn(NCS)_4]^{2-}$
(IV) = $(CH_3)_2Sn(NCS)_2\cdot$bipyridine
(VIII) = $[(CH_3)_4N]^+[NCS]^-$

(I)	*(II)*	*(III)*	*(IV)*	*(VIII)*	*Assignments*
2080 vs	2070 vs	2051 vs	2045 vs	2062 vs	N–C str.
			2033 vs		
945 m		972 vw	975 w		overtone of NCS bend.
		923 sh	957 vw		
	949 s	951 s		944 vs	(N–)CH_3 rock.
808 vw		815 sh	816 vw	740 s	C–S str.
787 vs	779 s	777 s br	794 s		(Sn–)CH_3 rock.
553 vs	552 s	581 m	579 s		SnC_3 or SnC_2 asym. str.
550 vs					
			515 vw		SnC_2 sym. str.
472 m	476 w	482 m	488 m	459 sh	NCS bend.
			479 m		
	454 w	463 w		456 m	NC_3 deform.

side of the SnC_3 plane. Further, the observation of only one N–C–S bending vibration band at 472 cm^{-1} indicates a linear arrangement of Sn–N–C–S linkage. The slight splitting of the degenerate, asymmetric SnC_3 stretching band may be understood as caused by the C_{2v} symmetry of coordinated pyridine molecule.

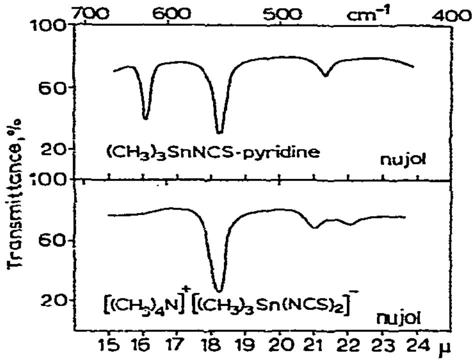
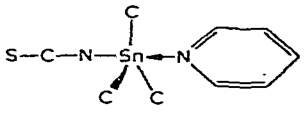
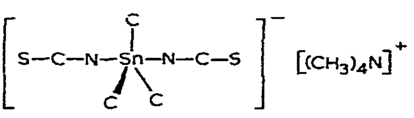


Fig. 2. Infrared absorption spectra of $(CH_3)_3SnNCS$·pyridine and $[(CH_3)_4N]^+ [(CH_3)_3Sn(NCS)_2]^-$.

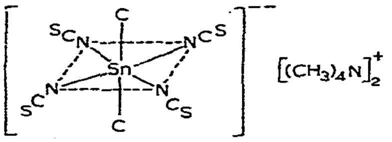
A bipyramidal, penta-coordinated tin structure may be assigned for the anion of (II), and a *trans*-octahedral arrangement for the anion of (III). These assignments seem further to be supported by the observations of only one band due to the N–C stretching vibration in each spectrum.



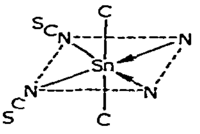
(I)



(II)



(III)



(IV)

As was proposed for R_2SnCl_2·bipyridine[11,16], (IV) may also preserve the *trans*-alignment of the alkyl groups. The existence of a very weak band due to symmetric SnC_2 stretching vibration in the spectra of IV may be accounted for as the slightly bent bonding of C–Sn–C moiety*. The observation of two bands near 2040 cm^{-1} and 2020 cm^{-1} due to the N–C stretching vibration of $R_2Sn(NCS)_2$·bipyridine (Table 4 and 5) indicates the *cis*-alignment of the two NCS groups.

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* Analogous observations of symmetric SnC_2 stretching band are known for $(CH_3)_2Sn(oxinate)_2$[2,4] or $(CH_3)_2Sn(OOCCH_3)_2$[17].

TABLE 5

INFRARED VIBRATIONAL FREQUENCIES OF $R_2Sn(NCS)_2 \cdot$ BIPYRIDINE

R	*C_2H_5*	*n-C_3H_7*	*n-C_4H_9*	*Assignments*
	2041 vs	2053 vs	2039 vs	N–C str.
	2024	2012	2020	
	812 sh	810 w	812 m	C–S str.
	489 m	481 m	480 m	NCS bend.
	478	476		

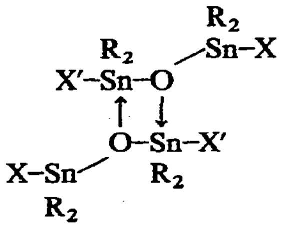
Dimeric distannoxane derivatives

In the infrared spectra of (SCN)R_2SnOSnR_2(NCS)(V) as given in Table 6, two bands due to the N–C stretching vibration are observed both in the solid state and in solution of non-polar solvent. This fact is consistent with the initially proposed, dimeric structure of the distannoxanes[18,19] (see below), in which two kinds of electronegative substituents (NCS group, for the present) are contained.

TABLE 6

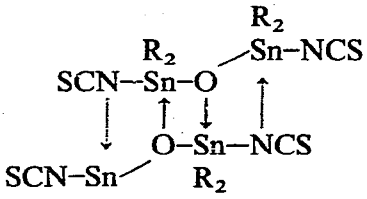
INFRARED VIBRATIONAL FREQUENCIES OF NC STRETCHING VIBRATION IN TETRAALKYL DISTANNOXANES AND R_2Sn(OXINATE)NCS

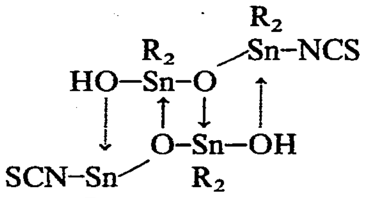
	CH_3	*C_2H_5*	*C_3H_7*	*C_4H_9*
(V) (SCN)R_2SnOSnR_2(NCS)				
nujol mull		2037	2042	2041
		1959	1961	1953
benzene soln.		2030	2020	2016
or CCl_4 soln.		1957	1959	1960
(VI) (SCN)R_2SnOSnR_2OH				
nujol mull	2070	2081	2062	2064
solution		2049 (acetophenone)	2045 (benzene)	2049 (benzene)
(VII) R_2Sn(oxinate)NCS				
nujol mull	2055	2053	2055	



The N–C stretching band at 1960 cm^{-1} for (V) is unique, since such a low frequency band has never been observed in the spectra of other alkyltin isothiocyanates and in the spectra of transition metal isothiocyanates[13]. The N–C stretching vibration band in the spectra of R_2Sn(oxinate)NCS, of which the NCS group is attached to the penta-coordinated tin atom[4], is observed at 2055 cm^{-1}. This fact implies that an NCS group does not give such a low frequency band at 1960 cm^{-1} even though it is bonded to a penta-coordinated tin atom in a dialkyltin derivative.

A lowering of the N–C stretching band frequency might be interpreted as being caused by the bridging to another tin atom by the nitrogen atom, and such a bridging is expected for the NCS group attached to the oxygen-coordinated tin atom in the dimeric distannoxanes. The absence of the band at 1960 cm^{-1} in the spectra of $(SCN)R_2SnOSnR_2(OH)$ (VI) indicates that the OH group has replaced the position of the bridging NCS group. This interpretation will predict the ladder type dimerization of the compounds, (V) and (VI), as shown below.


(V)


(VI)

An X-ray crystal study[20] has confirmed such a structure for $(CH_3)_3SiO(CH_3)_2SnOSn(CH_3)_2OSi(CH_3)_3$. The two absorption bands due to O–Si stretching vibrations at 980 cm^{-1} and 910 cm^{-1} of this compound[21] may be understood as originating from the nonbridging $(Sn-)OSi(CH_3)_3$ group and the bridging $(Sn-)OSi(CH_3)_3$ group, respectively. The infrared spectra of $R_3SnOSi(CH_3)_3$, which is monomeric, show[22] the band near 980 cm^{-1}. It has been shown that the oxygen atom of $OSi(CH_3)_3$ can bridge other two or three metal atoms, such as aluminium[23], gallium[23] or cadmium[24].

TABLE 7

THE CHARACTERISTIC FREQUENCIES (in cm^{-1}) ASSOCIATED WITH Sn–O–Sn LINKAGE FOR DIMERIC TETRAETHYL-1,3-DISUBSTITUTED DISTANNOXANES, $[X(C_2H_5)_2SnOSn(C_2H_5)_2X']_2$

X	*X'*			*Ref.*
$OSi(CH_3)_3$	$OSi(CH_3)_3$	622	570	21
NCS	NCS	612	563	3
Cl	Cl	607	558	19
Br	Br	596	532	19
NCS	OH	626	571	3
Cl	OH	637	569	19
Br	OH	638	564	19
I	OH	633	553	19
I	OCH_3	600	552	19
I	OC_2H_5	595	555	19
$[(C_2H_5)_2SnO]_x$			573	

Tetraalkyldistannoxane derivatives, $XR_2SnOSnR_2X'$, give rise to two characteristic absorption bands due to the Sn–O–Sn linkage in the region 650–530 cm^{-1}. Taking tetraethyldistannoxanes as examples, the frequencies of these bands are summarized in Table 7. Although there is a steady shift in the frequencies of two bands, an essential structural difference in these distannoxanes may not exist. The feature of shift seems to be connected with the properties of substituents. One of these properties may be the bridging ability of the substituent; the bromide of type (V) gives the lowest frequencies of each band. The iodide of type (V) could not be prepared[19]. However, the iodide of type (VI) was isolated, and the failure in preparing type (V) is understood as due to the poor bridging property of the iodine anion to form the ladder type dimeric distannoxane. The fact that hexaalkyldistannoxanes, $R_3SnOSnR_3$, are monomeric may be explained in the same way[19].

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SUMMARY

The infrared spectra of $(CH_3)_3SnNCS$, $(CH_3)_3SnNCS \cdot$pyridine, $[(CH_3)_4N]^+ \cdot [(CH_3)_3Sn(NCS)_2]^-$, $[(CH_3)_4N]_2^+[(CH_3)_2Sn(NCS)_4]^{2-}$, $R_2Sn(NCS)_2$, $R_2Sn(NCS)_2 \cdot$bipyridine, $(SCN)R_2SnOSnR_2(NCS)$ and $(SCN)R_2SnOSnR_2(OH)$ have been recorded in the region 4000–400 cm^{-1}. The spectra are discussed on the basis of the known or presumed structures of these alkyltin isothiocyanates.

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