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Metal Isotope Effect on Metal-Ligand Vibrations. X. Far-Infrared Spectra of Trans Adducts of Tin(IV) Tetrahalide with Unidentate Ligands

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Twelve 1:2 adducts of tin tetrahalides with various unidentate ligands, SnX_4L_2, have been prepared, and their far-infrared spectra have been assigned based on ^{116}Sn-^{124}Sn isotopic shifts. Cis and trans structures have been distinguished from the number of observed Sn-X and Sn-L stretching modes. It has been shown that all the complexes studied are trans.

Introduction

A system of 1:2 adducts of tin tetrahalides with unidentate ligands, SnX_4L_2, where X is a halogen and L is a unidentate ligand, represents a unique series for studying the metal-ligand interactions, cis-trans isomerism, and its relation to their thermodynamic stabilities, and has already been studied by many workers.[3] It is known from X-ray diffraction study that the adducts $SnX_4(py)_2$ where X is Cl or Br are trans octahedral.[4] Similarly, the adduct $SnCl_4(THT)_2$ is trans,[5] whereas the adducts $SnCl_4(POCl_3)_2$,[6] $SnCl_4(DMSO)_2$,[7] $SnCl_4(SeOCl_2)_2$[8] and $SnCl_4(CH_3CN)_2$[9] are all cis octahedral (THT = tetrahydrothiophene; DMSO = dimethyl sulfoxide). However, the stereochemistries of many other adducts have not yet been well established.

Vibrational spectroscopy has been utilized extensively to study tin tetrahalide adducts.[10] Theoretically, four Sn-X stretching vibrations are infrared active for the cis structure (C_{2v}) whereas only one infrared-active Sn-X stretching band is expected for the trans structure (D_{4h}).

Beattie, *et al.*,[11,12] have shown that the number of infrared-active Sn-Cl stretching bands is useful in determining the stereochemistry of these adducts. However, this method gives a clear-cut diagnosis only when the Sn-Cl stretching region (usually 350-300 cm^{-1}) is not obscured by other vibrations such as Sn-L stretching and ligand bands. As pointed out by Beattie, *et al.*,[11,12] certain Sn-Cl stretching bands of cis adducts may be coalesced or may be of low intensity, thus leading to an erroneous conclusion. On the other hand, the Sn-Cl stretching band (E_u mode) of a trans adduct may split into two peaks due to the solid-state effect. Thus, the assignment of stereochemistry by infrared spectroscopy is not always simple. The stereochemistry of the corresponding bromo and iodo derivatives is more difficult to determine from far-infrared spectra because Sn-Br and Sn-I stretching bands are closely located to Sn-L stretching and other skeletal bending vibrations. In fact, almost no definitive assignments are available on the bromo and iodo derivatives.

In the previous papers of this series,[13] we have demonstrated that the metal isotope technique is very useful in assigning the metal-ligand vibrations. In this paper, we have prepared a series of tin tetrahalide adducts of the SnX_4L_2 type in which the central metal is isotopically substituted by ^{116}Sn and ^{124}Sn and have examined their far-infrared and some Raman spectra to elucidate stereochemistry. The ligands studied in this paper include pyridine, γ-picoline, 4-*tert*-butylpyridine, tetrahydrofuran, tetrahydrothiophene, triphenylphosphine, and triphenylarsine.

Experimental Section

Preparation of SnX_4 Containing Pure ^{116}Sn and ^{124}Sn. Since pure tin isotopes are available as the oxides,[14] they were first converted to metallic tin by reducing the oxides with potassium cyanide,[15] and then the resulting metallic tin isotopes (^{116}Sn and ^{124}Sn) were allowed to react with chlorine or bromine gas to form the corresponding tin tetrahalides.[16] The purity of metal isotopes was as follows: ^{116}Sn, 95.74%; ^{124}Sn, 94.7%. The purity of each compound was checked by comparing the infrared spectrum with that of the corresponding halide containing tin of natural abundance.

Preparation of SnX_4L_2. All tin tetrahalides containing natural-abundance tin were purchased from Alfa Inorganics Inc. and used without further purification except tin tetrachloride which was distilled under vacuum. All ligands investigated were commercially available; pyridine and tetrahydrofuran were from Baker Chemical Co. and all other ligands were from Aldrich Chemical Co. Pyridine, γ-picoline, and tetrahydrofuran were purified by vacuum distillation. Triphenylphosphine was recrystallized from acetone-methanol. All other ligands were used without further purification.

Tin halide adducts were prepared typically by mixing a 20-ml benzene solution containing 0.5-1.2 g (about 2 mmol) of tin halide with a 10-ml benzene solution of each ligand in a 1:2.1 molar ratio. Preparation involving tin tetrahalides was carried out in a vacuum line or in a drybox filled with dry nitrogen. The addition reaction proceeded smoothly and the precipitate formed immediately. The reaction mixture was kept stirring for about 30 min after the first precipitation was observed. The precipitate was collected on a filter paper and washed several times with small portions of dry benzene. No further purification was undertaken, and the product was dried in a vacuum desiccator containing calcium chloride for 3-4 hr at

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room temperature. In the case of tetrahydrofuran, the precipitate did not form readily, and it was necessary to cool the reaction mixture in a refrigerator (about 5°) for several hours. The purity of each addition compound was checked by elemental analysis, by melting (decomposition) point, or by comparing its infrared spectrum with that reported in literature. Table I lists some analytical data. Similar procedures were used for the preparation of tin halide adducts containing ^{116}Sn and ^{124}Sn.

Spectral Measurements. Infrared spectra were measured on Beckman IR-12 (4000-250 cm^{-1}) and Hitachi Perkin-Elmer FIS-3 (410-33 cm^{-1}) infrared spectrophotometers. The Nujol-mull technique with CsI plates (4000-200 cm^{-1}) or polyethylene plates (410-33 cm^{-1}) was employed for all solid compounds. The spectra were run on an expanded scale with a scanning speed of 2-4 cm^{-1}/min. The low-frequency spectra (410-33 cm^{-1}) of most of the compounds were obtained under vacuum. However, the spectra of $SnX_4((CH_2)_4O)_2$ and $SnX_4((CH_2)_4S)_2$ were run in dry nitrogen atmosphere in order to prevent loss of samples or any dissociation of coordinated ligands under vacuum. Reproducibility of the spectra was checked by multiple scans of several samples over the desired frequency range. The spectral resolution was approximately 1 cm^{-1} with an accuracy of ±0.5 cm^{-1}. The frequencies were calibrated by using polystyrene, 1,3,5-trichlorobenzene, and water vapor.

The Raman spectra were recorded on a Spex Model 1401 Raman spectrophotometer equipped with an argon ion laser. The green excitation (5145 Å) was used. Calibration of frequency reading was made by using carbon tetrachloride. The reproducibility of Raman spectra was also checked by multiple scans over the desired frequency range and was found to be ±0.5 cm^{-1}.

Abbreviations Used. In describing the mode of vibrations and intensity the following symbols were used: ν, stretching; δ, bending; π, out-of-plane bending; s, symmetric; a, asymmetric; ir, infrared; R, Raman.

The following abbreviations were used to denote the ligands: py, pyridine; py-d_5, perdeuterated pyridine; γ-pic, γ-picoline; *t*-Bupy, 4-*tert*-butylpyridine; THF, tetrahydrofuran; THT, tetrahydrothiophene; PPh_3, triphenylphosphine; $AsPh_3$, triphenylarsine.

Results and Discussion

Theoretically, 15 normal vibrations (3 × 7 − 6) are expected for *trans*-SnX_4L_2 type molecules if the ligand L is assumed to be a point mass. These vibrations are classified into $2\ A_{1g}\ (R) + B_{1g}\ (R) + B_{2g}\ (R) + E_g\ (R) + 2\ A_{2u}\ (ir) + B_{2u}$ (inactive) $+ 3\ E_u$ (ir) under D_{4h} symmetry. As shown in our previous papers,[13] metal isotope shifts are much larger for stretching modes (10-2 cm^{-1}) than for bending modes (2-0 cm^{-1}). Thus, the metal isotope method has been used mainly to assign the metal-ligand stretching modes. In the present case, only two stretching modes, one Sn-X (E_u) and one Sn-L (A_{2u}) stretching, are infrared active, and both are expected to give large shifts relative to others when ^{116}Sn is substituted by ^{124}Sn.

In the case of *cis*-SnX_4L_2, the 15 vibrations are classified into $6\ A_1$ (ir, R) $+ 2\ A_2$ (R) $+ 3\ B_1$ (ir, R) $+ 4\ B_2$ (ir, R) under C_{2v} symmetry. Then, four Sn-X ($2\ A_1 + B_1 + B_2$) and two Sn-L ($A_1 + B_2$) stretching modes are infrared active. These six vibrations are expected to give relatively large shifts by the ^{116}Sn-^{124}Sn substitution. Thus, it is possible to distinguish the trans and cis structures by comparing the number of metal isotope sensitive bands in the far-infrared spectra.

$SnX_4(py)_2$. Pyridine (py) forms fairly stable 1:2 adducts with tetrahalides of group IV metals.[3] Cis-trans isomerism of the pyridine adducts of tin tetrahalides has been studied by X-ray methods,[4,17] ^{19}F nmr spectroscopy,[18] vibrational spectroscopy,[4,12,19-20] and more recently by ^{119}Sn Mossbauer spectroscopy.[21] There has been considerable controversy about the structure of the adducts $SnX_4(py)_2$ (X = F, Cl, Br, I). A ^{19}F nmr study of $SnF_4(py)_2$ in solution indicated a cis configuration,[18] while a trans configuration was suggested by its solid-state infrared spectrum.[19]

Table I. Analytical Results

Compd	% calcd C	% calcd H	% calcd Halogen	% found C	% found H	% found Halogen
$SnI_4(py)_2$	15.35	1.28		15.53	1.46	
$SnCl_4(t\text{-Bupy})_2$	40.70	4.74		40.39	5.44	
$SnCl_4(THT)_2$	22.06	3.73	32.36	22.24	3.87	31.98
$SnBr_4(THT)_2$	15.64	2.63	52.03	15.72	2.80	52.16
$SnBr_4(PPh_3)_2$	45.04	3.14	33.34	45.50	3.07	34.42
$SnCl_4(AsPh_3)_2$	49.60	3.46		44.76	3.02	

On the basis of the vibrational spectroscopic data, Beattie, *et al.*,[12] originally concluded that the chloride analog $SnCl_4(py)_2$ was in a trans configuration. However, Clark and Wilkins[17] showed by X-ray powder diagrams that $SnCl_4(py)_2$ and $SnBr_4(py)_2$ were isomorphous. They assigned cis configuration to both compounds, since the vibrational spectrum of the bromide analog shows three well-resolved bands in the Sn-Br stretching region. Later, Beattie, *et al.*,[4] succeeded in growing single crystals of both compounds from pyridine solution at elevated temperatures (in a sealed tube) and carried out X-ray analyses on them. The results have confirmed that these two compounds are indeed isomorphous. Although the accurate atomic coordinates were not determined, the gross structure was concluded to be trans. Tanaka, *et al.*,[10,20] also reported the infrared spectra of a series of 1:2 pyridine adducts $SnX_4(py)_2$ (X = Cl, Br, I) in the 1610-80-cm^{-1} range and assigned again cis configuration for all these adducts in accord with Clark and Wilkins. However, the conclusion made by Tanaka, *et al.*, was based on rather ambiguous assignments of the Sn-X stretching bands; they could not distinguish the Sn-X and Sn-N stretching bands.

$SnCl_4(py)_2$. Figure 1 shows actual tracings of the far-infrared spectra of $SnCl_4(py)_2$, $SnCl_4(py\text{-}d_5)_2$, and $^{116,124}SnCl_4(py)_2$. The Raman spectra of some of these complexes are also shown. Table II lists the observed and calculated frequencies of the skeletal vibrations of these isotopic compounds. As is seen in Figure 1, $SnCl_4(py)_2$ exhibits six infrared and five Raman bands in the low-frequency region (400-70 cm^{-1}). Upon the ^{116}Sn-^{124}Sn substitution, two infrared bands at 323.0 and 227.5 cm^{-1} show large isotopic shifts relative to others. This is in perfect agreement with the prediction from the trans configuration. Thus, $SnCl_4(py)_2$ must take a trans structure in agreement with the result of the single-crystal X-ray analysis.[4] This conclusion is further confirmed by our Raman study; no tin isotope effect was observed for all Raman-active fundamentals, since the central metal atom does not move in the g-type vibrations. Two infrared bands at 323.0 and 227.5 cm^{-1} which are metal isotope sensitive can be assigned to the Sn-Cl (E_u) and Sn-N (A_{2u}) stretching modes, respectively, because the former is insensitive but the latter is sensitive to the pyridine deuteration.

All other bands can be assigned as shown in Table II based on the isotope effects (^{116,124}Sn and pyridine deuteration) and the results of normal-coordinate analysis. Approximate normal-coordinate analysis[22] was carried out by assuming the pyridine ligand as a point mass of $C_5H_5N_5$. The set of force constants and the molecular dimensions used are listed in Table III. The agreement between the observed and calculated frequencies is fairly good. Some discrepancies in

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Table II. Comparison of Observed and Calculated Frequencies and Isotopic Shifts for $SnCl_4(py)_2$ (cm^{-1})

Symmetry species	Calcd			Obsd			Assignment
	$\nu(^{116}Sn)$	$\Delta\nu^a$	$\Delta\nu^b$	$\nu(^{116}Sn)$	$\Delta\nu^a$	$\Delta\nu^b$	
E_u	324.8	3.0	0.0	323.0[c]	5.0	0.0	ν(Sn-Cl)
A_{1g}	307.1	0.0	0.4	(307.1)[d]	0.3	· · ·	ν(Sn-Cl)
B_{1g}	254.2	0.0	0.0	(244.8)[d]	· · ·	· · ·	ν(Sn-Cl)
A_{2u}	234.6	3.8	3.4	227.5	4.0	3.0	ν(Sn-N)
B_{2g}	186.2	0.0	0.0	(173.5)[d]	· · ·	· · ·	δ(Cl-Sn-Cl)
E_g	172.6	0.0	1.8	(157.3)[d,e]	· · ·	· · ·	δ(N-Sn-Cl)
E_u	167.6	2.2	0.5	187.0	1.2	· · ·	δ(N-Sn-Cl)
A_{1g}	158.8	0.0	4.6	(157.3)[d,e]	· · ·	· · ·	ν(Sn-N)
B_{2u}	139.4	0.0	0.0	(Inactive)	· · ·	· · ·	δ(N-Sn-Cl)
E_u	116.3	0.1	1.8	170.0	1.0	∿1	δ(Cl-Sn-Cl)
A_{2u}	119.2	0.9	0.5	145.0	0.5	1.0	$\pi(SnCl_4)$
· · ·	· · ·	· · ·	· · ·	90	0	0	Lattice mode

[a] $\Delta\nu = \nu(^{116}Sn) - \nu(^{124}Sn)$. [b] $\Delta\nu = \nu(Sn, py) - \nu(Sn, py\text{-}d_5)$. [c] This band is sometimes accompanied by a shoulder band at *ca.* 305 cm^{-1}. The appearance of this shoulder band may indicate the splitting of the E_u mode due to lowering of the D_{4h} symmetry in the solid state. [d] Frequency of $SnCl_4(py)_2$ containing Sn in natural abundance. [e] Overlapped band.

Table III. Urey-Bradley Force Constants (mdyn/Å) and Molecular Dimensions (Å) Used for $SnCl_4(py)_2$ and $SnCl_4(THF)_2$[a]

		$SnCl_4$-$(py)_2$	$SnCl_4$-$(THF)_2$
Force constants	K(Sn-Cl)	1.10	1.25
	K(Sn-L)	0.85	0.75
	H(Cl-Sn-Cl)	0.25	0.25
	H(L-Sn-Cl)	0.30	0.20
	F(Cl· · ·Cl)	0.25	0.25
	F(L· · ·Cl)	0.30	0.30
Molecular dimensions	R(Sn-Cl)	2.40	2.35
	R(Sn-L)	2.20	2.20

[a] All angles were assumed to be 90°. F' was taken as $-(1/10)F$.

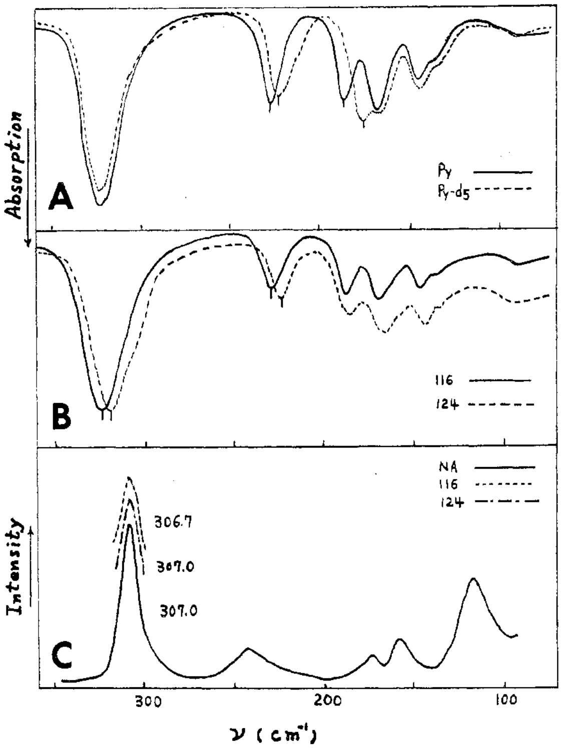

Figure 1. (A) Far-infrared spectra of $SnCl_4(py)_2$ and $SnCl_4(py\text{-}d_5)_2$, (B) far-infrared spectra of $^{116}SnCl_4(py)_2$ and its ^{124}Sn analog, and (C) Raman spectra of $SnCl_4(py)_2$ and its ^{116}Sn and ^{124}Sn analogs.

the bending modes are probably due to the approximations made in the calculation: (1) a point mass approximation for the pyridine ligand and (2) a simplified force field (UBF) employed.

Table IV correlates symmetry species and vibrational frequencies between $SnCl_6^{2-}$ (O_h)[23] and $SnCl_4(py)_2$ (D_{4h}). This table also supports the above band assignments. The present results do not agree with the previous assignments made by Tanaka, *et al.*,[20] who attributed the bands at *ca.* 323, 307, and 228 cm^{-1} to the Sn-Cl stretching and those at *ca.* 187 and 170 cm^{-1} to the Sn-N (or Sn-Cl) stretching modes, thus leading to the assignment of the cis configuration for $SnCl_4$-$(py)_2$. [The band at *ca.* 307 cm^{-1} is hardly recognizable (see Figure 1).]

Table IV. Correlation of Symmetry Species and Vibrational Frequencies between the $SnCl_6^{2-}$ Anion (O_h) and $SnCl_4(py)_2$ (D_{4h})

$SnCl_6^{2-}$	$SnCl_4(py)_2$
312 cm^{-1}, ν(Sn-Cl), A_{1g}	307.1 cm^{-1}, ν(Sn-Cl), A_{1g}
233 cm^{-1}, ν(Sn-Cl), E_g	244.8 cm^{-1}, ν(Sn-Cl), B_{1g}
	157.3 cm^{-1}, ν(Sn-N), A_{1g}
161 cm^{-1}, δ(Cl-Sn-Cl), F_{2g}	173.5 cm^{-1}, δ(Cl-Sn-Cl), B_{2g}
	157.3 cm^{-1}, δ(N-Sn-Cl), E_g
317 cm^{-1}, ν(Sn-Cl), F_{1u}	323.0 cm^{-1}, ν(Sn-Cl), E_u
	227.5 cm^{-1}, ν(Sn-N), A_{2u}
174 cm^{-1}, δ(Cl-Sn-Cl), F_{1u}	170.0 cm^{-1}, δ(Cl-Sn-Cl), E_u
	145.0 cm^{-1}, $\pi(SnCl_4)$, A_{2u}
Inactive, δ(Cl-Sn-Cl), F_{2u}	187.0 cm^{-1}, δ(N-Sn-Cl), E_u
	Inactive, δ(N-Sn-Cl), B_{2u}

$SnBr_4(py)_2$. As mentioned previously, X-ray studies have revealed that $SnBr_4(py)_2$ is isomorphous with $SnCl_4(py)_2$.[4,17] Since the latter is now proven to be trans, then the bromide analog must also be trans. The observed number of infrared bands and their frequencies in the present work (Table V and Figure 2) are in good agreement with those of the previous workers.[4,17,20] However, the number of infrared-active bands (eight in the 400-70 cm^{-1} range) is more than five which is expected for an ideal D_{4h} symmetry of the molecule. This contradiction was solved by Beattie, *et al.*,[4] who assumed D_{2h} symmetry for the *trans*-$SnBr_4(py)_2$ molecule in which the pyridine ligand does not rotate freely around the Sn-N bond. In this case, there are eight infrared-active skeletal modes, three of which are stretching vibrations. In fact, three bands at 246.5, 230.5, and 217.5 cm^{-1} of the ^{116}Sn complex show large isotopic shifts relative to others by the ^{116}Sn-^{124}Sn substitution. Thus, these three bands must be mainly due to the Sn-Br and Sn-N stretching modes. Upon the pyridine deuteration, the lowest frequency band at 217.5 cm^{-1} gives the largest shift (5.0 cm^{-1}) among these three bands and therefore must be assigned as the Sn-N stretching vibration. Then the remaining two bands can be assigned to the Sn-Br stretching bands which originate from the splitting of the doubly degenerate Sn-Br stretching mode (E_u) of D_{4h}

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Table V. Far-Infrared Frequencies and Isotope Shifts of $SnX_4(py)_2$ (X = Br, I) (cm^{-1})

Symmetry	$SnBr_4(py)_2$			$SnI_4(py)_2$		
species	$\nu(^{116}Sn)$	$\Delta\nu^a$	$\Delta\nu^b$	$\nu(Sn)$	$\Delta\nu^b$	Assignment^c
B_{3u}	246.5	4.5	3.6	195^c	*d*	ν(Sn-X)
B_{2u}	230.5	4.5	−1.4	185.0	2.0	ν(Sn-X)
B_{1u}	217.5	3.5	5.0	218.5	8.0	ν(Sn-N)
B_{3u}	202.5	0.5	8.0	163.0	4.0	δ(N-Sn-X)
B_{2u}	176.7	0.7	11.0	153.0	4.0	δ(N-Sn-X)
B_{1u}	126.0	1.2	1.2	104.0	2.0	δ(N-Sn-X)
B_{3u}	104.5	0.5	0.0	76	*d*	δ(X-Sn-X)
B_{2u}	92.0	0.5	0.0			δ(X-Sn-X)

^{a} $\Delta\nu = \nu(^{116}Sn) - \nu(^{124}Sn)$. ^{b} $\Delta\nu = \nu(Sn, py) - \nu(Sn, py\text{-}d_5)$. ^{c} Assignments are based on isotopic shifts and normal-coordinate analysis.[4] ^{d} Isotopic shifts could not be determined because of the poor shape of the band.

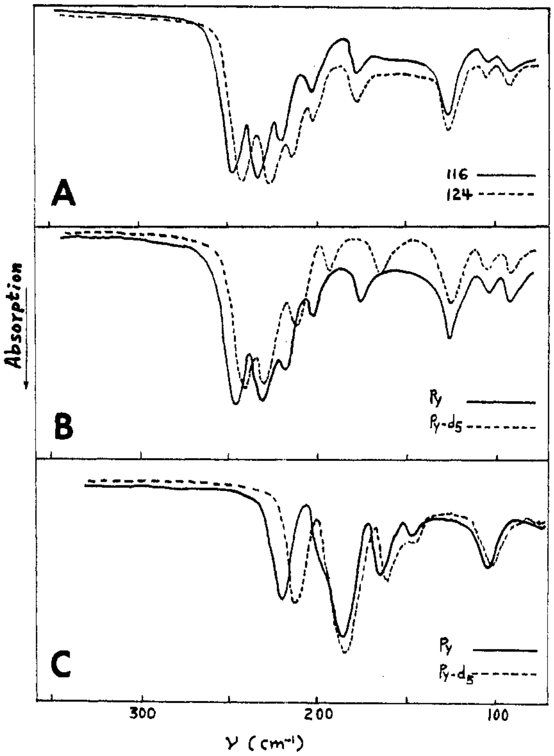

Figure 2. Far-infrared spectra of (A) $^{116}SnBr_4(py)_2$ and its ^{124}Sn analog, (B) $SnBr_4(py)_2$ and $SnBr_4(py\text{-}d_5)_2$, and (C) $SnI_4(py)_2$ and $SnI_4(py\text{-}d_5)_2$.

symmetry. The highest frequency band gives a relatively large shift upon the pyridine deuteration, which may indicate the presence of vibrational coupling between Sn-Br stretching and N-Sn-Br bending modes. The second Sn-Br stretching band increases its frequency slightly (1.4 cm^{-1}) upon the pyridine deuteration. This result may suggest that the magnitude of the splitting due to crystal field effect is different for the py and py-d_5 species. The remaining bands at 202.5, 176.6, and 126.0 cm^{-1} may be assigned to N-Sn-Br bending modes, since they are sensitive to the deuteration. On the other hand, two bands at 104.5 and 92.0 cm^{-1} can be assigned as the Br-Sn-Br bending modes since they are insensitive to the deuteration. These assignments are in general agreement with those made by Beattie, *et al.*,[4] but are different from those of Clark and Wilkins[17] and Tanaka, *et al.*[20]

$SnI_4(py)_2$. The observed number of infrared bands of this compound is in good agreement with that of Tanaka, *et al.*[20] (Table V). Although it is rather difficult to determine the structure based on pyridine deuteration data alone, it is probably trans since the number of infrared bands observed (seven including a weak shoulder at around 195 cm^{-1}) is closer to that of the trans (five or eight) than to that of the cis complex (13) (see Figure 2). Tentative band assignments have been made based on the D_{2h} symmetry (Table V). The highest frequency band with medium to strong intensity can be assigned as the Sn-N stretching since the observed deuteration shift (8.0 cm^{-1}) is close to the theoretical value of 6.9 cm^{-1} (diatomic model approximation). The most intense band at 185.0 cm^{-1} with a weak shoulder at around 195 cm^{-1} can be assigned as the Sn-I stretching mode. The appearance of a shoulder band may indicate the splitting of the E_u mode. The three bands at 163.0, 153.0, and 104.0 cm^{-1} may be assigned as the N-Sn-I bending since they are sensitive to the pyridine deuteration. The lowest frequency band at 76 cm^{-1} which is insensitive to the deuteration may then be assigned to the I-Sn-I bending. The present assignments are different from those of Tanaka, *et al.*,[20] who assigned all the bands except the two lowest frequency bands to the Sn-N and Sn-I stretching modes based on the cis configuration.

$SnCl_4(\gamma\text{-pic})_2$ and $SnCl_4(t\text{-Bupy})_2$. The observed frequencies are listed in Table VI and the vibrational spectra are shown in Figure 3. Both of these compounds must be trans since the spectra are very similar to that of $SnCl_4(py)_2$ (Figure 1). The Sn-Cl stretching frequencies (E_u, A_{1g}, and B_{1g}) of the γ-pic adduct (325, 308, and 251 cm^{-1}, respectively) and the *t*-Bupy adduct (325, 304, and 255 cm^{-1}, respectively) are similar to those of the py adduct (323, 307, and 245 cm^{-1}, respectively). The Sn-N stretching frequencies (A_{2u}) of the former two adducts (213 and 189 cm^{-1}, respectively) are lower than that of the py adduct (226 cm^{-1}).

$SnX_4(THF)_2$. THF is a weak donor toward tin tetrahalides. It forms a 1:1 adduct with SnF_4[24] while it gives 1:2 adducts with $SnCl_4$[5,11,25-27] and $SnBr_4$.[25] The latter two compounds are soluble in common organic solvents such as acetone, benzene, or THF itself. A value of 4.3 D has been quoted for the dipole moment of $SnCl_4(THF)_2$,[5] although the infrared studies[11,27] (only one band was observed in the Sn-Cl stretching region) tend to favor a trans configuration. The Mossbauer spectrum has also been obtained for $SnCl_4(THF)_2$.[26] Previous infrared study on $SnCl_4(THF)_2$ was not extended to the low-frequency region where the Sn-ligand vibrations appear. No structural information is available on $SnBr_4 \cdot (THF)_2$.

Table VII lists the observed and calculated frequencies and isotopic shifts for $^{116,124}SnCl_4(THF)_2$ and $SnBr_4(THF)_2$. The set of force constants used for the calculation is listed in Table III. It is obvious from the spectra that both compounds must be assigned as trans. In the case of the chloride complex two bands at 342.0 and 222.8 cm^{-1} can be assigned as Sn-Cl stretching (E_u) and Sn-O stretching (A_{2u}), respectively, since they give large isotopic shifts relative to others. The band at 278 cm^{-1} must be a ligand band since it does not give any isotopic shift and the bromide complex exhibits a similar band. In the case of the bromide complex, the Sn-Br and Sn-O stretching bands are at 247 and 204 cm^{-1}, respectively. As is seen in Table VII, the agreement between observed and calculated frequencies is fairly good except for two bending modes. The trans structure of $SnCl_4(THF)_2$ obtained in this work is in accord with that of the previous

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Table VI. Observed Frequencies and Band Assignments of $SnCl_4(\gamma\text{-pic})_2$ and $SnCl_4(t\text{-Bupy})_2$ (cm^{-1})

$SnCl_4(py)_2$		$SnCl_4(\gamma\text{-pic})_2$		$SnCl_4(t\text{-Bupy})_2$		
Ir	R	Ir	R	Ir	R	Assignment
323		325		325		ν(Sn-Cl), E_u
	307		308		304	ν(Sn-Cl), A_{1g}
	245		251		255	ν(Sn-Cl), B_{1g}
227		213		189		ν(Sn-N), A_{2u}
187		177		140		δ(N-Sn-Cl), E_u
	173.5		(162)[a]		(162)[a]	δ(Cl-Sn-Cl), B_{2g}
170		159		156		δ(Cl-Sn-Cl), E_u
	(157.3)[a]		(162)[a]		(162)[a]	δ(N-Sn-Cl), E_g
	(157.3)[a]		. . .		. . .	ν(Sn-N), A_{1g}
145		137		126		$\pi(SnCl_4)$, A_{2u}
	117		. . .		120	Other bands
			91		89	
			66			

[a] Overlapped band.

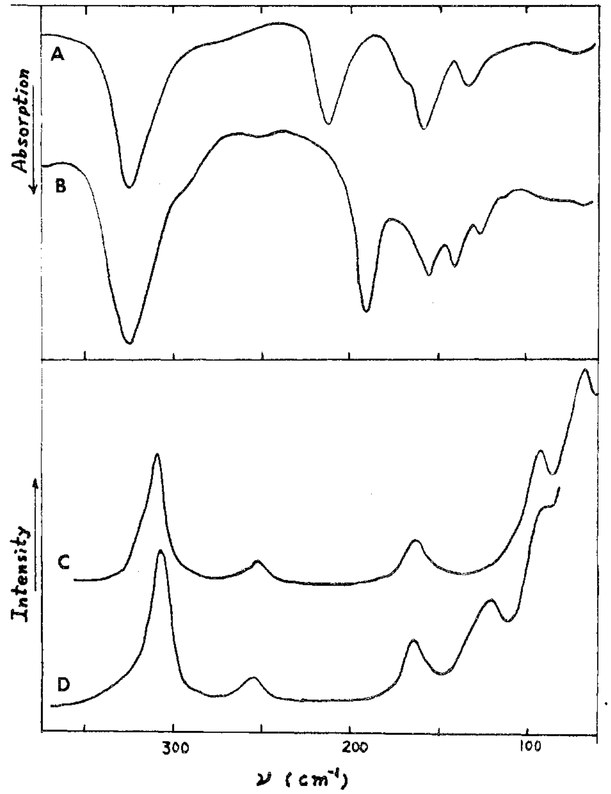

Figure 3. Far-infrared spectra of (A) $SnCl_4(\gamma\text{-pic})_2$ and (B) $SnCl_4(t\text{-Bupy})_2$ and Raman spectra of (C) $SnCl_4(\gamma\text{-pic})_2$ and (D) $SnCl_4(t\text{-Bupy})_2$.

workers.[11,27] The trans structure of the bromide complex has been proposed for the first time.

$SnX_4(THT)_2$. Tetrahydrothiophene (THT) adducts may be expected to take a similar configuration as that of THF adducts. As mentioned previously, the X-ray[5] and vibrational studies (Sn-Cl stretching region)[11,27] on the chloride complex strongly suggest that the adduct is centrosymmetric (trans). The present low-frequency infrared study is also in agreement with these previous observations. As is seen in Table VII, the band at 318 cm^{-1} can be assigned as the ν(Sn-Cl) (E_u). However, the Sn-S stretching band is rather difficult to assign without metal isotope data. No attempts have been made to obtain $^{116}SnCl_4(THT)_2$ and its ^{124}Sn analog, since it was rather difficult to prepare them on a milligram scale. No bands have been found in the 300-200-cm^{-1} region which can possibly be assigned to the Sn-S stretching mode.

The bromide complex can also be assigned to a trans configuration (Table VII). The strong band at 218 cm^{-1} is definitely due to the Sn-Br stretching mode (E_u). The shoulder at around 227 cm^{-1} may originate from the Sn-Br stretching (E_u) which splits into a doublet due to the lowering of symmetry in the solid state. The bromide complex shows a weak band at around 270 cm^{-1} which is probably due to the ligand.

$SnX_4(PPh_3)_2$ and $SnX_4(AsPh_3)_2$. Many tertiary phosphine complexes with $SnCl_4$ have been synthesized,[9,28-31] and the Mossbauer spectra[28,30,31] as well as infrared spectra (mostly above 200-cm^{-1} region)[9,28-30] have been reported. Triphenylphosphine is known to form both 1:1 and 1:2 adducts with $SnCl_4$.[28-31] For the 1:2 complex $SnCl_4(PPh_3)_2$, a trans structure has been assigned based on infrared evidence (only one strong band in the 300-cm^{-1} region).[28,30,31] In contrast to many phosphine complexes, only a few arsine complexes have been prepared.[29] The Sn-P and Sn-As stretching frequencies reported previously (513 and 330 cm^{-1}, respectively) seem to be too high.[29] In the present work, three 1:2 complexes ($^{116,124}SnCl_4(PPh_3)_2$, $SnBr_4(PPh_3)_2$, and $SnCl_4(AsPh_3)_2$) have been prepared and their low-frequency infrared spectra reinvestigated. The results are listed in Table VIII.

Upon the ^{116}Sn-^{124}Sn substitution, three bands at 307.0, 167.3, and 140.0 cm^{-1} of $^{116}SnCl_4(PPh_3)_2$ give large isotopic shifts (3.0, 1.4, and 1.7 cm^{-1}, respectively). The very strong band at 307.0 cm^{-1} can easily be assigned to the Sn-Cl stretching which is in complete agreement with the previous assignments by other workers.[28-30]

The Sn-P stretching band, however, is rather difficult to assign with certainty because metal-phosphine bands are generally weak in the infrared region. Furthermore, triphenylphosphine itself exhibits many bands in the low-frequency region where metal-ligand vibrations appear. Rivest, *et al.*,[29] previously assigned the Sn-P stretching band at 513 cm^{-1} which was not observed in the free ligand (in solid state). However, their assignment is obviously erroneous because the band in question (at 520.5 cm^{-1} in the present work) and all other bands above 390 cm^{-1} are not sensitive to the ^{116}Sn-^{124}Sn substitution. Thus, all of these bands must be assigned to the ligand vibrations. It is known that free triphenylphosphine exhibits two or three bands in the 500-cm^{-1} region (513, 499, and 492 cm^{-1} in the present work) which have been known as Whiffen's y vibrations or out-of-plane bending vibration of the phenyl ring.[32] Thus the 513-cm^{-1} band which was assigned to the Sn-P stretching must be one of these ligand vibrations.

It is not clear whether the band at 167.3 or 140.0 cm^{-1} is due to the Sn-P stretching mode. However, these frequencies do not seem to be unreasonable since the Ni-P stretching bands of $NiCl_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$ have been assigned in the 192-164 cm^{-1} region by the use of ^{58}Ni-^{62}Ni and ^{104}Pd-^{110}Pd substitution.[13b] Since Sn is much heavier than Ni, the Sn-P stretching frequency can be as low as those of

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Table VII. Far-Infrared Frequencies and Isotopic Shifts of $SnX_4(THF)_2$ and $SnX_4(THT)_2$ (X = Cl, Br) (cm^{-1})

$SnCl_4(THF)_2$				Obsd ν			
Calcd		Obsd					
$\nu(^{116}Sn)$	$\Delta\nu^a$	$\nu(^{116}Sn)$	$\Delta\nu^a$	$SnBr_4(THF)_2$	$SnCl_4(THT)_2$	$SnBr_4(THT)_2$	Assignment
341.5	3.2	342.0	4.0	247	318	218	ν(Sn-X), E_u
		278.0	0.0	282	270	270	Ligand
222.2	3.2	222.8	3.2	204	. . . ^{b}	227	ν(Sn-L), A_{2u}
171.9	2.0	163.0	$\sim$2	120	154	118	δ(L-Sn-X), E_u
116.8	0.3	154.0	c	108	145	105	δ(X-Sn-X), E_u
115.4	1.1	140		93	130	90	π(L-Sn-X), A_{2u}

[a] $\Delta\nu = \nu(^{116}Sn) - \nu(^{124}Sn)$. [b] Hidden by the ligand band at 270 cm^{-1}. [c] The ^{124}Sn complex shows a broad band at *ca.* 160 cm^{-1} due to overlapping of δ(O-Sn-Cl) and δ(Cl-Sn-Cl).

Table VIII. Far-Infrared Frequencies and Isotopic Shifts of $SnCl_4(PPh_3)_2$, $SnBr_4(PPh_3)_2$, and $SnCl_4(AsPh_3)_2$ (cm^{-1})

$SnCl_4(PPh_3)_2$		ν				
$\nu(^{116}Sn)$	$\Delta\nu^a$	PPh_3	$SnBr_4(PPh_3)_2$	$AsPh_3$	$SnCl_4(AsPh_3)_2$	Assignment^b
520.5	0.0	513	514			Ligand y vibration
501.0	0.0	499	497	474	470	
495	0	492				
447.0	0.2	423	434	312	333	Ligand t vibration
		421				
405.0	0.0	407		403	403	Ligand w vibration
395.0	0.0	397	397			
				314		
307.0	3.0		209	309		ν(Sn-Cl) or ν(Sn-Br)
265		272	251 br	250	250	Ligand x vibration
250		253	246 br			
		247				
203.5	0.4	215	(209)^c	192		
196		197		182	189	Ligand u vibration or ν(Sn-L)^d
		187				
167.3	1.4				152	δ(X-Sn-X) or δ(X-Sn-L)^d or ν(Sn-L)
140	1.7		113		136	
103					90	δ(Cl-Sn-P) or δ(Cl-Sn-As)

[a] $\Delta\nu = \nu(^{116}Sn) - \nu(^{124}Sn)$. [b] Ligand bands were assigned according to ref 31. [c] Hidden under the strong band at 209 cm^{-1}. [d] L indicates PPh_3 or $AsPh_3$.

Cl-Sn-Cl and Cl-Sn-P bending modes. The relatively large isotopic shift and broadness of the 140.0-cm^{-1} band may imply that this band could be an overlap of the Sn-P stretching and bending modes.

Previously, Harrison, *et al.*,[30] failed to prepare $SnBr_4(PPh_3)_2$ because it is easily oxidized in air. We have prepared this compound in the nitrogen atmosphere to avoid oxidation of the phosphine ligand. The Sn-Br stretching band can be easily assigned at 209 cm^{-1} since it is the strongest band in the far-infrared region. Assignments of other bands are listed in Table VIII. As mentioned before, the assignment of the Sn-P stretching band is not certain.

The triphenylarsine complex $SnCl_4(AsPh_3)_2$ shows three bands in the 350-300-cm^{-1} region (333, 314 (sh), and 309 cm^{-1}) consistent with the previous observation.[29,31] Rivest, *et al.*,[29] assigned the highest frequency band at 333 cm^{-1} to the Sn-As stretching mode. However, this band may be due to a ligand vibration since free ligand exhibits a strong band at 312 cm^{-1}. The fact that this band is virtually insensitive to the halogen substitution (chloride-bromide) seems to support the present assignment. The strong band at 309 cm^{-1} may be assigned to the Sn-Cl stretching mode as previously assigned by other workers.[29,31] The shoulder band at 314 cm^{-1} may be due to a splitting of this E_u mode. Three bands at 152, 136, and 90 cm^{-1} may be assigned to the skeletal bending modes.

Summary on Sn-X Stretching Frequencies. It is interesting to compare the Sn-X stretching frequencies thus far determined, *i.e.*

	L												
	THF		γ-pic		t-Bupy		py		THT		As-Ph_3		PPh_3
ν(Sn-Cl)	342	>	325	≈	325	>	323	>	318	>	309	>	307
ν(Sn-Br)	247	>	···		···	>	236	>	218	>	···	>	209

(The 236-cm^{-1} frequency for py is an average of two frequencies.) This result suggests that the Sn-X bond strength decreases in the same order. In general, the Sn-X bond becomes weaker as the Sn-L bond becomes stronger. If this is the case, PPh_3 forms the strongest and THF forms the weakest metal-ligand bond in this series. This interpretation is supported by an approximate normal-coordinate analysis on $SnCl_4(py)_2$ and $SnCl_4(THF)_2$. *K*(Sn-Cl) of the pyridine adduct is smaller than that of the THF adduct, while *K*(Sn-N) of the former is larger than *K*(Sn-O) of the latter (Table III). In fact, the Sn-N stretching frequencies (A_{2u}) of $SnCl_4(py)_2$ and $SnBr_4(py)_2$ (227.5 and 217.0 cm^{-1}, respectively) are higher than the Sn-O stretching frequencies of the corresponding THF adducts (22.8 cm^{-1} for the chloride complex and 204 cm^{-1} for the bromide complex) even though pyridine is heavier than THF. It is of particular interest to compare the order of the donor strength ($As \approx P > S > N > O$) derived from the present infrared work with the order of the effectiveness of the donor atoms in reducing the 5s electron density at the tin nucleus ($O > N > S > P$) obtained by Mossbauer studies.[21] Since ($As \approx P > S > N > O$) is the order of σ-electron release of the ligand atoms, the present infrared result may support the conclusion derived from the Mossbauer study that the tin-ligand bonds are mainly of σ-bond type.[21] On the basis of Mossbauer and vibrational studies of many phosphine complexes of $SnCl_4$, Carty, *et al.*,[28] also suggested that the Sn=P double bond is unimportant and proposed that as the s character of the Sn–P bond increases, that of the Sn–Cl bond decreases in $(PR_3)_2SnCl_4$. An extreme case for this may be seen in *trans*-$(CH_3)_2SnCl_4$ where the methide ions (CH_3^-) can be regarded as a very strong σ donor and the Sn-Cl (E_u) stretching band appears at a very low frequency region (235 cm^{-1}).[33]

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Registry No. *trans*-$SnCl_4(py)_2$, 22798-23-8; *trans*-$SnBr_4(py)_2$, 22798-24-9; *trans*-$SnI_4(py)_2$, 40802-54-8; *trans*-$SnCl_4(\gamma\text{-pic})_2$, 40802-55-9; *trans*-$SnCl_4(t\text{-Bupy})_2$, 40802-56-0; *trans*-$SnCl_4(THF)_2$, 40802-57-1; *trans*-$SnBr_4(THF)_2$, 40802-58-2; *trans*-$SnCl_4(THT)_2$, 40802-59-3; *trans*-$SnBr_4(THT)_2$, 40802-60-6; *trans*-$SnCl_4(PPh_3)_2$, 17668-11-0; *trans*-$SnBr_4(PPh_3)_2$, 40802-61-7; *trans*-$SnCl_4(AsPh_3)_2$, 17668-12-1; ^{116}Sn, 14191-70-9; ^{124}Sn, 14392-29-1.

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Metal Isotope Effect on Metal-Ligand Vibrations. XI. Far-Infrared Spectra of *cis*-SnX_4(L-L) Type Complexes

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Eleven tin tetrahalide adducts with various bidentate ligands, *cis*-SnX_4(L-L), have been prepared, and their far-infrared spectra have been assigned based on the observed ^{116}Sn–^{124}Sn isotope shifts.

Introduction

In the previous paper of this series,[2] we have reported the low-frequency vibrational spectra of *trans*-SnX_4L_2 type complexes where X is a halogen (Cl, Br, I) and L is a unidentate ligand such as pyridine and triphenylphosphine. In this paper, we report the far-infrared spectra of *cis*-SnX_4(L-L) type complexes where L-L denotes a bidentate chelating ligand. The ligands studied are 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 1,2-dimethylthioethane (DTE), and 1,2-bis(diphenylphosphino)ethane (DPE). The general pattern of the spectra of these compounds is expected to be similar to that of the *cis*-SnX_4L_2 type complexes which will be reported in a subsequent paper.

As discussed previously, only two (one Sn-X and one Sn-L) stretching vibrations are infrared active in a *trans*-SnX_4L_2 type complex of D_{4h} symmetry. A much more complicated spectrum is expected, however, for a *cis*-SnX_4(L-L) type complex of C_{2v} symmetry; four Sn-X (2 A_1, B_1, B_2) and two Sn-L (A_1, B_2) stretching modes are infrared as well as Raman active.

Experimental Section

Preparation of Compounds. The addition compounds were prepared by mixing solutions containing tin tetrahalide and a ligand in a 1:1.05 molar ratio.[2] The reaction was carried out in a drybox (for complexes containing tin in natural abundance) or in a vacuum line (for complexes containing tin isotopes). The precipitate was filtered and washed with a small portion of dry benzene. The complex was dried in a vacuum desiccator over calcium chloride. The chloride and bromide complexes are colorless, but the iodide complexes are reddish orange crystals. The purity of each compound was checked by elemental analysis or by comparing its infrared spectrum with that reported in literature. Table I lists some analytical data.

Spectral Measurements. Infrared spectra were measured on Beckman IR-12 (4000–200 cm^{-1}) and Hitachi Perkin-Elmer FIS-3 (410–33 cm^{-1}) infrared spectrophotometers. The Nujol-mull technique with CsI plates (4000–200 cm^{-1}) or polyethylene plates (410–33 cm^{-1}) was employed for all compounds. The spectra below 410 cm^{-1} were measured on an expanded scale with a scanning speed of 2–4 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans of several samples. The spectral resolution was approximately 1 cm^{-1} and the accuracy of frequency reading was ±0.5 cm^{-1}. The frequency reading was calibrated by using polystyrene and water vapor.

Table I. Analytical Results

	% calcd			% found		
Compd	C	H	Halogen	C	H	Halogen
$SnBr_4$(phen)	23.41	1.31		23.66	1.50	
SnI_4(phen)	17.94	1.00	64.43	18.13	1.02	64.97
$SnCl_4$(DTE)	12.62	2.64	36.80	12.75	2.77	37.13
$SnBr_4$(DTE)	8.64	1.80	57.03	8.93	1.71	57.42
SnI_4(DTE)	6.42	1.34	69.23	6.48	1.54	69.71

The Raman spectra were recorded on a Spex Model 1401 Raman spectrophotometer equipped with an argon ion laser. The green excitation (5145 Å) was used. Calibration of frequency reading was made by using carbon tetrachloride and indene.

Results and Discussion

(1) **2,2′-Bipyridine Complexes.** 2,2′-Bipyridine (bipy) is known to form 1:1 complexes, SnX_4 (bipy), with tin tetrahalides. The low-frequency infrared spectra[3-6] of SnX_4(bipy) (X = F, Cl, Br, I) and the Raman spectrum[7] of $SnCl_4$(bipy) have already been reported. However, previous band assignments were made without sufficient evidence. In this study, we have reexamined the far-infrared spectra of SnX_4(bipy) (X = Cl, Br, I) with the aid of ^{116}Sn and ^{124}Sn isotopes. The spectra of these complexes are shown in Figure 1, and

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