

Low frequency infrared spectral studies on some of the molecular addition compounds of tin(IV) halides with triphenylphosphine and triphenylarsine

ROLAND RIVEST, SURJIT SINGH, AND C. ABRAHAM
Department of Chemistry, University of Montreal, Montreal, Quebec

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Molecular addition compounds of tin tetrahalides with triphenylphosphine and triphenylarsine have been prepared. The analytical results show that triphenylphosphine forms both 1:2 ($\text{SnX}_4 \cdot 2\text{L}$) and 1:1 ($\text{SnX}_4 \cdot \text{L}$) adducts (L = ligand), whereas triphenylarsine forms only 1:2 adducts. The effect of addition of these ligands on the $\nu(\text{Sn}-\text{X})$ (where X = Cl, Br) of the Lewis acids has been studied. In all cases, $\nu(\text{Sn}-\text{X})$ have been found to shift to a lower frequency region on coordination. Tentative assignments for $\nu(\text{Sn}-\text{Y})$ (where Y = P, As) have been discussed on the basis of the experimental results.

Les complexes d'addition moléculaire de tetrahalogénures d'étain et la triphénylarsine et la triphénylphosphine ont été préparés. Les résultats analytiques indiquent que la triphénylphosphine forme deux sortes de complexes $\text{SnX}_4 \cdot \text{L}$ et $\text{SnX}_4 \cdot 2\text{L}$ (L est le ligand), tandis que la triphénylarsine ne forme qu'une sorte de complexes $\text{SnX}_4 \cdot 2\text{L}$. L'effet de l'addition de ces ligands sur la fréquence $\nu(\text{Sn}-\text{X})$ (où X = Cl ou Br) des acides de Lewis a été étudié. Dans chaque cas, $\nu(\text{Sn}-\text{X})$ diminue à cause de la coordination. On discute aussi de l'attribution possible de certaines bandes à $\nu(\text{Sn}-\text{Y})$ (où Y = P ou As).

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INTRODUCTION

In some of the early publications (1-3) the low frequency infrared spectra of coordination compounds of tin tetrahalides with various donors have been discussed. There appears to be considerable disagreement between these authors regarding the shift of the Sn—X stretching frequency on coordination. Beattie and co-workers (1) suggest a lowering in the $\nu(\text{Sn}-\text{Cl})$ on coordination, whereas Brown and Kubota (2) and Aggarwal and Singh (3) report that the $\nu(\text{Sn}-\text{Cl})$ remains almost at the same position when tin tetrachloride coordinates with donors. A number of other workers (4-10) have observed that when metal tetrahalides, MX_4 , form octahedral complexes, $\text{MX}_4 \cdot 2\text{donors}$, the M—X stretching vibrations are considerably shifted towards a low frequency region. Tertiary organo-derivatives of heavier elements of group VA are known to be fairly strong donors. These ligands are likely to form only *trans* adducts because of the steric hindrance of the phenyl groups attached. It was thus thought interesting to study systematically the low frequency infrared spectra of the addition compounds of tin(IV) halides with donors like tri-

phenylphosphine (LP) and triphenylarsine (LA) and give satisfactory assignments to the observed vibrations.

EXPERIMENTAL

All the solvents were of reagent grade and were purified and dried before use. Reagent grade tin tetrachloride from Fisher Scientific Company, after further distillation, was sealed in small ampuls of known contents. One such ampul was used for each experiment. Tin tetrabromide from K and K Laboratories and triphenylphosphine and triphenylarsine from Eastman Chemicals were used without further purifications. All reactions were carried out in a dry box under nitrogen atmosphere.

The complexes of tin tetrachloride were precipitated by adding the Lewis acid to a *n*-hexane solution of the ligands. The precipitates were washed with *n*-hexane and dried. Depending upon the ratio of the ligand to tin tetrachloride, complexes of two different compositions, $\text{MX}_4 \cdot \text{L}$ and $\text{MX}_4 \cdot 2\text{L}$, were obtained with LP. Only a 1:2 complex could be obtained with LA even in the presence of an excess of the Lewis acid. The complex $\text{SnBr}_4 \cdot 2\text{LA}$ was prepared by mixing the methylene chloride solutions of the ligand and the Lewis acid. An immediate precipitation occurred. The solvent was evaporated and the complex recrystallized by dissolving the precipitate in *n*-hexane. The complex $\text{SnBr}_4 \cdot \text{LA}$ could not be obtained even in an excess of Lewis acid.

All the complexes of tin tetrachloride were white powdery substances, whereas the complex $\text{SnBr}_4 \cdot 2\text{LA}$ was crystalline and orange in color.

TABLE I
Analytical data of tin(IV) halide complexes with triphenylphosphine and triphenylarsine

	% Sn		% Cl, Br		% C		% H		Melting point (°C)
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	
SnCl ₄ .LP	22.7	22.0	27.1	27.2	41.4	41.8	2.89	3.21	115-116
SnCl ₄ .2LP	15.1	15.8	18.1	17.5	55.1	55.2	3.85	4.42	132-134
SnCl ₄ .2LA	13.6	13.7	16.2	16.3	49.5	49.7	3.46	3.88	160-162
SnBr ₄ .2LA	11.3	10.7	30.4	30.7	—	—	—	—	104

The analytical results and the melting points of these complexes are given in Table I. The molecular weight of SnCl₄.LP was determined by osmometry using methylene chloride solvent, since the complex was insoluble in other solvents transparent in the far infrared. The molecular weight of SnBr₄.2LA was determined by cryoscopy using benzene as solvent.

The molecular weight of SnBr₄.2LA is in agreement with the monomeric composition. The SnCl₄.LP, on the other hand, exists as a dimer at higher concentrations and breaks into monomers in very dilute solutions. The molecular weight of SnCl₄.LP at 0.04 *M* and 0.014 *M* concentrations (using monomeric molecular weight of the complex) has been found to be 820 and 670 respectively. Higher concentrations could not be tried owing to the low solubility of the complex. The molecular weight of other complexes could not be determined because of solubility difficulties.

Infrared spectra of all the complexes and ligands were taken in the form of Nujol mulls. The infrared spectrum of SnCl₄.LP was also taken in methylene chloride solution (~0.04 *M*). A 1.0 mm thick stoppered polyethylene cell was used in taking the solution spectrum. Cells of bigger path length could not be used for dilute solutions, because of the high solvent absorbance in the far infrared region. A Perkin-Elmer 621 and a Beckman model IR-5A double-beam spectrophotometer fitted with cesium iodide optics were used for recording the spectra.

RESULTS AND DISCUSSION

The position of the bands recorded in the far infrared spectra of the complexes and their probable assignments are given in Table II. The low frequency infrared spectral assignments for the ligands have been given by Brown and co-workers (11) and are known as Whiffen's substituent sensitive bands. All the bands of the ligands appear in the complexes at a slightly shifted frequency.

Tin tetrahalides are known to have a tetrahedral symmetry and exhibit four fundamental vibrations (12). Out of these, two ($\nu_1 A_1$ and $\nu_3 F_2$) are stretching and the

remaining two ($\nu_2 E$ and $\nu_4 F_2$) are deformation vibrations. All the four vibrations are Raman active but only two ($\nu_3 F_2$ and $\nu_4 F_2$) are infrared active. The $\nu_4 F_2$ vibration occurs at 131 cm⁻¹ in SnCl₄ and therefore has not been of much interest, being out of range of the spectrophotometers generally used. The $\nu_3 F_2$ vibration appears at 403 cm⁻¹ and has been widely studied. The corresponding $\nu_3 F_2$ vibrations in SnBr₄ and SnI₄ appear at 279 and 216 cm⁻¹ respectively. On complex formation the symmetry of the molecule changes and accordingly, the number of infrared active vibrations also changes. The octahedral 1:2 complexes may have a *D*_{4h} or a *C*_{2v} symmetry, depending upon whether the ligands are arranged *trans* to each other or *cis* to each other. Based on the group theoretical requirements (13), the *trans* 1:2 complexes are expected to have one infrared active Sn—X and one Sn—Y stretching vibration (see Table III), whereas the *cis* 1:2 complexes are expected to have four Sn—X and two Sn—Y stretching vibrations. The bending vibrations, as has been seen above, appear at frequencies below the region studied and therefore have not been considered in Table III. From the steric hindrance of the ligands used and the number of bands observed (Table II), it appears that the 1:2 complexes exclusively have a *trans* configuration. The assignments have been given on the basis of a *trans D*_{4h} model for SnX₄.2L complexes. For convenience, a common term $\nu_d(\text{Sn—X})$ has been used to indicate the *F*₂ stretching vibration in tetrahedral *T*_d Lewis acids and *E*_u vibration in the *trans* octahedral *D*_{4h} addition complexes. In the spectrum of SnBr₄.2LA, two new bands have been observed. The 244 cm⁻¹

TABLE II

The far infrared spectral vibrations of tin(IV) halides complexes with triphenylphosphine and triphenylarsine

Assignments*	SnBr ₄ .2LA		SnCl ₄ .2LP		SnCl ₄ .2LA		SnCl ₄ .LP	
	Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex
Whiffen's s band	617 m,sh	615 m,sh	618 m,sh	618 m,sh	617 m,sh	615 m,sh	618 m,sh	615 m,sh
?†			540 m	536 m			540 m	536 m
ν (Sn—P)				513 sh				529 m,sh
Whiffen's y band	470 s	466 s	488 s	496 s	470 s	467 s	488 s	496 s
ν (Sn—As)		334 s				330 s		
Whiffen's t band	305 s	304 s	430 s	442 s	305 s	306 s	430 s	445 s
ν d(Sn—X)	311 sh	320 sh			311 sh	315 sh		
		244 s		306 s		306 s		328 s
								(equatorial)
ν (Sn—X) axial								350 s
ν (Sn—X) bridged								287 b,m
Whiffen's u band			245 s	238 s			245 s	238 s

*s = strong, m = medium, sh = shoulder, b = broad.

†This band appears in the complex and the ligand both and has probably been ignored by Brown *et al.* (11).

TABLE III

Selection rules for the Sn—L and Sn—X stretching modes for different configurations of SnX₄.2L complexes and SnX₄*

Molecule	Symmetry	Species of ν (Sn—L)	Species of ν (Sn—X)
SnX ₄	<i>T_d</i>	—	<u><i>A₁</i></u> + <u><i>F₂</i></u>
SnX ₄ .2L, <i>cis</i>	<i>C_{2v}</i>	<u><i>A₁</i></u> + <u><i>B₂</i></u>	<u><i>2A₁</i></u> + <u><i>B₁</i></u> + <u><i>B₂</i></u>
SnX ₄ .2L, <i>trans</i>	<i>D_{4h}</i>	<u><i>A_{1g}</i></u> + <u><i>A_{2u}</i></u>	<u><i>A_{1g}</i></u> + <u><i>B_{1g}</i></u> + <u><i>E_u</i></u>

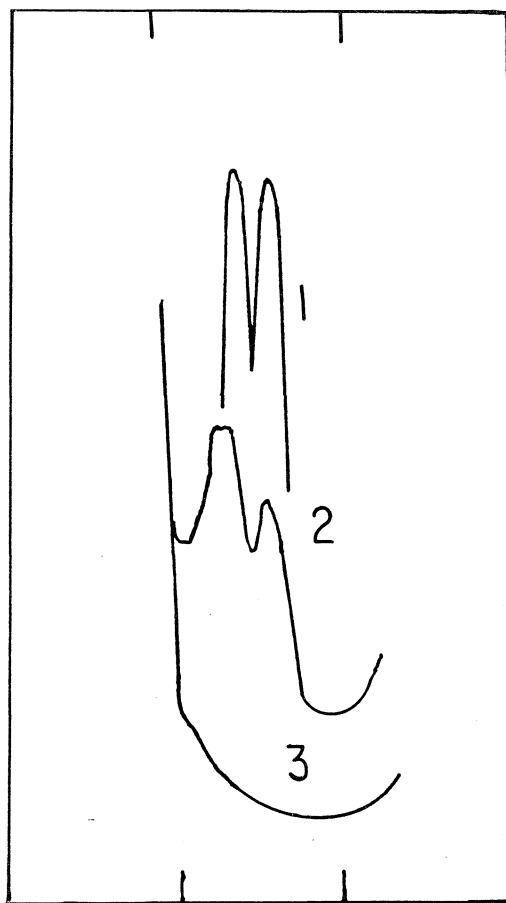
*The infrared active species have been underlined.

band has been assigned to the ν d vibration of SnBr₄, which has shifted by 35 cm⁻¹ on coordination. The band at 334 cm⁻¹ has been assigned to the Sn—As stretching vibration.

Two new bands have been observed in the spectrum of SnCl₄.2LP. The band at 306 cm⁻¹ has been assigned to the shifted ν d vibration of SnCl₄. The other band at 513 cm⁻¹ has been assigned to the Sn—P stretching mode. The difference in frequency between the Sn—P and Sn—As stretching modes may be due to two factors: the higher force constant of the Sn—P bond due to the higher donor properties of triphenylphosphine in comparison with the triphenylarsine ligand (14) and the lower reduced mass of the Sn—P species. The latter is not expected

to contribute much towards the frequency difference if triphenyl ligand is supposed to move as a whole in the Sn—P or Sn—As stretching modes. Such an assumption seems to be reasonable but is not completely justified. Cases are known in the literature (15) where no decrease in the metal—P stretching frequency is observed on changing from trimethylphosphine to triethylphosphine ligands (cf. *cis*-[(CH₃)₃P]₂PtCl₂ and *cis*-[(C₂H₅)₃P]₂PtCl₂), which is expected only if trialkyl ligands move as a whole in the Pt—P stretching modes.

The SnCl₄.2LA complex shows a band at 330 cm⁻¹ in addition to the ligand vibrations. As in the assignments given for SnBr₄.2LA, this band can be assigned to the Sn—As stretching vibration. The band



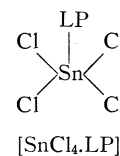
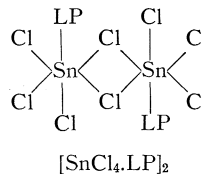
300 400
FREQUENCY, CM⁻¹

FIG. 1. The two bands of SnCl₄.LP as observed in [1] Nujol mull and [2] methylene chloride solution. Infrared trace of the solvent in this region is shown in [3].

at 306 cm⁻¹ due to the $\nu_d(\text{Sn}-\text{Cl})$ vibration as seen in the SnCl₄.2LP probably appears at the same position in the SnCl₄.2LA complex also but is overlapped by the strong band of the ligand (Whiffen's ν vibration) which appears exactly in the same region.

The SnCl₄.LP complex has four vibrational bands in addition to the ligand vibrations. The band at 529 cm⁻¹, similar

to the one at 513 cm⁻¹ in SnCl₄.2LP, may be assigned to the Sn—P stretching vibration. As has been mentioned in the experimental part, the complex exists as a dimer under normal conditions. This may involve bridging through chlorines. The remaining three bands at 287, 328, and 350 cm⁻¹ have been assigned to the three different modes of Sn—Cl vibrations. Though any conclusion about the configuration of the complex can not be reached on the basis of the observed vibrations, the hypothetical assignments for the Sn—Cl vibrations can be given on the basis of the following structures. The lowest energy band at 287 cm⁻¹ can be assigned to the bridged Sn—Cl vibration, since the bridged M—Cl vibrations are known to occur at a lower frequency than the terminal M—Cl vibrations (16). The remaining two vibrations at 328 and 350



cm⁻¹ can be assigned to the equatorial and the axial Sn—Cl vibrations respectively. The infrared spectrum taken in methylene chloride solution resembles the spectrum in Nujol mull except that the relative intensity of the band at 350 cm⁻¹ goes down appreciably and the band at 328 cm⁻¹ becomes broadened (Fig. 1). These results can be very nicely visualized in the light of the above assignments. The band at 350 cm⁻¹ is a characteristic band of the dimer as assigned above and really should decrease in intensity when dissolved in methylene chloride. On dissolving the complex, the dimers break into the monomeric species, and the axial Sn—Cl vibration, which is absent in monomers, falls in intensity. The broadening of the band at 328 cm⁻¹ in solution spectrum may probably be due to the combination of the dimeric equatorial Sn—Cl vibration with the monomeric Sn—Cl vibration which may be expected to appear in the close proximity. The 287 cm⁻¹ band could,

however, not be studied in solution because of solvent absorption in the same region.

CONCLUSION

From the far infrared spectral study of the addition compounds of tin(IV) halides with simple donors like triphenylphosphine and triphenylarsine, it becomes quite clear that the $\nu(\text{Sn}-\text{X})$ should shift to lower frequencies on coordination in all normal cases. The Sn—P and Sn—As stretching vibrations appear quite clearly in the far infrared range and their position is reasonable according to the reduced mass consideration and to the high donor properties of triphenylphosphine.

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