

study that the tin-ligand bonds are mainly of  $\sigma$ -bond type.<sup>21</sup> On the basis of Mossbauer and vibrational studies of many phosphine complexes of  $\text{SnCl}_4$ , Carty, *et al.*,<sup>28</sup> also suggested that the  $\text{Sn}=\text{P}$  double bond is unimportant and proposed that as the  $s$  character of the  $\text{Sn}-\text{P}$  bond increases, that of the  $\text{Sn}-\text{Cl}$  bond decreases in  $(\text{PR}_3)_2\text{SnCl}_4$ . An extreme case for this may be seen in *trans*- $(\text{CH}_3)_2\text{SnCl}_4$  where the methide ions ( $\text{CH}_3^-$ ) can be regarded as a very strong  $\sigma$  donor and the  $\text{Sn}-\text{Cl}$  ( $E_u$ ) stretching band appears at a very low frequency region ( $235\text{ cm}^{-1}$ ).<sup>33</sup>

(33) C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, **9**, 1037 (1970).

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**Registry No.** *trans*- $\text{SnCl}_4(\text{py})_2$ , 22798-23-8; *trans*- $\text{SnBr}_4(\text{py})_2$ , 22798-24-9; *trans*- $\text{SnI}_4(\text{py})_2$ , 40802-54-8; *trans*- $\text{SnCl}_4(\gamma\text{-pic})_2$ , 40802-55-9; *trans*- $\text{SnCl}_4(t\text{-Bupy})_2$ , 40802-56-0; *trans*- $\text{SnCl}_4(\text{THF})_2$ , 40802-57-1; *trans*- $\text{SnBr}_4(\text{THF})_2$ , 40802-58-2; *trans*- $\text{SnI}_4(\text{THF})_2$ , 40802-59-3; *trans*- $\text{SnBr}_4(\text{THT})_2$ , 40802-60-6; *trans*- $\text{SnCl}_4(\text{PPh}_3)_2$ , 17668-11-0; *trans*- $\text{SnBr}_4(\text{PPh}_3)_2$ , 40802-61-7; *trans*- $\text{SnCl}_4(\text{AsPh}_3)_2$ , 17668-12-1; <sup>116</sup>Sn, 14191-70-9; <sup>124</sup>Sn, 14392-29-1.

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## Metal Isotope Effect on Metal-Ligand Vibrations. XI. Far-Infrared Spectra of *cis*- $\text{SnX}_4(\text{L}-\text{L})$ Type Complexes

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Eleven tin tetrahalide adducts with various bidentate ligands, *cis*- $\text{SnX}_4(\text{L}-\text{L})$ , have been prepared, and their far-infrared spectra have been assigned based on the observed <sup>116</sup>Sn-<sup>124</sup>Sn isotope shifts.

### Introduction

In the previous paper of this series,<sup>2</sup> we have reported the low-frequency vibrational spectra of *trans*- $\text{SnX}_4\text{L}_2$  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*- $\text{SnX}_4(\text{L}-\text{L})$  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*- $\text{SnX}_4\text{L}_2$  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*- $\text{SnX}_4\text{L}_2$  type complex of  $D_{4h}$  symmetry. A much more complicated spectrum is expected, however, for a *cis*- $\text{SnX}_4(\text{L}-\text{L})$  type complex of  $C_{2v}$  symmetry; four Sn-X ( $2A_1, B_1, B_2$ ) 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.<sup>2</sup> 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  $\text{cm}^{-1}$ ) and Hitachi Perkin-Elmer FIS-3

(1) Submitted by N. Ohkaku to the faculty of Marquette University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, **12**, 2440 (1973).

Table I. Analytical Results

| Compd                        | % calcd |      |         | % found |      |         |
|------------------------------|---------|------|---------|---------|------|---------|
|                              | C       | H    | Halogen | C       | H    | Halogen |
| $\text{SnBr}_4(\text{phen})$ | 23.41   | 1.31 |         | 23.66   | 1.50 |         |
| $\text{SnI}_4(\text{phen})$  | 17.94   | 1.00 | 64.43   | 18.13   | 1.02 | 64.97   |
| $\text{SnCl}_4(\text{DTE})$  | 12.62   | 2.64 | 36.80   | 12.75   | 2.77 | 37.13   |
| $\text{SnBr}_4(\text{DTE})$  | 8.64    | 1.80 | 57.03   | 8.93    | 1.71 | 57.42   |
| $\text{SnI}_4(\text{DTE})$   | 6.42    | 1.34 | 69.23   | 6.48    | 1.54 | 69.71   |

(410-33  $\text{cm}^{-1}$ ) infrared spectrophotometers. The Nujol-mull technique with CsI plates (4000-200  $\text{cm}^{-1}$ ) or polyethylene plates (410-33  $\text{cm}^{-1}$ ) was employed for all compounds. The spectra below 410  $\text{cm}^{-1}$  were measured on an expanded scale with a scanning speed of 2-4  $\text{cm}^{-1}/\text{min}$ . Reproducibility of the spectra was checked by multiple scans of several samples. The spectral resolution was approximately 1  $\text{cm}^{-1}$  and the accuracy of frequency reading was  $\pm 0.5\text{ cm}^{-1}$ . The frequency reading was calibrated by using polystyrene 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 and indene.

### Results and Discussion

(1) **2,2'-Bipyridine Complexes.** 2,2'-Bipyridine (bipy) is known to form 1:1 complexes,  $\text{SnX}_4(\text{bipy})$ , with tin tetrahalides. The low-frequency infrared spectra<sup>3-6</sup> of  $\text{SnX}_4(\text{bipy})$  (X = F, Cl, Br, I) and the Raman spectrum<sup>7</sup> of  $\text{SnCl}_4(\text{bipy})$  have already been reported. However, previous band assignments were made without sufficient evidence. In this study, we have reexamined the far-infrared spectra of  $\text{SnX}_4(\text{bipy})$  (X = Cl, Br, I) with the aid of <sup>116</sup>Sn and <sup>124</sup>Sn isotopes. The spectra of these complexes are shown in Figure 1, and

(3) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Chem. Soc. A*, 1828 (1968).

(4) M. F. Faroni and J. G. Grasselli, *Inorg. Chem.*, **6**, 1675 (1967).

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(6) I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964).

(7) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *Spectrochim. Acta, Part A*, **25**, 1035 (1969).

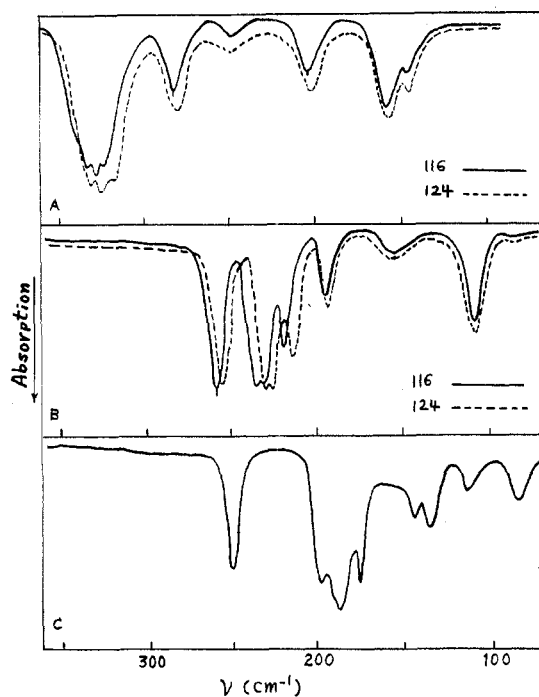


Figure 1. Far-infrared spectra of (A)  $^{116,124}\text{SnCl}_4(\text{bipy})$ , (B)  $^{116,124}\text{SnBr}_4(\text{bipy})$ , and (C)  $\text{SnI}_4(\text{bipy})$ .

the observed frequencies, isotope shifts, and band assignments are listed in Table II.

**$\text{SnCl}_4(\text{bipy})$ .** In accordance with the prediction for the *cis* structure, at least four Sn-Cl stretching bands have been observed between 340 and 280  $\text{cm}^{-1}$ . All these bands show relatively large shifts by  $^{116}\text{Sn}$ - $^{124}\text{Sn}$  substitution and disappear upon Cl-Br substitution. Previously, Clark, *et al.*,<sup>3</sup> assigned three bands (322, 302, and 279  $\text{cm}^{-1}$ ) and Forona and Grasselli<sup>4</sup> assigned five bands (337, 326, 318, 303, and 282  $\text{cm}^{-1}$ ) to the Sn-Cl stretching modes. We observed three bands (333, 328, and 322  $\text{cm}^{-1}$ ) relatively close together followed by a distant band (284  $\text{cm}^{-1}$ ) of lower intensity. This trend has been reported for *cis*- $\text{PtCl}_4(\text{NH}_3)_2$ .<sup>8</sup>

The bands at 204.0 and 158.0  $\text{cm}^{-1}$  are slightly sensitive to the tin isotope substitution and may be assigned to the Sn-N stretching modes. The weak band at 250.8  $\text{cm}^{-1}$  which is insensitive to the metal isotope substitution must be assigned to a ligand vibration activated by complex formation. Previously, this band was assigned to the Sn-N stretching mode.<sup>4</sup>

**$\text{SnBr}_4(\text{bipy})$ .** The bromide complex also exhibits four isotope-sensitive bands at 258.0, 235.0, 231.0, and 218.0  $\text{cm}^{-1}$ , all of which can be assigned to the Sn-Br stretching modes. Our assignments are different from those of Clark, *et al.*,<sup>3</sup> who assigned four bands at 256, 240, 216, and 192  $\text{cm}^{-1}$  to the Sn-Br stretching modes, or those of Forona and Grasselli,<sup>4</sup> who assigned two bands at 236 and 220  $\text{cm}^{-1}$  to the same modes. The bands at 194.0 and 156.0  $\text{cm}^{-1}$  may be assigned to the Sn-N stretching modes, although the latter is probably overlapped by a ligand vibration. In this case, strong vibrational coupling between the Sn-Br and Sn-N stretching modes may result in a pseudo totally symmetric vibration because the masses of Br and  $\text{C}_5\text{H}_5\text{N}$  are similar. This may account for the insensitivity of the 194.0- $\text{cm}^{-1}$  band to the isotopic substitution.

**$\text{SnI}_4(\text{bipy})$ .** The spectrum of the iodide complex can be assigned from the comparison with those of the chloride and

Table II. Far-Infrared Frequencies, Isotopic Shifts, and Band Assignments of  $\text{SnX}_4(\text{bipy})$  ( $\text{cm}^{-1}$ )

| bipy<br>$\nu$ | $\text{SnCl}_4(\text{bipy})$ |                    | $\text{SnBr}_4(\text{bipy})$ |               | $\text{SnI}_4(\text{bipy})$ |                      | Assignment <sup>d</sup>     |
|---------------|------------------------------|--------------------|------------------------------|---------------|-----------------------------|----------------------|-----------------------------|
|               | $\nu(^{116}\text{Sn})$       | $\Delta\nu^a$      | $\nu(^{116}\text{Sn})$       | $\Delta\nu^a$ | $\nu(\text{Sn})$            | $\nu(\text{Sn})$     |                             |
| 423           | 446.0                        | 0.0                | 444.0                        | 0.0           | 440                         |                      | Ligand                      |
| 404           | 419.5                        | 0.0                | 418.0                        | 0.0           | 416                         |                      | Ligand                      |
|               | 333.0                        | 3.0                | 258.0 <sup>b</sup>           | 2.0           | 198                         | } $\nu(\text{Sn-X})$ |                             |
|               | 327.5                        | 2.0                | 235.0                        | 3.5           | 191                         |                      |                             |
|               | 321.8                        | c                  | 231.0                        | 3.0           | 187.5                       |                      |                             |
|               | 283.5                        | 1.5                | 218.0                        | c             |                             |                      |                             |
| 250.8         | 0.0                          | 258.0 <sup>b</sup> |                              | 251           | Ligand                      |                      |                             |
| 168           | 204.0                        | 1.0                | 194.0                        | 0.2           | 176                         |                      | $\nu(\text{Sn-N})$          |
|               | 158.0                        | 1.0                | 156.0                        |               | 157                         |                      | $\nu(\text{Sn-N})$ , ligand |
|               | 146.6                        | 0.7                | 109.5                        |               | 136                         |                      | } $\delta(\text{skeletal})$ |
|               |                              |                    |                              |               | 115                         |                      |                             |
|               |                              |                    | 90                           |               | 84                          |                      |                             |

<sup>a</sup>  $\nu(^{116}\text{Sn}) - \nu(^{124}\text{Sn})$ . <sup>b</sup> Overlapped band. <sup>c</sup> This band is metal isotope sensitive. However, the isotopic shift could not be measured accurately because of poor band shape. <sup>d</sup> For the assignments of ligand vibrations, see ref 9. Abbreviations:  $\nu$ , stretching;  $\delta$ , bending.

bromide complexes (Table II). Four strong bands (198, 191, 187.5, and 176  $\text{cm}^{-1}$ ) have been observed in the region where the Sn-I and Sn-N stretching modes are expected. It is rather difficult, however, to distinguish these two modes empirically. Clark, *et al.*,<sup>3</sup> assigned three bands at 196, 185, and 173  $\text{cm}^{-1}$  to the Sn-I stretching modes, whereas Forona and Grasselli<sup>4</sup> assigned two bands at 186 and 176  $\text{cm}^{-1}$  to the same modes. Since the acceptor strength of  $\text{SnX}_4$  follows the order  $\text{X} = \text{Cl} > \text{Br} > \text{I}$ , the Sn-N stretching frequency of the iodide complex may not be higher than that of the bromide. We have, therefore, assigned three bands at 198, 191, and 187.5  $\text{cm}^{-1}$  to the Sn-I stretching and two bands at 176 and 157  $\text{cm}^{-1}$  to the Sn-N stretching modes.

**(2) 1,10-Phenanthroline Complexes.** The far-infrared spectra of  $\text{SnX}_4(\text{phen})$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>3</sup> and the Raman spectrum of  $\text{SnCl}_4(\text{phen})$ <sup>7</sup> have been reported previously. Figure 2 illustrates the far-infrared spectra of three  $\text{SnX}_4(\text{phen})$  type compounds. The observed frequencies, isotopic shifts, and band assignments are listed in Table III.

**$\text{SnCl}_4(\text{phen})$ .** The chloride complex exhibits four bands at *ca.* 341, 332, 326, and 278  $\text{cm}^{-1}$ , all of which give relatively large shifts by the  $^{116}\text{Sn}$ - $^{124}\text{Sn}$  substitution. Since these bands are not observed for the bromide and iodide complexes, they have been assigned to the Sn-Cl stretching modes. Clark, *et al.*,<sup>3</sup> assigned three bands at 319, 302, and 271  $\text{cm}^{-1}$  (ir) to the Sn-Cl stretching modes, whereas Fowles, *et al.*,<sup>7</sup> assigned four bands (338, 324, 305, and 275  $\text{cm}^{-1}$  in the ir and 341, 328, 312, and 277  $\text{cm}^{-1}$  in the Raman) to the same modes. The medium-intensity band at 310  $\text{cm}^{-1}$  in our spectrum is probably due to a ligand vibration; it is not sensitive to the metal isotope substitution and the bromide and iodide complexes also exhibit the same band.

The weak band at 245.2  $\text{cm}^{-1}$  must be assigned to a ligand vibration<sup>9</sup> since it is not sensitive to the metal isotope substitution. Fowles, *et al.*,<sup>7</sup> assigned it to the Sn-N stretching mode. We assigned this mode to the band at 183  $\text{cm}^{-1}$  which gives an isotopic shift of 1.2  $\text{cm}^{-1}$ . This frequency is close to 204  $\text{cm}^{-1}$  where the Sn-N stretching mode of  $\text{SnCl}_4(\text{bipy})$  has been assigned. The location of the other Sn-N stretching band is not clear since the spectrum between 160 and 140  $\text{cm}^{-1}$  is complicated.

**$\text{SnBr}_4(\text{phen})$ .** The Raman spectrum of this compound has been observed for the first time. As is seen in Table III, the

(8) D. M. Adams and P. J. Chandler, *J. Chem. Soc. A*, 1009 (1967).

(9) B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3335 (1970); Y. Saito, J. Takemoto, B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, **11**, 2003 (1972).

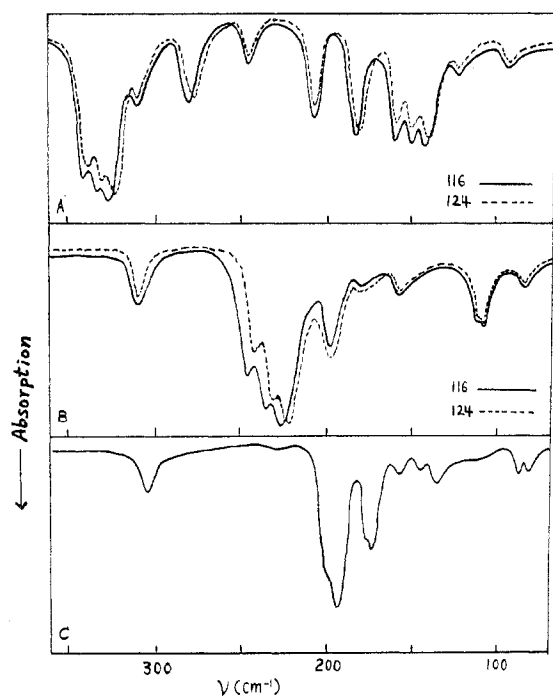


Figure 2. Far-infrared spectra of (A)  $^{116,124}\text{SnCl}_2(\text{phen})$ , (B)  $^{116,124}\text{SnBr}_2(\text{phen})$ , and (C)  $\text{SnI}_2(\text{phen})$ .

Table III. Far-Infrared Frequencies, Isotopic Shifts, and Band Assignments of  $\text{SnX}_4(\text{phen})$  ( $\text{cm}^{-1}$ )

| phen $\nu$ | $\text{SnCl}_4(\text{phen})$ |               | $\text{SnBr}_4(\text{phen})$ |               | $\text{SnI}_4(\text{phen})$ |                             | Assignment           |
|------------|------------------------------|---------------|------------------------------|---------------|-----------------------------|-----------------------------|----------------------|
|            | $\nu$ ( $^{116}\text{Sn}$ )  | $\Delta\nu^a$ | $\nu$ ( $^{116}\text{Sn}$ )  | $\Delta\nu^a$ | $\nu$ ( $^{116}\text{Sn}$ ) | $\nu$ ( $^{124}\text{Sn}$ ) |                      |
| 432        | 446.0                        | 0.0           | 447.0                        | 0.0           | 430                         | 446                         | Ligand               |
| 411        | 430.5                        | 0.0           | 429.0                        | 0.0           | 418                         | 428                         | Ligand               |
|            | 341.4                        | 1.2           | 244.0                        | 3.0           | 245                         | 195                         | } $\nu(\text{Sn-X})$ |
|            | 332.0                        | 3.0           | 231.5                        | 2.5           | 234                         | 191                         |                      |
|            | 326.0                        | 1.0           | 226.0                        | 3.8           | 223                         |                             |                      |
|            | 278.6                        | 1.1           |                              |               |                             |                             |                      |
|            | 309.8                        | 0.2           | 308.0                        | 0.0           | 310                         | 302                         | Ligand               |
| 259        | 245.2                        | 0.0           | c                            |               | c                           | 235                         | Ligand               |
| 242        |                              |               |                              |               |                             |                             |                      |
|            | 210.0                        | 0.4           | 196.5                        | 0.2           | 196                         | 176                         | Ligand               |
|            | 183.0                        | 1.2           | 180                          | d             | 183                         | 173                         | $\nu(\text{Sn-N})$   |
|            | 160.0                        | 0.2           | 158                          | ~0            | 158                         | 158                         | } Skeletal bending   |
|            | 149.0                        | 0.5           | 148                          | ~0            | 148                         | 145                         |                      |
|            | 143.5                        | 0.5           | 112                          | ~0            | 118                         | 134                         |                      |
|            | 127                          | ~0            | 107                          | 0.5           | 110                         | 113                         |                      |
|            | 94                           |               | 82                           |               | 85                          | 85                          |                      |

<sup>a</sup>  $\nu(^{116}\text{Sn}) - \nu(^{124}\text{Sn})$ . <sup>b</sup> Raman frequencies. <sup>c</sup> Overlapped band. <sup>d</sup> Too weak to be observed.

Raman frequencies are very similar to the infrared frequencies, indicating the lack of a center of symmetry. Three strong bands at 244.0, 231.5, and 226.0  $\text{cm}^{-1}$  of the  $^{116}\text{Sn}$  complex are metal isotope sensitive and can be assigned to the Sn-Br stretching modes. Clark, *et al.*,<sup>3</sup> assigned three bands at 240, 222, and 196  $\text{cm}^{-1}$  to the same modes. However, the last band is not sensitive to the metal isotope substitution. In the present work, this band has been assigned to a ligand vibration. The band at 180  $\text{cm}^{-1}$  has been assigned to the Sn-N stretching mode since its frequency is close to 183  $\text{cm}^{-1}$  of  $\text{SnCl}_4(\text{phen})$ .

**$\text{SnI}_4(\text{phen})$ .** Our spectrum shown in Figure 2 is in general agreement with that of Clark, *et al.*<sup>3</sup> No bands except two weak ligand bands (302 and 235  $\text{cm}^{-1}$ ) are observed between 400 and 200  $\text{cm}^{-1}$ . Four strong bands are observed at 195, 191, 176, and 173  $\text{cm}^{-1}$ . The first two bands have been

Table IV. Far-Infrared Frequencies and Band Assignments of  $\text{SnX}_4(\text{DTE})$  ( $\text{cm}^{-1}$ )

| DTE <sup>a</sup> | $\text{SnCl}_4(\text{DTE})$ | $\text{SnBr}_4(\text{DTE})$ | $\text{SnI}_4(\text{DTE})$ | Assignment           |
|------------------|-----------------------------|-----------------------------|----------------------------|----------------------|
| 442              | 450                         | 447                         | b                          | } Ligand             |
| 339              | d                           | 332                         | b                          |                      |
|                  | 326                         | 246 <sup>c</sup>            | 182                        | } $\nu(\text{Sn-X})$ |
|                  | 316                         | 223 <sup>c</sup>            | 170                        |                      |
|                  | 288 <sup>c</sup>            | 216                         |                            |                      |
|                  | 288 <sup>c</sup>            | 279                         | 264                        | } $\nu(\text{Sn-S})$ |
|                  | 240                         | 246 <sup>c</sup>            | 227                        |                      |
| 230              | 221                         | 223 <sup>c</sup>            | 220                        | Ligand               |
|                  | 156                         | 169                         | 148                        | } Skeletal bending   |
|                  | 144                         | 145                         |                            |                      |
|                  | 103                         | 114                         | 105                        |                      |
|                  |                             | 100                         | 77                         |                      |

<sup>a</sup> Measured in benzene solution. <sup>b</sup> This region was not measured. <sup>c</sup> Overlapped band. <sup>d</sup> Hidden by the Sn-Cl stretching band.

assigned to the Sn-I stretching modes whereas the last two bands have been attributed to a ligand vibration and the Sn-N stretching mode, respectively.

**(3) 1,2-Dimethylthioethane Complexes.** 1,2-Dimethylthioethane (DTE) is known to form a 1:1 cis complex with  $\text{SnCl}_4$ , and the Sn-Cl stretching bands have been assigned in the 327–285- $\text{cm}^{-1}$  region.<sup>7,10</sup> The bromide and iodide complexes have not been reported previously. In this study, we have synthesized all three complexes,  $\text{SnX}_4(\text{DTE})$  (X = Cl, Br, I). Figure 3 shows their infrared spectra and Table IV lists the observed frequencies and band assignments.

**$\text{SnCl}_4(\text{DTE})$ .** The spectrum shown in Figure 3 is in good agreement with those of previous workers.<sup>7,10</sup> A medium-intensity band at 450  $\text{cm}^{-1}$  corresponds to the 442- $\text{cm}^{-1}$  band of the free ligand. This band is observed at 445  $\text{cm}^{-1}$  for  $\text{TiCl}_4(\text{DTE})$ , 447  $\text{cm}^{-1}$  for  $\text{TiBr}_4(\text{DTE})$ , 450  $\text{cm}^{-1}$  for  $\text{NiI}_2(\text{DTE})$ , and 447  $\text{cm}^{-1}$  for  $\text{SnBr}_4(\text{DTE})$ . It is most reasonable to assign it to a ligand vibration. Previously,<sup>10</sup> this band was suggested to be a Sn-S stretching mode.

In agreement with previous workers,<sup>7,10</sup> three bands at 326, 316, and 288  $\text{cm}^{-1}$  are assigned to the Sn-Cl stretching modes. As will be shown later, the iodide complex exhibits two medium-intensity bands at 264 and 227  $\text{cm}^{-1}$  which can be assigned to the Sn-S stretching modes. In the case of the chloro complex, the corresponding bands are at *ca.* 290 (hidden by the Sn-Cl stretching band) and 240  $\text{cm}^{-1}$ . The Sn-S stretching vibrations of a series of complexes of the types  $\text{Sn}(\text{S-S})_2\text{L}_2$  and  $\text{Sn}(\text{S-S})_2(\text{L-L})$ , where S-S denotes the  $[\text{S}(\text{CH}_2)_2\text{S}]^{2-}$  ion and L (or L-L) represents a unidentate (or bidentate) ligand, have been assigned in the 350–300- $\text{cm}^{-1}$  region.<sup>11</sup> These frequencies are slightly higher than those of the present compounds possibly because the former involves the metal-thiolato bond rather than the metal-thioether bond.

**$\text{SnBr}_4(\text{DTE})$ .** As is shown in Table IV, five bands have been observed in the 400–200- $\text{cm}^{-1}$  region. The highest frequency band at 332  $\text{cm}^{-1}$  corresponds to the 339- $\text{cm}^{-1}$  band of the free ligand. The next band at 279  $\text{cm}^{-1}$  is assigned to the Sn-S stretching mode. The other Sn-S stretching band is probably hidden under the Sn-Br stretching modes near 230  $\text{cm}^{-1}$ .

**$\text{SnI}_4(\text{DTE})$ .** Two bands at 264 and 227  $\text{cm}^{-1}$  have been assigned to the Sn-S stretching modes. Two strong bands at 182 and 170  $\text{cm}^{-1}$  are reasonably assigned to the Sn-I

(10) R. J. H. Clark and W. Errington, *Inorg. Chem.*, **5**, 650 (1966).

(11) R. C. Poller and J. A. Spillman, *J. Chem. Soc. A*, 1024 (1966).

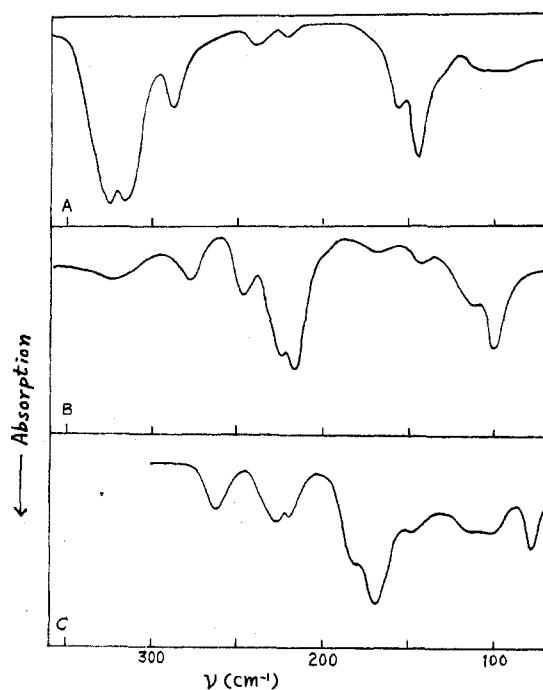


Figure 3. Far-infrared spectra of (A)  $\text{SnCl}_4(\text{DTE})$ , (B)  $\text{SnBr}_4(\text{DTE})$ , and (C)  $\text{SnI}_4(\text{DTE})$ .

stretching modes. The shoulder band at  $220\text{ cm}^{-1}$  is probably due to a ligand vibration.

(4) **1,2-Bis(diphenylphosphino)ethane Complexes.** This ligand (DPE) is known to form chelate compounds with a variety of metals. The infrared and Raman spectra of  $\text{SnCl}_4(\text{DPE})$  have been reported previously.<sup>12</sup> However, no spectral data are available on  $\text{SnBr}_4(\text{DPE})$ . Table V lists the observed frequencies and band assignments of these two compounds obtained in this work.

**$\text{SnCl}_4(\text{DPE})$ .** Carty, *et al.*,<sup>12</sup> observed only two strong ir bands ( $309$  and  $293\text{ cm}^{-1}$ ) in the Sn-Cl stretching region. Thus, the infrared spectrum did not unambiguously favor the cis structure although its Raman spectrum was indicative of cis stereochemistry. We observed three Sn-Cl stretching bands ( $320$ ,  $313$ , and  $297\text{ cm}^{-1}$ ) in the infrared spectrum.

The Sn-P stretching bands are difficult to assign in the infrared spectrum since they are relatively weak and the ligand itself exhibits a number of bands below  $400\text{ cm}^{-1}$ . As is shown in Table V, most of the bands observed are attributed to the ligand vibrations. In the previous paper,<sup>2</sup> we have suggested that the Sn-P stretching frequency of  $\text{SnX}_4(\text{PPh}_3)_2$  is lower than  $200\text{ cm}^{-1}$ . In the case of *cis*- $\text{SnCl}_4(\text{DPE})$ , the Sn-P stretching frequencies could be higher than those of *trans* complexes.<sup>13</sup> It is difficult, however, to give any definitive assignments without metal isotope data. Unfortunately, several attempts to prepare  $\text{SnCl}_4(\text{DPE})$  on a milligram scale were not successful.

(12) A. J. Carty, T. Hinsperger, L. Mihichuk, and H. O. Sharma, *Inorg. Chem.*, **9**, 2573 (1970).

(13) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Coord. Chem.*, **1**, 89 (1971).

Table V. Far-Infrared Frequencies and Band Assignments of  $\text{SnX}_4(\text{DPE})$  ( $\text{cm}^{-1}$ )

| DPE | $\text{SnCl}_4$ -<br>(DPE) <sup>a</sup> | $\text{SnBr}_4$ -<br>(DPE) | Assignment           |
|-----|---|----------------------------|----------------------|
| 399 | 413                                     | 409                        | } Ligand             |
|     | 391                                     |                            |                      |
| 337 | 363                                     |                            | } Ligand             |
|     | 342                                     | 343                        |                      |
| 300 | <i>b</i>                                | 310                        | Ligand               |
|     | 320                                     | 233                        | } $\nu(\text{Sn-X})$ |
|     | 313                                     | 217                        |                      |
|     | 297                                     | 207                        |                      |
| 284 | <i>b</i>                                | 281                        | } Ligand             |
|     |   | 276                        |                      |
| 259 | 260                                     | 265                        | } Ligand             |
| 248 | 245                                     | <i>b</i>                   |                      |
| 215 | 213                                     | <i>b</i>                   |                      |
| 150 | <i>b</i>                                | 149                        |                      |
|     | 161                                     | 139                        | } Skeletal bending   |
|     | 154                                     | 113                        |                      |
| 113 | 114                                     | 98                         |                      |

<sup>a</sup> Carty, *et al.*,<sup>12</sup> reported five Raman lines at  $357$ ,  $311$ ,  $290$ ,  $267$ , and  $250\text{ cm}^{-1}$ . <sup>b</sup> Hidden under the neighboring band.

**$\text{SnBr}_4(\text{DPE})$ .** Three strong bands at  $233$ ,  $217$ , and  $207\text{ cm}^{-1}$  can be assigned to the Sn-Br stretching modes. However, it was not possible to assign the Sn-P stretching modes due to lack of metal isotope data.

### Summary

Theoretically, four Sn-X stretching bands are expected to be ir active for the *cis*- $\text{SnX}_4(\text{L-L})$  type complexes. The present study shows, however, that the number of Sn-X stretching bands observed ranges from four to two, depending upon the nature of coordinating ligands. Some *trans*- $\text{SnX}_4\text{L}_2$  type complexes exhibit two Sn-X stretching bands although only one band is expected to be ir active.<sup>2</sup> Thus, the number of Sn-X stretching bands does not always provide clear-cut diagnosis on the stereochemistry of these complexes.

The Sn-L stretching bands are difficult to assign on an empirical basis. In the present work, the Sn-N stretching bands of the bipy and phen complexes have been located at  $210$ - $150\text{ cm}^{-1}$  based on metal isotope data. The Sn-S stretching modes of the DTE complexes have been assigned empirically in the range  $290$ - $220\text{ cm}^{-1}$ . It was not possible to locate the Sn-P stretching bands of the DPE complexes without metal isotope data.

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**Registry No.**  $\text{SnCl}_4(\text{bipy})$ , 23875-15-2;  $\text{SnBr}_4(\text{bipy})$ , 16918-62-0;  $\text{SnI}_4(\text{bipy})$ , 16918-63-1;  $\text{SnCl}_4(\text{phen})$ , 23917-59-1;  $\text{SnBr}_4(\text{phen})$ , 21220-35-9;  $\text{SnI}_4(\text{phen})$ , 21220-37-1;  $\text{SnCl}_4(\text{DTE})$ , 23875-14-1;  $\text{SnBr}_4(\text{DTE})$ , 21470-15-5;  $\text{SnI}_4(\text{DTE})$ , 40802-51-5;  $\text{SnCl}_4(\text{DPE})$ , 31080-28-1;  $\text{SnBr}_4(\text{DPE})$ , 40802-53-7; <sup>116</sup>Sn, 14191-70-9; <sup>124</sup>Sn, 14392-29-1.