

Dimethyltin Dihalide Complexes and Their Infrared Spectra

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Dimethyltin dichloride and dibromide form crystalline salts containing the ions $\text{Me}_2\text{SnX}_3^-$ as well as $\text{Me}_2\text{SnX}_4^{2-}$. The infrared spectra of the former are consistent with the methyl groups occupying equatorial rather than apical positions of a trigonal bipyramid. The spectra of complexes $\text{Me}_2\text{SnX}_2 \cdot 2\text{L}$ indicate the methyl groups to be in *trans* octahedral positions, with the remaining ligands in *cis* positions when $\text{X} = \text{Cl}$ and $\text{L} = \text{pyridine}$ or triphenylphosphine oxide.

THE identification of five-co-ordinate tin complexes in solution¹ and in crystalline compounds² including salts having ions of the type^{3,4} $\text{Me}_2\text{SnX}_3^-$ prompts closer examination of the co-ordination behaviour of the dimethyltin dihalides.⁵ It might be expected that the reduced electron-acceptor properties of the tin in these halides as compared with the tetrahalides would prejudice the co-ordination of a second ligand. This effect appears in halide ion complexes where the type

$\text{Me}_2\text{SnX}_3^-$ as well as $\text{Me}_2\text{SnX}_4^{2-}$ may be obtained even though the tetrahalides favour octahedral SnX_6^{2-} complexes. However, with stronger monodentate ligands, the only crystalline complexes obtained are of composition $\text{Me}_2\text{SnX}_2 \cdot 2\text{L}$. The infrared (i.r.) spectra of both the five- and six-co-ordinate complexes provide evidence on their configurations. The bands to 200 cm^{-1} given in Tables 1 and 2 include all Sn-Cl stretching frequencies and the Sn-Br bands from $\text{Me}_2\text{SnBr}_3^-$.

¹ T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 331; J. Laane and T. L. Brown, *Inorg. Chem.*, 1964, **3**, 148.

² R. Hulme, *J. Chem. Soc.*, 1963, 1524; H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 1963, **2**, 540, 1120; R. F. Bryan, *J. Amer. Chem. Soc.*, 1964, **86**, 733.

³ C. J. Wilkins and H. M. Haendler, *J. Chem. Soc.*, 1965, 3174.

⁴ F. W. B. Einstein and B. R. Penfold, private communication.

⁵ I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1963, 1519.

The Sn-Br bands from $\text{Me}_2\text{SnBr}_4^{2-}$ and $\text{Me}_2\text{SnBr}_4 \cdot 2\text{L}$ fall at lower frequencies, beyond the limit of the available instrument.

The capacity to form both $\text{Me}_2\text{SnX}_3^-$ and $\text{Me}_2\text{SnX}_4^{2-}$ ions extends over the fluoride,³ chloride, and bromide, but neither type of iodo-complex could be isolated. For the cations Cs^+ , NMe_4^+ , and NEt_4^+ there is a correlation between their increasing radii and capacity to produce salts of composition $\text{M}[\text{Me}_2\text{SnX}_3]$. Specific behaviour necessarily depends, however, upon both stability and solubility relationships. With the ammonium ion the only chloro-salt to crystallise is $\text{NH}_4[\text{Me}_2\text{SnCl}_3]$ and no complex bromide is obtainable from aqueous solution.

TABLE 1
Infrared spectra of halide ion complexes in the range 600–200 cm^{-1}

Compound	ν Sn-Me	ν Sn-X
$\text{Cs}_2\text{Me}_2\text{SnCl}_4$	580m	227s
$\text{Cs}_2\text{Me}_2\text{SnBr}_4$ ^a	571m	
$(\text{NMe}_4)_2\text{Me}_2\text{SnCl}_4$	578m ^b	227s
$\text{NH}_4\text{Me}_2\text{SnCl}_3$	581m, 519m	312sh, 306s, 300sh, 232s br
$\text{NMe}_4\text{Me}_2\text{SnCl}_3$...	574m, 432m, 520m	333sh, 322s, 235m br
$\text{NEt}_4\text{Me}_2\text{SnCl}_3$	574m, 568m, 501m	320s, 308s, 240m br
$\text{NMe}_4\text{Me}_2\text{SnBr}_3$...	566m, 522m	239sh, 228s, 222sh
$\text{NEt}_4\text{Me}_2\text{SnBr}_3$...	567m, 512m	228sh, 218s

^a Isomorphous with the chloride. ^b A band at 460 cm^{-1} is considered below the Sn-Me stretching frequency range.

The i.r. spectra (Table 1) of the octahedral halide ion complexes, $\text{Me}_2\text{SnX}_4^{2-}$, showing single Sn-Me and

dihalide complexes. The complexity of these spectra indicates that in the $\text{Me}_2\text{SnX}_3^-$ complexes the methyl groups are less symmetrically placed than at the apices of a regular trigonal bipyramid. The evidence is consistent with their lying in or near the equatorial plane as in the anion ⁴ of the salt $[\text{terpy} \cdot \text{Me}_2\text{SnCl}]^+ \text{Me}_2\text{SnCl}_3^-$, with the atoms of higher electronegativity in the polar positions, as seems usual.⁶

For the six-co-ordinate complexes formed by pyridine, dipyridyl, pyridine *N*-oxide, and triphenylphosphine oxide the single Sn-Me frequency is again indicative of a *trans* methyl configuration. The spectra of the pyridine *N*-oxide and triphenylphosphine oxide complexes contain ligand bands below 560 cm^{-1} (Table 2), but are identical with those of the corresponding complexes formed by the tin(IV) halides where no Sn-Me vibration is possible. In particular, no new band appears in the range 530–500 cm^{-1} , where the symmetric stretching frequency of the five-co-ordinate $\text{Me}_2\text{SnX}_3^-$ complexes is found.

In the bipyridyl complex $\text{Me}_2\text{SnCl}_2 \cdot \text{bipy}$, with the chlorine atoms necessarily in *cis* positions, the Sn-Cl absorption is very broad, with evidence of four components. Comparable broad bands present in the spectra of the pyridine and triphenylphosphine oxide complexes point to their having the same configuration. The pyridine *N*-oxide complex probably also has this configuration, though the evidence is less certain. The Sn-Cl band is not so broad, but has a contour suggesting closely spaced components at 233, 228, and 223

TABLE 2
Infrared spectra of other Me_2SnX_2 complexes in the range 600–200 cm^{-1}

Compound	ν Sn-Me	ν Sn-Cl ^a	ν Ligand	ν Sn-L
$\text{Me}_2\text{SnCl}_2 \cdot \text{bipy}$ ^b	575m	255sh, 248sh, 240s, 227sh	467w, 427m, 410m, 348w	
$\text{Me}_2\text{SnBr}_2 \cdot \text{bipy}$ ^b	574m		467w, 429w, 413m, 349w	(?) 217m
$\text{Me}_2\text{SnI}_2 \cdot \text{bipy}$ ^b	571m		467w, 428w, 410m, 350w	
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ^b	564m	248s, 241s, 228sh	424m	
$\text{Me}_2\text{SnBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ^{b, c}	560m		424m	
$\text{Me}_2\text{SnI}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ^b	550m		422m	
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{NO}$ ^b	574m	233s, 228s, 223sh	463m	321s
$\text{Me}_2\text{SnBr}_2 \cdot 2\text{C}_5\text{H}_5\text{NO}$ ^{b, c}	572m		463m	320s
$\text{Me}_2\text{SnI}_2 \cdot 2\text{C}_5\text{H}_5\text{NO}$ ^d	570m		463m	317s
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{Ph}_3\text{PO}$ ^b	577m	261s, 246s	543s, 505w, 465w, 451m ^e	
$\text{Me}_2\text{SnBr}_2 \cdot 2\text{Ph}_3\text{PO}$ ^d	575m		540s, 507w, 465w, 439w ^e	
$\text{Me}_2\text{SnI}_2 \cdot 2\text{Ph}_3\text{PO}$ ^d	573m		536s, 510w, 467m, 440m ^e	

^a These bands are poorly resolved. ^b X and L are in *cis* positions. ^c Isomorphous with the corresponding chlorides. ^d Positions of X and L not determined. ^e Bands at lower frequencies are omitted.

Sn-X stretching frequencies, point to a *trans* configuration. By contrast, the complexes of composition $\text{Me}_2\text{SnX}_3^-$ show a second Sn-Me stretching frequency 50–60 cm^{-1} below the first, with occasional doubling of one of the bands. There is also some complexity in the Sn-X region. For the bromides a broadened band comprising several components lies in the range 240–215 cm^{-1} . The chlorides show the corresponding band at 330–300 cm^{-1} , with a further very broad band having its maximum at 240–230 cm^{-1} also accessible. The frequency of the first Sn-Cl band is similar to that shown by the tin(IV) halide complexes; the frequency of the second is comparable with that of the dimethyl tin

cm^{-1} . The pyridine and pyridine *N*-oxide complexes from dimethyltin dibromide are isomorphous with those from the chloride.

The pyridine *N*-oxide complexes of the dimethyltin dihalides are characterised by strong Sn-O bands whose position continues to move to lower frequency with decreasing charge transfer within the bond, as in the tetrahalide complexes.³ These bands are broad, but symmetrical and without shoulders. The information on the pyridine and triphenylphosphine oxide complexes is insufficient to enable identification of metal-ligand

⁶ E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

frequencies. Comparison with other complexes of the former ligand⁷ suggests that the Sn-py frequencies could be below 200 cm.⁻¹, and with the latter the Sn-O band probably lies close to ligand bands in the range 400–300 cm.⁻¹.

The evidence for *cis* configurations in an increasing range of crystalline tin complexes encourages the belief that their isolation reflects a preponderance of this form in solution. From its i.r. spectrum it has been considered⁸ that the compound $\text{SnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ is more likely to be of *trans* than *cis* configuration. We confirm the presence of one strong and fairly sharp Sn-Cl band at 323 cm.⁻¹ (though with weak shoulders at 327 and 303 cm.⁻¹). Yet X-ray powder photographs show that the compound is of closely similar crystal structure to $\text{SnBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$, whose i.r. spectrum with three well-resolved Sn-Br bands (244s, 228s, and 215m cm.⁻¹) defines the configuration as *cis*.^{8,9} This configuration is therefore common to the pyridine complexes from tin(IV) chloride, tin(IV) bromide, dimethyltin dichloride, and dimethyltin bromide.

EXPERIMENTAL

Preparation and Analysis of Halide Ion Complexes.—Preparations were in general carried out using the components in equimolar proportions. The *caesium* and *ammonium* salts (Table I), and the *tetramethylammonium* salts of composition $\text{NMe}_4\text{Me}_2\text{SnX}_3$ were obtained by allowing aqueous solutions, containing a few drops of hydrochloric or hydrobromic acid as appropriate, to crystallise. The salt $(\text{NMe}_4)_2\text{Me}_2\text{SnCl}_4$ (analytically somewhat impure despite repetition of the preparation), was precipitated by mixing solutions of the components in dry ethanol. The *tetraethylammonium* salts $\text{NEt}_4\text{Me}_2\text{SnX}_3$ and $(\text{NEt}_4)_2\text{SnX}_6$ (X = Cl or Br) were likewise obtained from this solvent. The bromide $\text{NEt}_4\text{Me}_2\text{SnBr}_3$ required a few minutes to crystallise. The two *tetramethylammonium* compounds $\text{NMe}_4\text{Me}_2\text{SnCl}_3$ and $(\text{NMe}_4)_2\text{Me}_2\text{SnCl}_4$ were also obtained by heating *tetramethylammonium* chloride and dimethyltin dichloride in 1:1 and 2:1 molar proportions, respectively, in sealed tubes at 140°. These samples gave X-ray powder photographs and i.r. spectra which were identical with those of the compounds prepared from solution. All samples were dried under high vacuum before analysis. The following results were obtained, the figures for carbon, hydrogen, and nitrogen being from the micro-analytical laboratory, University of Otago.

(a) $\text{Cs}_2\text{Me}_2\text{SnCl}_4$ (Found: C, 4.4; H, 1.2; Cl, 25.6. $\text{C}_2\text{H}_6\text{Cl}_4\text{Cs}_2\text{Sn}$ requires C, 4.3; H, 1.1; Cl, 25.5%). (b) $\text{Cs}_2\text{Me}_2\text{SnBr}_4$ (Found: Br, 43.5. $\text{C}_2\text{H}_6\text{Br}_4\text{Cs}_2\text{Sn}$ requires Br, 43.5%). (c) $\text{NH}_4\text{Me}_2\text{SnCl}_3$ (Found: Cl, 38.8; 39.2; N, 4.6. $\text{C}_2\text{H}_{10}\text{Cl}_3\text{NSn}$ requires Cl, 39.0; N, 5.1%). (d) $\text{NMe}_4\text{Me}_2\text{SnCl}_3$ (Found: C, 23.0; H, 5.9; Cl, 32.3. $\text{C}_6\text{H}_{18}\text{Cl}_3\text{NSn}$ requires C, 21.9; H, 5.3; Cl, 32.4%). (e) $(\text{NMe}_4)_2\text{Me}_2\text{SnCl}_4$ (Found: C, 29.4; H, 7.5; Cl, 32.0.

$\text{C}_{10}\text{H}_{30}\text{Cl}_4\text{N}_2\text{Sn}$ requires C, 27.4; H, 6.9; Cl, 32.3%). (f) $\text{NMe}_4\text{Me}_2\text{SnBr}_3$ (Found: C, 15.7; H, 4.1; Br, 52.0. $\text{C}_6\text{H}_{18}\text{Br}_3\text{NSn}$ requires C, 15.55; H, 3.9; Br, 51.8%). (g) $\text{NEt}_4\text{Me}_2\text{SnCl}_3$ (Found: C, 31.3; H, 6.9; Cl, 27.8. $\text{C}_{10}\text{H}_{26}\text{Cl}_3\text{NSn}$ requires C, 31.2; H, 7.9; Cl, 27.6%). (h) $\text{NEt}_4\text{Me}_2\text{SnBr}_3$ (Found: C, 23.5; H, 5.1; Br, 46.5. $\text{C}_{10}\text{H}_{26}\text{Br}_3\text{NSn}$ requires C, 23.3; H, 5.0; Br, 46.2%). (i) $(\text{NEt}_4)_2\text{SnCl}_6$ (Found: C, 31.7; H, 5.2; Cl, 35.9. $\text{C}_{16}\text{H}_{40}\text{Cl}_6\text{N}_2\text{Sn}$ requires C, 32.4; H, 6.7; Cl, 36.0%). (j) $(\text{NEt}_4)_2\text{SnBr}_6$ (Found: C, 22.1; H, 4.7; Br, 55.5. $\text{C}_{16}\text{H}_{40}\text{Br}_6\text{N}_2\text{Sn}$ requires C, 22.4; N, 4.7; Br, 55.6%).

Preparation and Analysis of Other Complexes.—The bipyridyl complexes have been described previously.¹⁰ The *pyridine* adducts precipitated immediately from dry ethanol; the *pyridine N-oxide* and *triphenylphosphine oxide* complexes separated more slowly. The adducts were collected on a filter-crucible, washed successively with ethanol and light petroleum, and dried under high vacuum.

The following analyses were obtained. **Dimethyltin dichloride complexes.** (a) With pyridine (Found: C, 38.3; H, 4.5; Cl, 18.8. Calc. for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_2\text{Sn}$: C, 38.2; H, 4.2; Cl, 18.8%). (b) Pyridine *N-oxide* (Found: C, 35.3; H, 4.7; Cl, 17.6. $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_2\text{Sn}$ requires C, 35.2; H, 3.9; Cl, 17.3%). (c) Triphenylphosphine oxide (Found: C, 58.7; H, 4.7; Cl, 9.0. $\text{C}_{38}\text{H}_{36}\text{Cl}_2\text{O}_2\text{P}_2\text{Sn}$ requires C, 58.8; H, 4.7; Cl, 9.1%). **Dimethyltin dibromide complexes.** (d) With pyridine (Found: C, 31.0; H, 3.5; Br, 34.6. $\text{C}_{12}\text{H}_{16}\text{Br}_2\text{N}_2\text{Sn}$ requires C, 31.5; H, 3.5; Br, 34.2%). (e) Pyridine *N-oxide* (Found: C, 29.0; H, 3.6; Br, 32.5. $\text{C}_{12}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_2\text{Sn}$ requires C, 28.9; H, 3.2; Br, 32.0%). (f) Triphenylphosphine oxide (Found: C, 52.3; H, 4.3; Br, 18.4. $\text{C}_{38}\text{H}_{36}\text{Br}_2\text{O}_2\text{P}_2\text{Sn}$ requires C, 52.7; H, 4.2; Br, 18.5%). **Dimethyltin di-iodide complexes.** (g) With pyridine (Found: C, 25.8; H, 2.9; I, 45.6. $\text{C}_{12}\text{H}_{16}\text{I}_2\text{N}_2\text{Sn}$ requires C, 25.7; H, 2.9; I, 45.2%). (h) Pyridine *N-oxide* (Found: C, 24.6; H, 2.9; I, 43.4. $\text{C}_{12}\text{H}_{16}\text{I}_2\text{N}_2\text{O}_2\text{Sn}$ requires C, 24.3; H, 2.7; I, 42.8%). (i) Triphenylphosphine oxide (Found: C, 47.5; H, 3.85; I, 26.5. $\text{C}_{38}\text{H}_{36}\text{I}_2\text{O}_2\text{P}_2\text{Sn}$ requires C, 47.5; H, 3.8; I, 26.5%).

Infrared Spectra.—Spectra were recorded on Nujol mulls of the solid compounds. A Perkin-Elmer 221 spectrophotometer with potassium bromide optics was used to 400 cm.⁻¹. Spectra in the range 500–200 cm.⁻¹ were kindly recorded by Dr. N. S. Gill of the Australian National University, Canberra, using a Grubb-Parsons DM4 spectrophotometer, linear in wavelength. Some spectra were also run on a similar instrument linear in frequency.

X-ray powder photographs used for identification of solid phases and determination of isomorphism were taken using a Philips 114.8 mm. camera with Cu K_α radiation.

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