

620. *cis-trans-Isomerism in Octahedral SnCl_4L_2 Studied by Infrared Spectroscopy in the Cæsium Bromide Region.*

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Numerous addition compounds of tin tetrachloride have been prepared and characterised. On the basis of infrared spectroscopic examination it is suggested that the 1 : 2-adduct with acetone has a *cis*-octahedral configuration whereas more sterically hindered ligands such as trimethylamine, ether, tetrahydrofuran, tetrahydrothiophen, and diethyl sulphide result in adducts with *trans* stereochemistry. The 1 : 1 adduct with tetramethylethylenediamine is apparently not chelated. Where possible, both solution and solid-state spectra are reported. The infrared spectra of nitrile and phosphoryl chloride addition compounds of tin tetrachloride are also discussed.

THE general pattern of the stereochemistry of the non-transition elements is well understood.¹ However, very little is known about the influence of steric requirements of the ligands on the stereochemistry of co-ordination compounds, although the relationship between stability and steric hindrance has been quite extensively studied.² Similarly, it is usually difficult to predict the arrangement of the ligands in a complex unless π -bonding is of considerable importance, as, for example, in the compound $\text{py}_3\text{Mo}(\text{CO})_3$ in which

¹ See, *e.g.*, Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.

² See, *e.g.*, Wirth and Slick, *J. Phys. Chem.*, 1962, **66**, 2277, and references therein.

the carbon monoxide groups are mutually *cis*.³ Any study of the influence of stereochemistry of the ligand (and acceptor) on the stereochemical arrangement in the adduct should ideally be carried out under equilibrium conditions in solution (or in the gas phase), as solubility in many cases decides which isomer is produced from solution.⁴

We have attempted to assign the stereochemistry to 1:2 addition compounds of tin tetrachloride with organic ligands by examining their infrared spectra in the caesium bromide region. Our knowledge of the force constants in co-ordination compounds of

TABLE 1.

Main absorption bands in the infrared spectra of certain addition compounds of tin tetrachloride and related compounds in the 500—270 cm.⁻¹ range (mulls are in Nujol).

Compound	State		Stereochemistry
Acetone	Liquid	492sh, 389s	
SnCl ₄	In Me ₂ CO (380—290 cm. ⁻¹)	358s, 333s, 300w?	<i>cis</i>
SnCl ₄ .2Me ₂ CO	Mull	422m, 359s, 330s, 304s ^a	<i>cis</i> ^b
Pyridine <i>N</i> -oxide	Mull	460s, 305s	
SnBr ₄ .2C ₅ H ₅ NO	Mull	447m, 389m, 362m	
SnCl ₄ .2C ₅ H ₅ NO	Mull	441m, 397s, 366s, 337s, 323s, 281?	<i>cis</i> ^b
Me ₂ SO	In C ₆ H ₆ ^c	378s, 330s	
SnBr ₄ .2Me ₂ SO	Mull	464s, 338m, 313w, br	
SnCl ₄ .2Me ₂ SO	Mull	475s, 328vs, br, 302m, 270?	<i>cis</i> [*]
Ether	Liquid	498m, 436s, 374m, 308?	
SnCl ₄ .2Et ₂ O	Mull	436w, 341s	<i>trans</i>
SnCl ₄	In ether	497m ^d , 436s ^d , 374m ^d , 348m, 308? ^d	<i>trans</i>
SnCl ₄	In (CH ₂) ₄ O	343s	<i>trans</i>
SnCl ₄ .2(CH ₂) ₄ O	Mull	341s	<i>trans</i>
SnCl ₄ .2(CH ₂) ₄ O	In C ₆ H ₆ ^c	385w, 344s	<i>trans</i>
Diethyl sulphide	Liquid	380m, 340m, 303m	
SnCl ₄	In Et ₂ S	380m ^d , 331s, 304m ^d	<i>trans</i>
SnCl ₄ .2Et ₂ S	Mull	321s	<i>trans</i>
SnCl ₄ .2Et ₂ S	In C ₆ H ₆	369w, 328s	<i>trans</i>
Tetrahydrothiophen	Liquid	467w, 328w	
SnCl ₄	In (CH ₂) ₄ S	471w ^d , 328s	<i>trans</i>
SnCl ₄ .2(CH ₂) ₄ S	Mull	467w, 319s	<i>trans</i>
SnCl ₄ .2(CH ₂) ₄ S	In C ₆ H ₆ ^c	466w, 328s	<i>trans</i>
SnCl ₄ .2NMe ₃	Mull	319s	<i>trans</i>
SnCl ₄ .2NMe ₃	In C ₆ H ₆ ^c	367w, 329vs	<i>trans</i>
SnCl ₄ .Me ₂ N·[CH ₂] ₂ ·NMe ₂	Mull	316s	<i>trans</i> ^b bridged
UCl ₄ .MeO·[CH ₂] ₂ ·OMe	Mull	391m	
SnCl ₄ .MeO·[CH ₂] ₂ ·OMe	Mull	401m, 355s, 338s	
SnCl ₄	In MeO·CH ₂ ·CH ₂ ·OMe	348s	

* See Lindquist, "Inorganic Adduct Molecules of Oxo-compounds," Springer, Berlin, 1963.

^a Hydrolysis peak occurs at this point. ^b Assignment of stereochemistry in doubt. ^c Weak peaks near 400 cm.⁻¹ not given, as this is close to a benzene absorption. ^d Solvent peak.

the type under discussion is slight, but by use of the Raman⁵ data for SnCl₆²⁻ it is possible⁶ to obtain an approximate estimate of the positions of the tin-chlorine infrared-active stretching vibrations. Transference of the force-constant data from SnCl₆²⁻ directly to the SnCl₄ residue in a *cis*-adduct⁷ gives (approximately) $f_R = f_r = 1.4 \times 10^5$, $f_{Rr} = f_{rr} = 0.15 \times 10^5$, and $f_\alpha = f_\gamma = f_\beta = 0.13 \times 10^5$ dynes cm.⁻¹, when all other force

³ Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

⁴ See, e.g., Wilkins and Williams, "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience, New York, 1960.

⁵ Woodward and Anderson, *J.*, 1957, 1285.

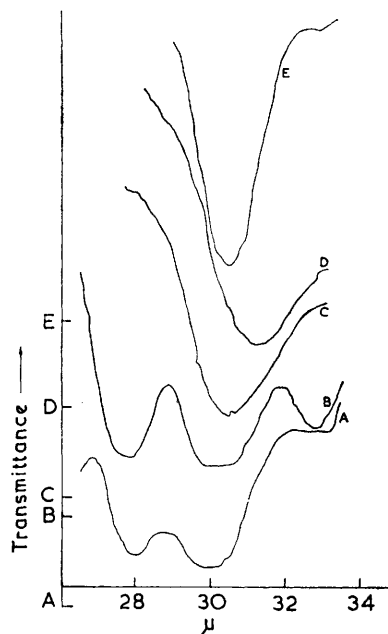
⁶ Pistorius, *J. Chem. Phys.*, 1958, 29, 1328.

⁷ Beattie, Gilson, Webster, and McQuillan, *J.*, 1964, 238.

constants are arbitrarily put equal to zero and the equalities shown are assumed. These very approximate calculations yield "stretching frequencies" a_1 243 and 310, b_1 332, and b_2 297 cm^{-1} ; these are comparable with the results of Brune and Zeil⁸ on SnCl_4L of symmetry C_{2v} (a_1 262 and 353, b_1 396, and b_2 388 cm^{-1}). Thus (as for 1:2 adducts of silicon tetrachloride⁷), we expect three fairly closely spaced absorption bands plus one of lower frequency (and probably off the range of our instrument). For a *trans*-adduct we expect⁹ one frequency only, around 330 cm^{-1} (e_u -type).

Our experimental observations are summarised in Table 1 and the Figure. The first point of interest that arises from Table 1 is that all the addition compounds of tin tetrachloride have bands in the region of 300 cm^{-1} , close to the antisymmetric stretching

The infrared spectra of some addition compounds of tin tetrachloride in "the Sn-Cl stretching region." A, SnCl_4 in acetone; B, $\text{SnCl}_4 \cdot 2\text{Me}_2\text{CO}$ as a Nujol mull; C, SnCl_4 in tetrahydrothiophen; D, $\text{SnCl}_4 \cdot 2(\text{CH}_2)_4\text{S}$ as a Nujol mull; E, $\text{SnCl}_4 \cdot 2(\text{CH}_2)_4\text{S}$ in benzene. Lines on the ordinate show zero transmittance for the various curves.



vibration of SnCl_6^{2-} [f_{1u} at 312 cm^{-1} in solid $(\text{NH}_4)_2\text{SnCl}_6$ ¹⁰]. The assignment of stereochemistry indicated in Table 1 is based on the above discussion. Our results on supposed *cis*-adducts could be interpreted in other ways, for example in terms of ionization to $\text{SnCl}_2\text{L}_4^{2+}$ and SnCl_6^{2-} . However, there is very little evidence to support this sort of behaviour for adducts of tin tetrachloride, and in acetonitrile (one of the solvents most likely to cause ionization) tin tetrachloride is effectively a non-conductor. The spectrum of the solid compound $\text{SnCl}_4 \cdot 2\text{MeCN}$ is almost identical¹⁰ with that of tin tetrachloride dissolved in acetonitrile, except for a solvent peak. Further, the only X-ray determinations carried out on adducts of tin tetrachloride show a *cis*-octahedral distribution.¹¹ Generally, where we have been able to obtain solution spectra these agree well with the corresponding solid-state spectra (except in the case of the 1:1 adduct of tin tetrachloride with dimethoxyethane).

Addition Compounds with Nitriles.—Although it has been suggested that two of the three strong absorptions found in the 300 cm^{-1} region for nitrile adducts are associated with tin-nitrogen vibrations,¹² this interpretation has been questioned¹⁰ since the spectrum of tin tetrachloride in acetonitrile in the "tin-chlorine stretching region" is virtually identical

⁸ Brune and Zeil, *Z. Phys. Chem. (Frankfurt)*, 1962, **32**, 384.

⁹ Pistorius, *Mol. Phys.*, 1958, **1**, 295.

¹⁰ Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.

¹¹ (a) Hermodsson, *Acta Cryst.*, 1960, **13**, 656; (b) Branden, *Acta Chem. Scand.*, 1963, **17**, 759.

¹² Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 4175.

(apart from a solvent peak) with that in propionitrile. A simple valence force field (SVFF) vibrational analysis of linear Me-C-N-Sn for the bond-stretching fundamentals, putting methyl as a point mass of 15 units with tin at 120 units, yields a tin-nitrogen frequency of 244 cm^{-1} if the C-C stretching force constant is taken as 5×10^5 , the C-N stretching force constant as 15×10^5 , and the Sn-N stretching force constant as $10^5 \text{ dynes cm}^{-1}$. Maintaining the same force constants, but extending the chain (assumed to be linear) by a methylene group to give Me-CH₂-C-N-Sn, yields a tin-nitrogen frequency of 201 cm^{-1} . Thus, on changing from acetonitrile as a ligand to propionitrile as a ligand, the tin-nitrogen frequency would be expected to decrease by about 40 cm^{-1} . No such change is observed for the three main peaks in the spectra of these compounds,¹⁰ and it may be assumed with confidence that they are tin-chlorine vibrations. These results are not in agreement with those of Brune and Zeil,⁸ who find only one peak in this region from the Raman spectrum ($\Delta\nu = 340 \text{ cm}^{-1}$) compared with the three in the infrared spectrum (365, 339, and 306 cm^{-1} , ref. 10; 367, 333—345, and 305 cm^{-1} , ref. 12). For C_{2v} symmetry the Raman and infrared spectra of the SnCl₄ residue should be identical (in position) in this region. It is possible that the solvent masked the peak at $\Delta\nu = 365 \text{ cm}^{-1}$ in the Raman effect, and that the intensity of the 306 cm^{-1} peak is low. The main peak observed in the infrared spectrum coincides with the one found in the Raman effect. There is no ambiguity from the point of view of the infrared spectrum; the assignment is *cis* (C_{2v}), although Brune and Zeil assign *trans* (D_{4h}) symmetry.

Generally the C-N stretching frequency in acetonitrile increases on co-ordination, and this has been taken to indicate an increase in the strength of this bond.¹³ We find from the above analysis that the change in the C-N frequency on co-ordination of acetonitrile to tin tetrachloride (assuming that there is no change in any force constant on co-ordination) is an increase of about 10 cm^{-1} . Increasing the mass of the tin atom from 120 to ∞ has virtually no effect on this frequency. The apparent lack of splitting of the C-N stretching frequency¹⁴ in a *cis*-adduct is explicable in terms of the mass of the tin atom and the weak coupling (due to the low value of the Sn-N stretching force constant).

In an earlier Paper we commented on the dissociation of the adduct SnCl₄.2MeCN in solution in benzene.¹⁰ We reported there that ν_3 of SnCl₄ was significantly less intense than the intensity of one of the Sn-Cl vibrations of a supposed 1 : 1 adduct. This is incorrect; the two intensities appear to be comparable. A careful examination of the spectra of SnCl₄ (SnCl₄.2MeCN), and (SnCl₄.2MeCN + excess acetonitrile) in benzene, and of SnCl₄ in acetonitrile suggests that the 1 : 1 adduct has a band at about 390 and another at about 347 cm^{-1} . SnCl₄.2EtCN shows a similar spectrum when dissolved in benzene, and here a 1 : 1 adduct is known to be formed.¹⁵

The Addition Compound SnCl₄.2POCl₃.—The 1 : 2 adduct of tin tetrachloride with phosphoryl chloride is the only one shown by the phase diagram, and is known to be *cis* from X-ray data, with co-ordination from the oxygen.^{11b} There were two previous Raman studies on this compound: Brune and Zeil,⁸ melt of SnCl₄.POCl₃ in POCl₃ at 30°, 397 (dep), 393 (dep), 359 (p, (267) (p), and 145; Kinnell, Lindquist, and Zackrisson,¹⁶ solution of SnCl₄ in POCl₃ (mole ratio 1 : 20) (read from a Figure), (586), 511, (481), (337), 312, 289, (266), 208, (191), 142, and 118. The Raman data for phosphoryl chloride show peaks at 194s, 269m, 339m, 482vs, and 584w, and we have placed brackets around frequency shifts close to these values in the above spectra. The agreement between the two sets of workers on tin tetrachloride solutions in phosphoryl chloride is almost negligible and suggests that they were studying different compounds (in solution). The experimental details in Brune and Zeil's Paper are slight, so that it is impossible to discuss these discrepancies adequately. We found that a Nujol mull of SnCl₄.2POCl₃ indicated that some

¹³ See, e.g., Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2182.

¹⁴ Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

¹⁵ Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, *B*, **17**, 21.

¹⁶ Kinell, Lindquist, and Zachrisson, *Acta Chem. Scand.*, 1959, **13**, 1159.

solution (and dissociation) of the adduct in Nujol had occurred. Mulling with phosphoryl chloride was attempted but the spectra were then complicated by the very intense band of phosphoryl chloride at 336 cm^{-1} . Under various conditions we appeared to obtain most of the bands in the $30\ \mu$ region mentioned by the previous Raman workers. A solid-state spectrum of $\text{SnCl}_4 \cdot 2\text{POCl}_3$ sublimed on to cooled caesium bromide plates showed main absorptions at 381, 368, 351, 342, 336, 318, and 289 cm^{-1} . We are unable to give intensity data, as the compound was found to sublime from the plate very readily.

Supposed cis-Adducts.—We selected a few ligands which were not sterically hindered, and where the donor atom was small (pyridine *N*-oxide, acetone, and dimethyl sulphoxide). The acetone adduct gave similar spectra in the solid state and in solution in the ligand, clearly indicating a *cis*-configuration. The normal infrared spectrum of this adduct closely resembled that of $\text{TiCl}_4 \cdot \text{Me}_2\text{CO}$.¹⁷ The solution spectrum in acetone could only be run over a short range, as some reaction between the tin tetrachloride and the solvent occurred (probably owing to difficulties experienced in the drying of acetone), whilst a solution in benzene gave evidence of extensive dissociation.¹⁵ Both the dimethyl sulphoxide adduct and the pyridine *N*-oxide adduct appear to be insoluble in organic solvents. Solid-state spectra of the chloride addition compounds, when compared with the corresponding bromide addition compounds, lead to a tentative *cis*-assignment for the pyridine *N*-oxide adduct of tin tetrachloride. The normal infrared spectra of these adducts agree closely with those for related addition compounds.^{18,19}

Supposed trans-Adducts.—Here we selected ligands which were likely to be more sterically hindered and/or had large donor atoms (ether, tetrahydrofuran, diethyl sulphide, tetrahydrothiophen, and trimethylamine). In all cases it was possible to obtain solution spectra which agreed closely with the relevant solid-state spectra. For the trimethylamine, tetrahydrofuran, and tetrahydrothiophen adducts a *trans* assignment appears to be unambiguous. In the case of the solution spectra in the free ligand, the assignment of stereochemistry is complicated to some extent in the ether and diethyl sulphide cases by the presence of solvent peaks. However, reliable spectra were obtained for all the supposed *trans*-adducts in benzene, with the exception of $\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$ which displayed the expected large degree of dissociation.²⁰

Bidentate Ligands.—1,2-Dimethoxyethane with tin tetrachloride yields a 1:1 adduct showing a main double peak, suggesting resolution of the e_u vibration with *trans* stereochemistry. In solution in the ligand the spectrum changes to that of a *trans*-adduct. In solution in benzene the spectrum shows a peak at 354 cm^{-1} with evidence of a shoulder at 348 cm^{-1} , possibly due to the presence of five- and six-co-ordinated tin. In the case of the tetramethylethylenediamine (TMEN) adduct the spectrum is that of a *trans*-complex with bridging TMEN. This is not unexpected, as both bridging and non-bridging ethylenediamine are well established. What is rather surprising is that the normal infrared spectrum of $\text{SnCl}_4 \cdot \text{TMEN}$ (assumed to be bridged-polymeric) closely resembles that of $\text{SiCl}_4 \cdot \text{TMEN}$ (assumed to be chelate).²¹ We find that for tin tetrachloride with strong chelate ligands there is a tendency for the two high-frequency bands to coalesce, and for the lower frequency band to lose intensity and be in a region where our spectrometer is losing sensitivity, so that a *trans* assignment here is open to criticism. Nevertheless, we would also point out that tetramethylethylenediamine chelated to silicon would almost certainly show a non-planar N-C-C-N grouping, leading to low symmetry, whilst with this group acting as a bridge for a multinuclear complex the symmetry could again be low, depending on the alignment of the two N-C groups about the C-C single bond, so that the importance of the spectral data in the normal infrared region should not be overstressed.

¹⁷ Susz, *Helv. Chim. Acta*, 1960, **43**, 855.

¹⁸ Lappert and Smith, *J.*, 1961, 3224.

¹⁹ Kida, Quagliano, Walmsley, and Tyree, *Spectrochim. Acta*, 1963, **19**, 189.

²⁰ Laubengayer and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5985.

²¹ Beattie and Webster, *J.*, 1963, 4285.

DISCUSSION

Our results at present fit into a tentative picture that "small" donors tend to give *cis*-adducts, whereas more bulky fairly symmetrical ligands tend to give *trans*-adducts. These conclusions rest largely on the relatively unambiguous *cis* assignments for adducts of acetonitrile, acetone, and phosphoryl chloride^{11b} plus the *trans* assignments for adducts of tetrahydrofuran, trimethylamine, ether, tetrahydrothiophen, and diethyl sulphide. The Raman spectrum of $\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$ has been reported⁸ to show a tin-chlorine stretching vibration at $\Delta\nu = 325 \text{ cm.}^{-1}$, about 20 cm.^{-1} from the corresponding band in the infrared spectrum of this adduct and supporting the suggestion that the SnCl_4 residue in this molecule has a centre of symmetry. The assumption that acetone and phosphoryl chloride are "small" ligands relies on the supposition that a lone-pair has a relatively small steric effect as far as the acceptor is concerned. Some doubt is cast on this facile explanation by recent observations on lone-pair-lone-pair repulsions.²² Further, ^{19}F resonance measurements²³ on several 1 : 2 addition compounds of tin tetrafluoride show that a *cis* configuration is adopted, suggesting the importance of $d_\pi-p_\pi$ bonding between the halogen and the tin. Similarly, $\text{Me}_2\text{SnCl}_4^{2-}$ is *trans*²⁴ although on steric grounds a *cis* configuration would have been expected. In view of the strength of the Sn-C bond this ion is perhaps best considered as a co-ordination compound of $\text{Me}_2\text{Sn}^{2+}$ and chloride ions. An equivalent point of view is to consider that a primary hybridisation occurs, to form linear $\text{Me}_2\text{Sn}^{2+}$, and that the more weakly held chloride ions use the remaining orbitals and take up a square-planar distribution about the central atom. This type of explanation suggests that a square-planar arrangement of four ligands about a non-transition element (or ion) might be found without the necessary presence of lone-pairs of electrons.

As we have pointed out, our observations on $\text{SnCl}_4 \cdot 2\text{MeCN}$ are not in agreement with the Raman work, although the main band in both spectra coincides (339 cm.^{-1} and $^8 \Delta\nu = 340 \text{ cm.}^{-1}$). The disagreement is probably explicable in terms of the adjacent solvent band and intensity effects. Similarly, there is an apparent disagreement with dipole moment data on $\text{SnCl}_4 \cdot 2(\text{tetrahydrothiophen})$. This compound has been reported²⁵ to have a dipole moment of about 5 D, but it is not clear whether any correction was made for electron and atom polarization. Further, the tetrahydrothiophen residues are attached through a Sn-S-C bond which will presumably be bent so that a *trans*-adduct with suitable alignment of the ligand rings could have a high moment.

We stress that our results should only be accepted with caution. Assignment of a *cis* configuration relies on the absence of impurity, ligand and (perhaps most important) metal-ligand vibrations in the 30μ region. We should not be aware of the presence of small amounts of *trans*-adduct in a *cis*-adduct, although in no case did we find evidence that mixtures of isomers were formed. The assignment of *trans* stereochemistry could be erroneous if certain bands coalesced or were of low intensity. We find that for strong donors there is a tendency for the low-frequency vibration of the group of three to lie in a region (near 270 cm.^{-1}) where our instrument is becoming less sensitive. Coalescence of the remaining two bands could lead to wrong stereochemical deduction. Ideally, a known chelate, closely related to the relevant unidentate ligand, should be examined to obtain the spectrum of a *cis*-adduct.

EXPERIMENTAL

Preparations.—Benzene, carbon tetrachloride, acetonitrile, propionitrile, trimethylamine, tetramethylethylenediamine, and tin tetrachloride were dried and purified as described previously.^{10, 21, 26} Ether, light petroleum (b. p. $100-120^\circ$), tetrahydrofuran, 1,2-dimethoxyethane, diethyl sulphide, toluene, and tetrahydrothiophen were dried with calcium hydride, the

²² Owen and Sheppard, *Proc. Chem. Soc.*, 1963, 264.

²³ Muettterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

²⁴ Beattie and McQuillan, *J.*, 1963, 1519.

²⁵ See, e.g., Gold'shtein, Gur'yanova, and Kocheshkov, *Proc. Acad. Sci. (U.S.S.R.)*, 1961, **138**, 566.

²⁶ Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.

tetrahydrofuran and 1,2-dimethoxyethane having been previously passed through an alumina column. Acetone was dried over calcium sulphate, and dimethyl sulphoxide with molecular sieve. Pyridine *N*-oxide and tin tetrabromide were vacuum-sublimed. The addition compounds were generally prepared by adding tin tetrachloride to a solution of the donor in a solvent [tetrahydrofuran, acetone, ether, and 1,2-dimethoxyethane in light petroleum (b. p. 100—120°); pyridine *N*-oxide, tetramethylethylenediamine, and dimethyl sulphoxide in benzene; acetonitrile in carbon tetrachloride], and the resultant white precipitate could be removed in a centrifuge and washed with light petroleum (b. p. 100—120°). In the case of the tin tetrachloride adduct with phosphoryl chloride, precipitation from light petroleum (b. p. 100—120°) occurred only on standing. With certain adducts it was necessary to remove the volatile compounds after mixing the reagents alone or in a solvent [tin tetrachloride added to diethyl sulphide or acetone (see also above) in benzene; tin tetrachloride dissolved in ethyl cyanide or tetrahydrothiophen]. The tin tetrabromide adducts of pyridine *N*-oxide and dimethyl sulphoxide were obtained as white precipitates after mixing benzene solutions of the reagents. The adduct SnCl₄.2NMe₃ was made, in a vacuum system, from tin tetrachloride and excess of trimethylamine.²⁷ The excess of trimethylamine was pumped away after standing at room temperature for 24 hr. All preparations not carried out in a vacuum system were carried out in a dry-box.

Spectra.—These were taken on a Perkin-Elmer model 221 infrared spectrometer equipped with grating, rock-salt, and caesium bromide optics. For spectra in acetonitrile Polythene plates were used, with toluene in low concentration as an internal reference to determine cell thickness. For other spectra caesium bromide plates were employed.

Characterization.—The compounds were analysed by total hydrolysis, followed by potentiometric determination of halide with a silver electrode. In the case of the 1 : 1 TMEN adduct hydrolysis was not successful and combustion analysis was necessary. Compounds were also examined by melting point, and solubility was (approximately) determined.

TABLE 2.
Analyses, melting points, and solubilities.

Compound	Found (%) Cl or Br	Formula	Reqd. (%) Cl or Br	M. p. (sealed tube)	Lit. value	Solubility
SnCl ₄ .2MeCN	41.3, 41.4	C ₈ H ₈ Cl ₄ N ₂ Sn	41.4	—	112—114 ^g 14	Sol. C ₆ H ₆ and MeCN
SnCl ₄ .2EtCN	38.2	C ₈ H ₁₀ Cl ₄ N ₂ Sn	38.3	72 or 92°	69—74 14 92 15 76.5 e	V. sol. C ₆ H ₆ , light petroleum (b. p. 100—120°), and EtCN
SnCl ₄ .2(CH ₃) ₂ O	34.8	C ₈ H ₁₆ Cl ₄ O ₂ Sn	35.0	—	180 b	Sol. C ₆ H ₆ and tetrahydro- furan
SnCl ₄ .2Et ₂ O	34.6	C ₈ H ₂₀ Cl ₄ O ₂ Sn	34.7	97	98 15 80.6 20	Sol. C ₆ H ₆ ; sl. sol. Et ₂ O
SnCl ₄ .MeO·CH ₂ ·CH ₂ ·OMe	40.1, 40.4	C ₈ H ₁₀ Cl ₄ O ₂ Sn	40.5	—	—	V. sol. MeO·CH ₂ ·CH ₂ ·OMe; sl. sol. C ₆ H ₆
SnCl ₄ .2Et ₂ S	32.1	C ₈ H ₂₀ Cl ₄ S ₂ Sn	32.2	104—108	101—102 d	Sol. C ₆ H ₆ and Et ₂ S
SnCl ₄ .2(CH ₃) ₂ S	32.2	C ₈ H ₁₆ Cl ₄ S ₂ Sn	32.5	162—163 (sl. decomp.)	154—157 e	Sol. C ₆ H ₆ and tetrahydro- thiophen
SnCl ₄ .2Me ₂ CO	37.0, 37.4	C ₈ H ₁₂ Cl ₄ O ₂ Sn	37.7	106—108 (decomp.)	—	Sol. Me ₂ CO and C ₆ H ₆
SnCl ₄ .2NMe ₃	37.3	C ₈ H ₁₈ Cl ₄ N ₂ Sn	37.4	164—166 (decomp.)	171 20 174—175 21	Sol. C ₆ H ₆
SnCl ₄ .2Me ₂ SO	33.9	C ₈ H ₁₂ Cl ₄ O ₂ S ₂ Sn	34.0	280 245 (decomp.)	270—300 18	—
SnCl ₄ .TMEN	*	—	—	59 220 250 (decomp.)	59 a	Sol. POCl ₃
SnCl ₄ .2POCl ₃	—	—	—	59	—	—
SnBr ₄ .2Me ₂ SO	53.1	C ₈ H ₁₂ Br ₄ O ₂ S ₂ Sn	53.8	220	198—204 18	—
SnBr ₄ .2py·N-O	50.4	C ₁₀ H ₁₆ Br ₄ N ₂ O ₂ Sn	50.9	250 (decomp.)	—	—
SnCl ₄ .2py·N-O	31.1	C ₁₀ H ₁₆ Cl ₄ N ₂ O ₂ Sn	31.5	235—245 (decomp.)	—	—

* Found: C, 19.4; H, 4.4; Cl, 33.0. C₈H₁₆Cl₄N₂Sn requires C, 19.1; H, 4.3; Cl, 37.37.

a Payne, *Rec. Trav. chim.*, 1956, **75**, 620. b Sisler, Batey, Pfahler, and Mattair, *J. Amer. Chem. Soc.*, 1898, **70**, 3821. c Puschin Rustic, Parchomenkov, and Ubovic, *Annalen*, 1942, **553**, 278. d Werner and Pfeiffer, *Z. anorg. Chem.*, 1989, **17**, 82. e Karaulova and Nekrasov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 73.

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