

301. The Structure of *trans*-Tetrachlorobis(tetrahydrothiophen)tin(IV) in the Solid State and in Solution

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The 1 : 2 addition compound formed between tin tetrachloride and tetrahydrothiophen is soluble in benzene with only slight dissociation and in this solvent has a dipole moment of about 4 Debye. Despite this high moment, Raman and infrared spectral investigations show that this compound has a *trans*-configuration in benzene solution. X-Ray analysis of the crystalline material indicates that the space group is $P2_1/n$ (No. 14) with $a = 10.1$, $b = 9.3$, $c = 7.9$ Å and $\beta = 98^\circ$. There are two molecules in the unit cell, requiring a centrosymmetric molecule with a *trans*-configuration.

X-RAY structural investigations of the 1 : 2 addition compounds formed between tin tetrachloride and phosphoryl chloride,¹ selenyl chloride,² or dimethyl sulphoxide³ show the presence of an approximately octahedral distribution about the tin(IV) with ligands in the *cis*-positions. However, on the basis of a study of the infrared spectra of several related 1 : 2 addition compounds of tin tetrachloride with a variety of donors,⁴ it has been suggested⁵ that ligands that are "small" tend to give *cis*-adducts, whereas more bulky ligands, which are sterically hindered in a fairly symmetrical fashion, tend to yield *trans*-adducts. In particular, it was suggested that the 1 : 2 addition compound with tetrahydrothiophen had *trans*-formulation, although from dielectrometric titration in benzene it has been found⁶ that the adduct has an electric moment of about 5 Debye. A similar value was found⁶ from a direct determination of the dipole moment in benzene-tetrahydrothiophen, although in neither case was the method of calculation made clear. As both cryoscopic⁶ and infrared⁴ spectroscopic investigation of this compound in benzene indicated only slight dissociation, the high dipole moment makes one question the *trans*-assignment. However, from the point of view of the infrared spectral results that assignment is unambiguous and, if incorrect, would throw as much doubt on the value of this technique in assigning molecular geometry as its being correct throws doubt on the dipole moment method for such compounds. In the region of 330 cm.⁻¹ only one smooth symmetrical absorption is observed, representing a classical example of the requirement for a *trans*-adduct, and in sharp contrast to the *three* absorptions found in this region for many *cis*-adducts.⁴ We felt that a complete investigation of this compound in the solid state and in solution was necessary, (a) because of the current trend towards the use of infrared spectroscopy in the region beyond 400 cm.⁻¹ for the assignment of the stereochemical formulation of metal halide addition compounds and, (b) to define a *trans*-addition compound of tin tetrachloride.

The determination (and interpretation) of the dipole moment of a compound such as SnCl₄.2C₄H₈S involves a number of difficulties. Hydrolysis is likely to lead to compounds of very high dipole moment, while dissociation to SnCl₄.C₄H₈S and free tetrahydrothiophen would similarly lead to a high apparent moment. Determination of the molecular weight of the 1 : 2 adduct in benzene showed the presence of a largely undissociated species, in agreement with earlier work.^{4,6} Similarly, studies of its dipole moment in benzene showed the presence of an adduct with a moment of about 4.2 Debye, again in reasonable agreement with previous results.⁶ Infrared spectroscopic examination of the solutions used for the dipole moment investigations suggested negligible hydrolysis. However, an examination of this compound in benzene by the technique of Raman spectroscopy showed an intense

¹ Branden, *Acta Chem. Scand.*, 1963, **17**, 759.

² Hermodsson, *Acta Cryst.*, 1960, **13**, 656.

³ Hanson and Brunge, private communication quoted in Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Springer, Berlin, 1963.

⁴ Beattie and Rule, *J.*, 1964, 3267.

⁵ Beattie, *Quart. Rev.*, 1963, **17**, 382.

⁶ Gol'dshtein, Gur'yanova, and Kocheshkov, *Proc. Akad. Sci., U.S.S.R.*, 1962, **144**, 456.

band at 301 cm.^{-1} with a depolarization ratio of 0.1 (see Table). The lack of a band at 300 cm.^{-1} in the infrared spectrum of this compound under comparable conditions strongly suggests D_{4h} rather than C_{2v} symmetry for the SnCl_4 residue. Similarly, the Raman polarization results identify the main band as a (perturbed) a_{1g} mode of *trans*- L_2MX_4 , essentially the breathing frequency of the MCl_4 residue. It can thus be assumed with some certainty that in solution in benzene the compound has a *trans*-configuration. The band at 336 cm.^{-1} , present in solution spectra but absent in the spectrum of the solid state, is not due to dissociation to a 1 : 1 adduct, since this band also occurs with tin tetrachloride dissolved in tetrahydrothiophen.

Raman and infrared results for $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{S}$ in the 300 cm.^{-1} region

Phase	Method	ν (in cm.^{-1})	
In benzene	R	336 ($\rho = 0.2$)(3)	301 ($\rho = 0.1$)(10) 259 (<1)
In tetrahydrothiophen *	IR	328s	
	R	334(3)	296(9)
Solid	IR	328s	
	R		299s 259w
(Nujol mull)	IR	319s	

ρ = Depolarization ratio; bracketed figures indicate approximate intensity of Raman lines.

* Tetrahydrothiophen has a weak depolarized Raman band at 297 cm.^{-1} , whereas the strong Raman band shown in the Table for the solution of the tetrachloride in tetrahydrothiophen is polarized. In a previous Paper by two of us⁴ (I. R. B. and L. R.) a weak band was reported at 328 cm.^{-1} in the infrared spectrum of tetrahydrothiophen. This observation is erroneous as is that of band at 305 cm.^{-1} in pyridine *N*-oxide. In the case of the tetrahydrothiophen it is apparent that slight contamination by tin tetrachloride occurred through the atmosphere of the dry box.

The high dipole moment is not easy to explain, although a variety of factors could lead to a moment of about 4 Debye. If we assume that the dipole moment of tetrahydrothiophen is unchanged on co-ordination, and that there is free rotation about the Sn-S bond (remembering that Sn-S-C is non-linear) the problem is reduced to that of a summation for the two vectors. Putting the dipole moment of tetrahydrothiophen equal to 1.9 Debye and the Sn-S-C angle (take by us to be the Sn-S-vector angle) equal to the tetrahedral angle, the calculated⁷ dipole moment for free rotation is about 2.5 Debye. A further difficulty lies in the atom polarization, which is probably underestimated by us in calculating the dipole moment from the experimental results (by Guggenheim's method,⁸ equation 7.3, and noting that the multiplier in the numerator should be 4 and not 3). Thus, although the adduct $\text{SnCl}_4 \cdot 2\text{NMe}_3$ would be expected to have zero moment, a dipole moment of 0.4 Debye has been reported.⁹ Other factors that could *raise* the apparent dipole moment are slight hydrolysis (unlikely to be serious here), slight dissociation to yield a 1 : 1 adduct of high moment and tetrahydrothiophen, suitably *coupled* rotation of the tetrahydrothiophen ligands, and (by comparison with the calculated value above by using a vector model) an enhanced dipole moment for tetrahydrothiophen due to co-ordination.

A value of 4.3 Debye has been quoted for the dipole moment of $\text{SnCl}_4 \cdot 2\text{tetrahydrofuran}$,⁶ although here again the infrared results point unambiguously to a *trans*-formulation. Similarly, the adduct $\text{VCl}_3 \cdot 2\text{Et}_2\text{S}$, although almost certainly a *trans* trigonal bipyramidal adduct, is reported to have a dipole moment of 2.6 Debye.¹⁰ This work thus confirms that dipole moment measurements on compounds where the direction of the ligand dipole does not coincide with the co-ordinate bond direction are unlikely to be helpful stereochemically.

⁷ See, e.g., Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, London, 1955, p. 231 *et seq.*

⁸ Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

⁹ Brune and Zeil, *Z. phys. Chem. (Frankfurt)*, 1962 **32**, 384.

¹⁰ Duckworth, Fowles, and Williams, *Chem. and Ind.*, 1962, 1285.

X-Ray Results.—Crystals of the SnCl_4 -tetrahydrothiophen complex were obtained from benzene. Oscillation and Weissenberg photographs taken with $\text{Cu-K}\alpha$ radiation about the *c*-axis show that the single crystal is monoclinic with $a = 10.1$, $b = 9.3$, $c = 7.9 \text{ \AA}$, β (by angular lag) $= 98^\circ$, $V = 732 \text{ \AA}^3$. Systematic absences are $h0l$ when $(h + l)$ is odd, and $0k0$ when k is odd, so that the space group must be $P2_1/n$ (No. 14). From packing considerations, we conclude that there can only be two molecules in the unit cell. This is supported by a rough density measurement (1.9 g./c.c.) obtained by flotation; the calculated density is 1.98 g./c.c. for $M = 437$, $Z = 2$. To fit two molecules into a cell that has four general positions, it is necessary to place them in a mirror plane, on a two-fold axis or at a centre of symmetry. Only the latter element is available in the space group $P2_1/n$, so that the molecules must lie at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and themselves be centrosymmetric. This is only possible if the molecule has the *trans*-configuration. An electron-density projection, constructed from 65 $hk0$ intensities, confirmed this interpretation and, together with a generalized projection (using 113 hkl intensities) suggested the molecule shown in the

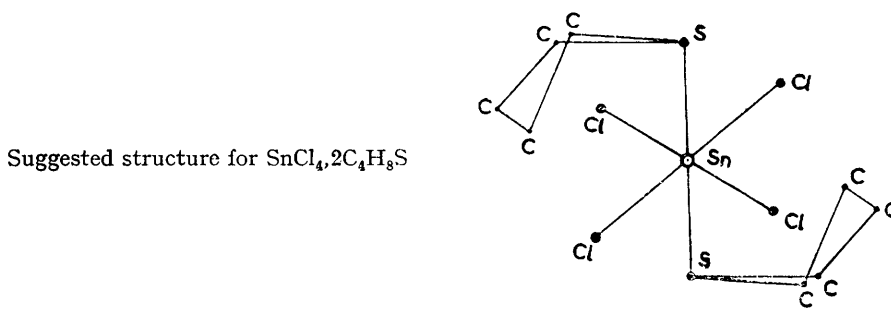


Figure. The *X*-ray diffraction results are thus in agreement with the deductions based on infrared spectroscopic examination of this compound.⁴ Similarly, the only Raman band of appreciable intensity in the region of $\Delta\nu = 300 \text{ cm.}^{-1}$ is one at 299 cm.^{-1} , very close to that observed with Raman spectra of benzene solutions of this compound, but 20 cm.^{-1} from the relevant infrared absorption.

EXPERIMENTAL

The $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{S}$ and the solvents for this investigation were prepared as described previously.⁴ The demountable dipole-moment-cell consisted of an outer jacket silvered on the inside and an inner closed cylinder platinized on the outside. The total capacity was $86.42 \mu\mu\text{F}$. Capacitance measurements were made on a megacycle bridge described by Buckingham *et al.*¹¹ Refractive index measurements were made with an Abbe refractometer inside a welded polythene "dry-bag" and all measurements were corrected to 17° . The molecular-weight measurements were made cryoscopically in benzene, a five-junction copper-constantan thermocouple being used (0.0958 g. of compound in 8.797 g. of benzene and 0.0602 g. of compound in 8.835 g. of benzene gave depressions of the freezing-point corresponding to molecular weights of 406 and 443, respectively. Theory = 437).

Spectra were recorded with a Perkin-Elmer 221 infrared spectrometer equipped with sodium chloride grating and caesium bromide optics or with a Cary 81 Raman spectrophotometer.

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¹¹ Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.