540. *The Raman Spectra of Some Adducts of Tin Tetrachloride*

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BRUNE AND ZEIL[1] have reported the Raman spectra (in solution) of a number of 1 : 1 and 1 : 2 adducts of tin tetrachloride with donor molecules. The assignment of D_{4h} symmetry for these adducts (assumed to be of the form L_2SnCl_4) has been disputed[2,3] in the case of $SnCl_4$,2MeCN and $SnCl_4$,2EtCN, and, in the light of elementary stereochemical considerations,[4] is surprising for $SnCl_4,2H_2O$ and $SnCl_4$,2ROH. We now report the Raman spectra of several adducts of tin tetrachloride in solution and in the solid state; the data are listed in the Table, earlier infrared data being included for ease of comparison. The most striking

The Raman (R) and infrared (i.r.) spectra of some adducts of tin tetrachloride

Compound	Technique	ν or Δν (in cm.$^{-1}$)				Lit.
			cis-Adducts			
Solid $SnCl_4$,2EtCN	R		336s		264w	
$SnCl_4$ in EtCN[a]	R		341			1
$SnCl_4$ in EtCN	i.r.	362s	339s	314m		
Solid $SnCl_4$,2MeCN	i.r.	365s	339vs	306s		3
$SnCl_4$ in MeCN[a]	R		340			
$SnCl_4$ in MeCN	i.r.	362s	340s	310m		
Solid $SnCl_4,2Me_2CO$	R		333			
Solid $SnCl_4,Me_2CO$	i.r.	359s	330s	304s[d]		2
$SnCl_4$ in Me_2CO[b]	R		335	301?sh		
$SnCl_4$ in Me_2CO	i.r.	358s	333s	300w?		2
			trans-Adducts			
$SnCl_4$ in $(CH_2)_4O$[c]	R		*ca.* 338 (*ca.* 4)	324 (*ca.* 8)		
$SnCl_4$ in $(CH_2)_4O$	i.r.		343			2
$SnCl_4,2(CH_2)_4O$ in PhH[e]	R		*ca.* 349 (*ca.* 4)	325 (*ca.* 12)		
$SnCl_4,2(CH_2)_4O$ in PhH	i.r.		344s			2
Solid $SnCl_4,2(CH_2)_4O$	R		324 (*ca.* 9)		264 (*ca.* 2)	
Solid $SnCl_4,2(CH_2)_4O$	i.r.		341s			2
$SnCl_4,2(CH_2)_4S$ in PhH	R		336 (3)	301 (10)	259 (<1)	5
$SnCl_4,2(CH_2)_4S$ in PhH	i.r.		328s			2, 5
$SnCl_4$ in $(CH_2)_4S$[c]	R		334 (3)	296 (9)		5
$SnCl_4$ in $(CH_2)_4S$	i.r.		328s			2, 5
Solid $SnCl_4,2(CH_2)_4S$	R			299s	259w	5
Solid $SnCl_4,2(CH_2)_4S$	i.r.		319s			2, 5
$SnCl_4$ in Et_2S[f]	R		332 (*ca.* 4)	299 (*ca.* 11)		2
$SnCl_4$ in Et_2S	i.r.		331s			
$SnCl_4,2NMe_3$ in PhH	R			300		
$SnCl_4,2NMe_3$ in PhH	i.r.		329			2
Solid $SnCl_4,2Et_2O$	R		322 (*ca.* 9)		261 (*ca.* 2)	6
Solid $SnCl_4,2Et_2O$	i.r.		341s			2

[a] EtCN and MeCN have bands at about 380 cm.$^{-1}$ (EtCN also at 220 cm.$^{-1}$ in R). [b] Unstable; rapid decomposition in arc. [c] Fluoresces. [d] Hydrolysis peak appears at this point. [e] $(CH_2)_4S$ has band at 297 cm.$^{-1}$ in R. [f] Et_2S has bands at 305, 334, 380 cm.$^{-1}$ in R; 303, 340, 380 cm.$^{-1}$ in i.r.

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[1] H. A. Brune and W. Zeil, *Z. phys. Chem.* (*Frankfurt*), 1962, **32**, 384.

[2] I. R. Beattie and L. Rule, *J.*, 1964, 3267.

[3] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J.*, 1963, 1514.

[4] I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.

[5] I. R. Beattie, R. Hulme, and L. Rule, *J.*, 1965, 1581.

[6] G. Briegleb and W. Lauppe, *Z. phys. Chem.*, 1937, *B***35**, 42.

point to arise during this study was that, in the region of $\Delta\nu = 300$ cm.$^{-1}$, the suggested [2] *cis*-adducts (L = MeCN, EtCN, or Me_2CO) showed only *one* intense Raman band, compared with three of roughly equal intensity in the infrared spectrum. For C_{2v} symmetry of L_2SnCl_4, the three bands active in the infrared should also be active in the Raman effect.[7] The single intense band in the Raman effect was coincident with the central one of the group of three present in the infrared spectrum for all the *cis*-adducts, and, where measurements were possible, was, as expected, strongly polarised (essentially an a_1 mode of C_{2v} $SnCl_4$). We should like to state that, from Raman-spectral studies alone, we should have assigned D_{4h} symmetry. Clearly, the intensity of the *b*-type stretching modes is particularly weak for these compounds in the Raman effect (the ratio of the intensity of *a* to *b* M–Cl stretching modes for solid $SnCl_4$,2EtCN being at least 20 : 1).

For the *trans*-adducts, we expect, by analogy with previous work,[1] two strong Raman bands, one at about 300 cm.$^{-1}$ (a_{1g}) and one at about 250 cm.$^{-1}$ (b_{1g}). For solid L_2SnCl_4 [L = Et_2O, $(CH_2)_4O$, and $(CH_2)_4S$], these bands are evident. In the case of the solution spectra, the low-frequency band is not clear. This is partly due to the low solubility of several of the adducts in the free ligand (frequently 0·1M in tin tetrachloride) and the decomposition reaction occurring during the exposure to the Toronto arc. However, it is interesting that the solution spectra of both $SnCl_4,2(CH_2)_4O$ and $SnCl_4,2(CH_2)_4S$ show additional high-frequency bands (at about 340 cm.$^{-1}$) not shown in the corresponding solid-state Raman spectra. It is possible that this is due to a breakdown of the selection rules, as clearly, in these last two adducts, the molecule does not have D_{4h} symmetry and the ligand dipole direction makes an angle with the L–Sn–L bond. It is noteworthy that, in $SnCl_4,2NMe_3$ in solution, no additional high-frequency band is observed, and here the ligand dipole direction coincides with the L–Sn–L axis.

It has been argued [1] that the position of the totally symmetric stretching frequency is indicative of the stability of the adduct for D_{4h} symmetry. While we do not altogether accept this argument, it is interesting to note that, on this basis, the sulphur donors are better than the oxygen donors. This is not particularly unexpected, as we have previously noticed [2] that $SnCl_4,2Et_2S$ is appreciably more stable than $SnCl_4,2Et_2O$ in benzene. However, the ether adduct is appreciably less stable than the tetrahydrofuran adduct, although the significant Raman shifts are almost identical.

Finally, we should like to point out that we took no exceptional precautions in obtaining these Raman spectra, beyond crystallising the adducts to obtain larger particles and thus reduce the amount of scattering of the incident (and Raman) radiation. Summarising, we note that for a *cis*-adduct of tin tetrachloride, the Raman spectrum (for the SnCl stretching vibrations) will show one intense absorption in the 300-cm.$^{-1}$ region probably coincident with the central line of the group of three present in the infrared spectrum. For a *trans*-adduct (in the solid state) the single intense Raman line near 300 cm.$^{-1}$ will be about 25 cm.$^{-1}$ lower than the frequency of the corresponding infrared-active vibration.

Experimental.—The compounds were prepared as described previously,[2] but for the solid-state Raman spectra, the acetone and ether adducts were recrystallised from benzene. Solvents were distilled to reduce the incidence of fluorescence. The compounds $SnCl_4,2(CH_2)_4S$ and $SnCl_4,2(CH_2)_4O$ were relatively stable to hydrolysis, and could be studied as pressed discs. In the case of the more easily hydrolysed materials, a recently developed solid-state technique was used.[8] All spectra were recorded on a Cary 81 Raman spectrophotometer.

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[7] See, for example, I. R. Beattie and M. Webster, *J.*, 1964, 6166.

[8] I. R. Beattie and M. Webster, *J.*, 1965, in the press.