Vibrational Spectra of Some Chloro- and Methylchloro-species of Cadmium, Indium, Tin, Antimony, Tellurium, and Iodine

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Vibrational spectra of the following species are reported: $SbCl_3$(gas), $SnCl_4$(gas), $(NH_4)_2SbCl_5$, $MeTeCl_3$, Me_2TeCl_2, Me_2SbCl_3, $MeTeCl_4^-$, $Me_2SbCl_4^-$, $Me_3SnCl_2^-$, $Me_2SnCl_3^-$, $MeSnCl_4^-$, $MeSnCl_5^{2-}$, and $SbCl_6^{3-}$. In the case of $Me_2SnCl_4^-$ and $Me_3SnCl_2^-$ deuteriation studies are also given. The values of the frequencies of the most intense ' metal–chlorine stretching mode ' in the Raman effect are compared with those of related compounds. It is suggested that in the six-co-ordinated species $LMCl_5^{n-}$ (where L = a lone pair or methyl group) the M–Cl bond *trans* to a lone pair or methyl group will be short relative to those in the planar MCl_4 residue. Similarly in five-co-ordinated trigonal bipyramidal species $LMCl_4^{n-}$ and $L_2MCl_3^{n-}$ it is suggested that M–Cl bonds in the same equatorial plane as a lone pair or methyl group will be shortened relative to those in the linear MCl_2 residue. On the basis of this discussion suggestions are made about the acceptor properties and shapes of several species.

IN 1967 two reports [1,2] appeared on the vibrational spectrum of crystalline $(NH_4)_2SbCl_5$, which from *X*-ray analysis [3] was thought to contain square pyramidal $SbCl_5^{2-}$ ions. The spectral data showed clearly that the two sets of authors were dealing with different compounds or with (structurally) different crystalline modifications of the same compound. More recently a spectrum of $(NH_4)_2SbCl_5$ agreeing with that of ref. 2 was reported.[4] In the Raman effect the most intense stretching vibration of $SbCl_5^{2-}$ occurs at 290 cm^{-1} (ref. 1) or at 348 cm^{-1} (refs. 2 and 4). The corresponding vibration of the square pyramidal [5] $InCl_5^{2-}$ ion in $(Et_4N)_2InCl_5$ occurs [6] at 294—287 cm^{-1}. As the two ions ($InCl_5^{2-}$ and $SbCl_5^{2-}$) differ only in the addition of a pair of electrons (coupled with a corresponding change in nuclear charge) we felt the 290 cm^{-1} result for $SbCl_5^{2-}$ to be the more likely to be correct. We therefore re-examined the Raman spectrum of a single crystal of $(NH_4)_2SbCl_5$ but obtained results closely similar to those reported in refs. 2 and 4. Thus the addition of a pair of electrons on passing from $InCl_5^{2-}$ to $SbCl_5^{2-}$ *raises* the most intense stretching vibration by over 50 cm^{-1}. In view of this result Keats and Webster [7] re-examined the *X*-ray structure of $(NH_4)_2SbCl_5$ which confirmed the presence of a (distorted) square pyramid. Because of problems of polymorphism with this compound, Raman spectral studies were carried out on the same crystal as that used in the *X*-ray determination.

It appeared to us that the results for $InCl_5^{2-}$ and $SbCl_5^{2-}$ were of sufficient interest to warrant further examination. Table 1 summarises the totally symmetric modes of species MCl_n as a function of their symmetry. Force-constant calculations on such molecules are open to question. As a first approximation we (*a*) neglect *G*-matrix coupling because of the mass difference between chlorine and the central atom, (*b*) neglect *F*-matrix coupling between stretches and deformations, (*c*) assume that for species where there are two totally symmetric stretching modes there will be an intense in-phase stretch and a weak out-of-phase stretch. Thus the position of the most intense Raman band in the metal–chlorine stretching region of a species MCl_n may crudely be taken as a measure of the force constant [f_r plus $(n-1)f_{rr}$ terms] of the M–Cl bond.

TABLE 1

Totally symmetric modes of MCl_n as a function of symmetry

Species	Symmetry	Stretch	Deformation	Coupling
MCl_2	$D_{\infty h}$	1	—	—
MCl_2	C_{2v}	1	1	*F* and *G*
MCl_3	D_{3h}	1	—	—
MCl_3	C_{3v}	1	1	*F* and *G*
MCl_4	T_d	1	—	—
MCl_4	D_{4h}	1	—	—
MCl_4	C_{2v}	2	2	*F* and *G*
MCl_5	D_{3h}	2	—	*F*
MCl_5	C_{4v}	2	1	*F* and *G*
MCl_6	O_h	1	—	—

In Figure 1 we plot this most intense Raman band of a range of chloro-compounds [6-18] containing the elements Cd, In, Sn, Sb, Te, or I. In examining this Figure a number of points should be borne in mind: (*a*) there is no necessary relationship between bond strength and force constant,[8] (*b*) the results quoted for the uncharged species refer to gases and are therefore more acceptable than those for the anionic species, where additional interactions may be present owing to the use of both

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[1] H. A. Szymanski, R. Yelin, and L. Marabella, *J. Chem. Phys.*, 1967, **47**, 1876.

[2] T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *J. Chem. Soc.* (*A*), 1967, 1810.

[3] M. Edstrand, N. Ingri, and M. Inge, *Acta Chem. Scand.*, 1955, **9**, 122.

[4] E. Martineau and J. B. Milne, *J. Chem. Soc.* (*A*), 1970, 2971.

[5] D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 1969, **8**, 14.

[6] D. F. Shriver and I. Wharf, *Inorg. Chem.*, 1969, **8**, 2167; S. R. Leone, B. Swanson, and D. F. Shriver, *ibid.*, 1970, **9**, 2189.

[7] S. Keats and M. Webster, *J. Chem. Soc.* (*A*), 1971, 298.

[8] T. L. Cottrell, ' The Strengths of Chemical Bonds,' Butterworths, London, 1968.

[9] A. G. Maki and R. Forneris, *Spectrochim. Acta*, 1967, **23** *A*, 867.

[10] I. R. Beattie and R. O. Perry, *J. Chem. Soc.* (*A*), 1970, 2429.

[11] J. H. R. Clarke and Y. Kuroda, personal communication.

[12] K. Nakamoto, ' Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, London, 1963.

[13] G. Conteras and D. G. Tuck, *Chem. Comm.*, 1971, 1552.

[14] I. R. Beattie and J. R. Horder, *J. Chem. Soc.* (*A*), 1969, 2655.

[15] M. J. Deveney, Ph.D. Thesis, St. Andrews, 1968.

[16] J. E. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1971, 1273.

[17] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 1691.

[18] J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968, 808.

solution and solid-state data, (*c*) tellurium tetrachloride[19] has been omitted from the Figure as two intense bands are observed in the ' stretching region '.

The full line in Figure 1 shows the effect of the addition of one negative charge in an isoelectronic series. In the series $SbCl_3$(382), $SnCl_3^-$(297), $InCl_3^{2-}$(252) the mean difference is 65 cm^{-1}; in the series $SnCl_4$(367), $InCl_4^-$(321), $CdCl_4^{2-}$(261) the mean difference is 53 cm^{-1}; in the series $SbCl_5$(355), $SnCl_5^-$(331), $InCl_5^{2-}$(290 Change of shape) it is 33 cm^{-1}; and in the series $SbCl_6^-$(329), $SnCl_6^{2-}$(311), $InCl_6^{3-}$(277) it is 26 cm^{-1}. There appear to be no anomalies here. The smaller the number of chlorine atoms in any series, the greater the effect of the addition of negative charge (in terms of mean wavenumber shift). The broken line in Figure 1 shows the effect of adding a chloride ion. The wavenumbers are $InCl_3$(350), $InCl_4^-$(321), $InCl_5^{2-}$ (290), $InCl_6^{3-}$ 277 cm^{-1} and $SnCl_4$ (367), $SnCl_5^-$(331), $SnCl_6^{2-}$(311 cm^{-1}). The shifts are again regular and range from 13 to 36 cm^{-1} between any two adjacent species. However, the change of 81 cm^{-1} between $SbCl_5^{2-}$(348) and $SbCl_6^{3-}$(267) is clearly anomalous.* Since the lone-pair ions $TeCl_6^{2-}$ and $SbCl_6^{3-}$ are not anomalous with respect to $SnCl_6^{2-}$ and $InCl_6^{3-}$, the position of $SbCl_5^{2-}$ must be anomalous.

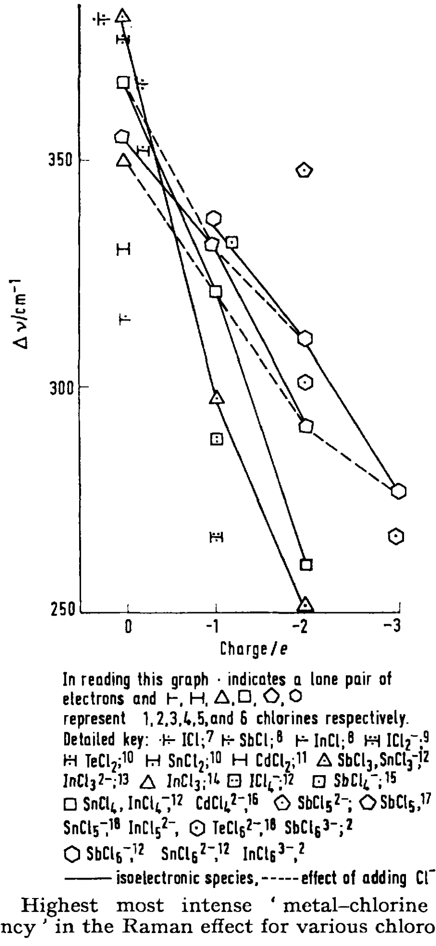

FIGURE 1 Highest most intense ' metal–chlorine stretching frequency ' in the Raman effect for various chloro-species

An examination of the relevant structural studies shows that $SbCl_5$ has approximately equal axial and equatorial bond lengths (2·34 and 2·29 Å) as does $SnCl_5^-$(2·37 Å).[21] Similarly $InCl_5^{2-}$ has[5] apical and basal bond lengths which are nearly equal (2·42 and 2·46 Å). By contrast $SbCl_5^{2-}$ has[7] bond lengths of 2·36 Å (apical) and 2·58—2·69 Å (basal), the apical bond length being close to that found[22] in $SbCl_3$(2·33 Å). Thus the high frequency observed in Figure 1 for $SbCl_5^{2-}$ can be associated with the short apical Sb–Cl distance which, in Sidgwick and Powell terms, is *trans* to a lone pair. It is noteworthy that in $(pyH^+)SbCl_4^-$ the antimony(III) species lie in a grossly distorted octahedron[23] leading to an approximately C_{2v} $SbCl_4^-$ ion with equatorial bond lengths of 2·38 Å and axial bond lengths of 2·64 Å. The additional interactions to complete the octahedron are at the much larger Sb–Cl distance of 3·12 Å. Thus the two chlorines ' in the same equatorial plane as the lone pair ' also show distinctly shorter distances than those found for the axial chlorines.

Boal and Ozin[24] report the totally symmetric mode of $XeCl_2$ at 253 cm^{-1}. This result is anomalous in terms of the data in Figure 1. It is interesting that ν_3 of $XeCl_2$ is at[25] 313 cm^{-1} while ν_3 of the isoelectronic species[9] ICl_2^- is at 226 cm^{-1}, giving a shift of 87 cm^{-1} on addition of a negative charge in an isoelectronic series containing only two chlorines, and similar to that expected for the shift in ν_1 for these species.

Because in many respects methyl groups behave rather like ' lone pairs ' of electrons we examined a number of species containing both chlorine and methyl as ligands. For the purposes of this paper we assume that $MeSnCl_4^-$, $MeTeCl_3$, Me_2SbCl_3, and $Me_3SnCl_2^-$ may, like Me_2TeCl_2,[26] Me_3SbCl_2,[22] and $Me_2SnCl_3^-$,[27] be regarded as based on a trigonal bipyramidal distribution about the central atom with ' lone pairs ' and methyl groups showing a preference for equatorial positions. It is, however, also important to note that there is evidence for polymerisation in species such as $MeTeCl_3$[28] and Me_2SnCl_2.[29]

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* Previous assignments[2] of the Raman spectrum of $Co(NH_3)_6SbCl_6$ have been criticised.[4] However, the band assigned by Martineau and Milne[4] as a fundamental of $SbCl_6^{3-}$ moves at least 30 cm^{-1} on deuteriation of the $Co(NH_3)_6^{3+}$ ion. It is not our purpose here to discuss the complicated features present in aqueous hydrochloric acid solutions of antimony trichloride.[20]

[19] I. R. Beattie, J. R. Horder, and P. J. Jones, *J. Chem. Soc.* (*A*), 1970, 329.

[20] C. J. Adams and A. J. Downs, *Chem. Comm.*, 1970, 1699.

[21] H. Freedman and A. E. Young, *J. Amer. Chem. Soc.*, 1964, **86**, 733.

[22] A. F. Wells, ' Structural Inorganic Chemistry,' Oxford Univ. Press, London, 1962.

[23] S. K. Porter and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1970, 1356.

[24] D. Boal and G. A. Ozin, *Spectroscopy Letters*, 1971, **4**, 43.

[25] L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, 1967, **6**, 1758.

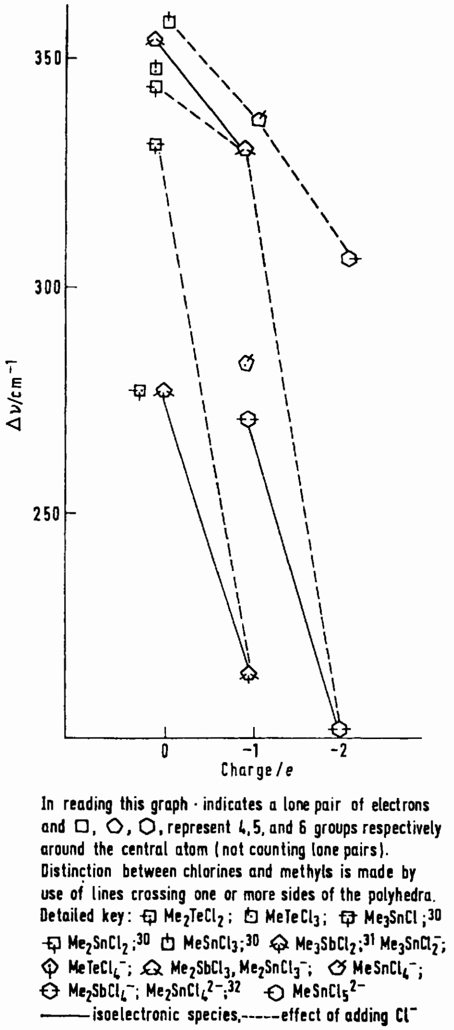
[26] G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 782.

[27] F. W. B. Einstein and B. R. Penfold, *Chem. Comm.*, 1966, 780.

[28] D. Kobelt and E. F. Paulus, *Angew. Chem.*, 1971, **10**, 74; K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, 1970, **9**, 106.

[29] A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2862; but see P. T. Greene and R. F. Bryan, *ibid.*, 1971, 2549.

In Figure 2 we plot the most intense Raman band [30-32] in the metal–chlorine stretching region for a variety of methylchloro-species. The results again show a fairly monotonous change in frequency from one species to the next in a sequence, the frequency difference between any two adjacent pairs lying in the range 10—30 cm^{-1}. However, there are clear cut exceptions: the broken line of Figure 2 shows that the addition of a chloride ion between Me_3SnCl and $Me_3SnCl_2^-$ gives $\Delta\nu = 102$ cm^{-1}, and between $Me_2SnCl_3^-$ and $Me_2SnCl_4^{2-}$ $\Delta\nu$ is 129 cm^{-1}. The full line shows that the addition of a negative charge in an isoelectronic series gives $\Delta\nu = 56$ cm^{-1} between Me_3SbCl_2 and $Me_3SnCl_2^-$ and 69 cm^{-1} between $Me_2SbCl_4^-$ and $Me_2SnCl_4^{2-}$.



In reading this graph · indicates a lone pair of electrons and □, ⬠, ⬡, represent 4, 5, and 6 groups respectively around the central atom (not counting lone pairs). Distinction between chlorines and methyls is made by use of lines crossing one or more sides of the polyhedra. Detailed key: □ Me_2TeCl_2; □ $MeTeCl_3$; □ Me_3SnCl;[30] □ Me_2SnCl_2;[30] □ $MeSnCl_3$;[30] ⬠ Me_3SbCl_2;[31] $Me_3SnCl_2^-$; ⬠ $MeTeCl_4^-$; ⬠ Me_2SbCl_3, $Me_2SnCl_3^-$; ⬠ $MeSnCl_4^-$; ⬡ $Me_2SbCl_4^-$; $Me_2SnCl_4^{2-}$;[32] ⬡ $MeSnCl_5^{2-}$

——— isoelectronic species, - - - - - effect of adding Cl^-

FIGURE 2 Highest most intense 'metal–chlorine stretching frequency' in the Raman effect for various methyl-chloro species

Unfortunately there is little structural information for these species. For the $Me_2SnCl_3^-$ ion the equatorial tin–chlorine bond length is [27] 2·35 Å while the axial lengths are 2·54 Å which can be rationalised as due to an equatorial 'sp^2' dimethylchloro-group, leaving essentially p-bonded chlorine in the axial direction. The anomalously low totally symmetric M–Cl stretching frequencies of $Me_3SnCl_2^-$ and $Me_2SnCl_4^{2-}$ can be rationalised as due to the presence of essentially sp^2-bonded Me_3Sn^+ and sp-bonded Me_2Sn^{2+}. The degree of ionic character in the bonds for the (axial) $SnCl_2$ residue or the (planar) $SnCl_4$ residue is illustrated by the weakness of these bands in the Raman effect, making unambiguous identification difficult.

With these features in mind it is easy to make some rather qualitative predictions. Me_3SbCl_2 and Me_2TeCl_2 are expected to be extremely weak acceptors. Their spectra in pyridine are essentially the same as their spectra in non-donor solvents. No 1 : 2 adduct of trimethyltin chloride with unidentate ligands is known or expected. We would predict that for $MeSnCl_5^{2-}$ the Sn–Cl bond *trans* to the methyl group would be shorter than the Sn–Cl distance in the planar $SnCl_4$ residue. $MeInCl_4^{2-}$, if monomeric, would either be square pyramidal with a basal methyl group or trigonal bipyramidal with an equatorial methyl group. The trigonal bipyramidal model is favoured if it is assumed that the methyl group will be essentially s-bonded.

It is well known that $TeCl_6^{2-}$ is obtained readily from the addition of chloride ions to tellurium(IV). The $TeCl_6^{2-}$ ion in $(NH_4)_2TeCl_6$ is a regular octahedron.[33] However, the ion $TeCl_5^-$ is not well characterised. This behaviour contrasts sharply with the fluoride complexes where TeF_6^{2-} is unknown whereas TeF_5^- is well characterised.[34] This can be rationalised by assuming that electron repulsions in TeF_5^- do not allow the 'lone pair' to enter a spherically symmetrical orbital to form TeF_6^{2-}. In TeF_5^- the additional two valence electrons would effectively form a Sidgwick and Powell 'stereochemically active lone pair.' Similar reasoning predicts the formation of 1 : 1 adducts between $MeTeCl_3$ and unidentate ligands (L). The shape of the species $MeTeCl_3,L$ is easily predicted as a square pyramid with an apical methyl group, leaving a T-shaped $TeCl_3$ residue. Finally, we note that if discrete, monomeric $Me_2TlCl_3^{2-}$ can be prepared it is possible that this will show a trigonal bipyramidal shape with axial methyl groups (owing to the tendency to behave as an essentially Me_2Tl^+ ion with weak co-ordination).

EXPERIMENTAL

Me_3SbCl_2,[35] Me_2SbCl_3,[36,37] and $MeTeCl_3$ [28] were prepared by standard literature methods. $(NH_4)_2SbCl_5$ was prepared as described by Edstrand, Ingri, and Inge,[3] but it was

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[30] W. F. Edgell and C. H. Ward, *J. Mol. Spectroscopy*, 1962, **8**, 343.

[31] R. G. Goel, E. Maslowsky, and C. V. Senoff, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 833; C. Wood and G. G. Long, *J. Mol. Spectroscopy*, 1971, **38**, 387.

[32] C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1037.

[33] A. C. Hazell, *Acta Chem. Scand.*, 1966, **20**, 165.

[34] A. J. Edwards and M. A. Mouty, *J. Chem. Soc.* (*A*), 1969, 703.

[35] G. O. Doak, G. G. Long, and M. E. Key, *Inorg. Synth.*, 1967, **9**, 93.

[36] G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, 1926, **110**, 523.

[37] O. J. Scherer, P. Hornig, and M. Schmidt, *J. Organometallic Chem.*, 1966, **6**, 259.

found possible to obtain a variety of products, including apparently polymorphs of $(NH_4)_2SbCl_5$, from this preparation. Me_3SnCl and Me_2SnCl_2 were obtained commercially and purified by sublimation. $MeSnCl_3$ was prepared by treatment of methylstannonic acid[38] with thionyl chloride, followed by recrystallisation from light petroleum (b.p. 40—60 °C) and sublimation. Me_2TeCl_2 was kindly provided by Dr. M. Gall. Et_4NCl was either dried *in vacuo* at 120 °C or used as the monohydrate where thionyl chloride was used as the solvent.

$Sn(CD_3)_4$ was prepared by the reaction of deuteriomethylmagnesium iodide with tin tetrachloride.[39] $Sn(CD_3)_4$ was then treated with $HgCl_2$ in ethanol to obtain $(CD_3)_3SnCl$ and $(CD_3)_2SnCl_2$.[40] Both were sublimed, but still contained traces of impurity. However, the adducts prepared from these compounds appeared, by spectral comparison with the undeuteriated adducts, to be free from impurity.

TABLE 2

Analyses (%)

	Halide		Tin	
	Calc.	Obs.	Calc.	Obs.
$(Et_4N)Me_3SnCl_2$	19·5	19·1	32·9	31·5 30·5
$(Et_4N)_2Me_2SnCl_4$	25·6	25·5	21·5	21·0
$Cs_2Me_2SnCl_4$	25·6	25·6		
$(Et_4N)Me_2SnCl_3$	27·7	27·5	30·8	31·1
$Cs_2Me_2SnBr_4$	43·5	43·0		
$(Et_4N)_2MeSnCl_5$	31·0	31·1	20·8	20·9
$(Ph_4As)MeSnCl_4$	21·7	21·6		
$(Et_4N)Me_2SbCl_4$	33·5	32·9		
$(Et_4N)MeTeCl_4$	34·3	33·8		

TABLE 3

Infrared spectra

Compound	Phase *	Bands (cm^{-1})
$(Et_4N)_2MeSnCl_5$	Mull	159s, 186s, 250s, 310s, 536m
$(Ph_4As)MeSnCl_4$	Mull	154m, 282s, 338s, 355s, 459s, 477s, 540w
$Et_4NCl + MeSnCl_3$ 1 : 1	$MeNO_2$ soln.	157s, 276s, 343s, 541w
$(Et_4N)_2Me_2SnCl_4$	Mull	150s, 225s, 392vw, 473vw, 582s
$(Et_4N)Me_2SnCl_3$ [a]	Mull	120m,sh, 150s, 250s, 310s, 510w, 564m, 572m
$Cs_2Me_2SnCl_4$	Mull	145sbr, 200m, 235s, 286w, 581m
$Cs_2(CD_3)_2SnCl_4$	Mull	145sbr, 181w,sh, 222s, 529m
$Cs_2Me_2SnBr_4$ [b]	Mull	~130sbr, 263w, 290w, 570m
$(Et_4N)Me_3SnCl_2$ [b, c]	Mull	107s,sh, 150sbr, 225s, 342m, 470m, 544s
$(Et_4N)Me_2SbCl_4$ [d]	Mull	272s
$(Et_4N)Me_2SbCl_4$	$MeNO_2$ soln.	280s
$(Et_4N)MeTeCl_4$	$MeNO_2$ soln.	250s,br, 310m,sh, 521m

* $MeNO_2$ has a band at 480 cm^{-1}.

[a] See also ref. 41. [b] Poor-quality spectrum. [c] 342 Band probably Me_3SnCl. [d] Not recorded below 200 cm^{-1}.

The adducts were prepared by addition of halide ion to the acceptor in a suitable solvent: $Et_4NMe_2SnCl_3$ from Et_4NCl and Me_2SnCl_2 in 1 : 1 mole ratio in dry ethanol;[41] $Cs_2Me_2SnCl_4$ (and the deuterio-analogue) from excess of CsCl and Me_2SnCl_2 in hydrochloric acid;[41] and $Cs_2Me_2SnBr_4$ from

TABLE 4

Raman spectra

Solids

Compound	Bands (cm^{-1})
$(Et_4N)_2MeSnCl_5$	96w, 140m, 158ms, 184w, 229w, 311s, 392s, 467vw, 533w
$(Ph_4As)MeSnCl_4$	155m, 179m, 230ms, 329s, 534w
$(Et_4N)_2Me_2SnCl_4$	100w, 128ms, 199ms, 214m,sh, 314vw, 382w, 516s
$(Et_4N)Me_2SnCl_3$	114vw, 177mw, 207w, 311mw, 421w, 515s, 565vw
$Cs_2Me_2SnCl_4$	47w, 140w, 200m,sh, 207m, 232vw, 507s
$Cs_2(CD_3)_2SnCl_4$	142w, 185ms, 203w, 220w, 462s
$Cs_2Me_2SnBr_4$	92w, 136w, 176w,sh, 185mw, 196vw, 499s
$Cs_2(CD_3)_2SnBr_4$	88w, 93w, 134mw, 162ms, 175wsh, 453s
$(Et_4N)Me_3SnCl_2$	97w, 147ms, 178m, 216w, 391w, 509s, 543ms
$(Et_4N)(CD_3)_3SnCl_2$	96ms, 136ms, 160m, 216vw, 240vw, 393w, 426vw, 464s, 496ms
$(Et_4N)Me_2SbCl_4$	213m, 252m, 272s, 418w, 508s
Me_2SbCl_3	180w, 195w, ~223w, 338w, 353m, 506s
Me_3SbCl_2	172m, 270s, 534s, 577m
$(Et_4N)MeTeCl_4$	256ms, 283s, 420vw, 546mw
$MeTeCl_3$	226w, 314m, 334ms, 356s, 538mw
Me_2TeCl_2	276s, 540ms
$(NH_4)_2SbCl_5$ (single crystal)	349s, 230m, 250m, ~168mw, ~118w

Solution

Sample	Solvent *	Bands (cm^{-1})
Me_2SnCl_2	$MeNO_2$	
0·12M		342ms,pol, 526s,pol
+0·5 equiv. Et_4NCl		332m,pol, 342m,pol, 525s,pol, 570w, depol
+1·5 equiv. Et_4NCl		326m,pol, 419mw,pol,† 518s,pol, 567vw,depol.
+4·0 equiv. Et_4NCl		326m,pol, 391mw,pol,† 420ms,pol,† 504mw,pol, 518s,pol
$MeSnCl_3$	$MeNO_2$	
0·07M		364s,pol, 527vw,[a]pol, 553,mpol
+0·7 equiv. Et_4NCl		338ms,pol, 362m,pol, 543m,pol
+1·0 equiv. Et_4NCl		310w,pol, 337s,pol, 392vw,pol,† 420w,pol,† 523w,pol, 541m,pol
+1·5 equiv. Et_4NCl		308ms,pol, 333m,pol, 390w,pol,† 418mw,pol, 518m,pol, 540w,pol
+2·0 equiv. Et_4NCl		307s,pol, 327w,pol, 389w,pol,† 417mw,pol,† 519m,pol, 542,vw, pol
+4·0 equiv. Et_4NCl		305s,pol, 389w,pol,† 418,mpol,† 521m,pol
Me_3SnCl	$MeNO_2$	
0·28M		312w,pol, 517s,pol, 547w,depol
+5·0 equiv. Et_4NCl		388vw,pol,† 416w,pol,† 508s,pol, 546w,depol
$(Et_4N)Me_2SbCl_4$	$MeNO_2$	248m,depol, 272ms,pol, 334w,pol,[b] 420w,pol,† 509s,pol
Me_3SbCl_2	$MeNO_2$	268m,pol, 526s,pol, 576w,depol
$MeTeCl_3$	Benzene	280mw,pol, 314m, 341s,pol, 364m,pol 539m,pol
$(Et_4N)MeTeCl_4$	$MeNO_2$	255w,depol, 283s,pol, 546w,pol

* $MeNO_2$ has a band at 481 cm^{-1}. † Et_4N^+.

[a] Me_2SnCl_2?. [b] $SbCl_6^-$?.

Gases

Compound	Bands (cm^{-1})
$SnCl_4$	403w, 367vs,pol, $\overbrace{\text{140w,sh, 128m, 118m,sh,}}$ $\overbrace{\text{108m, 97s, 89m}}$
$SbCl_3$	382vs,pol, 354m, 153s,pol, 141w,sh,* 124m

* Impurity?

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[38] H. Lambourne, *J. Chem. Soc.*, 1922, 2533.

[39] W. F. Edgell and C. H. Ward, *J. Amer. Chem. Soc.*, 1954, **76**, 1169.

[40] Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 235.

[41] J. P. Clark and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1966, 871.

CsBr and Me_2SnBr_2 in 2 : 1 mole ratio in water containing a few drops of hydrobromic acid. $Cs_2(CD_3)_2SnBr_4$ was obtained by dissolving $(CD_3)_2SnO$ [obtained by the ammoniacal hydrolysis of $(CD_3)_2SnCl_2$] in hydrobromic acid, followed by the addition of CsBr in 2 : 1 mole ratio. $(Et_4N)_2Me_2SnCl_4$ was prepared from gradual addition of Et_4NCl to Me_2SnCl_2 in dry nitromethane. (Crystalline material deposited as a 2 : 1 adduct after the addition of about 1 mole ratio of Et_4NCl.) $(Et_4N)_2MeSnCl_5$ was prepared similarly. $(Ph_4As)MeSnCl_4$ was prepared from Ph_4AsCl and $MeSnCl_3$ in 1 : 1 mole ratio in dry ethanol; $(Et_4N)Me_3SnCl_2$ and $(Et_4N)(CD_3)_3SnCl_2$ from Et_4NCl and Me_3SnCl or $(CD_3)_3SnCl$ in dry ethanol; $(Et_4N)Me_2SbCl_4$ from Et_4NCl and Me_2SbCl_3 in thionyl chloride and recrystallised from hydrochloric acid–ethanol; $(Et_4N)MeTeCl_4$ from Et_4NCl and $MeTeCl_3$ in 1 : 1 mole ratio in dichloromethane.

Where necessary glove-box techniques were used. Solvents were dried (CaH_2) and distilled.

Analyses.—Compounds were analysed for halide by hydrolysis, followed by potentiometric titration. Tin analyses were carried out by reduction with nickel foil followed by titration with KI–KIO_3. The results are summarised in Table 2.

Spectra.—Spectral studies were carried out with a Spex 1401 or a Cary 81 instrument with He-Ne, Ar-Kr, or Ar^+ excitation. I.r. spectra were measured on a Beckman IR11 instrument. The results are summarised in Tables 3 and 4.

Individual Systems (*Raman Spectra*).—$MeSnCl_3$–Cl^-. Results for $MeSnCl_3$ were similar to those of Edgell and Ward.[30,42] Solution of $MeSnCl_3$ in nitromethane followed by addition of Et_4NCl led to clear-cut assignments. A strong polarised band at 364 cm^{-1} for pure $MeSnCl_3$ in nitromethane gradually decreased on addition of Et_4NCl while a new strongly polarised band appeared at 337 cm^{-1}. At 1 : 1 mole ratio the 364 cm^{-1} band had disappeared, and a strong polarised band at 337 cm^{-1} dominated the spectrum. A new band began to appear at 310 cm^{-1} and as more Et_4NCl was added the 337 cm^{-1} band decreased until at a mole ratio of 2 : 1 Et_4NCl : $MeSnCl_3$ a 307 cm^{-1} band dominated the spectrum. At a mole ratio of 4 : 1 this band remained polarised at 305 cm^{-1}. These results demonstrate the successive formation of $MeSnCl_4^-$ and $MeSnCl_5^{2-}$.

Me_2SnCl_2–Cl^-. Data on the pure compound agree with Edgell and Ward.[30,42] A solution of Me_2SnCl_2 in nitromethane showed a strong band at 342 cm^{-1} in the Raman effect. Addition of Et_4NCl decreased the intensity of this band while a new band which was also strongly polarised appeared at 326 cm^{-1}. We interpret this as due to the formation of the $Me_2SnCl_3^-$ ion. Addition of excess of Et_4NCl decreased the intensity of this band but we were not able to observe the formation of a new band corresponding to the hoped-for $Me_2SnCl_4^{2-}$ ion.

Solid-state spectra of $Cs_2Me_2SnCl_4$ are essentially the same as those reported by Hobbs and Tobias.[32] Our interpretation of the data is different. The band at 207 cm^{-1} previously assigned [32] as an Sn–Cl stretching mode is clearly, from the deuteriation studies, a tin–carbon deformation. Similar arguments apply to the 183 cm^{-1} band in $Cs_2Me_2SnBr_4$. These assignments also suggest that the band at 224 cm^{-1} in $K_2Me_2SnF_4$ is not a lattice mode,[32] but is also a tin–carbon deformation. It is clear that the totally symmetric stretching mode of the $SnCl_4$ residue in Me_2SnCl_4 is unexpectedly extremely weak in the Raman effect, suggesting a considerable degree of ionic character in the bonding. In the i.r. spectrum Hobbs and Tobias [32] assigned a band at 235 cm^{-1} to an Sn–Cl mode. This shifts to 222 cm^{-1} on deuteriation, which is acceptable in this case as the i.r.-active tin–carbon deformation is of the same symmetry as the antisymmetric stretching mode of a planar MCl_4 unit.[31] We further note that in the i.r. spectrum of $Cs_2Me_2SnBr_4$ there is no band in this region.

If the assignment of 235 cm^{-1} is correct for the i.r.-active Sn–Cl stretching mode, then the symmetric stretching mode would be expected to occur at a similar frequency, or a little lower. We therefore assign the 203 cm^{-1} band in $Cs_2(CD_3)_2SnCl_4$ as the totally symmetric Sn–Cl stretching mode, but the assignment is tentative.

Me_3SnCl–Cl^-. Data for the pure compound again agree with Edgell and Ward.[30] In solution in nitromethane addition of Et_4NCl merely caused a reduction in intensity of the polarised band at 312 cm^{-1} without the appearance of a new band which could be attributed to the formation of the hoped-for adduct $Me_3SnCl_2^-$. Again the lack of a totally symmetric mode in the Raman spectrum suggests a largely ionic Sn–Cl interaction.

Because of the weakness of the totally symmetric Sn–Cl stretching vibration of $Me_3SnCl_2^-$ and its deuterio-analogue we were not able to make an unambiguous assignment. The i.r. spectrum shows a strong band at 225 cm^{-1} which could reasonably be attributed to a tin–chlorine stretching mode. On this basis we tentatively assign the Raman-active mode of $Me_3SnCl_2^-$ at 216 cm^{-1}. (The totally symmetric Sb–Cl stretching mode of Me_3SbCl_2 occurs [31] at 266 cm^{-1} while the antisymmetric stretching mode occurs at 280 cm^{-1}.)

Me_3SbCl_2. Me_3SbCl_2 does not apparently show acceptor properties. A solution in pyridine showed a strong band at 268 cm^{-1}, in the same position as that found for solutions in nitromethane.

Me_2SbCl_3. This compound is insoluble in common solvents and decomposes at, or just below, its m.p. It is probable that strong interactions occur *via* chlorine bridges, leading to an increase in the Me–Sb–Me angle over that expected for a monomer. The band at 353 cm^{-1} is arbitrarily assigned to an antimony–chlorine stretching mode. It is possible to obtain solutions of $(Et_4N)Me_2SbCl_4$ in nitromethane and these show a strong polarised band at 272 cm^{-1} which is attributed to the totally symmetric stretching mode of the $SbCl_4$ residue.

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[42] See also H. Kriegsman and S. Pauly, *Z. anorg. Chem.*, 1964, **330**, 275.