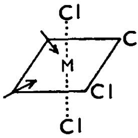
285. *The Infrared Spectra of Certain Addition Compounds of Germanium and Tin Tetrachlorides in the Cæsium Bromide Region.*

By I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster.

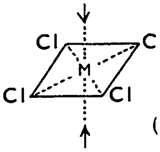
The value of infrared spectroscopy in the cæsium bromide region is briefly pointed out and transmittance data are given for a number of useful solvents and ligands. The infrared spectra, for this region, of a number of adducts of germanium tetrachloride and tin tetrachloride with tertiary aromatic bases are given and discussed. Previous work on the adducts $SnCl_4,2MeCN$ and $TiCl_4,2$pyridine is discussed and alternative assignments are made.

Although fundamental vibrations of many inorganic species occur in the range 400—250 cm.$^{-1}$ (*i.e.*, between the limits of a potassium bromide and a cæsium bromide prism), this region has been largely ignored by chemists.[1] Information on the stereochemistry and stability of co-ordination compounds in non-aqueous solution may be obtained by studying absorption spectra in this range. Fig. 1 summarises transmittance data for a number of potentially useful solvents and ligands, showing the large " windows " frequently available beyond 25 μ. Nujol is effectively transparent in the region as is hexachlorobutadiene below 500 cm.$^{-1}$.

To take a particular case, instead of attempting to examine the stereochemistry of $MCl_4,2py$ (where py = pyridine) from observations of the relatively small changes in the infrared spectrum of the ligand on co-ordination,[2] the grossly altered acceptor skeleton may be studied. If we assume the presence of discrete six-co-ordinate octahedral species, it is here necessary to decide between the *cis*- (I) and the *trans*-configuration (II). The assignment of metal–nitrogen vibrations in co-ordination compounds involving an amine donor is in doubt even for highly symmetrical species such as $[Co(NH_3)_6]^{3+}$. However, it appears[3] that the force constant for the cobalt–nitrogen bond is likely to be about 10^5 dynes cm.$^{-1}$. As this is rather less than half that of the M–Cl bond in ions[4] such as $[SnCl_6]^{2-}$, we shall initially disregard coupling between the M–Cl and the pyridine vibrations. The *trans*-adduct is thus considered to be similar to a perturbed square planar MCl_4 unit, so that only one infrared active fundamental M–Cl stretching vibration is predicted,[5] of symmetry type e_u. For the *cis*-configuration there would be at least two fundamentals associated with M–Cl stretching modes and expected to be observed[6] in the region under discussion. Therefore, in principle, we can distinguish between the two cases (*cis* and *trans*) although the arguments have not been rigorous.



(I)



(II)

There are numerous flaws in this simple approach. Only a very restricted range of the spectrum of M–Cl vibrations has been discussed, which is as if an organic chemist were restricted to using only the C–H stretching region. Fermi resonance[7] may make a combination band intense enough to be accepted as a fundamental Alternatively, certain

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[1] See, however, Cotton, " Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960.

[2] See, *e.g.*, Hulme, Leigh, and Beattie, *J.*, 1960, 366.

[3] Shimanouchi and Nakagawa, *Spectrochim. Acta*, 1962, **18**, 89.

[4] Redlich, Kurz, and Rosenfeld, *Z. phys. Chem.*, 1932, *B*, **19**, 231.

[5] Pistorius, *Mol. Phys.*, 1958, **1**, 295.

[6] See, *e.g.*, Dodd, Woodward, and Roberts, *Trans. Faraday Soc.*, 1956, **52**, 1052; Shaffer and Herman, *J. Chem. Phys.*, 1944, **12**, 494.

[7] Herzberg, " Molecular Spectra and Molecular Structure," Van Nostrand, New York, 1945.

fundamentals may be very weak (as for gaseous antimony trichloride,[8] whose a_1 fundamental is very strong relative to the weak e fundamental). Accidental degeneracies may occur or bands may be unresolved. Electronic transitions and lattice vibrations may appear (for example calcium fluoride has a broad infrared absorption band [9] at about 270 cm.$^{-1}$). Finally, and perhaps most frequently, crystal-field effects may resolve degeneracies. Thus one triply degenerate f_{1u} fundamental of symmetrical SiF_6^{2-} is

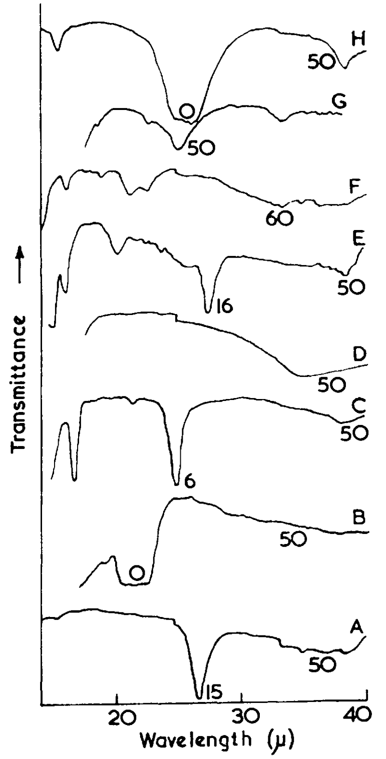

FIG. 1. Spectra of some solvents and ligands in the range 14—40 μ. Solvent (approximate film thickness in mm.): (A) Acetonitrile (0·1). (B) Acetic Acid (0·2). (C) Pyridine (0·1). (D) Tetrahydrofuran (0·2). (E) Chloroform (0·5). (F) Carbon tetrachloride (0·2). (G) Benzene (1·0). (H) Carbon disulphide (0·5). Figures on curve represent approximate percentage transmittance.

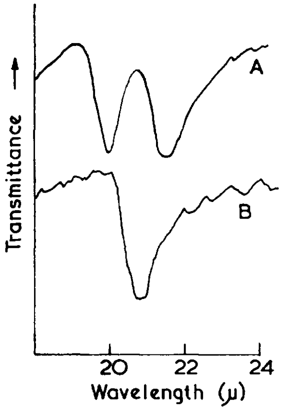

FIG. 2. The infrared spectrum of the SiF_6^{2-} ion in the region of 500 cm.$^{-1}$. (A) $BaSiF_6$; (B) K_2SiF_6.

resolved into two peaks in the crystalline compound $BaSiF_6$ (probably owing to elongation of the octahedron along the three-fold axis,[10] causing a lowering of the symmetry from O_h to D_{3d} so that [11] $f_{1u} \longrightarrow a_{2u} + e_u$). In the regular octahedron found in potassium or ammonium salts [12] no such splitting occurs (see Fig. 2).

In the solid state it is unlikely that stereochemical predictions will be unambiguous except in certain fortuitous cases. However, the information obtained in the cæsium

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[8] Wilmshurst, *J. Mol. Spectroscopy*, 1960, **5**, 343.

[9] Shimanouchi, Tsuboi, and Miyazawa, *J. Chem. Phys.*, 1961, **35**, 1597.

[10] Hoard and Vincent, *J. Amer. Chem. Soc.*, 1940, **62**, 3126.

[11] Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, London, 1955.

[12] Ketelaar, *Z. Krist.*, 1935, **92**, 155.

bromide region may still be of value and in *solution* can lead to unambiguous stereochemical assignments or can help in determining stability constants.

The Table summarises our values for fundamental M–Cl vibrations of some addition compounds of germanium and tin tetrachloride. Considerable shifts have occurred in these vibrations relative to those of the free tetrachlorides (ν_3 for $GeCl_4$ = 453 cm.$^{-1}$, for $SnCl_4$ = 403 cm.$^{-1}$), suggesting by analogy with $GeCl_6^{2-}$ and $SnCl_6^{2-}$ ions [ν_3/f_{1u} at 312 cm.$^{-1}$ in Cs_2GeCl_6 and $(NH_4)_2SnCl_6$] a co-ordination number of six. Further, the increased complexity of the spectra of the (presumed) chelate adducts relative to *trans*-[$GeCl_4py_2$] (ref. 2) is in agreement with the earlier qualitative discussion. On this basis the complex $SnCl_4$,2py is predicted to be a *trans*-form. However, pyridinium hexachlorostannate(IV), unlike the corresponding hexachloroantimonate(V),[13] exhibits two M–Cl vibrations ($\sim$310vs,br; $\sim$280vs,v.br) suggesting a deformation of the octahedron. Had this occurred for a complex MX_4,2L a *cis*-configuration might have been assumed for a *trans*-adduct.

Absorption bands in the region 26—40 μ for addition compounds of germanium and tin tetrachlorides.

Compound (Nujol mull)	Frequencies (cm.$^{-1}$)	Compound (Nujol mull)	Frequencies (cm.$^{-1}$)
$GeCl_4$,2py	$\sim$330vvs,br	$GeCl_4$,bipy	$\sim$330vs,br, $\sim$300s
$SnCl_4$,2py	$\sim$324vvs,br	$SnCl_4$,bipy	$\sim$327vs,br, $\sim$280s,br
$GeCl_4$,phen	351vs, 333vs, 325vs,br	$SnCl_4$,2MeCN	365s, 339vs, 306s
$SnCl_4$,phen	$\sim$328vs,br, $\sim$275s,br		

py = Pyridine. phen = 1,10-Phenanthroline. bipy = 2,2′-Bipyridyl.

We only know of two previous studies of the infrared spectra of addition compounds of tetrahalides of metals of Group IV in the region beyond 15 μ. In both cases we disagree with the assignments. Rao[14] assigns a band at 436 cm.$^{-1}$ for the titanium compounds in $TiCl_4$,2py, to a Ti–Cl vibration. In adducts of Lewis acids with pyridine we always find a band at about 430 cm.$^{-1}$ ($GeCl_4$,2py, 449; $SnCl_4$,2py, 431; $SbCl_5$,py, 437; $MeSnCl_3$,2py, 428; Me_2SnCl_2,2py, 422; Me_3SnCl,py, 417; I py_2^+,I_3^-,$2I_2$, 434; $CoCl_2$,4py, 432 cm.$^{-1}$). A band occurs for free pyridine at 403 cm.$^{-1}$. Thus although our spectrum of the compound $TiCl_4$,2py agrees with Rao's, we assign the band at 436 cm.$^{-1}$ to ligand pyridine. The main Ti–Cl vibrations occur around 368 and 280 cm.$^{-1}$.

Brown and Kubota[15] have examined the adduct $SnCl_4$,2MeCN. Our spectra in the cæsium bromide region are generally in agreement with theirs. Acetonitrile has one medium band in this region (Fig. 1), at 377 cm.$^{-1}$, assigned to a C–C–N wagging mode. The weak bands around 400 cm.$^{-1}$ are probably due to ligand acetonitrile (Fig. 3). A weak band also occurs[13] at 400 cm.$^{-1}$ in the adduct $SbCl_5$,MeCN. The main bands mentioned in the Table are attributed by us to fundamental Sn–Cl stretching vibrations of a *cis*-adduct. The spectrum of the solid complex $SnCl_4$,2MeCN closely resembles that of a solution of stannic chloride in acetonitrile (Fig. 3), suggesting that the observation of three main peaks in the solid is not due to crystal-field effects. Further, the spectrum of a solution of stannic chloride in propionitrile (which has no intense solvent band in the 25—35 μ region) is almost identical with that in acetonitrile (apart from the peak due to the free solvent in the latter case), confirming the view that these are not tin–nitrogen vibrations. Further confirmation is afforded by the observation by Brown and Kubota[15] that the analogous compound $SnCl_4$,2(*p*-MeO·C_6H_4·CN) shows bands at 360vs, 337vs, and 303w cm.$^{-1}$, again very close to those of the acetonitrile adduct. It is interesting that the Sn–Cl vibrations with the weak ligand acetonitrile occur at higher frequencies than with the stronger aromatic tertiary (Lewis) bases. It has recently been suggested[13] that the ion $[SbCl_4(MeCN)_2]^+$ has a *trans*-configuration, although it is isoelectronic with the

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[13] Beattie and Webster, *J.*, 1963, 38.

[14] Rao, *Z. Naturforsch.*, 1959, **14**b, 689.

[15] Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 4175.

proposed *cis*-[$SnCl_4(MeCN)_2$]. We are carrying out further work to confirm these stereochemical assignments and it is interesting that antimony pentachloride in solution in propionitrile shows only two main peaks around 30 μ, one (345 cm.$^{-1}$) attributable to the $SbCl_6^-$ ion and the other (369 cm.$^{-1}$) to *trans*-[$SbCl_4(EtCN)_2$]$^+$.

In solution in benzene we find, under the conditions of our experiment, that the complex $SnCl_4$,2MeCN is largely dissociated, yielding acetonitrile and other species. An examination of the infrared spectrum (4000—250 cm.$^{-1}$) of this complex in benzene at various concentrations indicated the absence of appreciable quantities of a 1 : 2 adduct, but the probable presence of a 1 : 1 adduct. The Sn–Cl stretching vibration of stannic chloride of symmetry type f_2 (ν_3) lies at 403 cm.$^{-1}$, very close to one of the Sn–Cl vibrations of the supposed 1 : 1 adduct (402 cm.$^{-1}$). However, the vibration associated with ν_3 of stannic chloride is much less intense than that found for the 1 : 1 adduct (Fig. 4) so that the observed spectrum would be essentially that of a material $SnCl_4$,MeCN. The band at 347 cm.$^{-1}$ could be considered as an antisymmetric stretching vibration (very crudely analogous to ν_3 of stannic chloride), while the band at 402 cm.$^{-1}$ would be analogous to the a_1 mode of stannic chloride (Raman-active here at 366 cm.$^{-1}$). The conclusion that, in benzene, dissociation of the complex $SnCl_4$,2MeCN occurs to free acetonitrile and a species $SnCl_4$,MeCN is in general agreement with the results of earlier workers[16,17] on related systems, but not with those of Coerver and Curran on this diacetonitrile complex.

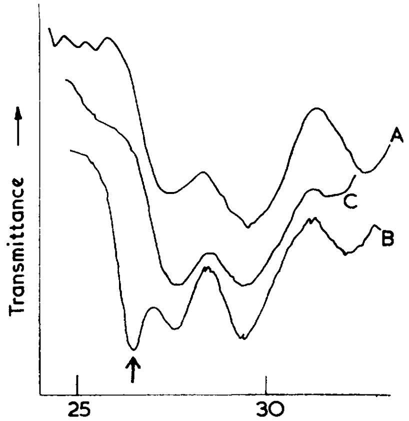

FIG. 3. The infrared spectrum of: (A) the addition compound $SnCl_4$,2MeCN as a Nujol mull; (B) $SnCl_4$ in solution in acetonitrile (0·1 mm. cell); (C) $SnCl_4$ in propionitrile (0·1 mm. cell). The arrow indicates the solvent absorption peak at 377 cm.$^{-1}$ due to acetonitrile.

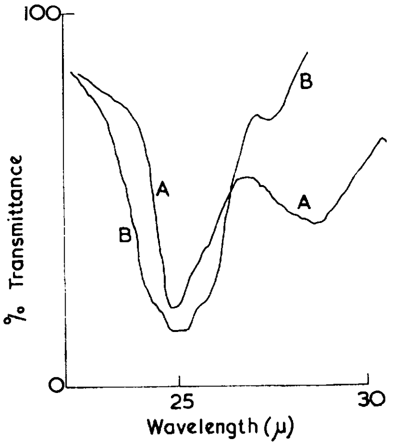

FIG. 4. The infrared spectrum of: (A) the addition compound $SnCl_4$,2MeCN in benzene (0·054M); (B) $SnCl_4$ in benzene (0·43M).

EXPERIMENTAL

Manipulations were carried out either in dry-boxes or on a vacuum-system.

Preparations.—2,2′-Bipyridyl and 1,10-phenanthroline were dried by repeated sublimations *in vacuo*. Pyridine was dried by silicon tetrachloride and distilled in a vacuum into ampoules which were then sealed. Germanium tetrachloride and tin tetrachloride were purified by vacuum-distillation into ampoules, and antimony pentachloride was purified as described previously.[13] Solvents were usually refluxed over calcium hydride and vacuum-distilled into

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[16] See, *e.g.*, Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, *B*, **17**, 21; Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 331.

[17] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

ampoules (acetonitrile and propionitrile) or distilled on to calcium hydride (benzene, carbon tetrachloride, and carbon disulphide). Addition compounds of tertiary bases with tin tetrachloride were prepared by mixing solutions of the reactants in an inert solvent (carbon tetrachloride for pyridine and 2,2′-bipyridyl, carbon disulphide for 1,10-phenanthroline). In the case of germanium tetrachloride adducts the free tetrachloride was added to solutions of the bases in solvents as above. The addition compound $SnCl_4,2MeCN$ was prepared by adding free tetrachloride to a solution of the nitrile in carbon tetrachloride.

Analyses.—The germanium tetrachloride adducts were hydrolysed readily and were analysed by pH titration.[18] For addition compounds of stannic chloride with tertiary bases hydrolysis was slow, and anion determination [19] was successful only for $SnCl_4,2py$ and $SnCl_4,2MeCN$. The 1,10-phenanthroline and 2,2′-bipyridyl compounds were therefore analysed by combustion. Results are tabulated.

		Found (%)				Required (%)		
Complex	Mol. ratio found	C	H	Cl	Formula	C	H	Cl
$GeCl_4,2py$	1 : 1·97							
$GeCl_4,bipy$	1 : 1·02							
$GeCl_4,phen$	1 : 1·04							
$SnCl_4,2py$	—	—	—	33·8	$C_{10}H_{10}Cl_4N_2Sn$	—	—	33·9
$SnCl_4,bipy$	—	29·0	2·3	—	$C_{10}H_8Cl_4N_2Sn$	28·8	1·9	—
$SnCl_4,phen$	—	33·4	1·5	—	$C_{12}H_8Cl_4N_2Sn$	32·7	1·8	—
$SnCl_4,2MeCN$	—	—	—	41·3, 41·4	$C_4H_6Cl_4N_2Sn$	—	—	41·4

Infrared Spectra.—Cæsium bromide windows are suitable in general for mull spectra and solution spectra when non-polar solvents are used. This salt is, however, soluble in solvents such as acetonitrile. High-density Polythene at a thickness of about 0·8 mm. is fairly rigid, is free from absorption bands beyond about 600 cm.$^{-1}$, and gives ~75% transmittance over most of its useful range. Many compounds are soluble in Polythene, so that it is necessary to renew the windows frequently to avoid the appearance of spurious peaks. All spectra were taken on a Perkin-Elmer model 221 infrared spectrometer equipped with grating, rock-salt, and cæsium bromide optics. For solution work specially designed "Teflon" cells with a "Teflon" O-ring and spacers were necessary. It is advisable to run the spectra of highly reactive compounds at least twice (successively on the same sample) to see if any peaks change (owing to hydrolysis) or new peaks appear. Similarly the cell may be opened (to allow hydrolysis), then resealed, and the spectrum again taken.

For the complex, $SnCl_4,2MeCN$ in benzene, free acetonitrile was determined as suggested by Coerver and Curran [17] from the band at 2253 cm.$^{-1}$; infrared spectra from 4000 to 250 cm.$^{-1}$ were studied for benzene solutions in the concentration range 0·02—0·06M (calculated on $SnCl_4,2MeCN$).

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University of London King's College,
Strand, London, W.C.2.

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[18] Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.

[19] Beattie and McQuillan, *J.*, following paper.