39. *The Stereochemistry of Addition Compounds of Silicon Tetrahalides, Studied by Their Spectra in the Cæsium Bromide Region.*

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The formation of a 4 : 1 adduct between pyridine and silicon tetraiodide is verified from vacuum experiments. It is suggested on the basis of infrared spectroscopic examination that this compound should be formulated as *cis*-[$SiI_2(C_5H_5N)_4$]$^{2+}$ $2I^-$. A 1 : 1 addition compound of silicon tetraiodide with 1,10-phenanthroline is also described. Addition compounds of silicon tetrachloride and silicon tetrabromide with pyridine, 1,10-phenanthroline, and 2,2'-bipyridyl are prepared and in the case of the pyridine adducts a *cis*-octahedral structure is assigned. Germanium tetraiodide does not appear to form an addition compound with pyridine at normal temperatures.

ADDITION compounds of the type MX_4L_2 (where M is silicon, germanium, or tin, X is halogen and L is a monodentate ligand) are well known [1] although their stereochemistry has only recently [2-6] been at all extensively studied. Compounds of the type MX_4L_4 have also been reported but are not well substantiated. Thus the work leading to $SiCl_4,4py$ (where py = pyridine) has been shown to be erroneous,[7] and one compound reported in a paper [8] on adducts of phosphine oxides and amine oxides with silicon tetrahalides has been shown not to exist at room temperature;[9] doubt is thus thrown on the 1 : 4 adducts reputedly discovered at the same time. The compound $SiI_4,4py$ has been reported by

[1] See, *e.g.*, Beattie, *Quart. Rev.*, 1963, **17**, 382.
[2] Branden, *Acta Chem. Scand.*, 1963, **17**, 759.
[3] Hermodsson, *Acta Cryst.*, 1960, **13**, 656.
[4] Hulme, Leigh, and Beattie, *J.*, 1960, 366.
[5] Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.
[6] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.
[7] Wannagat and Vielberg, *Z. anorg. Chem.*, 1957, **291**, 310.
[8] Issleib and Reinhold, *Z. anorg. Chem.*, 1962, **314**, 113.
[9] Beattie and Webster, *J.*, 1963, 4285.

Wannagat *et al.*[10] and by Muetterties.[11] It has been referred to [12] (before the work of Muetterties) as an ill-defined compound. The only physical technique used to study this compound has been X-ray powder photography, yielding a diffraction pattern very similar to that given for pyridinium iodide.[10] It is very difficult to distinguish between a true adduct $SiI_4,4py$ and the total hydrolysis product $(py \; HI)_4SiO_2$ solely by analysis. Germanium tetraiodide is reported to be decomposed by pyridine,[13] while tin tetraiodide yields a 1 : 2 adduct [14,15] which is presumably octahedral. (Ratios other than 1 : 2 have been reported for adducts of pyridine with tin tetraiodide,[16,17] but these can probably be disregarded.) We reinvestigated the reactions of silicon and germanium tetraiodide with pyridine, examining the stereochemistry of the adducts and the stereochemistry of related compounds of silicon tetrachloride and tetrabromide.

Addition of pyridine to a solution of silicon tetraiodide in benzene in a vacuum system yielded an immediate pale yellow precipitate with an iodine analysis close to that required for the adduct $SiI_4,4py$. Addition of pyridine to solid silicon tetraiodide in a vacuum system showed that reaction is extremely slow at room temperature. However, condensation of an excess of pyridine on to silicon tetraiodide followed by heating at 110° with subsequent removal (and measurement) of the residual pyridine showed that a 1 : 4 adduct was formed. This compound sublimed *in vacuo*, apparently with decomposition to the constituents. In contrast, addition of pyridine to germanium tetraiodide, dissolved in benzene, in a vacuum system followed by removal of the volatile materials left unchanged germanium tetraiodide.

The annexed Table records the infrared spectra of several addition compounds of silicon tetrahalides. In many addition compounds metal–halogen vibrations are much more intense than ligand vibrations. In Group IVb, this is most marked for adducts of tin tetrahalides and least marked for adducts of silicon tetrahalides where intensities are frequently comparable. Inspection of the Table shows that in the case of $SiBr_4,2py$ the

The infrared spectra of several addition compounds of silicon tetrahalides (as Nujol mulls) in the range 500—270 cm.$^{-1}$.

Compound	Frequencies (cm.$^{-1}$)						
$SiCl_4,2py$	482s	469sh	412s	382s	301w		
$SiBr_4,\; 2py$	469s	418s	369vs, br	353s, sh, br			
$SiI_4,4py$	465s	403s	367s				
$SiCl_4,1,10$-phenanthroline ...	475s	462m	443s	425s	397?		
$SiBr_4,1,10$-phenanthroline ...	452sh	445m	406m	390m	352s, br	325w	
$SiI_4,1,10$-phenanthroline......	463w, br	447w	435m	385s	350s	310sh	298s, br
$SiCl_4,2,2'$-bipyridyl	488sh	480s	463s	444s	435s		
$SiBr_4,2,2'$-bipyridyl............	469m	423s	388m	370m	356s		

Very weak absorptions and ill-defined shoulders are not shown.

only band which can reasonably be attributed to pyridine is that found at 469 cm.$^{-1}$ (ν_3 of $SiBr_4$ [18] is at 487 cm.$^{-1}$), the observed silicon–bromine stretching vibrations of all the adducts lying within the extremes 425 and 360 cm.$^{-1}$. A shoulder at 469 cm.$^{-1}$ in $SiCl_4,2py$ is attributable to a pyridine vibration, the observed silicon–chlorine stretching vibrations all lying within the extremes 482 and 382 cm.$^{-1}$ (ν_3 of $SiCl_4$ [18] is at 608 cm.$^{-1}$). The complexity of the spectra of the pyridine adducts of silicon tetrachloride and tetrabromide

[10] Wannagat, Schwarz, Voss, and Knauff, *Z. anorg. Chem.*, 1954, **277**, 73.
[11] Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 182.
[12] Eaborn, " Organosilicon Compounds," Butterworths Scientific Publns., London, 1960.
[13] Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 2854.
[14] Dimitriou, *Praktika*, 1927, **2**, 496 (*Chem. Abs.*, 1929, **23**, 4904).
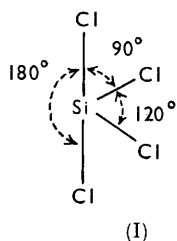[15] McQuillan, Thesis, London, 1962.
[16] Cooper and Wardlaw, *J.*, 1930, 1141.
[17] Pfeiffer, *Z. anorg. Chem.*, 1911, **71**, 97.
[18] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945.

in the Si–X stretching region clearly points to a *cis*-stereochemistry, in agreement with predictions based on d_π–p_π bonding and M–X repulsions.[1]

It is difficult to predict how many M–X vibrations one should observe in the " M–X stretching region " for a *cis*-adduct. It has been suggested[5] that " at least two fundamentals " are " expected to be observed " and that [19] of the four infrared active M–Cl stretching vibrations of MCl_4L (L = bidentate ligand) the symmetric M–Cl stretching vibrations (a_1 type) may be weaker than the antisymmetric bands. Distortion of MCl_4 from T_d to C_{2v} symmetry results in $a_1 \longrightarrow a_1$, and $f_2 \longrightarrow a_1 + b_1 + b_2$.[20] In C_{2v} symmetry all vibrations except a_2 are both infrared- and Raman-active. If the distortion were small, the effect would essentially be a resolution of the f_2 mode to give a closely spaced triplet plus a weak vibration near the Raman-active a_1 mode of the original (T_d) tetrachloride. Thus in the case of silicon tetrachloride, allowing for the weakening of the Si–Cl bond on co-ordination of two donor atoms, we might expect three vibrations around
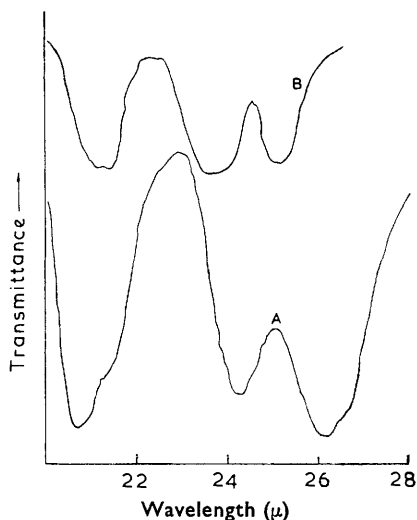
The infrared spectrum of (A) $SiCl_4,2py$ and (B) $SiCl_4,TMEN$ (TMEN = tetramethylethylenediamine) in the 24 μ region.

500 cm.[-1] and one low-intensity vibration at about 320 cm.[-1] (the a_1 mode of silicon tetrachloride is at 424 cm.[-1]). An alternative approach, yielding similar results, is to use the normal co-ordinate treatment of the sulphur tetrafluoride molecule due to Chantry and Ewing.[21] If we consider the $SiCl_4$ residue (I) to have the symmetry shown (C_{2v}), with all bond lengths equal, we may apply their F and G matrix elements directly. As so little is known of force constants in molecules of this type we used the S.V.F.F. approximation, putting off-diagonal elements in the F matrix equal to zero. We further assumed that the force constant for stretching the equatorial bonds equalled that for stretching the axial bonds.* We took the stretching constants as 1.4×10^5 dyne cm.[-1] and all the bending constants as one-tenth of this value. Calculation then yielded the values for silicon tetrachloride: a_1 390 and 260, b_1 514, and b_2 462 cm.[-1]. Only " stretching " vibrations are recorded here. We then obtain three bands quite closely spaced around 450 cm.[-1] and one a_1 mode

* In sulphur tetrafluoride these force constants are equal.[21] An earlier treatment[22] showing considerable differences between axial and equatorial stretching constants contains a number of errors in the analysis leading to wrong force constants.[23]

[19] Clark, *J.*, 1963, 1377.
[20] Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.
[21] Chantry and Ewing, *Mol. Phys.*, 1962, **5**, 209.
[22] Venkateswarlu and Pillai, *Optics and Spectroscopy*, 1961, **11**, 26.
[23] Chantry, personal communication.

(probably of low intensity, although there will be considerable coupling with the other a_1 mode) further out around 250 cm.$^{-1}$.

In the complex, $SiCl_4py_2$, apart from the pyridine vibrations, we observe bands at 482, 412, and 382 cm.$^{-1}$ with a very weak band at 301 cm.$^{-1}$ that may be an a_1 fundamental. The spectrum bears a very close relation [9] to that found for the chelate adduct, $SiCl_4(TMEN)$ (where TMEN = tetramethylethylenediamine) as shown in the Figure. There can be little doubt that a *cis*-assignment is correct for these adducts. Similar arguments apply to the adduct $SiBr_4py_2$, although here one a_1 mode would be well below the limit of our instrument (ν_1 of $SiBr_4$ is at 249 cm.$^{-1}$). A final point of interest concerns the possibility of distortion of a *trans*-adduct. Only one stretching vibration in the MCl_4 residue of a *trans*-adduct is infrared-active, namely, the doubly degenerate e_u vibration.[24] Calculations based on a stretching force constant of 1.4×10^5 dyne cm.$^{-1}$ and with all bending constants one-tenth of this value put the e_u vibration at 513 cm.$^{-1}$ in *trans*-$[SiCl_4L_2]$. Crystal-field effects are thus only likely to cause the appearance of two peaks in the region, by resolution of the double degeneracy. The next nearest fundamental is a_{2u} at 285 cm.$^{-1}$. Very considerable distortion of a *trans*-adduct would be necessary to yield three peaks in the 24 μ region. Similarly, small distortions of a *cis*-adduct would not alter the complexity of the spectrum in this region.

The spectra of the 1,10-phenanthroline and 2,2'-bipyridyl adducts of silicon tetrachloride and tetrabromide are much as expected, ligand vibrations in the region of the silicon–halogen vibrations rendering assignment difficult. Perhaps the most striking aspect of the work is the sequence *cis*-$SiCl_4py_2$, *trans*-$GeCl_4py_2$,[4] *trans*-$SnCl_4py_2$.[5] Further in contrast to their spectra in the cæsium bromide region, the infrared spectra of the germanium and silicon adducts are virtually identical in the range 500—1700 cm.$^{-1}$.

X-Ray Examination.[25]—Crystals of $SiCl_4py_2$ or $SiBr_4py_2$ can be grown from hot pyridine solutions. The former have a density of about 1.72 g. c.c.$^{-1}$. Single-crystal oscillation and Weissenberg photographs about the a- and b-axes with Cu-$K\alpha$ radiation and small crystals sealed in glass gave the triclinic body-centered cell [hkl absent when $(h + k + l)$ was odd]; $a' = 7.82$, $b' = 8.23$, $c' = 10.04$ Å, $\alpha' = 92.30°$, $\beta' = 92.30°$, $\gamma' = 102.13°$, $V' = 630$ Å^3, and $D_c = 1.73$ g. c.c.$^{-1}$, for two molecules of $SiCl_4py_2$ per unit cell. A primitive unit cell containing one molecule is obtained by taking new axes: $a = a' = 7.82$, $b = \frac{1}{2}[111] = 6.89$, $c = \frac{1}{2}[11\bar{1}] = 7.34$ Å, $\alpha = 90.30°$, $\beta = 116.25°$, $\gamma = 114.10°$, $V = 315$ Å^3.

Statistical tests [26] were performed with the corrected intensity data. For each zone the $N(z)$—z plot lay between the centro- and non-centrosymmetric curves. No final assignment of space group or molecular symmetry is possible at this stage, though a structure similar to that [4] of *trans*-tetrachlorodipyridinegermanium(IV) can be excluded. A *cis*-configuration is most likely.

The Adduct, $SiI_4,4py$.—Inspection of the spectrum of the 1 : 4 adduct of silicon tetra-iodide and pyridine shows immediately that it is not based on 8-co-ordinate silicon (nor would such an entity have been expected). For a (mononuclear) 8-co-ordinate species the silicon–iodine stretching vibrations would have been predicted to occur below 380 cm.$^{-1}$ (ν_3 is at 401 cm.$^{-1}$). Thus, in the 1 : 1 adduct (presumably an octahedral chelate) SiI_4L (L = 1,10-phenanthroline), the silicon–iodine stretching vibrations occur between the limits 385 and 298 cm.$^{-1}$. Further co-ordination of donor molecules would be expected to result in shifts to even lower frequencies. The main possibilities which then arise are (*a*) that the pyridine is co-ordinated to iodine,[12] (*b*) that part of the halogen is ionised,[10] and (*c*) that only two of the four pyridine molecules are co-ordinated. The third possibility is discounted by the near-infrared spectrum, which shows the presence of co-ordinated pyridine and the absence of pyridinium and, because of its simplicity, that all four pyridine

[24] Pistorius, *Mol. Phys.*, 1958, **1**, 295.
[25] Hulme, personal communication.
[26] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

residues act as ligands. In contrast to Wannagat *et al.*[10] we found that the adduct, $SiI_4,4py$, is extremely susceptible to hydrolysis and it was very difficult to avoid traces of pyridinium ion and silica in our infrared spectra of this compound. In the cæsium bromide region the infrared spectrum is relatively simple and the band at 465 cm.[-1] or the one at 403 cm.[-1] evidently contains the pyridine out-of-plane deformation vibration. We have found that the position of this pyridine vibration is sensitive to the element to which it is co-ordinated, but *relatively* insensitive to the nature of the groups attached to this element. Further, certain apparently regular trends appear in the position of this band ($SnI_4,2py$, 427; $MeSnI_3,2py$, 425; $MeSnCl_2,2py$, 428; $Me_2SnCl_2,2py$, 417; $SnCl_4,2py$, 431; $GeCl_4,2py$, 449; $GeBr_4,2py$, 443; $SiCl_4,2py$, 469; $SiBr,2py$, 469 cm.[-1]). Thus, for adducts where tin is the central atom the band is at about 425 cm.[-1], for germanium at 446 cm.[-1], for silicon at 469 cm.[-1]. By contrast, the band for py_2I^+ occurs at 434 cm.[-1], while that in ICl,py[27] is at about 430 cm.[-1]. It is thus reasonable to assign the band at 465 cm.[-1] in $SiI_4,4py$ to pyridine co-ordinated to silicon. We attempted to study the effect of co-ordination of pyridine to iodine in the adduct $CHI_3,3py$ (known from phase-diagram studies[28] and presumed by us to be similar in structure to $CHI_3,3quinoline$[29]). However, the spectrum of a solution of iodoform in pyridine at room temperature and after solidification was essentially that of the constituents.[30]

The unassigned bands at 403 and 366 cm.[-1] in the spectrum of the adduct, $SiI_4,4py$, are most likely to be associated with silicon–iodine stretching modes. The whole spectrum can then be quite elegantly explained in terms of the ionic model, *cis*-$[SiI_2,py_4]^{2+}2I^-$. The high value for the symmetric and the antisymmetric silicon–iodine stretching vibrations is due to the fact that the main vibration is undergone by the silicon. The frequency of these vibrations would be raised relative to those of a simple octahedral adduct $SiI_4,2L$ owing to the presence of a double positive charge on the complex ion.

Chemically the formulation of the adduct as $[SiI_2,py_4]^{2+}2I^-$ is satisfactory. Donation from pyridine to the iodine of silicon tetraiodide, yielding a 1 : 4 adduct of considerable thermal stability [m. p. 150—160° (decomp.)], could be interpreted in terms of strong $d_\pi-p_\pi$ bonding between silicon and iodine, rendering the iodine a better acceptor than in carbon tetraiodide (where a pyridine adduct is unknown). However, it would require a quite unreasonable change between silicon and germanium in π-bonding ability to account for lack of adduct formation between pyridine and germanium tetraiodide. If ionisation is invoked to explain the formation of an adduct with silicon tetraiodide, this is capricious and cannot be predicted. Similarly, silicon tetraiodide is apparently very insoluble in pyridine, unlike carbon tetraiodide and germanium tetraiodide. Finally a model shows that it is possible to pack four pyridine (or quinoline or acridine) molecules around the SiI_2^{2+} ion.

Silicon–Nitrogen Vibrations.—It could be argued that the main weakness in the above discussion of the infrared spectra of co-ordination compounds is the possibility of element–ligand vibrations being mistaken for element–halogen vibrations. Perhaps the strongest argument against the presence of element–ligand vibrations is that in all our spectra of co-ordination compounds with donors such as pyridine, 2,2'-bipyridyl, and 1,10-phenanthroline we have never needed to invoke such vibrations to assign the main bands. For confusion to arise the element–ligand bands would need to occur always in the region of the element–halogen bands, which seems most unlikely.

The assignment of element–nitrogen bands in co-ordination compounds has caused much confusion in the literature. The B–N bond stretch in the adduct BCl_3,py has been given[31,32] as above 1100 cm.[-1] although a comprehensive study[33] has established the

[27] Popov, Marshall, Stute, and Person, *J. Amer. Chem. Soc.*, 1961, **83**, 3586.
[28] Davidson, Van der Werf, and Boatright, *J. Amer. Chem. Soc.*, 1947, **69**, 3045.
[29] Bjorvatten and Hassel, *Acta Chem. Scand.*, 1959, **13**, 1261.
[30] See also Stammreich and Forneris, *Spectrochim. Acta*, 1956, **8**, 52.
[31] Greenwood and Wade, *J.*, 1960, 1130.
[32] Waddington and Klanberg, *J.*, 1960, 2339.
[33] Taylor and Cluff, *Nature*, 1958, **182**, 390.

B–N stretch at 667 cm.$^{-1}$ in trimethylaminoborane. In several cases it is difficult to assign a vibration solely to the B–N (or Al–N or Ga–N) stretch. However, it appears that the force constant for the B–N stretching is at least 2.5×10^5 dyne cm.$^{-1}$. This high value can be correlated with the fact that it is a vacant, low-lying, *p*-orbital of boron which acts as the acceptor. It appears likely that the force constants for the Al–N and Ga–N bonds will be correspondingly high. However, in the case of silicon the acceptor orbitals are in the $3d$-level and the general properties of the addition compounds indicate a weak linkage. Thus the 1 : 1 adduct of silicon tetrachloride with tetramethylethylenediamine is effectively fully dissociated in solution at room temperature.[9] In contrast, the complex, BF$_3$,py, is only 11% dissociated in the gas phase at 300°/1 atm.[34] Further, borane (BH$_3$) is such a powerful acceptor that in the absence of donors it forms the hydrogen-bridged dimer (B$_2$H$_6$), whereas silane apparently exhibits no acceptor properties even towards strong nitrogen donors.

If the Si–N force constant for bond stretching is as low as $<10^5$ dyne cm.$^{-1}$ it is unlikely that we should observe such a vibration where the nitrogen is contained in a heavy heterocyclic residue.

EXPERIMENTAL

Purification of Solvents and Reagents.—Pyridine, 1,10-phenanthroline, 2,2′-bipyridyl, carbon disulphide, benzene, and silicon tetrachloride were purified and dried by methods previously described.[4,5] Chloroform was dried over molecular sieve. Silicon tetrabromide was fractionally crystallised *in vacuo*, then distilled into ampoules. Germanium tetraiodide was prepared as described by Foster and Williston[35] and recrystallised from chloroform. Silicon tetraiodide was purified by vacuum-sublimation.

Preparation of Adducts.—(*a*) *In the dry-box.* Generally the halide was dissolved in a solvent (carbon tetrachloride, carbon disulphide, chloroform, or benzene) and the aromatic base added directly (pyridine) or in a solvent (carbon disulphide or chloroform for 1,10-phenanthroline, carbon tetrachloride or benzene for 2,2′-bipyridyl). (*b*) *In vacuo.* The adduct of pyridine with silicon tetraiodide was prepared by distilling pyridine into a solution of silicon tetraiodide in benzene, resulting in the immediate formation of a pale yellow precipitate. Similarly, silicon tetraiodide (2·139 g.) was heated with an excess of pyridine at about 110° for 10 hr. The excess of pyridine was distilled off and measured. Addition of pyridine to germanium tetraiodide in benzene yielded no precipitate, and removal of volatile material left unchanged germanium tetraiodide (m. p. 141—149°, infrared spectrum showing no bands in the 2·5—37 μ region). Although germanium tetraiodide is apparently stable to hydrolysis, the addition of " wet " pyridine to a solution of germanium tetraiodide in a solvent such as benzene yields pyridinium iodide.

Analyses.—Generally analyses were carried out by total hydrolysis followed by pH titrations or determination of halide potentiometrically at a silver electrode; the results are tabulated here.

Adduct	Molar ratio (pH titration)	Found (%) Cl or Br	Formula	Required (%) Cl or Br
SiCl$_4$,1,10-phenanthroline	1 : 1·01			
SiCl$_4$,2,2′-bipyridyl	1 : 1·04			
SiBr$_4$,2py	1 : 2·04	62·6	C$_{10}$H$_{10}$Br$_4$N$_2$Si	63·2
SiBr$_4$,1,10-phenanthroline	1 : 1·10			
SiBr$_4$,2,2′-bipyridyl....................	1 : 1·08	62·1	C$_{10}$H$_8$Br$_4$N$_2$Si	63·5
SiI$_4$,4py *		58·8	C$_{20}$H$_{20}$I$_4$N$_4$Si	59·6
SiI$_4$,1,10-phenanthroline †	1 : 1·05			

* Molar ratio of 1 : 3·88 from vacuum-experiment with solid SiI$_4$ and pyridine. † Molar ratio of 1 : 1·03 by precipitation-titration of SiI$_4$ and 1,10-phenanthroline dissolved in carbon disulphide.

Infrared Spectra.—Spectra were taken on a Perkin-Elmer model 221 infrared spectrometer equipped with grating and rock-salt and cæsium bromide optics. For the adducts, SiCl$_4$,2py and SiBr$_4$,2py, the spectra changed to some extent depending upon the crystallinity of the

[34] Greenwood and Martin, *Quart. Rev.*, 1954, **8**, 1.
[35] Foster and Williston, *Inorg. Synth.*, 1946, **2**, 112.

sample: samples recrystallised from hot (~150°) pyridine generally showed less resolution of the peaks. Similarly the very finely divided sample of $SiCl_4$,1,10-phenanthroline from carbon disulphide gave better resolution than did that obtained from chloroform solution.

The near-infrared spectrum of SiI_4,4py as a Nujol mull showed bands at 638w, 659s, 670sh, 691s, 699s, 741w, 761m, 768m, 771sh, 958w, 985w, 994w, 1009vs, 1059s, 1068sh, 1152w, 1207m, 1338w, 1441s cm.$^{-1}$

<div align="center">APPENDIX [23]</div>

F and G matrix elements are for XY_4 (C_{2v}) having the dimensions shown for the $SiCl_4$ residue (I) and with all bond lengths equal. The matrices are symmetrical about the diagonal, and zero elements are not given. The secular equation is derived from the F and G matrices by use of the relationship [20] $|FG-E\lambda| = 0$. Symbols have the significance given by Chantry and Ewing.[21] μ = reciprocal mass in atomic-weight units.

F matrix elements:

<div align="center">

Class a_1

$f_{11} = f_r + f_{rr}$
$f_{12} = 2f_{Rr}$
$f_{13} = (\sqrt{2}/\sqrt{5})[\phi_{r\gamma} + 2\phi_{r\gamma\alpha}]$
$f_{14} = \sqrt{2}f_{r\beta}$
$f_{22} = f_R + f_{RR}$
$f_{23} = (\sqrt{2}/\sqrt{5})[\phi_{R\gamma} + 2\phi_{R\gamma\alpha}]$
$f_{24} = \sqrt{2}f_{R\beta}$
$f_{33} = 1/5[\phi_\gamma + \phi_{\gamma\gamma} + \phi_{\gamma\gamma}' + 4\phi_\alpha]$
$f_{34} = (2/\sqrt{5})\phi_{\alpha\beta\gamma}$
$f_{44} = f_\beta$

Class a_2

$f_{55} = \phi_\gamma - \phi_{\gamma\gamma} - \phi_{\gamma\gamma}'$

</div>

<div align="center">

Class b_1

$f_{66} = f_R - f_{RR}$
$f_{67} = \sqrt{2}\phi_{R\gamma}$
$f_{77} = \phi_\gamma - \phi_{\gamma\gamma} + \phi_{\gamma\gamma}'$

Class b_2

$f_{88} = f_r - f_{rr}$
$f_{88} = \sqrt{2}\phi_{r\gamma}$
$f_{99} = \phi_\gamma + \phi_{\gamma\gamma} - \phi_{\gamma\gamma}'$

</div>

G matrix elements:

<div align="center">

Class a_1

$g_{11} = \mu_y + \frac{1}{2}\mu_x$

$g_{13} = \dfrac{-\sqrt{5}}{\sqrt{2}}\mu_x$

$g_{14} = -\dfrac{\sqrt{3}}{\sqrt{2}}\mu_x$

$g_{22} = \mu_y$

$g_{33} = \dfrac{5}{2}\mu_y + 5\mu_x$

$g_{34} = \sqrt{15}\mu_x$

$g_{44} = 2\mu_y + 3\mu_x$

Class a_2

$g_{55} = \dfrac{7}{2}\mu_y$

Class b_1

$g_{66} = \mu_y + 2\mu_x$
$g_{67} = -2\sqrt{2}\mu_x$
$g_{77} = \dfrac{5}{2}\mu_y + 4\mu_x$

Class b_2

$g_{88} = \mu_y + \dfrac{3}{2}\mu_x$

$g_{89} = -\dfrac{3}{\sqrt{2}}\mu_x$

$g_{99} = \dfrac{3}{2}\mu_y + 3\mu_x$

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