Preparation, Vibrational Spectra, Normal Coordinate Analysis, and Structures of bis-Pyridine and Orthophenanthroline Complexes of Mixed Halogenosilanes

D. H. Boal and G. A. Ozin[1]

Lash Miller Chemistry Laboratory and Erindale College, University of Toronto, Toronto, Ontario

Received February 17, 1972

The compounds py_2SiCl_3X (where X = H, F, or Br), $py_2SiCl_2X_2$ (where X = F or Br) and the corresponding orthophenanthroline complexes are prepared and the vibrational spectra reported for the first time. Using a combination of the vibrational data and normal coordinate calculations, the stereochemistries may be defined for most of the complexes. Preferences for certain configurations in the series are qualitatively discussed in terms of the spatial requirements of the various atoms and groups within each complex.

Les composés py_2SiCl_3X (où X = H, F, ou Br), $py_2SiCl_2X_2$ (où X = F ou Br) et les complexes ortho-phénantroline correspondants ont été préparés et leurs spectres de vibration rapportés pour la première fois. En utilisant une combinaison des données vibrationnelles et des calculs des coordonnées normales, les stéréochimies ont pu être établies pour la plupart des complexes. Les préférences pour certaines configurations dans la série sont discutées qualitativement en fonction des exigences spatiales des divers atomes et groupes à l'intérieur de chaque complexe.

Introduction

There has been considerable interest in the molecular structures of pyridine complexes of the main group halides, especially those of group IVB (1). Certain trends have emerged as definitive structural information (usually from X-ray, infrared, and Raman data) has gradually appeared in the literature.

One finds an apparently universal preference for *trans*-octahedral stereochemistries for bis-pyridine adducts; for example, py_2SiF_4 (2), py_2SiCl_4 (3), py_2GeCl_4 (4), py_2SnCl_4, py_2SnBr_4, py_2SeCl_4, and py_2TeCl_4 (5). Monopyridine complexes, such as $pyAlCl_3$ (6) and $pyPCl_5$ (7) have the molecular structures which would be predicted on simple electron-pair repulsion principles. When pyridine is reacted with silicon halides containing SiI bonds, ionization often occurs. This may be illustrated by the unusual compounds py_3SiCl_3I and $py_4SiCl_2I_2$ which were shown to contain the cations $py_3SiCl_3^+$ and $py_4SiCl_2^{2+}$ having C_{2v} and D_{4h} symmetries, respectively (7).

A group of molecules for which stereochemical information has not yet been reported are the bis-pyridine and orthophenanthroline complexes of the mixed halogenosilanes. A

---

[1]To whom correspondence should be addressed.

combination of infrared and Raman data should allow their stereochemistries to be determined.

As the parent species py_2SiX_4 (where X = F, Cl, or Br) are all *trans*-octahedral, it is reasonable to assume that all combinations of F, Cl, or Br in the *mixed* halide complexes $py_2SiX_nY_{4-n}$ contain *trans*-pyridine ligands.

Results

bis-Pyridine Complexes

(A) Py_2SiCl_3F, py_2SiCl_3Br, and py_2SiCl_3H

Let us consider the complexes py_2SiCl_3X (where X = F, Br, or H) which would be expected to yield very similar infrared and Raman spectra, characteristic of *trans*-pyridine ligands with a *T*-shaped $SiCl_3$ skeleton (1 to 3) shown below
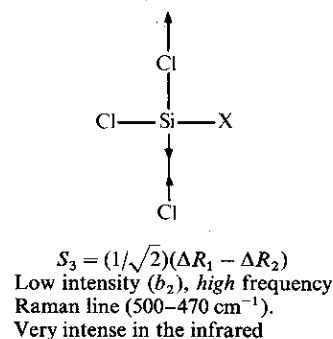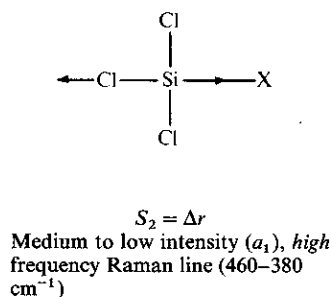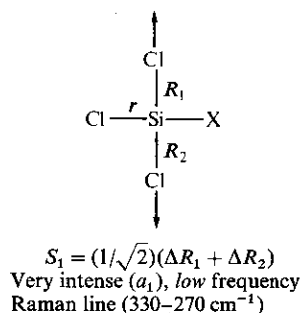

1 (C_{2v}) 2 (C_{2v}) 3 (C_{2v})
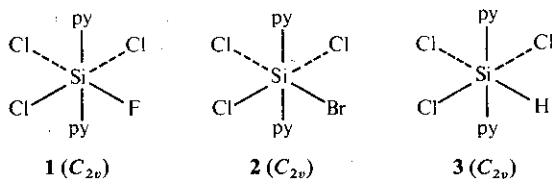
The *T*-shaped $SiCl_3$ grouping is easily recognized by a diagnostic pattern of *three* Raman lines, illustrated schematically by their symmetry coordinates below

TABLE 1. Vibrational spectra* of py$_2$SiCl$_3$X, X = H, F, and Br

| Frequency (cm^{-1}) | | | | | | |
| py$_2$SiCl$_3$H | | py$_2$SiCl$_3$F | | py$_2$SiCl$_3$Br | | Approximate description of mode |
Infrared	Raman	Infrared	Raman	Infrared	Raman	
	2085w					νSiH
	2065w					
		855vw	860vw			νSiF
482s	482w	486s	480vvw	489s	—	$S_3\nu$SiCl (asym)
447vs br	449mw	463m	458vw	466s	460vw	⎧pyridine out-of-plane
		425s br	430vw			⎨ring mode +
				410s	411vvw	⎩$S_2\nu$SiCl (sym)
374vs br	372vw	376ms	371ms	387s br	386vvw	νSiN (asym)
		337vw	332w			δSiF
301w	305vs	306w	303s		312vs	$S_1\nu$SiCl (sym)
				282w	285m	νSiBr (sym)
		252m	252ms		261mw	
	244ms					
		215m	215w	232w	223m	
	203w			202w		
		196m	184w		188ms	
		178w	175vw sh		170vw	
					156vw	
			134s		129s	
		110m	102s	106m		
		73w	65m		83s	

*SiCl and SiBr stretching modes are in italics (see text for description of S_1, S_2, and S_3).

Cl
 |R_1
Cl —r— Si —— X
 |R_2
Cl

$S_1 = (1/\sqrt{2})(\Delta R_1 + \Delta R_2)$
Very intense (a_1), *low* frequency Raman line (330–270 cm^{-1})

Cl
 |
←—Cl — Si —→ X
 |
Cl

$S_2 = \Delta r$
Medium to low intensity (a_1), *high* frequency Raman line (460–380 cm^{-1})

Cl
 |
Cl — Si —— X
 |
Cl

$S_3 = (1/\sqrt{2})(\Delta R_1 - \Delta R_2)$
Low intensity (b_2), *high* frequency Raman line (500–470 cm^{-1}). Very intense in the infrared

Thus, for py$_2$SiCl$_3$X we calculate and observe (Tables 1 and 2) a *low* frequency, totally symmetrical SiCl stretching mode S_1 at 303 cm^{-1} (X = H), 304 cm^{-1} (X = F), and 312 cm^{-1} (X = Br) characteristic of T-shaped SiCl$_3$. We note that S_1 occurs at low frequency because the central silicon atom remains stationary during the mode and cannot make a contribution to the respective G matrix element. This is not so for S_2 which appears at higher frequencies, 448 cm^{-1} (X = H), 427 cm^{-1} (X = F), and 410 cm^{-1} (X = Br). The monotonical drop to lower frequency parallels the increasing mass of the X grouping *trans* to chlorine and the resulting decreasing motion of the central silicon atom. The asymmetrical SiCl stretching mode S_3 is calculated and observed at *high* frequencies in the range 482–489 cm^{-1} for X = F, Br, and H.

The complex [py$_3$SiCl$_3^+$]I$^-$ which has also been assigned a T-shaped SiCl$_3$ residue (7) displays a *similar* pattern of SiCl$_3$ stretching modes at 315(S_1), 410(S_2), and 482(S_3) cm^{-1}.

TABLE 2. Calculated vibrational spectra of py$_2$SiCl$_3$X*

| Frequency (cm^{-1}) | | | Approximate description of mode‡ |
py$_2$SiCl$_3$H	py$_2$SiCl$_3$F	py$_2$SiCl$_3$Br	
1722			A_1 νSiH
	744		A_1 νSiF
463	479	470	B_1 νSiCl (S_3)
428	385	477†	A_1 νSiCl (S_2)
411	492	462	B_2 νSiN
279	272	322†	A_1 νSiCl (S_1)
		226†	A_1 νSiBr
133	135	131	A_1 νSiN

*Deformational modes are not listed.
†Highly coupled modes.
‡See text for description of S_1, S_2, and S_3.

TABLE 3. Vibrational spectra† of py$_2$SiCl$_2$X$_2$*

| Frequency (cm^{-1}) | | | | Approximate description of mode |
| py$_2$SiCl$_2$F$_2$ | | py$_2$SiCl$_2$Br$_2$ | | |
Infrared	Raman	Infrared	Raman	
489s	490vw	484s	—	νSiCl (asym)
455s	458w	458s br	—	py out-of-plane ring mode
420s	425w	408m	—	νSiN (asym)
	384s		—	νSiBr (asym)
352m	357w			
340w				δSiF
	279vs		311m	νSiCl (sym)
		280m	284ms	
		225m	225vs	νSiBr (sym)
230m	222w	207mw	210w	
192w	202w	191w	192w	
175m	174mw		176w	
	140w		153w	
108m	110m	102w		
90w				
	74m			

*SiCl and SiBr stretching modes are in italic.

(B) py$_2$SiCl$_2$F$_2$ and py$_2$SiCl$_2$Br$_2$

Having established the spectral characteristics of a T-shaped SiCl$_3$ grouping we will extend the method to the stereochemical problem presented by the complexes py$_2$SiCl$_2$X$_2$ (where X = F or Br). Using the *trans*-pyridine approximation described previously, it remains to distinguish the *cis* and *trans* possibilities (**4** and **5**) shown below

py   Cl   X   Si   Cl

4 (D_{2h})   **5** (C_{2v})
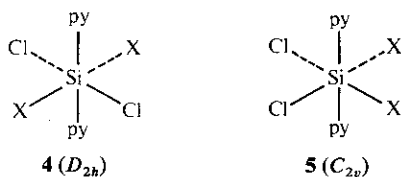
A mode involving little or no motion of the central silicon atom is expected to appear as an intense, low frequency line in the Raman spectrum of the above complexes.

We find that the Raman spectrum of py$_2$SiCl$_2$Br$_2$ displays a *low* frequency SiBr (225 cm^{-1} vs) and *low* frequency SiCl (311 cm^{-1} vs) stretching mode characteristic of *trans*-SiBr$_2$ and *trans*-SiCl$_2$ residues, respectively (configuration **4** and Table 3). Similarly, the Raman spectrum of py$_2$SiCl$_2$F$_2$ shows an intense, *low* frequency SiCl stretching mode (279 cm^{-1} vs) which also favors the all *trans* configuration **4**. The characteristic *high* frequency asymmetrical SiCl stretching mode appears in the infrared at 484 and 489 cm^{-1} for py$_2$SiCl$_2$Br$_2$ and py$_2$SiCl$_2$F$_2$, respectively (Table 3).

Additional evidence for the all *trans* assignment for py$_2$SiCl$_2$F$_2$ and py$_2$SiCl$_2$Br$_2$ may be obtained by comparing the observed and calculated vibrational spectra for the molecules in the possible conformations, that is, *trans*-pyridines, *trans*-halogens (D_{2h}), and *trans*-pyridines, *cis*-halogens (C_{2v}). The results of the calculations are shown in Table 4 and strongly favor the D_{2h} structure for py$_2$SiCl$_2$X$_2$.

Orthophenanthroline Complexes

It is interesting to consider the stereochemical behavior of the silicon–halogen residue when the complexes are locked in a *cis* configuration with the bulky chelate ligand orthophenanthroline. We have prepared the compounds o-phen.SiCl$_2$X$_2$ and o-phen.SiCl$_3$X (where X = F or Br) and will discuss their infrared and Raman spectra using stereochemical arguments similar to those described for the analogous pyridine complexes.

(A) o-phen.SiCl$_2$Br$_2$ and o-phen.SiCl$_2$F$_2$

The spectra of the orthophenanthroline adducts are more complex than the corresponding pyridine adducts mainly because of (a) the lower molecular symmetries and (b) the complexity of the ligand modes in the SiCl stretching region (510–350 cm^{-1}).

Careful examination of the Raman spectrum of o-phen.SiCl$_2$Br$_2$ (Table 5) shows only one intense, *low* frequency SiBr stretching mode

TABLE 4. Calculated vibrational spectra for $py_2SiCl_2X_2$*

| Frequency (cm⁻¹) for D_{2h} model		Approximate description of mode	Frequency (cm⁻¹) for C_{2v} model		Approximate description of mode
$py_2SiCl_2F_2$	$py_2SiCl_2Br_2$		$py_2SiCl_2F_2$	$py_2SiCl_2Br_2$	
836		B_{3u} νSiF			
			758		A_1 νSiF
606		A_g νSiF	739		B_1 νSiF
517	468	B_{1u} νSiCl	517	458	B_2 νSiN
517	458	B_{2u} νSiN			
	440	B_{3u} νSiBr	433	457	A_1 νSiCl
			355	454	B_1 νSiCl†
284	307	A_g νSiCl			
				292	A_1 νSiBr
	174	A_g νSiBr			
				212	B_1 νSiBr†
137	126	A_g νSiN	138	128	A_1 νSiN

*Deformational modes are not listed.
†Highly coupled mode.

TABLE 5. Vibrational spectra of o-phen.SiCl₂X₂*

Frequency (cm⁻¹)				
o-phen.SiCl₂F₂		o-phen.SiCl₂Br₂		Approximate description of mode
Infrared	Raman	Infrared	Raman	
	506w	506w	503vw	o-phen ring mode
476s		464s		νSiCl (asym)
448w	447ms	449ms		o-phen ring mode
430w	429mw	429s	430m	
418s	414m	406s	405mw	
350vw	346w	360w	359w br	
332w	331vw	332w	333vw	
306vw	298vs			νSiCl (sym)
	273s	282m	283m br	
		234m	237vs	νSiBr (sym)
		206m	197m	
		172m	168m	
		154w	152m	
		114w	114ms	

*SiCl and SiBr stretching modes are in italic.

(237 cm⁻¹) characteristic of *trans*-bromines shown below (6)
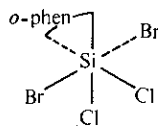
6

The absence of a *low* frequency SiCl stretching mode also supports the *cis*-chlorine assignment for o-phen.SiCl₂Br₂. Examination of the corresponding data for o-phen.SiCl₂F₂ (Table 5) shows an intense, *low* frequency SiCl stretching

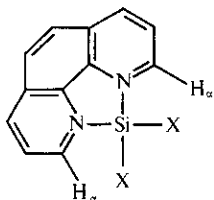mode (298 cm⁻¹) characteristic of *trans*-chlorines shown below (7)
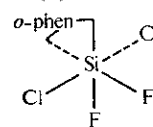
7

The different stereochemical arrangements for o-phen.SiCl₂F₂ and o-phen.SiCl₂Br₂ may be rationalized by considering the steric properties of the orthophenanthroline ring and the repulsion between *cis*-halogens. For example, it is

TABLE 6. The infrared and Raman spectra* of o-phen.SiCl₃X (where X = F or Br) and bipy.SiCl₃F

| Frequency (cm⁻¹) | | | | | | |
| o-phen.SiCl₃F | | bipy.SiCl₃F | | o-phen.SiCl₃Br | | Approximate description of mode |
Infrared	Raman	Infrared	Raman	Infrared	Raman	
509w	508m				506w	o-phen ring mode
477s			~487w	470s	478ww	vSiCl (asym)
467s	465vw		~460w	488s		vSiCl (sym)
427s br	432s		~420vvw	430s	428vs	vSiCl and o-phen ring mode
	413w		384w	403s	410vwsh	
371w	369w		360ms			
331m	330m		317w	~330vw	343w	
306w	304ms			291w	307vwsh	
					290mw	
278m	276ms		273vs		276wsh	vSiCl (sym)
247m	242ms		252m		263w	
222m	230msh			233w	244w	
210w	210w		211msh		229mw	
190m	191m		201m	193w	198wsh	
167m				182w	178msh	
122w				153w	159ms	
				124w		

*SiCl stretching modes are in italic.

known (8) that [(o-phen)₂py₂Ru]³⁺3Cl⁻ will not adopt conformations in which the ortho-phenanthroline rings are *trans* to one another (*i.e.* it will only adopt optically active *cis* conformations). This would indicate that the hydrogens Hₐ shown below can interact sterically with atoms occupying the other two positions in the plane about silicon. With this in mind, the con-


figurations 6 and 7 which we favor for o-phen.-SiCl₂Br₂ and o-phen.SiCl₂F₂ are those which would have been preferred simply from steric arguments. That is, one would predict that the *larger* halogens would chose positions in the complex such that they were both *out* of the plane of the bulky orthophenanthroline ligand and *as far apart* (*trans*) from each other as possible. In this way the repulsions between (a) the hydrogens Hₐ and the *cis*-halogens in the plane and (b) *cis*-halogens are both minimized.

(B) o-phen.SiCl₃F and o-phen.SiCl₃Br

In the above complexes containing the SiCl₃

residue we do have a stereochemical ambiguity, which was not the case for py₂SiCl₃X. The possible configurations for o-phen.SiCl₃F and o-phen.SiCl₃Br (8 and 9) are shown below
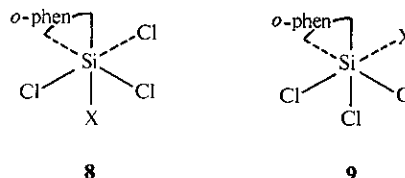
o-phen.SiCl₃Br shows an exceptionally intense, *high* frequency Raman line at 428 cm⁻¹ (Table 6) (its unusually high intensity makes it unlikely to be an orthophenanthroline mode, by comparison with Raman data for many ortho-phenanthroline complexes), which favors a pyramidal SiCl₃ residue as shown in configuration 9. However, o-phen.SiCl₃F shows a characteristic intense, *low* frequency SiCl stretching mode (276 cm⁻¹ and for comparison at 273 cm⁻¹ in the analogous bipy.SiCl₃F) which strongly favors the *T*-shaped SiCl₃ residue of configuration 8 (Table 6).

As with o-phen.SiCl₂X₂ we find that the configurations favored for o-phen.SiCl₃X (where X = F or Br) are those which would have been predicted from simple steric arguments. That is, the larger halogen prefers a molecular site in the

TABLE 7. Analyses of bispyridine and orthophenanthroline complexes of mixed halogenosilanes

Complex	% halide		Base:metal
	Observed	Calculated	
py$_2$SiCl$_3$F	34.4	34.2 (Cl)	1.96:1
py$_2$SiCl$_3$Br	28.2	28.0 (Cl)	2.07:1
	21.3	21.5 (Br)	
py$_2$SiCl$_2$F$_2$	18.5	18.0 (Cl)	1.90:1
py$_2$SiCl$_2$Br$_2$	16.0	17.7 (Cl)	2.05:1
	39.0	38.0 (Br)	
o-phen.SiCl$_3$F	31.6	31.8 (Cl)	1.06:1
o-phen.SiCl$_3$Br	23.0	23.4 (Cl)	1.04:1
	17.9	17.5 (Br)	
o-phen.SiCl$_2$F$_2$	22.4	22.6 (Cl)	1.03:1
o-phen.SiCl$_2$Br$_2$	14.5	16.2 (Cl)	0.94:1
	36.0	36.4 (Br)	

complex, such that it is out of the plane occupied by the bulky orthophenanthroline ligand and minimizes cis-halogen repulsions.

Conclusion

We may summarize the data for the pyridine and orthophenanthroline complexes of mixed halogenosilanes by stating that interesting structural trends are observed, which appear to be controlled by the spatial requirements of the respective ligands and halogens in the molecule. It appears that electronegativity and π bonding arguments do not have to be invoked in order to explain the data.

Experimental

Trichlorosilane was purchased from Matheson.

The chlorofluorosilanes were prepared using the method of Booth and Swineheart (9) in which a Swarts type reaction was involved. Here, SiCl$_4$ was partially fluorinated using SbF$_3$, incorporating SbCl$_5$ as a catalyst. The mixed chlorofluorosilanes were initially passed through cold traps, at ice/salt, CO$_2$/acetone, and liquid nitrogen temperatures, respectively, which thereby achieved a crude separation. Each crude fraction was introduced in turn into a specially designed, double vacuum jacketed, low temperature fractionation column, with a finely controlled take off head. Yields of SiCl$_3$F and SiCl$_2$F$_2$ were collected; their vapor pressure/temperature dependence agreed very closely with those quoted by Schumb and Gamble (10). These were separately stored in 5 l bulbs, each having a finger immersed continuously in liquid nitrogen. The latter precaution was to prevent the disproportionation of the gases to SiF$_4$ and SiCl$_4$. It was found that after a period of three months, on refractionating the gases, no detectable sign of disproportionation was observable. Infrared spectra of the gases

SiCl$_3$F and SiCl$_2$F$_2$ were taken and were in agreement with those of Stokr and Schneider (11).

The chlorobromosilanes were initially prepared by refluxing SiBr$_4$ and SbCl$_3$ using phosphorus pentoxide guard tubes. The resulting mixture was then fractionated but yielded mainly SiCl$_3$Br. The preparation was repeated, using the method of Forbes and Anderson (12), where a 1:1 mixture of SiCl$_4$ and SiBr$_4$ was sealed off in a thick walled glass bomb which was then heated at 140 °C for 72 h. Again the resulting mixture was fractionated producing SiCl$_3$Br and SiCl$_2$Br$_2$ in reasonable yields, b.p. 78 and 103 °C, respectively. The infrared spectra agreed with those of Mlle. Delwaulle (13) where the presence of one fraction in the other was negligible. Pyridine was dried with SiCl$_4$ and then vacuum distilled. Orthophenanthroline and bipyridyl were dried by slow, repeated vacuum sublimation. All solvents were dried with CaH$_2$ and vacuum distilled. A typical preparation involved the reaction of the appropriate halogenosilane with a slight excess of the ligand in either the pure state or in chloroform solution. The complexes always formed as white precipitates, which remained as white powders after removal of the excess ligand and solvent. All manipulations where possible were carried out in all glass vacuum systems. Raman spectra were recorded for the powdered solids in glass ampoules which had been sealed off directly from the vacuum line preparation. Samples for infrared mull spectra were handled in glove boxes which were continuously purged with dry air. Nujol was dried over molten sodium for 24 h prior to use.

Infrared spectra were recorded on a Beckmann IR 11 spectrometer and Raman spectra on a Spex 1401 spectrometer using krypton or argon ion laser excitation.

Analyses

Analyses were performed by quantitatively hydrolyzing the product and analyzing for halide and py:Si by using argentometric (14) and pH titrations, respectively. The preparation of the known compound py$_2$SiCl$_3$H was exactly the same as that reported (1). Results of analyses are shown in Table 7.

TABLE 8.   Force constants used in normal coordinate calculations of py_2SiX_4

	Value			
Force constant*	X = H†	X = F	X = Cl	X = Br
f_R	1.72	3.89	1.57	1.45
f_l	1.00	1.00	1.00	1.00
$f_{RR}^{cis} = f_{Rl}$	0.28	0.28	0.28	0.28
$f_{RR}^{trans} = f_{ll}$	0.14	0.14	0.14	0.14
f_α	0.55	1.18	0.70	0.60
$f_{R\alpha}$	0.18	0.34	0.20	0.17
$f_{\alpha\alpha} = f_{\alpha\beta} = f_{\beta\beta}$	0.10	0.10	0.10	0.10

*Force constants in units of mdyn/Å, mdyn/rad or mdyn Å/rad².
†Force constants for the hypothetical molecule py_2SiH_4.

Normal Coordinate Calculations

Force fields for the parent molecules py_2SiX_4 were derived using methods similar to those described previously for py_2SiCl_4 (1) and $pyPCl_5$ (7). These force constants were transferred directly to the respective mixed halogeno–pyridine complexes. The pyridine ligand was treated as a point mass with a SiN bond stretching constant of about 1.0 mdyn/Å. Force constants not listed in Table 8 for the parent molecules were set equal to zero in the mixed halo species. Table 9 contains the bond lengths used in the calculations.

The calculated spectra for py_2SiCl_3X are shown in Table 2 for a molecular symmetry of C_s. In the case of $py_2SiCl_2X_2$ the spectra were computed for *trans*-pyridines but with both *trans*-halogens (D_{2h}) and *cis*-halogens (C_{2v}). Within the approximations made in the force fields only the D_{2h} $py_2SiCl_2X_2$ calculated frequencies gave a satisfactory fit with the observed spectra.

The computer programs used for the calculation of the vibrational spectra are based on those of Schactschneider's G.MAT, F.MAT, and EIGV. and were run on an IBM 7094 computer system.

1. I. R. BEATTIE. Quart. Rev. 17, 383 (1963). H. J. CAMPBELL-FERGUSSON and E. A. V. EBSWORTH. J. Chem. Soc. (A), 1508 (1966); 705 (1967). I. R. BEATTIE, T. R. GILSON, and G. A. OZIN. J. Chem. Soc. 2773 (1968).

TABLE 9
(a)   Internal coordinates of parent molecules py_2SiX_4
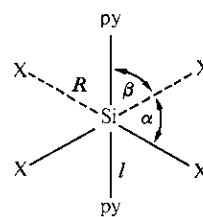
(b)   Bond distances used in vibrational analysis of py_2SiX_4

Bond	Distance (Å)
Si—H	1.55
Si—F	1.62
Si—Cl	2.13
Si—Br	2.28
Si—py	2.01

2. V. BAIN, R. C. G. KILLEAN, and M. WEBSTER. Acta Cryst. B25, 156 (1969).

3. R. C. G. KILLEAN. J. Chem. Soc. A, 2772 (1968).

4. R. HULME, G. O. LEIGH, and I. R. BEATTIE. J. Chem. Soc. 366 (1960).

5. I. R. BEATTIE, P. JONES, M. MILNE, and M. WEBSTER. J. Chem. Soc. A, 482 (1969).

6. I. R. BEATTIE, T. R. GILSON, and G. A. OZIN. J. Chem. Soc. A, 2373 (1968).

7. I. R. BEATTIE and G. A. OZIN. J. Chem. Soc. A, 370 (1969).

8. B. BOSNICH and F. P. DWYER. Aust. J. Chem. 19, 2227 (1969).

9. H. A. BOOTH and C. F. SWINEHEART. J. Am. Chem. Soc. 57, 1333 (1935).

10. W. C. SCHUMB and E. L. GAMBLE. J. Am. Chem. Soc. 54, 3943 (1932).

11. JAN STOKR and BOHDAN SCHNEIDER. Chem. listy, 52, 985 (1958).

12. G. S. FORBES and H. H. ANDERSON. J. Am. Chem. Soc. 66, 931 (1944).

13. M. L. DELWAULLE. J. Phys. Rad. [8], 7 (1946).

14. V. J. SHINER and M. L. SMITH. Anal. Chem. 28, 1043 (1956).