Vibrational Spectra, Vibrational Analysis and Stereochemistries of the Pentacoordinate Molecules $SiCl_3X \cdot N(CH_3)_3$ and $SiCl_3X \cdot N(CD_3)_3$ where X = H, F, Br, or I

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The thermally unstable compounds $SiCl_3X.N(CH_3)_3$ and $SiCl_3X.N(CD_3)_3$ where X=H, F, Br, or I are studied at −196 °C by infrared and Raman spectroscopy. The data are compatible with molecular five coordinate compounds having a trigonal bipyramidal stereochemistry with the ligand trimethylamine always in the axial position. Using the vibrational data and normal coordinate analyses in both the C_s and C_{3v} configurations, X is suggested to be equatorial for H and F and axial for Br and I. The factors influencing the position of X in the compounds are discussed.

Les composés thermiquement instables $SiCl_3X.N(CH_3)_3$ et $SiCl_3X.N(CD_3)_3$ où X=H, F, Br, où I ont été étudiés à −190 °C par spectroscopie infrarouge et Raman. Les résultats peuvent être attribués à des composés moléculaires de coordination cinq (5) possédant une stéréochimie bipyramidale trigonale avec le coordinat triméthylamine toujours en position axiale. En utilisant les données vibrationnelles et les analyses en coordonnées normales pour les configurations C_s et C_{3v}, on peut supposer que X est équatorial pour H et F, axial pour Br et I. Les facteurs influençant la position de X dans les composés sont discutés. [Traduit par le journal]

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Introduction

Stereochemical information for the compounds $SiCl_3X.NMe_3$ where X = H, F, Br, or I have not previously been reported although the existence of the hydride and fluoride has been known for some time (1, 2). The compounds are found to be stable at −196 °C, yet completely dissociated into free halide and amine at room temperature. Dissociation pressure measurements have been reported for the series $SiCl_nH_{4-n}.NMe_3$ and $SiCl_nF_{4-n}.NMe_3$ where the results indicated the influence of steric and electronegativity effects on the stability order of the molecules (3, 4). With recent improvements in low temperature infrared and Raman techniques, there has been renewed interest in vibrational and structural studies of unstable co-ordination compounds.

In an attempt to study these complexes, it was assumed that the basic shape at silicon was trigonal bipyramidal, with the trimethylamine ligand lying axially. Vibrational and single crystal Raman spectra and x-ray data (5, 6) for the complexes $MX_4.NMe_3$ (M = Si, Ge, or Sn and X = F or Cl), $MX_3.2NMe_3$ (M = Al, Ga, or In and X = H, Cl, or Br) and $MX_3.NMe_3$ (M = P or As and X = Cl or Br) have been reported and the evidence is overwhelmingly in favor of the amine lying axially. Assuming this, the question is then whether the X atom will reside in the equatorial or axial position for the series $SiCl_3X.NMe_3$. An argument has been put forward (7) that for trigonal bipyramidal molecules, the most electropositive atom will lie in the equatorial plane and hence one would expect to find Cl, F, Cl, and Cl in the axial positions for the series X = H, F, Br, and I. If the trimethylamine ligand were sterically bulky enough to crowd the atoms in the equatorial plane, then one might expect to find Cl, Cl, Br, and I for the same series. A third hypothesis based on molecular orbital theory is put forward in this paper, and leads to the same predictions as the steric argument. By examining the vibrational spectra of the complexes and their perdeutero analogs, it was found that the axial atoms were Cl, Cl, Br, and I for the series X = H, F, Br, and I.

Before going into detail, it is worthwhile to discuss the spectrum of the parent molecule $SiCl_4.NMe_3$ (8, 9), which has been reported to have C_{3v} symmetry with the trimethylamine ligand in the axial position. Its spectrum is very close to that of $GeCl_4.NMe_3$ which has been shown from single crystal Raman (9) and X-ray (10) data to have the above structure. The vibrational spectrum is easily divided into ligand and acceptor modes (9), the former experiencing

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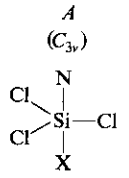
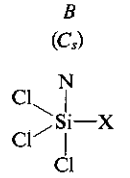
50–80 cm^{-1} shifts upon deuteration of the trimethylamine. The Si—Cl stretching modes are easily discernible because of their much smaller shifts upon deuteration. The asymmetric E mode of the equatorial chlorines is found at 582 cm^{-1} (high frequency), being strong in the infrared and weak in the Raman. The symmetrical A_1 of the equatorial chlorines comes at low frequency, 361 cm^{-1}, and is strong in the Raman. This low frequency (300–380 cm^{-1}) mode is common for light central metal atoms, for example, aluminum, silicon, and phosphorus. The other A_1 mode involves the axial silicon–chlorine stretch. This mode, because it contains motion of the silicon atom (whereas the other A_1 does not), is expected to come at higher frequencies, and indeed is observed at 385 cm^{-1}. It is significant to note that in the vibrational analysis of this complex, the axial stretching force constant was found to have one half the value of the equatorial one. In addition, the crystal structure of $AsCl_3.NMe_3$ (12) (which is based on a trigonal bipyramid with an equatorial lone pair) and $GeCl_4.NMe_3$ (10) shows the axial bond to be significantly longer than the equatorial one. The trimethylamine complex with $SiCl_3X$ can then have two possible stereochemistries



$$\Gamma_{vib}^{\nu SiCl} = A_1 + E$$



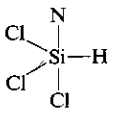
$$\Gamma_{vib}^{\nu SiCl} = 2A' + A$$

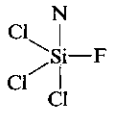
In configuration A, one would expect to find only one strong Raman peak in the Si—Cl stretching region due to the A_1 mode at about 370 cm^{-1}, as with monomeric $AlCl_3$ (11) (371 cm^{-1}). In B, however, there should be an A' mode due to the axial stretch above 380 cm^{-1}, and another A' mode having frequency greater than 400 cm^{-1} (the high frequency caused by both the motion of the silicon atom and the higher equatorial force constant compared to the axial one).

On the basis of the silicon–chlorine symmetric stretches, the stereochemistries were assigned. The perdeutero analogs were prepared to distinguish donor from acceptor modes, and normal coordinate calculations on each possible configuration were carried out.

$SiCl_3H.NMe_3$ and $SiCl_3F.NMe_3$

The spectra, observed and calculated, are tabulated in Tables 1 and 2. Both molecules show no silicon–chlorine stretching frequencies below 400 cm^{-1}, but rather two *high* frequency modes in the Raman. This strongly favors the hydrogen and fluorine atoms occupying the equatorial positions.





νSiCl	588 cm^{-1} A''	νSiCl	580 cm^{-1} A''
	517 cm^{-1} A'		460 cm^{-1} A'
	489 cm^{-1} A'		424 cm^{-1} A'

No serious attempt is made to assign the region under 300 cm^{-1} as the spectrum is far too complex (also indicating C_s symmetry). The low frequency calculated for the silicon–chlorine axial stretch in $SiCl_3H.NMe_3$ is due simply because of the very low force constant. If this force constant was raised to 3/4 of the equatorial, one obtains a frequency in the region observed. The calculations for a C_{3v} configuration are shown in Table 3. The Si—Cl stretching frequency calculated is significantly lower than that observed, and in order to raise this calculated value to even 470 cm^{-1}, a force constant of about double the $SiCl_4$ value must be employed. Clearly this is unacceptable since the $SiCl_4$ force constant should decrease, not increase, upon coordination. The C_{3v} model is also unable to explain the presence of two high frequency SiCl stretching modes; it predicts only one.

$SiCl_3Br.NMe_3$ and $SiCl_3I.NMe_3$

The spectra for these complexes are very different from the previous two (Tables 4 and 5). Both show only one strong band in the *low* frequency silicon–chlorine stretching region at about 370 cm^{-1}, and no acceptor modes between 400–550 cm^{-1}.

Evidence against an ionic formulation $[SiCl_3.NMe_3^+]$ $[X^-]$ for the bromide and iodide adducts stems from three observations: (*i*) the observed νSiBr and νSiI (382 and 332 cm^{-1} respectively) stretching modes are far too high and indicate normal covalently bonded halogen; (*ii*) the a_1 and e νSiCl frequencies for a "pyrami-

TABLE 1. Vibrational spectrum of $SiCl_3H.NMe_3$*

$SiCl_3H.N(CH_3)_3$† Raman (solid at −196 °C)	$SiCl_3H.N(CD_3)_3$† Raman (solid at −196 °C)	Calculated‡ $SiCl_3H.N(CH_3)_3$	Approximate description of mode
588vvw	—	593	A'' $\nu SiCl_{eq}$
517s br	*522mw*	508	A' $\nu SiCl_{eq}$
		545	A' δNMe_3
489ms	*492s*	434	A' $\nu SiCl_{ax}$
435m	434w	430	$A' + A''$ δNMe_3
		425	A' $\delta N(CD_3)_3$
423w sh			A' $\delta N(CD_3)_3$
	378w	396	A'' $\delta N(CD_3)_3$
346mw	331m		
322mw			
305w			
	296mw		
280mw			
	268mw		
252w sh	252mw		
243mw			
226ms	222ms		
	217ms		
213ms			
	192mw		
154w			
	148w		
113m			
	107m		

*Frequencies are reported in units of cm^{-1}.
†Metal–halogen skeletal stretching modes are in italics.
‡Only the Si—Cl stretching and NMe_3 deformation region is shown in the calculations.

TABLE 2. Vibrational spectrum of $SiCl_3F.NMe_3$*

$SiCl_3F.N(CH_3)_3$†		$SiCl_3F.N(CD_3)_3$†	Calculated‡	Approximate
Infrared	Raman	Raman	$SiCl_3F.N(CH_3)_3$	description of mode
857s	*868w*	*869mw*	984	A' νSiF
578vs	*580vw*	*582vw*	648	A'' $\nu SiCl_{eq}$
538m	535mw		581	A' δNMe_3
460vw	*460mw*	*464ms*	469	A' $\nu SiCl_{eq}$
			430	A''
	442w		429	A' $\delta NMe_3 + A'\delta N(CD_3)_3$
	424vs	*430vs*	434	A' $\nu SiCl_{ax}$
390s				
		392mw	396	A' $\delta N(CD_3)_3$
	378w	379w sh		
360s		362vw		
	330mw	302w br		
283w				
	268w			
254w	250mw	255m		
235w	236mw			
	225mw	223ms br		

*Frequencies are reported in units of cm^{-1}.
†Metal–halogen skeletal stretching modes are in italics.
‡Because of C_s symmetry, the region below 400 cm^{-1} is very complex and is therefore not assigned.

TABLE 3. Calculated frequencies for $SiCl_3X.NMe_3$ (X=H and F), C_{3v} symmetry*

$SiCl_3H.NMe_3$			$SiCl_3F.NMe_3$		
H9	Approximate description of mode	*D9*	*H9*	Approximate description of mode	*D9*
612	*E* νSiCl	612	643	*E* νSiCl	643
563	A_1 δNMe_3	532	545	A_1 δNMe_3	515
430	*E* δNMe_3	396	430	*E* δNMe_3	396
376	A_1 νSiCl	376	378	A_1 νSiCl	378
334	A_1 νSiN	328			
			269	A_1 νSiN	263
247	*E* $\rho_r NMe_3$	231	249	*E* $\rho_r NMe_3$	236
			218	*E* δFSiCl	215
161	*E* δSiCl i.p.	160			
			156	*E* δSiCl i.p.	155
135	A_1 δSiCl o.p.	130	134	A_1 δSiCl o.p.	129
84	*E* δNSiCl	82	81	*E* δNSiCl	79

*Frequencies are reported in units of cm^{-1}; i.p. = in plane, o.p. = out of plane.

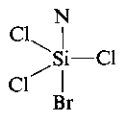
TABLE 4. Vibrational spectrum of $SiCl_3Br.NMe_3$*

$SiCl_3Br.N(CH_3)_3$†		$SiCl_3Br.N(CD_3)_3$†	Calculated for C_{3v} symmetry		
Infrared	Raman	Raman	*H9*	*D9*	Assignment
580vs	*580vw*‡	*576vw*‡	636	635	*E* νSiCl
	570vw‡	*567vw*‡			
537m	539w		572	542	A_1 δNMe_3
	451w	452w	430	396	*E* δNMe_3 + $A_1\delta N(CD_3)_3$
386s	*384w*	*382w*	415	410	A_1 νSiBr§
367s	*369s*	*368s*	372	370	A_1 νSiCl§ + $E\delta N(CD_3)_3$
	342w				
		326w			
300ms	312w				
	293w	290w br			
			248	230	*E* $\rho_r NMe_3$
	228mw	221mw			
	207m	209mw			
	193w	190w			
	179ms	170ms	166	165	*E*
	161w		155	147	A_1
		136w	126	125	*E*
	103m		132	122	A_1
	96m	95m br	70	68	*E*

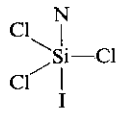
*Frequencies reported in cm^{-1}.
†Metal–halogen skeletal stretching modes are in italics.
‡Split degeneracy in solid.
§Very mixed modes.

dal'' C_{3v} $SiCl_3$ residue in $[SiCl_3.NMe_3^+]$ are calculated to be in the range 500–460 cm^{-1} (*c.f.* ν_1 (507 cm^{-1}) and ν_3 (494 cm^{-1}) of PCl_3) considerably higher than the observed a_1 νSiCl frequency (374–369 cm^{-1}) which is more consistent with a ''planar'' $SiCl_3$ residue in a molecular adduct $SiCl_3X.NMe_3$; (*iii*) point (*ii*) would be further emphasized by the presence of a positive charge on the cation.

On the basis of the experimental data, a molecular pentacoordinate (C_{3v}) formulation is preferred as shown below:



νSiCl 580 cm^{-1} *E*
369 cm^{-1} A_1



νSiCl 605 cm^{-1} *E*
374 cm^{-1} A_1

TABLE 5. Vibrational spectrum of $SiCl_3I.NMe_3$*

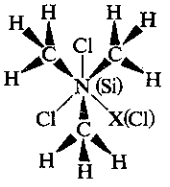
$SiCl_3I.N(CH_3)_3$†		$SiCl_3I.N(CD_3)_3$†	Calculated for C_{3v} symmetry		Approximate description
Infrared	Raman	Raman	*H*9	*D*9	of mode
604s br	*605vvw*	*597w br*	634	634	*E* νSiCl
	544w →	→ 464w br	569	539	A_1 δNMe_3
					A_1 $\delta N(CD_3)_3$
	453w →	→ 393w	430	396	*E* δNMe_3
					E $\delta N(CD_3)_3$
375w	*374s*	*371mw*	365	362	A_1 νSiCl
334s	*329ms*	*332s*	399	396	A_1 νSiCl + νSiI‡
281m	285vvw		247	232	*E* $\rho_r NMe_3$
240w		235vw			
213mw	215ms	217w	164	163	*E*
		197mw			
	168ms	166ms	142	134	A_1
			118	118	*E*
	109w		101	101	A_1
			66	64	*E*

*Frequencies are reported in units of cm^{-1}.
†Metal–halogen skeletal stretching modes are in italics.
‡Very mixed modes.

The calculations (Tables 4 and 5) give a very good match for C_{3v} symmetry, but a poor one for C_s. In the latter geometry, the bands were predicted to come at frequencies greater than 400 cm^{-1} as with the previous complexes, and very low force constants would have to be used to bring the frequencies down to 370 cm^{-1}.

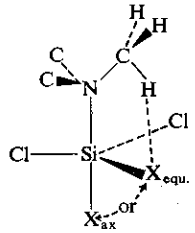
Discussion

Having defined the configurations of the molecules $SiCl_3X.NMe_3$, it is necessary to discuss the various factors which may influence the change in stereochemistry from C_s for X = H or F to C_{3v} for X = Br and I. It has been found that for trigonal bipyramidal trimethylamine complexes (5, 6, 10, 12), the bulky NMe_3 grouping adopts an axial staggered configuration with respect to the rest of the molecule. A staggered



configuration of the ligand would of course present the least amount of steric strain to the molecule.

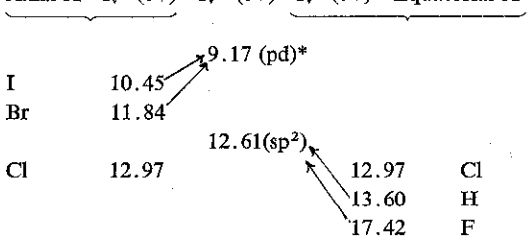
An estimate of the degree of "ligand hydrogen – equatorial halogen" steric interaction (illustrated below) can be determined from a molecular model of $SiCl_3X.NMe_3$, based on a trigonal bipyramidal stereochemistry, having an axial staggered NMe_3 with respect to a coplanar arrangement of equatorial atoms. Placing the atom X = H, F, Cl, Br, or I in either the axial or equatorial sites, assuming tetrahedral angles at N and C and using single bond covalent radii, the maximum distances of H····X closest approach were calculated.



The computed H····X distances were all larger than a H—X single bond distance although the bromide H····Br (2.46 Å) and iodide H····I (2.56 Å) distances were considerably shorter than the corresponding Van der Waal's distances, 3.15 and 3.35 Å respectively.

From simple steric arguments one would tend to favor equatorial H and F atoms but axial Br and I atoms which is in agreement with our experimental observations. It is perhaps interesting to note that intramolecular ligand hydrogen – equatorial fluorine (H····F) hydrogen bonding would also probably favor an equatorial F atom in $SiCl_3F.NMe_3$.

A semi-quantitative molecular orbital approach which can be considered when discussing the configurations of these trigonal bipyramidal molecules involves the energy gain on combining the orbitals of atom X and those of the central silicon atom. The sp^3d hybridized orbitals on the central atom of the trigonal bipyramidal molecule have been considered to be approximately divided into two orbital sets (7); axial linear pd hybrids and equatorial planar sp^2 hybrids. If the greatest energy to be gained by combining two orbitals occurs when the orbitals are evenly matched in energy, it is appropriate to consider as a first approximation the valence state ionization potentials (13) of the combining atom X = H, F, Br, and I and compare them with the values for the pd axial and sp^2 equatorial orbitals on silicon shown in Scheme 1. This



*In this approximation $E(pd) \simeq E(p_z)$.

SCHEME 1

simple scheme predicts that equatorial H and F atoms and an axial I atom are energetically favored in $SiCl_3X.NMe_3$, which agrees with our experimental observation and favors the geometries predicted from simple steric arguments. Although the fate of bromine is not clear cut on this scheme, perhaps the steric effect of Br predominates to favor the axial position.

Normal Coordinate Analysis For $SiCl_3X.NMe_3$ in C_s and C_{3v} Symmetry

The bond lengths used are listed in Table 6; the equatorial bond length is taken as the SiX_4 length while the axial one is taken as being 5% longer, in anticipation of the weakness of the axial bond, and in accordance with the $AsCl_3.NMe_3$ and $GeCl_4.NMe_3$ X-ray data (10, 12). The silicon–nitrogen length is set at 2.01 Å. The methyl groups were treated as point masses. The internal and symmetry coordinates are shown in the appendix.

The force field for the calculations on $SiCl_3X.NMe_3$ was assumed to be roughly the same as the previously published $SiCl_4.NMe_3$. The equatorial stretching force constants were set equal to the parent SiX_4 stretching constants while the axial stretching constants were given half this value. The f_β in the C_{3v} configuration was the average of the $SiCl_4$ and SiX_4 angle bending force constants and varied for each X. The f_α was given the same value as the parent SiX_4 molecule, in this case, $SiCl_4$. The f_γ was set at 3/4 of the f_α. The stretching

TABLE 6. Bond distances used in vibrational analysis

Bond	Distance (Å)
Si—N	2.01
N—Me	1.47
Si—H_{eq}	1.47
Si—H_{ax}	1.54
Si—F_{eq}	1.54
Si—F_{ax}	1.62
Si—Cl_{eq}	2.01
Si—Cl_{ax}	2.11
Si—Br_{eq}	2.28
Si—Br_{ax}	2.40
Si—I_{eq}	2.46
Si—I_{ax}	2.58

TABLE 7. Force constants for $SiCl_3X.NMe_3$ (C_{3v})

	Value for X =			
Force constant*	H	F	Br	I
f_R	2.70	2.70	2.70	2.70
f_D	1.35	3.05	0.98	0.70
f_d	1.20	1.20	1.20	1.20
f_{RR}	0.15	0.15	0.15	0.15
f_{RD}	0.15	0.15	0.15	0.15
f_α	0.489	0.489	0.489	0.489
f_β	0.648	0.665	0.669	0.642
f_γ	0.367	0.367	0.367	0.367
f_l	4.86	4.86	4.86	4.86
f_δ	1.010	1.010	1.010	1.010
$f_{\gamma'}$	0.638	0.638	0.638	0.638
$f_{l\delta}$	0.065	0.065	0.065	0.065

*In units of mdyn/Å, and mdyn/rad or mdyn Å/rad².

TABLE 8. Force constant* changes for $SiCl_3X.NMe_3$ (C_s)

X	f_R	f_r	f_D
H	2.70	1.35	2.70
F	2.70	1.35	6.11
Br	2.70	1.35	1.96
I	2.70	1.35	1.40

*In units of mdyn/Å, mdyn/rad, or mdyn Å/rad².

force constant for the Si–N bond was arbitrarily set at 1.20 mdyn/Å. The actual numbers used in the C_{3v} calculations are shown in Table 7. Only the stretching force constants changed in going to C_s symmetry, and the changes are shown in Table 8. Interaction constants not listed, as well as torsional force constants, were set equal to zero.

Experimental

Trichlorosilane (from Matheson Co.) was purified by trap-to-trap distillation and outgassed at −78 °C prior to use. Trichlorofluorosilane, trichlorobromosilane, and trichloroiodosilane were prepared by standard literature procedures (14–16) and purified by trap to trap distillation prior to use. The infrared and Raman spectra of the starting materials were found to be identical to those in the literature (17–18). Trimethylamine was dried and purified as described previously (19).

Dissociation pressure measurements have been reported for the systems $SiCl_3H/NMe_3$ and $SiCl_3F/NMe_3$ and clearly establish that only 1:1 complexes are capable of formation at low temperatures (1, 2). The $SiCl_3I.NMe_3$ adduct prepared for the first time in this study proved to be the most stable of the series and could be analyzed directly from a vacuum ampoule by hydrolysis followed by conventional argentrometric and p*H* titration techniques.

Anal. Calcd. for $SiCl_3I.NMe_3$: Cl, 33.2; I, 39.6; Me_3N: Si = 1. Found: Cl, 33; I, 38.7; Me_3N: Si = 1.10.

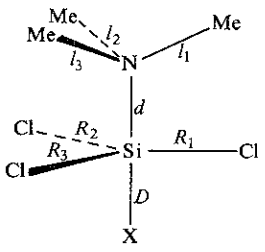
Vibrational spectra were recorded for thin films of the compounds formed by the slow deposition of a gaseous mixture of the appropriate halide with a slight excess of trimethylamine (approximately 1:1) onto the cold tip (−196 °C) of a low temperature infrared or Raman cell.

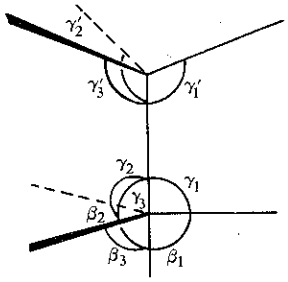
The infrared spectra were recorded on a Beckman IR 11 and Perkin–Elmer 180 and 221 spectrometers. Raman spectra were recorded on a Spex 1401 spectrometer using krypton and argon ion laser excitation.

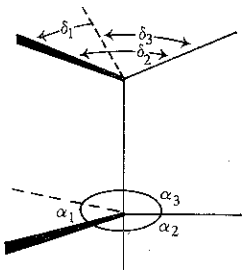
We wish to thank the National Research Council of Canada for financial support and for an NRCC scholarship (D.B.).

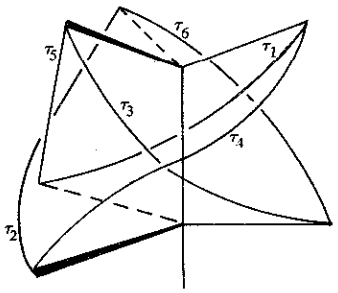
Appendix

C_{3v} Internal Coordinates









C_{3v} Symmetry Coordinates

Type A_1

$$S_1 = (1/\sqrt{3})(\Delta R_1 + \Delta R_2 + \Delta R_3)$$
$$S_2 = \Delta D$$
$$S_3 = \Delta d$$
$$S_4 = (1/\sqrt{3})(\Delta l_1 + \Delta l_2 + \Delta l_3)$$
$$S_5 = (1/\sqrt{3})(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)$$
$$S_6 = (1/\sqrt{3})(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)$$
$$S_7 = (1/\sqrt{3})(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3)$$
$$S_8 = (1/\sqrt{3})(\Delta\gamma_1' + \Delta\gamma_2' + \Delta\gamma_3')$$
$$S_9 = (1/\sqrt{3})(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)$$
$$S_{10} = (1/\sqrt{6})(\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 - \Delta\tau_4 - \Delta\tau_5 - \Delta\tau_6)$$

Type A_2

$$S_{11} = (1/\sqrt{6})(\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4 + \Delta\tau_5 + \Delta\tau_6)$$

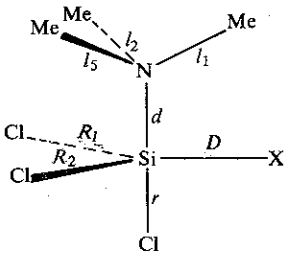
Type E_a

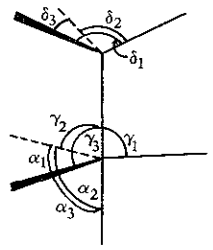
$$S_{12} = (1/\sqrt{6})(2\Delta R_1 - \Delta R_2 - \Delta R_3)$$
$$S_{13} = (1/\sqrt{6})(2\Delta l_1 - \Delta l_2 - \Delta l_3)$$
$$S_{14} = (1/\sqrt{6})(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$$
$$S_{15} = (1/\sqrt{6})(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$
$$S_{16} = (1/\sqrt{6})(2\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3)$$
$$S_{17} = (1/\sqrt{6})(2\Delta\gamma_1' - \Delta\gamma_2' - \Delta\gamma_3')$$
$$S_{18} = (1/\sqrt{6})(2\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3)$$
$$S_{19} = (1/2\sqrt{3})(2\Delta\tau_1 - \Delta\tau_2 - \Delta\tau_3 - 2\Delta\tau_4 + \Delta\tau_5 + \Delta\tau_6)$$
$$S_{20} = (1/2)(\Delta\tau_2 - \Delta\tau_3 - \Delta\tau_5 + \Delta\tau_6)$$

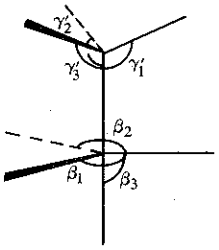
Type E_b

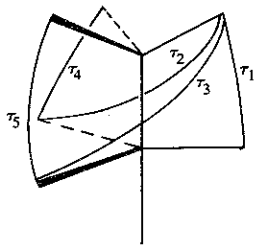
$$S_{21} = (1/\sqrt{2})(\Delta R_2 - \Delta R_3)$$
$$S_{22} = (1/\sqrt{2})(\Delta l_2 - \Delta l_3)$$
$$S_{23} = (1/\sqrt{2})(\Delta\alpha_2 - \Delta\alpha_3)$$
$$S_{24} = (1/\sqrt{2})(\Delta\beta_2 - \Delta\beta_3)$$
$$S_{25} = (1/\sqrt{2})(\Delta\gamma_2 - \Delta\gamma_3)$$
$$S_{26} = (1/\sqrt{2})(\Delta\gamma_2' - \Delta\gamma_3')$$
$$S_{27} = (1/\sqrt{2})(\Delta\delta_2 - \Delta\delta_3)$$
$$S_{28} = (1/2)(\Delta\tau_2 - \Delta\tau_3 + \Delta\tau_5 - \Delta\tau_6)$$
$$S_{29} = (1/2\sqrt{3})(2\Delta\tau_1 - \Delta\tau_2 - \Delta\tau_3 + 2\Delta\tau_4 - \Delta\tau_5 - \Delta\tau_6)$$

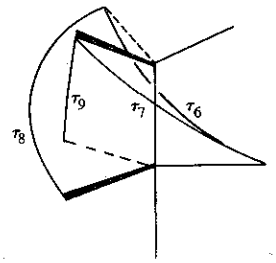
C_s Internal Coordinates











C_s Symmetry Coordinates

Type A'

$$S_1 = \Delta D$$
$$S_2 = (1/\sqrt{2})(\Delta R_1 + \Delta R_2)$$
$$S_3 = \Delta r$$
$$S_4 = \Delta d$$
$$S_5 = \Delta l_1$$
$$S_6 = (1/\sqrt{2})(\Delta l_2 + \Delta l_3)$$
$$S_7 = \Delta\alpha_1$$
$$S_8 = (1/\sqrt{2})(\Delta\alpha_2 + \Delta\alpha_3)$$
$$S_9 = (1/\sqrt{2})(\Delta\beta_1 + \Delta\beta_2)$$
$$S_{10} = \Delta\beta_3$$
$$S_{11} = \Delta\gamma_1$$
$$S_{12} = (1/\sqrt{2})(\Delta\gamma_2 + \Delta\gamma_3)$$
$$S_{13} = \Delta\gamma_1'$$
$$S_{14} = (1/\sqrt{2})(\Delta\gamma_2' + \Delta\gamma_3')$$
$$S_{15} = (1/\sqrt{2})(\Delta\delta_1 + \Delta\delta_3)$$
$$S_{16} = \Delta\delta_3$$
$$S_{17} = (1/\sqrt{2})(\Delta\tau_2 - \Delta\tau_3)$$
$$S_{18} = (1/\sqrt{2})(\Delta\tau_4 - \Delta\tau_5)$$
$$S_{19} = (1/\sqrt{2})(\Delta\tau_6 - \Delta\tau_7)$$
$$S_{20} = (1/\sqrt{2})(\Delta\tau_8 - \Delta\tau_9)$$

Type A''

$$S_{21} = (1/\sqrt{2})(\Delta R_1 - \Delta R_2)$$
$$S_{22} = (1/\sqrt{2})(\Delta l_2 - \Delta l_3)$$
$$S_{23} = (1/\sqrt{2})(\Delta\alpha_2 - \Delta\alpha_3)$$
$$S_{24} = (1/\sqrt{2})(\Delta\beta_1 - \Delta\beta_2)$$
$$S_{25} = (1/\sqrt{2})(\Delta\gamma_2 - \Delta\gamma_3)$$
$$S_{26} = (1/\sqrt{2})(\Delta\gamma_2' - \Delta\gamma_3')$$
$$S_{27} = (1/\sqrt{2})(\Delta\delta_1 - \Delta\delta_2)$$
$$S_{28} = \Delta\tau_1$$
$$S_{29} = (1/\sqrt{2})(\Delta\tau_2 + \Delta\tau_3)$$
$$S_{30} = (1/\sqrt{2})(\Delta\tau_4 + \Delta\tau_5)$$
$$S_{31} = (1/\sqrt{2})(\Delta\tau_6 + \Delta\tau_7)$$
$$S_{32} = (1/\sqrt{2})(\Delta\tau_8 + \Delta\tau_9)$$

1. A. B. BURG. J. Am. Chem. Soc. **76**, 2674 (1954).
2. J. E. FERGUSSON, D. K. GRANT, H. H. HICKFORD, and C. J. WILKINS. J. Chem. Soc. 99 (1959).
3. H. J. CAMPBELL-FERGUSON and E. A. V. EBSWORTH. J. Chem. Soc. (A), 1508 (1966).
4. H. J. CAMPBELL-FERGUSON and E. A. V. EBSWORTH. J. Chem. Soc. (A), 705 (1967).
5. I. B. BEATTIE and G. A. OZIN. J. Chem. Soc. (A), 542 (1969).
6. I. R. BEATTIE and G. A. OZIN. J. Chem. Soc. (A), 2535 (1969).
7. E. L. MUETTERTIES, W. MAHLER, and R. SCHMUTZLER. Inorg. Chem. **2**, 613 (1963).
8. I. R. BEATTIE and G. A. OZIN. J. Chem. Soc. (A), 370 (1970).
9. I. R. BEATTIE and T. R. GILSON. J. Chem. Soc. 6595 (1965).
10. M. S. BITTON and M. WEBSTER. J. Chem. Soc. (A), 722 (1972).
11. I. R. BEATTIE and J. HORDER. J. Chem. Soc. (A), 2655 (1969).
12. M. WEBSTER and S. KEATS. J. Chem. Soc. (A), 836 (1971).
13. J. HINZE and H. H. JAFFÉ. J. Am. Chem. Soc. **84**, 540 (1962).
14. H. H. ANDERSON. J. Am. Chem. Soc. **72**, 2091 (1950).
15. W. C. SCHUMB and H. H. ANDERSON. J. Am. Chem. Soc. **59**, 651 (1937).
16. R. WEST and E. G. ROCHOW. *In* Inorganic syntheses. Vol. 4. *Edited by* J. Bailar. McGraw–Hill, New York. 1953. p. 41.
17. M-L. DELWAULLE. J. Phys. Chem. **56**, 355 (1952).
18. K. HAMADA, G. A. OZIN, and E. A. ROBINSON. Can. J. Chem. **49**, 477 (1971).
19. I. R. BEATTIE and G. A. OZIN. J. Chem. Soc. (A), 2373 (1968).