abilities. In the present case with the hydride present, the cobalt will favor the best π-bonding ligand. It has been suggested by Cotton[17] and Horrocks[18] among others that PF_3 is slightly better at π bonding than CO. This might explain the preference for PF_3. We are attempting to test this idea.

The equilibrium constant data, combined with the rapid reaction rates, clearly demonstrate that $HCo(CO)(PF_3)_3$ should never result as a single product from a reaction involving only cobalt hydrides and the ligand gases CO and PF_3. Calculations show that major concentrations of the other species will also be present in most $CO:PF_3$ mole ratios. Kruck's work[4] in the isolation of $HCo(CO)(PF_3)_3$ must then force one to the conclusion that the hydrogen fluoride impurity either added deliberately or in the form of impure phosphorus trifluoride must play some rather unique role in the formation of the monocarbonyl.

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Vibrational Spectra and Structure of Some Silicon-Containing Compounds. II. Hexachlorodisiloxane

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The Raman spectrum of liquid hexachlorodisiloxane $[(SiCl_3)_2O]$ was recorded with both Toronto arc and He–Ne laser excitation. Quantitative depolarization values were measured for all lines of reasonable intensity. The mid-infrared spectrum was recorded of a contact film and the far-infrared spectrum was recorded to 33 cm^{-1} of solutions in both benzene and cyclohexane. The spectra have been interpreted in detail and it was found that D_{3h} or D_{3d} symmetry selection rules are most satisfactory for spectral interpretation. Such high symmetry is indicative of a very large Si–O–Si angle; however, the spectra clearly indicate that the molecule is not linear. The assignments are tabulated and discussed in detail.

Introduction

The surprisingly large Si–O–Si bond angles reported for disiloxanes and related molecules[2–4] have stimulated particular interest in the vibrational spectra of these molecules.[5–24] The majority of these spectra (Raman and infrared) display a simplicity suggestive of the operation of selection rules of high symmetry. Indeed the vibrational spectra of disiloxane and disiloxane-d_6 have been observed to follow the selection rules of D_{3d} symmetry.[13] The vibrational spectra of hexamethyldisiloxane which have been studied repeatedly[7,12,14,18,20–22,24] furnish another case in point. Scott, *et al.*, have selected frequencies "that appear well established" for this molecule and assigned them to the fundamental modes of vibration according to C_{2v} symmetry; such an assignment scheme requires numerous accidental degeneracies.

In order that a disiloxane derivative have a symmetry higher than C_{2v}, the Si–O–Si bond angle must approach linearity. To explain the wide Si–O–Si bond angles observed, $d\pi$–$p\pi$ interaction between silicon and oxygen atoms has been suggested. Since such interaction might be enhanced by electronegative sub-

[1] Taken from the thesis submitted by K. L. Hellams to the Department of Chemistry in partial fulfillment for the Ph.D. degree; presented at the 23rd Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Sept 4, 1968.

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stituents on the silicon atoms,[25] hexachlorodisiloxane might be expected to exhibit an Si–O–Si angle larger than disiloxane or alkylated disiloxane. This supposition is only feebly supported by electron diffraction experiments because of lack of precision in measurements.[2–4] Yokoi found the angle in hexamethyldisiloxane to be 130 ± 10°. Since the over-all scattering intensity was found to be insensitive to this angle in hexachlorodisiloxane, he assumed the Si–O–Si angle in this compound to be 130°. More precise data on the structure of this molecule are not available.

The Raman spectrum of hexachlorodisiloxane has been published twice[9,23] but with serious discrepancies between the two reports. Lazarev, *et al.*,[9] have reported infrared data above 400 cm^{-1}, but no far-infrared data have been published for this compound. Quite significantly, the present investigation has permitted elimination of several bands (due to impurities) from each of the spectra published by the other workers. Complete spectral data have made possible plausible assignments of all the observed bands.

Experimental Section

The Raman spectrum of hexachlorodisiloxane was recorded on a Cary Model 81 Raman spectrophotometer. Two excitation sources were used—a Toronto arc and a laser accessory. A circulating filter solution composed of 125 ml of *o*-nitrotoluene and 1.75 g of ethyl violet in 2.9 l. of 2-propanol was used to isolate the 4538-Å mercury excitation line produced by the Toronto arc. The He–Ne laser provided a 6328-Å excitation line.

Depolarization measurements of the arc-excitation spectra were determined by using cylindrical Polaroid sheets in the usual manner.[26] Qualitative polarization measurements of the laser-excitation spectrum were obtained in the manner described by Hawes, *et al.*[27] Values of polarization and intensity measurements reported here were obtained from the arc-excitation spectrum.

Far-infrared spectra of solutions of hexachlorodisiloxane first in benzene[28] and then in cyclohexane were obtained by using a Beckman IR-11 spectrophotometer. Each solution was approximately 10 vol % hexachlorodisiloxane. Polyethylene cells of 1-mm path length were used. The spectra were compared with spectra of the appropriate solvents to remove bands due to solvent or cell absorptions. The mid-infrared spectrum was recorded by using a Perkin-Elmer Model 521 spectrophotometer. The sample used was a contact film of the pure liquid between cesium iodide plates. The mid-infrared instrument was calibrated in the high-frequency region in the usual manner.[29] Both infrared spectrophotometers were calibrated in the low-frequency region by using water vapor and data reported by Randall, *et al.*[30] The housing of each instrument was continously flushed with dry air to remove atmospheric water vapor while measurements were being made. With exception of the weak Raman bands at 367 and 484 cm^{-1}, which lie partially underneath strong bands, all frequencies reported are expected to be accurate within 2 cm^{-1}.

The hexachlorodisiloxane was purchased from Pierce Chemical Co. Samples used in this investigation were very carefully purified. First, an aliquot of the compound was distilled under reduced pressure at 80° into a Pyrex ampoule which was sealed while the distillation system was maintained at reduced pressure. This fraction of the distillate was then transferred into another ampoule fitted with a rubber septum; transference was accomplished inside a "glove bag" flushed with dry nitrogen. The septum allowed convenient withdrawal of aliquots for injection into a vapor-phase chromatograph without exposing the sample to moist air. (Hexachlorodisiloxane is extremely labile toward hydrolysis.) A 5-ft column with Se-30 packing was used in the chromatographic purification. The column was operated at 70°. The flow rate of the helium carrier was set at 80 ml/min (at approximately 23° and 750 mm). The 5-ml sample used to obtain the arc-excitation Raman spectrum did not receive chromatographic purification. Rather the sample was distilled at reduced pressure directly into a Pyrex cell and sealed while the distillation system remained at reduced pressure. By comparison with the laser-excitation spectrum of the chromatographically pure sample, bands which arose from impurities were readily discerned in the Raman spectrum obtained by using the arc source. During preparation of samples for recording the infrared and laser-excitation Raman spectra, transferences of the chromatographically pure material were always performed within an atmosphere of dry nitrogen.

Results and Discussion

For convenience of comparison, Table I presents previously published infrared and Raman data from the spectra of hexachlorodisiloxane alongside the results of the present investigation. It is readily apparent that the previously published infrared spectrum bears little resemblance to that of this work. The Raman data are in somewhat better agreement, but

TABLE I

COMPARISON OF THE SPECTRAL DATA OF HEXACHLORODISILOXANE

Raman data						Infrared data		
Ref 23		This work		Ref 9		This work		Ref 9
$\Delta\bar{\nu}$, cm^{-1}	Rel intens	$\Delta\bar{\nu}$, cm^{-1}	Rel intens	$\Delta\bar{\nu}$, cm^{-1}	Rel intens	$\bar{\nu}$, cm^{-1}	Rel intens	$\bar{\nu}$, cm^{-1}
131	7	133	100	130	5	181	m	
143	6	143	32	146	4	222	w	
177	5	179	31	178	4	247	s	
220	6	220	44	217	5	335	s	
245	0					432	mw	
				274	2			465
285	1					474	s	475
333	5	332	12	329	3			610
				353	7	618	s	
		367	1					634
				388	2	686	w	695
412	7					726	w	
424	7	422	61	421	8	935	mw	
475	0					1115	s	1131
		484	1					1170
				589	3	1534	w	
520	00					1831	w	
612	5	612	11	618	3			
		651	2					
675	0							
718	3	715	2	718	2			
		729	4					
				797	0			
817	0							
862	0							
				1104	1			

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(25) A. N. Lazarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 235 (1964); *Bull. Acad. Sci. USSR, Chem. Ser.*, 218 (1964).

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(27) R. C. Hawes, K. P. George, D. C. Nelson, and R. Beckwith, *Anal. Chem.*, **38**, 1846 (1966).

(28) The benzene solution was yellow, possibly indicating formation of a π complex; however, with the exception of the presence of a possible weak band at 303 cm^{-1} in the spectrum of the benzene solution, the two solutions yielded identical spectra.

(29) IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth Inc., Washington, D. C., 1961.

(30) H. H. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937).

each spectrum exhibits several bands unique among the data collated.

Bands observed *only* in this investigation are centered at 367, 484, 651, and 729 cm^{-1}. It is readily apparent that the first three of these bands might not be observed in a study of the photographic Raman spectrum since they are broad and lie partially underneath other bands as can be seen in Figure 1. One band unique to this set of Raman data remains; it is the more intense member of the doublet near 720 cm^{-1}. It seems quite reasonable that this doublet, made up of a pair of broad and weak bands, might not have been resolved previously. This suggestion is consistent with the fact that each of the earlier reports lists a single band at 718 cm^{-1} which is between the positions of the pair constituting the doublet reported here.

Significantly, regarding those bands previously tabulated but not observed in this work, the earlier reports are not mutually supporting. Of this group of bands, none was observed in both investigations. Furthermore, the sample used in the present investigation after distillation without further purification showed moderately intense Raman bands at 355 and 387 cm^{-1}; that these bands arose from impurities is indicated by their disappearance upon purification of the sample by vapor-phase chromatography. Nevertheless, one of the previous reports indicated bands at 353 and 388 cm^{-1}. In addition, exposure of the chromatographically pure sample to moist air was observed to produce a shoulder on the high-frequency side of the infrared band at 474 cm^{-1} as well as a band at 634 cm^{-1}.

Figures 2 and 3 show the mid-infrared and the far-infrared spectra of hexachlorodisiloxane, respectively. All spectral measurements are listed in Table II where the assignments of the vibrational modes to all bands observed are indicated.

The bands at 651, 715, and 729 cm^{-1} in the Raman spectrum are apparently overtones and combination bands since no fundamentals are to be expected in this region; the bands at 367 and 484 cm^{-1} are very weak and are also taken to be a combination band and an overtone, respectively. Previous characterization of the vibrational spectra of the $SiCl_3$ group[31] provides a very helpful basis for beginning the assignment of fundamental vibrations of hexachlorodisiloxane. For convenient reference in the course of subsequent discussion, this characterization is summarized in Table III.

The spectra of hexachlorodisiloxane are too simple to permit satisfactory assignments according to the selection rules of C_{2v} symmetry which allow all 21 fundamentals to be active in the Raman effect and 16 of them to appear in the infrared spectrum. The observed Raman spectrum shows only seven lines that can plausibly be assigned to fundamental vibrations. Similarly, the infrared spectrum shows only seven bands. More satisfactory assignment schemes can be constructed according to the selection rules of D_{3d} symmetry or those of D_{3h} symmetry. In each case, two violations of selection rules result and the violations in each case can be dismissed with equal facility; the violations are of the same nature and involve the same bands. The selection rules of D_{3d} symmetry and those of D_{3h} symmetry are very similar. The only differences involve the degenerate species. According to D_{3d} symmetry, in-phase degenerate motions (E_g species)

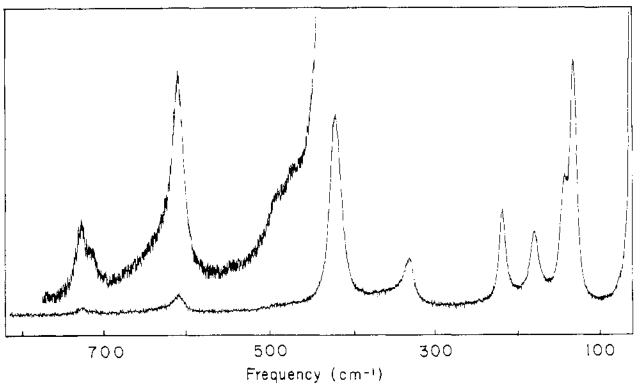

Figure 1.—Raman spectrum of hexachlorodisiloxane, laser excitation.

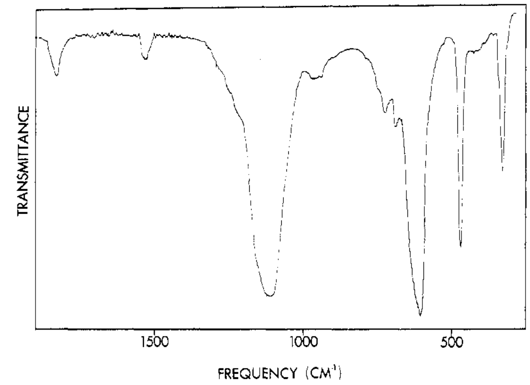

Figure 2.—Mid-infrared spectrum of hexachlorodisiloxane.

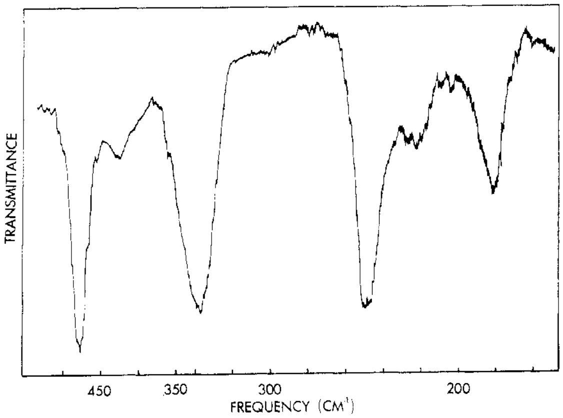

Figure 3.—Far-infrared spectrum of hexachlorodisiloxane.

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TABLE II

VIBRATIONAL DATA OF HEXACHLORODISILOXANE[a]

Raman			Infrared					
			Soln		Neat			
$\Delta\bar{\nu}$, cm^{-1}	Rel intens	Dep ratio	$\bar{\nu}$, cm^{-1}	Rel intens	$\bar{\nu}$, cm^{-1}	Rel intens	Symmetry species	Assignments
133	100	dp					E′	ν_{10}
143	32	dp					E″	ν_{14}
179	31	dp					E′	ν_3
			181	m			A_2''	ν_7
220	44	dp	222	w			E″	ν_{13}
			247	s			E′	ν_9
332	12	0.25	335	s	332	ms	A_1'	ν_2
367	1	?					$E' + A_1' + A_2'$	(143 + 220 = 363)
422	61	0.13					A_1'	ν_1
			432	mw	430	mw	$E' + A_1'$	(2 × 220 = 440)
							$E' + A_1' + A_2'$	(179 + 247 = 426)
			474	s	472	s	A_2''	ν_6
484	1	?					$E' + A_1'$	(2 × 247 = 494)
612	11	dp					E″	ν_{12}
					618	s	E′	ν_8
							A_1'	(181 + 472 = 653)
651	2	?					E″	(179 + 472 = 651)
							A_1'	(2 × 332 = 664)
					686	w	$E' + A_1'$	(2 × 133 + 422 = 688)
715	2	?					E″	(247 + 472 = 719)
729	4	p?			726	w	$E' + A_1' + A_2'$	(133 + 179 + 422 = 734)
					935	mw	E′	(332 + 618 = 950)
					1115	s	A_2''	ν_5
					1534	w	A_2''	(1115 + 422 = 1536)
					1831	w	E′	(247 + 472 + 1115 = 1832)

[a] Abbreviations used: m, medium; s, strong; w, weak; dep, depolarization; rel intens, relative intensity; dp and p are depolarized and polarized, respectively.

TABLE III

CHARACTERISTIC FREQUENCY RANGES OF THE NORMAL MODES OF THE $SiCl_3$ GROUP AS DETERMINED FROM A STUDY OF A SERIES OF ORGANOTRICHLOROSILANES[31]

Descriptions of vib	Freq ranges, cm^{-1}
Rock	86–166
Sym def	176–204
Asym def	208–226
Sym str	450–486
Asym str	510–613

TABLE IV

SUMMARY OF ACTIVITIES PREDICTED AND OBSERVED FOR THE FUNDAMENTAL VIBRATIONS OF HEXACHLORODISILOXANE

	Band description				
	Raman				
Symmetry	dp	p	Ir	Coincident	Total bands
C_{2v}	15	6	16	16	21
D_{3h}	7	3	7	4	17
D_{3d}	3	3	7	0	13
Obsd	5	2	7	3	14

are Raman active only and similar out-of-phase motions (E_u species) are infrared active only. If the symmetry is D_{3h}, in-phase degenerate vibrations (E′ species) are both Raman and infrared active whereas out-of-phase motions (E″ species) are Raman active only. Table IV summarizes the activity of fundamentals expected in case of C_{2v}, D_{3d}, and D_{3h} symmetries as well as the activity actually observed.

The most plausible scheme according to D_{3d} symmetry possesses one disadvantage not imposed by D_{3h} symmetry: either (1) an intense Raman band must be assigned to a $SiCl_3$ rocking mode which should be infrared active only or else (2) the degeneracy of one of the rocking modes must be assumed to be removed by interaction with a skeletal mode in which case the remaining rocking mode must presumably be unobserved. Consequently, assignments of spectral bands to vibrational modes will be discussed in terms of D_{3h} symmetry, but all differences, which would arise were assignments made according to D_{3d} symmetry, will be explicitly but parenthetically indicated. Descriptions of the fundamental modes and D_{3h} selection rules are stated in Table V.

Of the three skeletal vibrations, the two Si–O–Si stretching modes and the Si–O–Si bending mode, only the symmetric Si–O–Si stretching mode can be reasonably expected to lie within the frequency range (86–613 cm^{-1}) of the data of Table III. The Si–O–Si antisymmetric stretching modes of substituted disiloxanes have been found to exhibit relative constancy from one compound to the next.[5] For example, bands arising from this mode of vibration appear at 1107 cm^{-1} in

TABLE V

SYMMETRY SPECIES, SELECTION RULES, AND FREQUENCY ASSIGNMENTS OF FUNDAMENTALS OF HEXACHLORODISILOXANE (D_{3h} SYMMETRY)

Species	No.	Vibration, schematic description	Selection rules		Assignment	
			Raman	Ir	Raman	Ir
A_1'	1	$SiCl_3$ sym str (in phase)	Polarized	Forbidden	422	
	2	Si–O–Si sym str			332	332
	3	$SiCl_3$ sym def (in phase)			179	
A_1''	4	$SiCl_3$ torsion	Forbidden	Forbidden		
A_2'	...	(No vibration belongs to A_2' species)	Forbidden	Forbidden		
A_2''	5	Si–O–Si antisym str	Forbidden	Active		1115
	6	$SiCl_3$ sym str (out of phase)				474
	7	$SiCl_3$ sym def (out of phase)				181
E'	8	$SiCl_3$ degenerate str (in phase)	Depolarized	Active	...	618
	9	$SiCl_3$ degenerate def (in phase)			...	247
	10	$SiCl_3$ rock (in phase)			133	...
	11	Si–O–Si bend			...	...
E''	12	$SiCl_3$ degenerate str (out of phase)	Depolarized	Forbidden	612	
	13	$SiCl_3$ degenerate def (out of phase)			220	222
	14	$SiCl_3$ rock (out of phase)			143	

the spectrum of disiloxane,[13] at 1060 cm^{-1} in that of hexamethyldisiloxane,[7] and at 1075 cm^{-1} in that of hexaphenyldisiloxane.[11] The only band appearing in the spectrum of hexachlorodisiloxane within this wave number region is the strong infrared band at 1115 cm^{-1}. Therefore, this band is confidently assigned to the antisymmetric Si–O–Si stretching mode. The Si–O–Si bending mode is expected to lie at a very low frequency,[32] considerably below the lowest band in the observed spectrum.

A correlation between the observed frequencies of the symmetric Si–O–Si stretching mode and the square root of the mass of the SiX_3 group in disiloxane and substituted disiloxanes[5] suggests that this mode should occur at about 475 cm^{-1} in the spectrum of hexachlorodisiloxane. This consideration immediately poses the infrared band at 474 cm^{-1} to be assigned to the Si–O–Si symmetric stretching mode. However, this mode is expected to give rise to a relatively intense line in the Raman effect and the band at 474 cm^{-1} is not accompanied by a Raman band at all. Moreover, the infrared band at 474 cm^{-1} is more satisfactorily assigned to a $SiCl_3$ stretching mode. The moderately weak band at 430 cm^{-1} is an even less likely candidate; in fact, it is most likely a combination or overtone band, as is the Raman band at 484 cm^{-1}. Thus, the suggestion that the symmetric Si–O–Si stretching mode lies among the $SiCl_3$ stretching motions appears to be inconsistent with our data.

The $SiCl_3$ stretching modes are well characterized and readily assigned. The data of Table III indicate that they should lie close to the range 450–613 cm^{-1}. The most prominent band in the Raman spectra of organotrichlorosilanes has been observed[31] to arise from the $SiCl_3$ symmetric stretching mode; this band is always strong and highly polarized and occurs within the 450–486-cm^{-1} wave number range. Such a band appears in the Raman spectrum of hexachlorodisiloxane at a slightly lower wave number. The lower frequency can plausibly be attributed to interaction between vibrations of the two $SiCl_3$ groups and/or coupling with the Si–O–Si stretching mode, and the band at 422 cm^{-1} is, therefore, assigned to the $SiCl_3$ symmetric in-phase stretching mode. According to the selection rules of D_{3h} (and D_{3d}) symmetry the corresponding out-of-phase mode is infrared active but silent in the Raman effect. The infrared band at 474 cm^{-1} is accordingly assigned to the $SiCl_3$ symmetric out-of-phase stretching mode. Thus, this mode lies well within the expected frequency range. This assignment places the frequency of the out-of-phase $SiCl_3$ symmetric stretching mode 52 cm^{-1} above the corresponding in-phase mode. Such a large separation is to be expected if the symmetric stretching modes of the $SiCl_3$ groups are strongly coupled with each other or with the Si–O–Si stretching modes. Otherwise, the in-phase and the out-of-phase modes should lie very close together.

The degenerate stretching modes are expected to lie at still higher wave numbers (*cf.* Table III); the infrared band at 618 cm^{-1} is assigned to the $SiCl_3$ degenerate in-phase stretching mode, the Raman counterpart being unobserved. A second band arising from $SiCl_3$ degenerate stretching is expected. Within the frequency range of such vibrations as indicated by Table III are the Raman bands at 484 and 612 cm^{-1}. The former is very weak and is discounted as a fundamental. The band at 612 cm^{-1} is assigned to the $SiCl_3$ degenerate out-of-phase stretching mode. (Assignments according to D_{3d} selection rules would require reversing these two assignments.)

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(32) D. W. Robinson, W. J. Lafferty, J. R. Aronson, J. R. Durig, and R. C. Lord, *J. Chem. Phys.*, **35**, 2245 (1961).

The remaining modes arising from the $SiCl_3$ groups lie at low frequencies and are assigned with reference to the data of Table III. The lowest two bands at 133 and 143 cm^{-1} in the Raman spectrum are assigned to rocking modes of the $SiCl_3$ groups. The mode of lower frequency is described as in-phase $SiCl_3$ rocking motion, and the mode of higher frequency, as out-of-phase $SiCl_3$ rocking motion. (The selection rules of D_{3d} symmetry require the in-phase mode to be only Raman active and the out-of-phase motion to be only infrared active. Neither of the two Raman bands is accompanied by an infrared band. To reconcile these facts with D_{3d} selection rules, it may be supposed that both bands arise from in-phase motions, this mode not being truly degenerate because the molecular skeleton is slightly bent. The out-of-phase rocking mode would be considered as unobserved.)

Previous data (*cf.* Table III) indicate that the deformational modes of the $SiCl_3$ group typically fall within the range 176–226 cm^{-1}. Accordingly, the Raman and infrared bands falling within this frequency range are assigned to $SiCl_3$ deformational modes as is the infrared band at 247 cm^{-1}. In view of the different environment of the $SiCl_3$ groups in hexachlorodisiloxane as compared with organotrichlorosilanes, it is not objectionable to include this band among the deformational modes even though it lies slightly above the highest deformational modes observed for organotrichlorosilanes. The selection rules require both the symmetric in-phase and the degenerate out-of-phase deformational modes to be Raman active only, whereas the symmetric out-of-phase deformational mode is required to be infrared active only. The degenerate in-phase deformational mode is active in both the Raman and the infrared spectra. The totally symmetric mode is expected to have the lowest frequency; therefore, the Raman line at 179 cm^{-1} is assigned to the symmetric in-phase deformational mode. This line is observed to be depolarized, but totally symmetric deformational modes are often observed to give rise to depolarized Raman bands. Since the corresponding out-of-phase mode is expected to give rise to an infrared band of similar frequency, the band at 181 cm^{-1} is assigned to the symmetric out-of-phase deformational mode.

Within the frequency range of the deformational modes, only one Raman line and two infrared bands remain to be assigned and both the remaining deformational modes are Raman active but only the degenerate in-phase motion is infrared active. Consequently, the strong infrared band at 247 cm^{-1} is assigned to this mode. The Raman counterpart is unobserved. The Raman band at 220 cm^{-1} is assigned to the corresponding out-of-phase mode; this band is coincident with a weak infrared band at 222 cm^{-1} in violation of D_{3h} (and D_{3d}) selection rules. (The selection rules of D_{3d} symmetry require only that the assignments of the two degenerate deformational modes be reversed. Such a scheme, like the D_{3h} assignment scheme, results in a violation of selection rules since the degenerate in-phase deformational mode should be only Raman active.)

Now only one Raman band below 484 cm^{-1} remains to be considered, and two fundamental modes of hexachlorodisiloxane have not been assigned. Of these modes, the Si–O–Si bending mode has been discounted as being either too weak or too low in frequency to be observed. As a result, the remaining mode, the Si–O–Si symmetric stretching mode, appears to give rise to the Raman band at 332 cm^{-1} which is coincident with a moderately strong to strong infrared band. Coincidence of infrared and Raman bands constitutes a violation of D_{3h} selection rules. (A similar violation would result under D_{3d} selection rules.) However, slight deviation of the Si–O–Si angle from 180° would permit infrared activity. Furthermore, the Raman band should be highly polarized as is the band at 332 cm^{-1}. Therefore, the most important objection to this assignment is that the frequency might be too low. But as was suggested in the discussion of the $SiCl_3$ symmetric stretching modes, there may exist coupling between these motions and the Si–O–Si stretching mode. In view of this argument, the Si–O–Si symmetric stretching might occur at a lower frequency than Gillespie's collation[5] would suggest.

Moreover, calculation of the Si–O force constant on the basis of the observed band at 1115 cm^{-1} which is attributed to the Si–O–Si antisymmetric stretching mode indicates a low frequency for the symmetric stretching mode. If anharmonicity of the ground state of the Si–O–Si antisymmetric stretching vibration is neglected and the $SiCl_3$ groups are considered as infinite point masses located in line with the oxygen atom, calculation yields 5.87×10^{-5} dyn/cm for the Si–O stretching force constant. This value leads to a calculated frequency of 381 cm^{-1} for the symmetric Si–O–Si stretching vibration. If this calculation is considered to give a rough estimate of the frequency, it is not at all surprising that this normal mode lies as low as 332 cm^{-1} in view of the possibility of coupling of this motion with other symmetric stretching modes.

With the notable exceptions of the Raman band at 651 cm^{-1} for which three equally good assignments are indicated in Table II and the infrared band at 430 cm^{-1} for which two acceptable assignments are presented, assignments to overtones and combination bands prove rather straightforward; in each case the second-choice assignment for combinations is at least 9 cm^{-1} removed from the observed band to be assigned; the first-choice binary combinations are always within 4 cm^{-1} of the bands to receive the assignments excepting the infrared band at 935 cm^{-1}. The situation as regards assignments of overtones is similar. In all cases bands to be assigned fall either at least 25 cm^{-1} below twice the frequencies of the fundamentals or else at least 10 cm^{-1} *above* twice the frequencies of all fundamentals other than those actually considered to give rise to the overtones. The choice of triple combinations is equally clear-cut.

Summary

The vibrational spectra of hexachlorodisiloxane have been described in terms of D_{3h} symmetry. Since the experimental data do not discriminate between D_{3h} and D_{3d} symmetry, differences that would arise if the description were according to D_{3d} symmetry have been explicitly indicated. The data have been interpreted to indicate that the molecular skeleton is quasilinear and that the symmetric $SiCl_3$ stretching modes are coupled with the Si–O–Si stretching motion.

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The Structure of μ-Oxo-μ-chloro-di-μ-propionato-bis(chlorotriphenylphosphinerhenium). A New Metal–Metal Bond[1a]

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The crystal and molecular structures of one of the substances reported by Rouschias and Wilkinson to have the general formula $Re_2Cl_3(O_2CR)_2[P(C_6H_5)_3]_2$, namely, the one with R = C_2H_5, have been determined in an X-ray crystallographic study. It was found that the formula as previously given is incorrect, lacking one oxygen atom. The $Re_2OCl_3(O_2CC_2H_5)_2[P(C_6H_5)_3]_2$ molecule consists of two structurally equivalent Re atoms each surrounded by six ligand atoms at the vertices of a slightly distorted octahedron. The octahedra are joined on a common edge formed by bridging O and Cl atoms. The other two Cl atoms occupy positions *trans* to the bridging O atom, and the P atoms occupy positions *trans* to the bridging Cl atom. The pairs of vertices above and below the plane defined by these six ligand atoms and the two Re atoms are occupied by bridging bidentate C_2H_5COO groups. The symmetry of the two Re atoms and the ten atoms coordinated to them is C_{2v} neglecting small packing distortions. The Re–Re distance is 2.514 (1) Å. The entire structure is nearly identical with that of $Re_2OCl_5(O_2CC_2H_5)[P(C_6H_5)_3]_2$ except for the replacement of two Cl atoms by a propionato group. The crystals studied belong to space group $P2_1/c$ with dimensions $a = 14.059 \pm 0.003$ Å, $b = 17.477 \pm 0.003$ Å, $c = 17.556 \pm 0.003$ Å, and $\beta = 97.80 \pm 0.01°$. The observed and calculated densities were 1.81 ± 0.01 and 1.82 g cm^{-3} (for $Z = 4$), respectively. The structure was solved and refined using 2125 statistically significant independent reflections. Refinement was by a full-matrix, least-squares program in which the phenyl groups were treated as rigid bodies with separate isotropic temperature parameters for each carbon atom; anisotropic temperature parameters were used for Re, Cl, and P atoms. Final weighted and unweighted discrepancy indexes were 0.034 and 0.031, respectively. Mean values of bond lengths to rhenium atoms are (Å): Re–Cl(terminal), 2.360 (3); Re–Cl(bridge), 2.403 (3); Re–P, 2.455 (3); Re–O(carboxyl), 2.108 (5); Re–O(bridge), 1.916 (6).

Introduction

Dinuclear and trinuclear complexes of rhenium in oxidation state III have been well characterized.[2] Further, compounds containing rhenium in mean oxidation states between II and III appear to involve strong metal–metal interactions (Re–Re ≈ 2.29 Å).[3,4] Compounds containing rhenium in oxidation states near IV fall into two groups: (1) $La_4Re_6O_{19}$ (mean oxidation state $+4^1/_3$, Re–Re = 2.42 Å)[5] and $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ (Re–Re = 2.52 Å);[2,6] and (2) $ReCl_4$ (Re–Re = 2.73 Å)[7] and $Re_2Cl_9^-$ (Re–Re = 2.71 Å).[8] In $Re^V{}_2Cl_{10}$, a dinuclear species, the metal–metal distance is quite long (3.74 Å),[9] consistent with the suggestion[2] that the border line, in terms of oxidation state, between pronounced and negligible tendency to metal–metal bond formation occurs around oxidation number IV for rhenium.

As part of our continuing study of polynuclear

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