

Table 5. *Bond lengths and angles*

Standard deviations are given in parentheses.

Mn-Br tetrahedron					
Mn ⁱ	Br(1 ⁱ)	2.460 (27) Å	Br(1 ⁱ)-Mn ⁱ -Br(2 ⁱ)	116.7 (1.0)°	
	Br(2 ⁱ)	2.448 (36)	Br(1 ⁱ)-Mn ⁱ -Br(3 ^{i,iii})	109.9 (9)	
	Br(3 ^{i,iii})	2.444 (19)	Br(2 ⁱ)-Mn ⁱ -Br(3 ^{i,iii})	106.2 (9)	
Br(1 ⁱ)	Br(2 ⁱ)	4.178 (30)	Br(3 ⁱ)-Mn ⁱ -Br(3 ⁱⁱⁱ)	107.5 (8)	
	Br(3 ^{i,iii})	4.015 (20)			
Br(2 ⁱ)	Br(3 ^{i,iii})	3.913 (28)			
Br(3 ⁱ)	Br(3 ⁱⁱⁱ)	3.940 (18)			
Cs(1)-Br distances			Cs(2)-Br distances		
Cs(1 ⁱⁱ)	Br(1 ⁱⁱ)	4.472 (29) Å	Cs(2 ^x)	Br(1 ^{v,vii})	4.070 (8) Å
	Br(1 ^{ix})	3.618 (21)		Br(1 ^x)	3.685 (29)
	Br(2 ⁱ)	4.113 (25)		Br(2 ⁱ)	3.619 (27)
	Br(2 ^{vi,viii})	3.941 (3)		Br(2 ^x)	3.596 (21)
	Br(3 ^{i,iii})	3.792 (15)		Br(3 ^{v,vii})	3.635 (13)
	Br(3 ^{ii,iv})	4.363 (20)		Br(3 ^{vi,viii})	3.624 (17)
	Br(3 ^{vi,viii})	4.002 (20)			

i	x	y	z
ii	$\frac{1}{2} + x$	y	$\frac{1}{2} - z$
iii	x	$\frac{1}{2} - y$	z
iv	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$\frac{1}{2} - z$
v	$\frac{1}{2} - x$	1 - y	$\frac{1}{2} + z$
vi	1 - x	1 - y	1 - z
vii	$\frac{1}{2} - x$	$-\frac{1}{2} + y$	$\frac{1}{2} + z$
viii	1 - x	$-\frac{1}{2} + y$	1 - z
ix	1 + x	y	z
x	$\frac{1}{2} + x$	y	$\frac{3}{2} - z$

tion, with those observed for the zincate. The latter distance almost equals the sum of the ionic radii (3.63 Å) given by Clark (1955). The angular distortion of the tetrahedral unit, which occurs in the two structures, has been adequately explained by Morosin & Lingafelter.

Finally, it is interesting to note that Pauling's second rule is not quite obeyed in this structure; the sum of the bond strengths to Br(1), Br(2) and Br(3) are 201/198, 197/198 and 197/198, respectively.

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The Crystal and Molecular Structure of Dodecachloropentasilane Silicon Tetrachloride

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The structure of dodecachloropentasilane silicon tetrachloride, Si₅Cl₁₂·SiCl₄, has been determined and refined by three-dimensional least-squares methods, using 67 reflexions, to an *R* index of 0.044. The substance crystallizes in the cubic space group *F* $\bar{4}3c$, with *a* = 17.344 Å. The two types of molecule, Si₅Cl₁₂ and SiCl₄, are simply stacked together with intermolecular distances corresponding to van der Waals type interactions.

Introduction

The perchloropolysilanes, Si_{*n*}Cl_{2*n*+2}, could be described as the chlorosilicon analogues of the alkanes, C_{*n*}H_{2*n*+2}. But whereas C-C linkages are very common, Si-Si linkages are somewhat rare, Si-O bonds being much preferred when possible.

Some of the higher perchloropolysilanes form 1:1 adducts with silicon tetrachloride (Urry, 1964) which are crystalline and suitable for study by X-ray methods. For example, dodecachloropentasilane silicon tetrachloride was prepared. It was of interest to see which isomer of the dodecachloropentasilane was formed: *n*-pentyl, isopentyl or neopentyl:

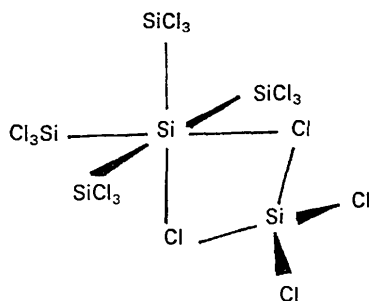
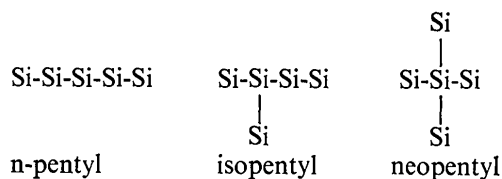
Fig. 1. A suggested structure for $\text{Si}_5\text{Cl}_{12} \cdot \text{SiCl}_4$.

Table 1. Observed and calculated structure amplitudes with calculated phase angles

h	k	l	$ F_o $	$ F_c $	α°	h	k	l	$ F_o $	$ F_c $	α°
2	0	0	203	186	180	10	6	4	121	117	34.2
2	2	0	315	311	0	10	8	2	95	96	92
4	0	0	229	220	180	10	8	4	209	115	273
4	2	0	322	309	0	10	8	6	103	94	4.7
4	4	0	152	144	180	10	10	4	83	65	12
6	0	0	44.1	44.4	180	11	3	1	108	91	283
6	2	2	128	120	210	11	5	1	75	78	50
6	4	0	95	95	0	11	7	1	117	131	176
6	4	2	164	171	27	11	7	5	114	110	12
6	6	0	44.5	465	0	12	0	0	359	340	0
6	6	2	140	146	106	12	2	0	133	135	180
7	3	1	142	138	335	12	2	2	206	211	12
7	5	1	117	116	174	12	4	4	141	142	283
7	5	3	195	196	313	12	6	0	160	162	180
8	2	2	170	163	150	12	6	4	64	57	292
8	4	0	134	134	0	12	6	6	62	53	355
8	4	2	140	141	94	12	8	4	121	118	29
8	4	4	211	230	324	12	8	6	128	119	153
8	6	0	222	230	180	12	8	8	171	167	352
8	6	2	339	356	34.5	12	10	6	84	95	26
8	8	0	217	230	0	12	12	6	127	116	356
8	8	2	183	185	309	13	3	1	131	131	112
8	8	4	83	79	105	13	5	3	93	91	220
9	3	1	252	265	259	13	7	3	85	71	77
9	5	1	174	174	95	14	2	0	119	102	0
9	5	3	158	152	100	14	2	2	136	144	251
9	7	1	109	114	34.9	14	4	2	98	94	8
9	7	3	150	153	24.8	14	4	4	131	134	215
9	7	5	119	118	132	14	6	0	101	107	180
10	0	0	208	203	180	14	6	4	112	116	28
10	4	0	58	51	0	14	6	6	72	79	14.5
10	4	2	293	300	294	14	8	6	128	121	332
10	4	4	185	188	115	14	10	4	70	50	34.3
10	6	0	175	183	0						

Table 2. Fractional atomic coordinates and thermal parameters

Values (except those marked with an asterisk) are multiplied by 10^5 .The temperature factor is of the form $\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	0	0	0	304 (38)	304 (38)	304 (38)	0	0	0
Si(2)	17237 (27)	17237 (27)	17237 (27)	281 (18)	281 (18)	281 (18)	-48 (21)	-48 (21)	-48 (21)
Si(3)	$\frac{1}{4}$ *	$\frac{1}{4}$ *	$\frac{1}{4}$ *	173 (30)	173 (30)	173 (30)	0	0	0
Cl(1)	-6509 (38)	-6509 (38)	-6509 (38)	984 (50)	984 (50)	984 (50)	-362 (40)	-362 (40)	-362 (40)
Cl(2)	23228 (28)	13447 (34)	8188 (35)	523 (34)	498 (28)	368 (27)	65 (28)	100 (26)	111 (28)

Further interest was generated in the adduct crystal by the suggestion (Nuss & Urry, 1964) that the two molecules were linked by chlorine bridges, giving a silicon atom with octahedral coordination, as in Fig. 1.

Preliminary X-ray work

The product from an $\text{Si}_5\text{Cl}_{12}$ preparation turned out to be microcrystalline (*cf.* Kaczmarczyk, Millard, Nuss & Urry 1964), and a powder photograph was all that could be attempted. The product from a preparation for giving $\text{Si}_6\text{Cl}_{14} \cdot \text{SiCl}_4$ turned out to be clear cube-shaped crystals (*cf.* Kaczmarczyk, Nuss & Urry 1964). These readily lost silicon tetrachloride to give a microcrystalline product which was also examined by powder photography. This photograph matched the previous one both in line spacings and in intensities. The Raman spectra of the two samples were also identical (Cradock & Bentham, unpublished). Clearly the two powders were the same and therefore at least one of the products was not what had been expected. Addition of silicon tetrachloride to the microcrystalline powder again produced the cube-shaped crystals.

Under an oscillation photograph and a zero-layer Weissenberg photograph the adduct crystal was found to have a cubic unit cell, $a = 17.344(25)$ Å, which was face-centred. This meant that the compound was the neopentyl isomer of dodecachloropentasilane, for it is the only possibility that can be accommodated within the symmetry requirements. Reflexions for which h , k and l were either not all even or not all odd were seen to be absent. Also, no reflexions of odd indices were observed with any two or all three indices equal. These absences correspond to space group $F\bar{4}3c$ which has the general conditions for reflexion:

$$hkl: h+k, k+l, l+h=2n$$

$$hhl: l, h=2n.$$

Because of their instability and reactivity towards air the crystals were handled under dry nitrogen and in sealed glass capillary tubes for photographing.

Crystal data

$\text{Si}_5\text{Cl}_{16}$, M.W. 735.8. Cubic, $a = 17.344$ Å,

$$V = 5217.3 \text{ \AA}^3, Z = 8.$$

$D_c = 1.87$, $F(000) = 2848$, $F\bar{4}3c$, Mo $K\alpha$ radiation, $\mu = 19.2 \text{ cm}^{-1}$.

Intensity data and structure refinement

Because of the difficulties experienced in trying to obtain upper-layer Weissenberg photographs, and indeed of getting photographs at all, it was decided to use oscillation photographs which had originally only been intended for preliminary work. These were indexed, and as many intensities as possible were carefully measured visually by comparison with an intensity strip. The measured intensities were L_p corrected and a weighted mean $|F_o|$ for each unique index set was calculated. Zirconium-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was used and no corrections were made for absorption.

A successful trial structure refined isotropically to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0810$ with 67 reflexions and 11 variable parameters, using a full-matrix least-squares computer program, a modified version of that written by Busing, Martin & Levy (1962). A further three cycles of anisotropic refinement gave $R = 0.0437$ with 67 reflexions and 18 variable parameters.

Observed and calculated structure amplitudes with calculated phase angles are given in Table 1.

Description and discussion of structure

The fractional atomic coordinates and temperature parameters are given in Table 2. The corresponding bond lengths and angles are shown in Table 3.

Table 3. *Observed bond lengths and angles with their standard deviations*

Si(1)–Cl(1)	1.955 (12) Å	Cl(2)–Si(2)–Cl(2')	108.8 (5)°
Si(2)–Cl(2)	1.994 (7)	Cl(2)–Si(2)–Si(3)	110.1 (5)
Si(2)–Si(3)	2.332 (9)		

The Si–Si bond length of 2.332 Å agrees well with other determinations of Si–Si bonds in other compounds (Table 4).

The Si–Cl bond of 1.994 Å in the dodecachloropentasilane molecule is in reasonable agreement with

other determinations of the Si–Cl bond (Table 5). However the Si–Cl bond of 1.955 Å in the silicon tetrachloride molecule in the crystal is clearly on the short side. This was taken to be the result of the time average effect which occurs in the X-ray method. For a terminal atom vibrating in an angular fashion the centre of mass of its time-average electron density distribution is moved towards the point about which the bond pivots. Since the measured X-ray intensities are determined by the time-average structure, the resultant bond length appears shortened. In the case of the silicon tetrachloride molecule this effect can be achieved by the molecule as a whole having a rotational vibration. Since the shortening appears greatest for this molecule it would be expected to have higher thermal parameters. This is in fact the case, the silicon tetrachloride thermal parameters being approximately double those found for the dodecachloropentasilane molecule.

Applying corrections for thermal librations by the method of Busing & Levy (1964), the following bond lengths were obtained:

$$\text{Si(1)–Cl(1)} = 2.036 (12) \text{ \AA}$$

$$\text{Si(2)–Cl(2)} = 2.012 (7)$$

$$\text{Si(2)–Si(3)} = 2.342 (9) .$$

These are also shown in Fig. 2. The standard deviations, in parentheses, are those obtained for the observed bond lengths. All the corrected values (within their respective limits of accuracy) are in very good agreement with the determinations quoted in Tables 4 and 5.

Both the silicon tetrachloride molecules and the dodecachloropentasilane molecules lie on special positions with the point group symmetry 23. The silicon tetrachloride molecules themselves possess the higher symmetry $\bar{4}3m$. It is the configuration of the surrounding dodecachloropentasilane molecules which reduces the overall symmetry. Although it is possible for the dodecachloropentasilane molecule to adopt the symmetry $\bar{4}3m$ in which each chlorine is *trans* to the op-

Table 4. *Some Si–Si bond lengths*

Compound	Bond length	Method	Reference
Si (diamond lattice)	2.35 Å	X-ray crystallography	Straumanis & Aka (1952)
Si ₂ Cl ₆	2.32 (6)		Brockway & Beach (1938)
	2.34 (6)	Electron diffraction	Iwasaki, Kotera, Tatematsu & Yamasaki (1948)
Si ₂ H ₆	2.24 (6)		Swick & Karle (1955)
Si ₂ (CH ₃) ₆	2.32 (3)		Brockway & Beach (1938)
	2.34 (10)		Brockway & Davidson (1941)

Table 5. *Some Si–Cl bond lengths*

Compound	Bond length	Method	Reference
SiCl ₄	2.01 (2) Å	Electron diffraction	Iwasaki <i>et al.</i> (1948)
Si ₂ Cl ₆	2.00 (5)		Brockway & Beach (1938)
	2.02 (2)		Iwasaki <i>et al.</i> (1948)
	2.01 (1)		Swick & Karle (1955)
SiH ₃ Cl	2.0479 (7)	Infrared and microwave Microwave	Bak, Bruhn & Rastrup-Andersen (1954)
SiHCl ₃	2.021 (2)		Mockler, Bailey & Gordy (1953)

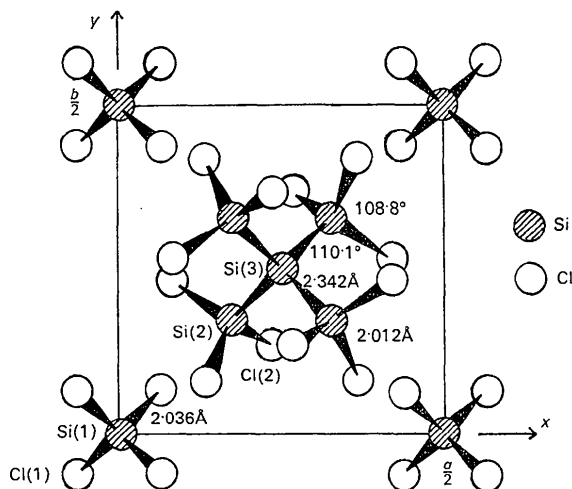


Fig. 2. Projection of one octant of the unit cell on to the (001) plane.

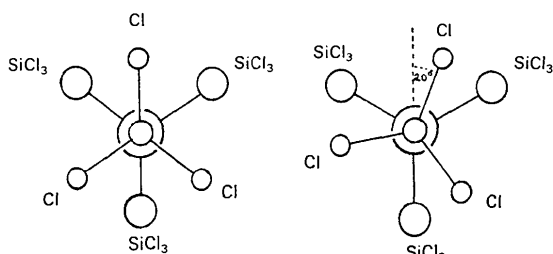


Fig. 3. $\text{Si}_5\text{Cl}_{12}$ projection along a Si-Si bond, (a) *trans* conformation, (b) skew conformation.

posite trichlorosilyl group, in fact the molecule in the crystal adopts a skew formation in which each trichlorosilyl group has been rotated through 20° with respect to the *trans* conformation (Fig. 3). Because of the symmetry, the angles at Si(1) and Si(3) are tetrahedral. In addition the angles at Si(2) are not significantly different from tetrahedral.

Finally a comment must be made on the overall structure. This is clearly not a bridged compound, nor is there any indication of bonding between the molecules. The closest contact between the silicon tetrachloride and the dodecachloropentasilane is 4.04 \AA . The crystal structure must therefore be the result of van der Waals-type interactions and stacking effects.

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