

Fig. 4. Electron density in the $(0\bar{4}4)$ plane containing the molecule. Contours are at $1 \text{ e.}\text{\AA}^{-3}$ starting at $2 \text{ e.}\text{\AA}^{-3}$. The \times marks are projections onto $(0\bar{4}4)$ from the electron density maxima, which in most cases are a short distance from $(0\bar{4}4)$.

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The Crystal and Molecular Structure of Tetrafluorobispyridinesilicon(IV)

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The crystal and molecular structure of tetrafluorobispyridinesilicon(IV), $\text{SiF}_4 \cdot 2(\text{NC}_5\text{H}_5)$, has been determined by a three-dimensional X-ray analysis and is shown to have a centrosymmetric *trans* configuration. The crystals are triclinic with $a = 7.23 \pm 0.01$, $b = 6.42 \pm 0.01$ and $c = 6.99 \pm 0.01 \text{ \AA}$, $\alpha = 109^\circ 43' \pm 10'$, $\beta = 114^\circ 35' \pm 10'$, $\gamma = 95^\circ 42' \pm 10'$; space group $P\bar{1}$ with $Z = 1$. The silicon-nitrogen distance is 1.93 \AA and the pyridine-silicon-pyridine part of the molecule is planar.

Introduction

Long wavelength infrared spectroscopy is now widely used to investigate the structure of coordination com-

pounds, and it is important that in some selected cases other physical techniques should be used to confirm the spectroscopic conclusions. No adducts of silicon tetrahalides – of the type $\text{Si}(\text{halogen})_4 \cdot 2(\text{ligand})$ – have been examined in detail by single-crystal X-ray techniques, although the infrared spectra have been reported and interpreted usually in terms of six-coordinate *cis* or *trans* geometrical isomers. The infrared

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spectrum of solid tetrafluorobispyridinesilicon(IV), $\text{SiF}_4 \cdot 2(\text{NC}_5\text{H}_5)$ has been interpreted in terms of a *trans* octahedral stereochemistry (Beattie & Webster, 1965; Campbell-Ferguson & Ebsworth, 1967) and the infrared spectrum of the related solid tetrachloride compound (Beattie, Gilson, Webster & McQuillan, 1964) was thought to indicate a *cis* octahedral isomer although this interpretation has been recently questioned (Campbell-Ferguson & Ebsworth, 1967). This present paper describes an X-ray investigation of the crystal structure of the fluoride; investigation of the chloride to be reported elsewhere shows the fluoride and the chloride to have similar configurations.

Preparation and crystal data

Crystals, suitable for X-ray examination, were obtained by heating the compound $\text{SiF}_4 \cdot 2(\text{NC}_5\text{H}_5)$ with excess pyridine in sealed tubes and allowing the tubes to cool slowly. Selected crystals were transferred in a dry box

to lithium-borate-glass capillary tubes. The unit-cell dimensions were obtained from rotation, Weissenberg and precession photographs. The crystallographic data are:

$$a = 7.23 \pm 0.01, \quad b = 6.42 \pm 0.01, \quad c = 6.99 \pm 0.01 \text{ \AA},$$

$$\alpha = 109^\circ 43' \pm 10', \quad \beta = 114^\circ 35' \pm 10', \quad \gamma = 95^\circ 42' \pm 10'.$$

$$\rho(X\text{-ray}) = 1.63 \text{ g.cm}^{-3}; \quad \rho(\text{measured}) = 1.61 \pm 0.04 \text{ g.cm}^{-3}; \quad Z = 1; \quad \text{space group } P1 \text{ or } P\bar{1}.$$

The space-group ambiguity exists because the molecule may have a centre of symmetry.

Experimental

Equi-inclination integrated Weissenberg photographs were taken about the *b* axis, up to the seventh layer. It was not possible to obtain intensity data about the other axes because of the orientation of the crystals in the glass tubes. The intensities were measured with a microdensitometer, corrected for Lorentz and polar-

Table 1. Observed and calculated structure factors

The first number in each column is *h*, the second 100 $F_o(hkl)$ and the third 100 $F_c(hkl)$.

1	h,0,0	5	2,4	198	1	252	198	h,0,-3	1	525	534	1	468	472	5	198	122	-3	1044	918	-8	248	308	-1	480	368	h,-4,5	h,-7,6				
-2	-1568	-1082	1	150	152	-2	150	152	-1	525	534	2	468	472	-3	198	122	-4	1044	918	-5	248	308	-6	480	368	-7	1116	1102	-1	114	106
-3	-3136	-2164	2	300	304	-3	300	304	-2	1050	1068	3	936	944	-4	396	244	-5	2088	1836	-6	496	616	-7	960	736	-8	2232	2204	-2	162	152
-4	-4704	-3246	3	450	456	-4	450	456	-3	1575	1596	4	1404	1408	-5	594	366	-6	3176	2754	-7	792	984	-8	1344	1048	-9	1584	1556	-3	296	296
-5	-6272	-4328	4	600	608	-5	600	608	-4	2100	2112	5	2100	2112	-6	840	516	-7	4352	3726	-8	1184	1488	-9	1808	1408	-10	2160	2132	-4	464	464
-6	-7840	-5410	5	750	756	-6	750	756	-5	2625	2634	6	2625	2634	-7	1125	684	-8	5712	4818	-9	1568	1968	-10	2208	1708	-11	2592	2574	-5	640	640
-7	-9408	-6492	6	900	908	-7	900	908	-6	3150	3156	7	3150	3156	-8	1470	888	-9	7024	5886	-10	2016	2416	-11	2656	2056	-12	3024	3006	-6	800	800
-8	-11000	-7574	7	1050	1056	-8	1050	1056	-7	3675	3678	8	3675	3678	-9	1890	1146	-10	8448	6942	-11	2464	2864	-12	3104	2504	-13	3472	3454	-7	960	960
-9	-12600	-8656	8	1200	1208	-9	1200	1208	-8	4200	4204	9	4200	4204	-10	2280	1332	-11	9536	7746	-12	2712	3112	-13	3352	2752	-14	3760	3742	-8	1120	1120
-10	-14200	-9738	9	1350	1356	-10	1350	1356	-9	4725	4728	10	4725	4728	-11	2670	1554	-12	10672	8586	-13	3152	3552	-14	3600	3000	-15	4008	3990	-9	1280	1280
-11	-15800	-10820	10	1500	1508	-11	1500	1508	-10	5250	5254	11	5250	5254	-12	3060	1806	-13	11808	9546	-14	3592	3992	-15	4152	3552	-16	4560	4542	-10	1440	1440
-12	-17400	-11902	11	1650	1656	-12	1650	1656	-11	5775	5778	12	5775	5778	-13	3450	2058	-14	13056	10506	-15	4032	4432	-16	4608	4008	-17	5072	5054	-11	1600	1600
-13	-19000	-12984	12	1800	1808	-13	1800	1808	-12	6300	6304	13	6300	6304	-14	3840	2316	-15	14304	11466	-16	4576	4976	-17	5120	4520	-18	5584	5566	-12	1760	1760
-14	-20600	-14066	13	1950	1956	-14	1950	1956	-13	6825	6828	14	6825	6828	-15	4230	2574	-16	15552	12306	-17	5016	5416	-18	5632	5032	-19	6080	6062	-13	1920	1920
-15	-22200	-15148	14	2100	2108	-15	2100	2108	-14	7350	7354	15	7350	7354	-16	4620	2932	-17	16800	13254	-18	5456	5856	-19	6128	5528	-20	6608	6590	-14	2080	2080
-16	-23800	-16230	15	2250	2256	-16	2250	2256	-15	7875	7878	16	7875	7878	-17	5010	3190	-18	18048	14094	-19	5904	6304	-20	6624	6024	-21	7184	7166	-15	2240	2240
-17	-25400	-17312	16	2400	2408	-17	2400	2408	-16	8400	8404	17	8400	8404	-18	5400	3448	-19	19296	14850	-20	6344	6744	-21	7232	6632	-22	7744	7726	-16	2400	2400
-18	-27000	-18394	17	2550	2556	-18	2550	2556	-17	8925	8928	18	8925	8928	-19	5790	3706	-20	20544	15606	-21	6784	7184	-22	7784	7184	-23	8240	8222	-17	2560	2560
-19	-28600	-19476	18	2700	2708	-19	2700	2708	-18	9450	9454	19	9450	9454	-20	6180	3964	-21	21792	16362	-22	7224	7624	-23	8288	7688	-24	8744	8726	-18	2720	2720
-20	-30200	-20558	19	2850	2856	-20	2850	2856	-19	9975	9978	20	9975	9978	-21	6570	4222	-22	23040	17118	-23	7664	8064	-24	8792	8192	-25	9248	9230	-19	2880	2880
-21	-31800	-21640	20	3000	3008	-21	3000	3008	-20	10500	10504	21	10500	10504	-22	6960	4480	-23	24288	17874	-24	8104	8504	-25	9344	8744	-26	9808	9790	-20	3040	3040
-22	-33400	-22722	21	3150	3156	-22	3150	3156	-21	11025	11028	22	11025	11028	-23	7350	4738	-24	25536	18630	-25	8544	8944	-26	9896	9296	-27	10368	10350	-21	3200	3200
-23	-35000	-23804	22	3300	3308	-23	3300	3308	-22	11550	11554	23	11550	11554	-24	7740	5000	-25	26784	19386	-26	9088	9488	-27	10496	9896	-28	10928	10910	-22	3360	3360
-24	-36600	-24886	23	3450	3456	-24	3450	3456	-23	12075	12078	24	12075	12078	-25	8130	5262	-26	28032	20142	-27	9528	9928	-28	10640	10040	-29	11440	11422	-23	3520	3520
-25	-38200	-25968	24	3600	3608	-25	3600	3608	-24	12600	12604	25	12600	12604	-26	8520	5524	-27	29280	20904	-28	10072	10472	-29	11184	10584	-30	11888	11870	-24	3680	3680
-26	-39800	-27050	25	3750	3756	-26	3750	3756	-25	13125	13128	26	13125	13128	-27	8910	5786	-28	30528	21660	-29	10512	10912	-30	11728	11128	-31	12336	12318	-25	3840	3840
-27	-41400	-28132	26	3900	3908	-27	3900	3908	-26	13650	13654	27	13650	13654	-28	9300	6048	-29	31776	22416	-30	10952	11352	-31	12272	11672	-32	12784	12766	-26	4000	4000
-28	-43000	-29214	27	4050	4056	-28	4050	4056	-27	14175	14178	28	14175	14178	-29	9690	6310	-30	33024	23172	-31	11392	11792	-32	12816	12216	-33	13232	13214	-27	4160	4160
-29	-44600	-30296	28	4200	4208	-29	4200	4208	-28	14700	14704	29	14700	14704	-30	10080	6572	-31	34272	23928	-32	11832	12332	-33	13264	12664	-34	13784	13766	-28	4320	4320
-30	-46200	-31378	29	4350	4356	-30	4350	4356	-29	15225	15228	30	15225	15228	-31	10470	6834	-32	35520	24684	-33	12272	12772	-34	13712	13112	-35	14336	14318	-29	4480	4480
-31	-47800	-32460	30	4500	4508	-31	4500	4508	-30	15750	15754	31	15750	15754	-32	10860	7096	-33	36768	25440	-34	12712	13242	-35	14256	13656	-36	14888	14870	-30	4640	4640
-32	-49400	-33542	31	4650	4656	-32	4650	4656	-31	16275	16278	32	16275	16278	-33	11250	7358	-34	38016	26196	-35	13152	13722	-36	14704	14104	-37	15440	15422	-31	4800	4800
-33	-51000	-34624	32	4800	4808	-33	4800	4808	-32	16800	16804	33	16800	16804	-34	11640	7620	-35	39264	26952	-36	13592	14162	-37	15152	14552	-38	15992	15974	-32	4960	4960
-34	-52600	-35706	33	4950	4956	-34	4950	4956	-33	17325	17328	34	17325	17328	-35	12030	7882	-36	40512	27708	-37	14032	14642	-38	15600	15000	-39	16544	16526	-33	5120	5120
-35	-54200	-36788	34	5100	5108	-35	5100	5108	-34	17850	17854	35	17850	17854	-36	12420	8144	-37	41760	28464	-38	14472	15072	-39	16048	15448	-40	17096	17078	-34	5280	5280
-36	-55800	-37870	35	5250	5256	-36	5250	5256	-35	18375	18378	36	18375	18378	-37	12810	8406	-38	43008	29220	-39	14912	15642	-40	16496	15896	-41	17648	17630	-35	5440	5440
-37	-57400	-38952	36	5400	5408	-37	5400	5408	-36	18900	18904	37	18900	18904	-38	13200	8668	-39	44256	29976	-40	15352	16102	-41	16944	16344	-42	18200	18182	-36	5600	5600
-38	-59000	-40034	37	5550	5556	-38	5550	5556	-37	19425	19428	38	19425	19428	-39	13590	8930	-40	45504	30732	-41	15792	16542	-42	17392	16792	-43	18752	18734	-37	5760	5760
-39	-60600	-41116	38	5700	5708	-39	5700	5708	-38	19950	19954	39	19950	19954	-40	13980	9192	-41	46752	31488	-42	16232	17042	-43	17840	17240	-44	19304	19286	-38	5920	5920
-40	-62200	-42198	39	5850	5856	-40	5850	5856	-39	20475	20478	40	20475	20478	-41	1																

ization factors in the usual way, and the layers approximately scaled to each other by comparison with diffractometer data for the same crystal.

Structure determination

An unsharpened Patterson map was computed and the sphere containing the ends of vectors of length 1.7 Å was plotted, it being expected that the silicon-fluorine bond would be about this length. The centres of the three largest peaks gave vectors which were mutually orthogonal to within a few degrees. The four fluorine atoms and the two nitrogen atoms of the pyridine rings were placed in a *cis* configuration and a three-dimensional electron-density map was calculated on the basis of the resulting structure-factor calculation. Ten additional peaks appeared on this electron-density map in positions consistent with the *trans*-configuration structure, although the possibility still existed that the pyridine rings were not quite related by a centre of symmetry. Least-squares refinement with the use of individual isotropic temperature factors was commenced on the assumption that the space group was *P*1, and a few cycles of refinement sufficed to show that the departure of the structure from *P*1 was less than the standard deviation of the coordinates of related atoms. Least-squares refinement was continued in space group *P*1, first with individual isotropic and then with anisotropic temperature factors, and discontinued when the shifts in the parameters were considerably smaller than their standard deviations and the value of $\Sigma w\Delta^2$ began to oscillate about its minimum. The value of *w* was chosen to be

$$w = \left[1 + \left\{ \frac{K|F_o| - 5F_{\min}}{8F_{\min}} \right\}^2 \right]^{-1} \quad (\text{Hughes, 1941}).$$

The positions of the hydrogen atoms were calculated and a layer-by-layer scaling of the data carried out. The final *R* value obtained after further minimizing $\Sigma w\Delta^2$ was 0.098. In view of the quality of the crystal, which was surface powdered, and the encapsulation this was thought to be satisfactory.

Observed and calculated structure factors are given in Table 1 and the coordinates and thermal parameters in Tables 2 and 3. The poor agreement between the observed and calculated value of the $\bar{6}02$ reflexion is probably due to double reflexion involving the $\bar{4}01$ and $20\bar{1}$ reflexions.

Table 3. *Anisotropic thermal parameters* ($\times 10^5$) defined as $\exp(-\sum_i \sum_j h_i h_j B_{ij})$

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Si	1124	3253	1543	1450	1422	344
F(1)	1791	4037	2179	1654	853	1875
F(2)	2013	3897	2407	1397	2568	-402
N	1236	3220	1954	1517	1279	963
C(1)	1595	3092	2046	953	1552	1084
C(2)	1844	3352	2842	1701	1811	626
C(3)	1646	4422	2500	882	2078	1340
C(4)	1996	4892	1517	1094	1694	468
C(5)	1584	3706	1727	1227	1349	632

Discussion

The projection of the structure down the *b* axis is shown in Fig. 1 and the bond lengths and bond angles are

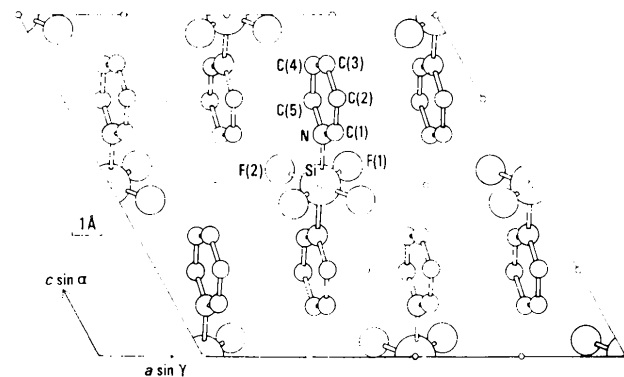


Fig. 1. Projection of structure along the *b* axis viewed in the direction of increasing *b*.

Table 2. *Final coordinates and standard deviations of the atoms*

The hydrogen atom coordinates were obtained by geometry and not refined.

	<i>x/a</i>	$\sigma(x/a)$	<i>y/b</i>	$\sigma(y/b)$	<i>z/c</i>	$\sigma(z/c)$
Si	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
F(1)	0.1721	0.0008	-0.1309	0.0010	0.1090	0.0008
F(2)	-0.1511	0.0008	-0.0984	0.0010	0.0894	0.0008
N	0.1422	0.0010	0.2706	0.0013	0.2910	0.0011
C(1)	0.2054	0.0013	0.4781	0.0017	0.3026	0.0015
C(2)	0.3100	0.0014	0.6750	0.0018	0.5067	0.0016
C(3)	0.3482	0.0014	0.6608	0.0020	0.7111	0.0016
C(4)	0.2804	0.0014	0.4432	0.0020	0.6988	0.0015
C(5)	0.1809	0.0013	0.2525	0.0017	0.4898	0.0014
H(1)	0.1765		0.4861		0.1500	
H(2)	0.3555		0.8313		0.5059	
H(3)	0.4174		0.7991		0.8658	
H(4)	0.3076		0.4286		0.8462	
H(5)	0.1325		0.0954		0.4800	

given in Tables 4 and 5. Owing to steric hindrance of the hydrogen atoms with the fluorine atoms of adjacent molecules the plane of the pyridine ring does not bisect the angle F(1)-Si-F(2); it is rotated about the Si-N-O(3) axis towards F(2). There are no unduly short intermolecular distances, and the angle Si-N-C(3) is 180.00°. The silicon-nitrogen bond is 1.93 Å (*cf* 1.74 Å in trisilamine).

Table 4. *Intramolecular bond lengths*

The mean standard deviation, excluding bonds to hydrogen atoms, is 0.015 Å

Si—F(1)	1.64 Å	C(4)—C(5)	1.38 Å
Si—F(2)	1.64	C(5)—N	1.35
Si—N	1.93	C(1)—H(1)	1.02
N—C(1)	1.33	C(2)—H(2)	1.03
C(1)—C(2)	1.38	C(3)—H(3)	1.01
C(2)—C(3)	1.38	C(4)—H(4)	1.01
C(3)—C(4)	1.40	C(5)—H(5)	1.00

Table 5. *Intramolecular bond angles*

The mean standard deviation, excluding angles containing a hydrogen atom, 0.9°

F(1)—Si—F(2)	90.1°	C(3)—C(2)—H(2)	120.3°
F(1)—Si—N	90.2	C(1)—C(2)—H(2)	120.5
F(2)—Si—N	89.5	C(4)—C(3)—C(2)	117.1
Si—N—C(5)	120.2	C(4)—C(3)—H(3)	119.4
Si—N—C(1)	121.8	C(2)—C(3)—H(3)	123.4
C(1)—N—C(5)	118.0	C(5)—C(4)—C(3)	120.8
N—C(1)—C(2)	123.6	C(5)—C(4)—H(4)	120.8
N—C(1)—H(1)	116.3	C(3)—C(4)—H(4)	118.5
C(2)—C(1)—H(1)	120.0	N—C(5)—C(4)	121.2
C(3)—C(2)—C(1)	119.2	N—C(5)—H(5)	117.7
C(4)—C(5)—H(5)	121.1°		

A least-squares fit of the best plane passing through the five carbon atoms in the pyridine ring gave deviations from this plane for C(1) through C(5) of 0.008, 0.009, 0.002, 0.006, 0.007 Å. The nitrogen atom of the pyridine ring deviates from this plane by 0.002 Å and the silicon atom by 0.001 Å showing that the pyridine-silicon-pyridine part of the molecule is planar.

The *trans* configuration of tetrafluorobispyridine-silicon(IV) is similar to that claimed for dipyridine-tetrachlorogermanium(IV) (Hulme, Leigh & Beattie, 1960).

Conclusions

The structure of tetrafluorobispyridinesilicon(IV) has been shown to have the centrosymmetric *trans* configuration in the solid state, confirming the conclusions obtained from infrared spectroscopy.

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