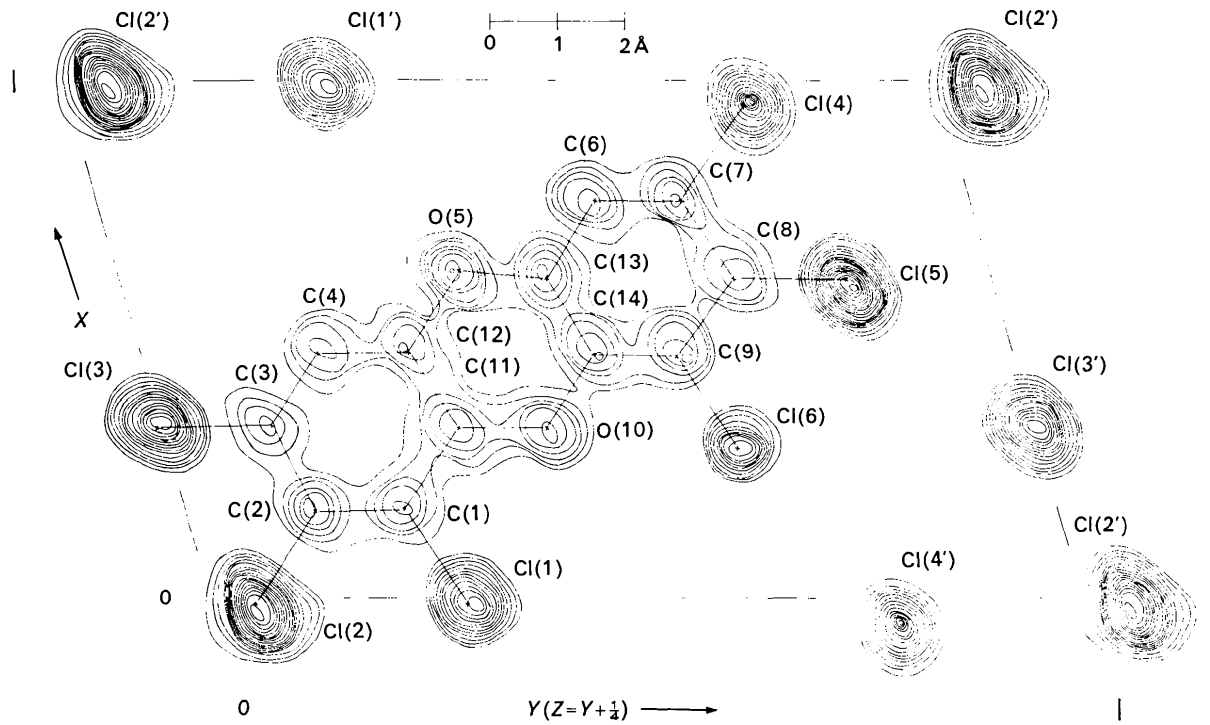

Fig. 4. Electron density in the (0$\bar{4}$4) plane containing the molecule. Contours are at 1 e.Å^{-3} starting at 2 e.Å^{-3}. The × marks are projections onto (0$\bar{4}$4) from the electron density maxima, which in most cases are a short distance from (0$\bar{4}$4).

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The Crystal and Molecular Structure of Tetrafluorobispyridinesilicon(IV)

BY VALERIE A. BAIN*, R.C.G. KILLEAN* AND M. WEBSTER†
The University, St. Andrews, Scotland

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The crystal and molecular structure of tetrafluorobispyridinesilicon(IV), $SiF_4.2(NC_5H_5)$, has been determined by a three-dimensional X-ray analysis and is shown to have a centrosymmetric *trans* configuration. The crystals are triclinic with $a=7{\cdot}23\pm0{\cdot}01$, $b=6{\cdot}42\pm0{\cdot}01$ and $c=6{\cdot}99\pm0{\cdot}01$ Å, $\alpha=109°43'\pm10'$, $\beta=114°35'\pm10'$, $\gamma=95°42'\pm10'$; space group $P\bar{1}$ with $Z=1$. The silicon-nitrogen distance is 1·93 Å 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 compounds, 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 Si(halogen)$_4$.2(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

* Department of Physics.
† Department of Chemistry. Present address: Department of Chemistry, The University, Southampton, England.

spectrum of solid tetrafluorobispyridinesilicon(IV), $SiF_4.2(NC_5H_5)$ 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 $SiF_4.2(NC_5H_5)$ 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:

$a = 7{\cdot}23 \pm 0{\cdot}01$, $b = 6{\cdot}42 \pm 0{\cdot}01$, $c = 6{\cdot}99 \pm 0{\cdot}01$ Å,
$\alpha = 109°43' \pm 10'$, $\beta = 114°35' \pm 10'$, $\gamma = 95°42' \pm 10'$.
ϱ(X-ray) = 1·63 g.cm^{-3}; ϱ(measured) = 1·61 ± 0·04 g.cm^{-3}; $Z = 1$; space group $P1$ 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 $F_c(hkl)$.

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 $P1$, and a few cycles of refinement sufficed to show that the departure of the structure from $P\bar{1}$ was less than the standard deviation of the coordinates of related atoms. Least-squares refinement was continued in space group $P\bar{1}$, 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

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

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

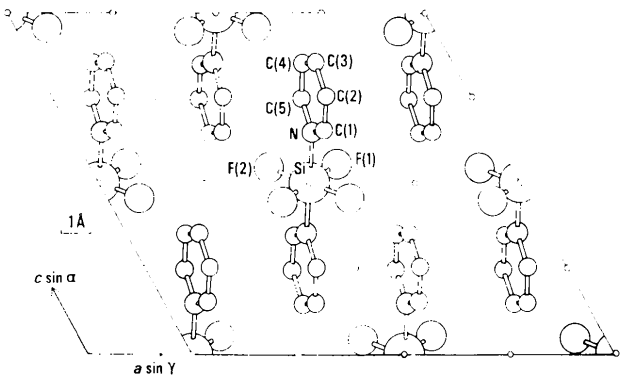

Fig. 1. Projection of structure along the b axis viewed in the direction of increasing b.

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

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

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
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 tetrafluorobispyridinesilicon(IV) is similar to that claimed for dipyridinetetrachlorogermanium(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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