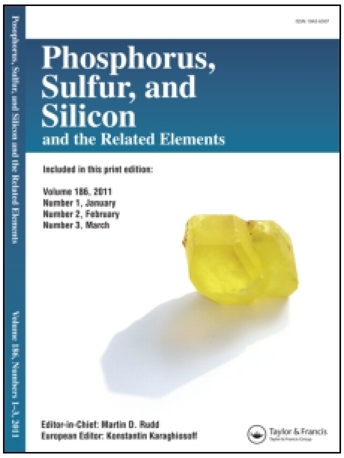

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# A NEW GEOMETRICAL FORM OF SILICON, SYNTHESIS AND STRUCTURE OF TETRAETHYLAMMONIUM BIS(1,2-BENZENEDIOLATO)FLUOROSILICATE(IV)

John J. Harland[a]; Roberta O. Day[a]; Jean F. Vollano[a]; Arjun C. Sau[a]; Robert R. Holmes[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

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# A NEW GEOMETRICAL FORM OF SILICON. SYNTHESIS AND STRUCTURE OF TETRAETHYLAMMONIUM BIS(1,2-BENZENEDIOLATO)FLUOROSILICATE(IV)

JOHN J. HARLAND, ROBERTA O. DAY, JEAN F. VOLLANO,
ARJUN C. SAU and ROBERT R. HOLMES*

*Department of Chemistry, University of Massachusetts,*
*Amherst, Massachusetts 01003*

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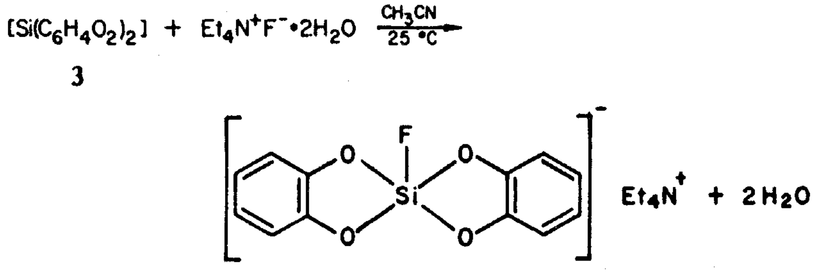
Anionic pentacoordinated silicon compounds,[1] isoelectronic with phosphoranes, are extremely rare. Of those synthesized, X-ray structural characterization of a spirocyclic derivative $[(C_6H_4O_2)_2SiPh]^-Me_4N^+$ (**1**) has been reported[2] and reveals a trigonal-bipyramidal form displaced about one-third the way toward a square pyramid.

We report here the preparation and X-ray crystal structure of the first pentacoordinated Si(IV) compound having a square-pyramidal conformation. The compound, tetraethylammonium bis(1,2-benzenediolato)fluorosilicate(IV) (**2**), mp 208–210°C, was prepared by the reaction of bis(catecholato)silicon(IV) (**3**)[3] with $Et_4N^+F^- \cdot 2H_2O$ in methyl cyanide at room temperature. Crystals suitable for X-ray diffraction analysis were grown from a 1:2 mixture of methyl cyanide–diethyl ether at 0°C. Anal. Calcd for $C_{20}H_{28}O_4NFSi$: C, 61.04; H, 7.17; N, 3.55. Found: C, 60.79; H, 7.15; N, 3.49.



**2**

**Crystal Data** for $C_{20}H_{28}O_4NFSi$ (**2**): Space group *C*2/*c* ($C^6_{2h}$, No. 15),[4] with $a = 28.091(4)$, $b = 11.213(1)$, $c = 33.582(8)$ Å; $\beta = 128.76(1)°$; $Z = 16$. Independent reflections (4711) were measured on an Enraf–Nonius CAD4 automated diffractometer, using graphite monochromated Mo $K\bar{\alpha}$ radiation and the $\theta$–$2\theta$ scan mode, to a maximum $2\theta_{MoK\bar{\alpha}}$ of 43°. The structure was solved by using direct methods (MULTAN). Full-matrix least-squares refinement[5] (54 independent nonhydrogen

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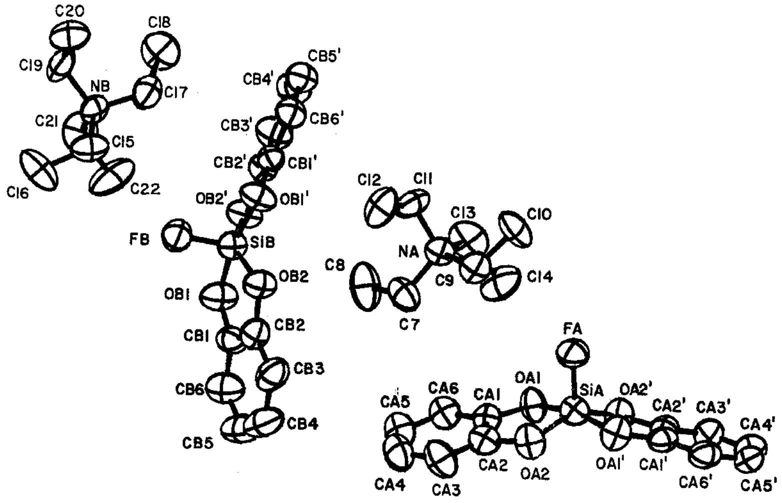

FIGURE 1 ORTEP plot of $[(C_6H_4O_2)_2SiF]^- Et_4N^+$ (**2**), with thermal ellipsoids shown at the 50% probability level. Bond parameters for anion A (those for anion B are in parentheses), lengths (Å): Si—F = 1.607 (4) (1.599 (4)), Si—O1 = 1.742 (5) (1.741 (5)), Si—O1′ = 1.736 (5) (1.738 (5)), Si—O2 = 1.704 (5) (1.699 (5)), Si—O2′ = 1.706 (5) (1.701 (5)). Angles (deg): O1—Si—O1′ = 164.0 (2) (168.4 (3)), O2—Si—O2′ = 145.5 (3) (140.7 (3)).

atoms, anisotropic, varied; 32 independent hydrogen atoms, excluding methyl hydrogen atoms, isotropic, fixed) led to a conventional unweighted residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.064 for the 2705 independent reflections having $I \geq 2\sigma(I)$.

Two discrete molecules of **2** are present in the unit cell shown in the ORTEP plot of Figure 1. The bond angle data given in the legend indicate that the structure of the molecule labeled A is more square pyramidal than the B molecule. On the basis of the dihedral angle data, as applied to cyclic phosphoranes,[6,7] the geometry about the silicon atom for molecule A is displaced by 70.5% (68.7% using unit vectors) from the trigonal bipyramid toward the square-pyramidal configuration. The structure of the B molecule is displaced 54.6% (52.8%) toward the square pyramid. Both molecules follow the local $C_{2v}$ constraint of the coordinate connecting the trigonal bipyramid to the rectangular pyramid. Each molecule has approximate 2-fold symmetry with the 2-fold axis coincident with the Si—F bond. Following the trend observed for cyclic phosphoranes,[6–8] the "axial" Si—O bonds are longer than the "equatorial" Si—O bonds, averaging 0.03 Å longer for each independent molecule.

Although crystal packing effects exert some influence on the structural form obtained for **2**, the recent discovery of the rectangular pyramidal geometry for related pentacoordinated Ge(IV)[9] and Sn(IV)[10] species suggests the operation of substituent effects as the principal structural determinant.

For each of these pentacoordinated derivatives, the structures obtained follow the factors deemed important in forming the rectangular pyramidal geometry for phosphoranes.[7,8]

The placement of the structures for **1** and **2** on the ligand exchange coordinate connecting the trigonal bipyramid and square pyramid suggests that fluxional behavior, common for phosphoranes,[8,11,12] should be an observable characteristic of pentacoordinated silicon.

## ACKNOWLEDGEMENT

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*Supplementary Material Available*: Atomic coordinates (Table I) and anisotropic thermal parameters (Table II) (4 pages). Ordering information is given on any current masthead page.

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