Bis(trifluoromethanesulfonato)(tetra-*p*-tolylporphyrinato)silicon(IV), (TTP)Si(OTf)₂: The First Structurally Characterized (Porphyrinato)silicon(IV) Complex

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The silicon metalloporphyrin (TTP)SiCl₂ (**1**) (TTP = dianion of tetra-*p*-tolylporphyrin) has been prepared by the condensation of [Li₂(THF)₂][TTP] with HSiCl₃ in methylene chloride at −78 °C. The reaction proceeds *via* the apparent loss of LiCl *and* LiH. The compounds (TTP)SiF₂ (**2**) and (TTP)Si(O₃SCF₃)₂ (**3**) were prepared by the reaction of **1** with SbF₃ (or AgBF₄) and Me₃SiO₃SCF₃ (or AgO₃SCF₃), respectively. Compound **1** is extremely water sensitive in solution, yielding [(TTP)H₄]Cl₂, yet **2** is insensitive to water. Bis(triflate) **3** is converted to (TTP)Si(OH)₂ upon exposure to water in solution and quenching with base. The single-crystal X-ray structure of **3** has been determined. The silicon lies in a slightly distorted octahedral geometry with the triflates in a *trans* configuration, and the porphyrin is in a *ruf* nonplanar form. The structure of **3** is compared to those of other main-group metalloporphyrins. Crystallographic data for **3**: orthorhombic, space group *Pca*2₁, $a = 24.740(5)$ Å, $b = 11.940(2)$ Å, $c = 15.514(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4583(2)$ Å³, $Z = 4$, R1 = 0.0414.

Introduction

Hypercoordinate silicon complexes have attracted interest because of their unusual structural and physical properties, their implication as reactive intermediates in catalysis, and the potential for coordination numbers about the silicon atom greater than 6.[1-6] Although there are many reports concerning hexacoordinate silicon, there is a paucity of chemical and structural studies of silicon complexes with a restricted geometry.[6] Phthalocyanines and porphyrins are macrocyclic ligands which provide a restricted, planar geometry and generally yield hexacoordinate complexes with substituents disposed above and below the plane of the macrocycle in a *trans* configuration. When the central atom is too large to fit in the cavity of the macrocycle, the substituents are disposed in a *cis* configuration on one side of the macrocycle (*e.g.* (TTP)ZrCl₂[7]). Whereas there are numerous reports of silicon phthalocyanine complexes with a variety of axial substituents, many of these compounds suffered from poor solubility. Thus, we found that porphyrins are more attractive candidate ligands for silicon complexes because of their improved solubility and variety of pendant groups.

The porphyrin chemistry of group 14 elements contains numerous examples of germanium and tin complexes which incorporate both octaalkyl- and tetraarylporphyrins.[8-16] On the other hand, only a few (porphyrinato)silicon complexes are known. The octaethylporphyrin complex (OEP)SiCl₂ (OEP = dianion of octaethylporphyrin) and its derivatives (OEP)SiX₂ (X = Me, Ph, OMe, OPh) have been known[11,17,18] for over 20 years; however, prior to our work, tetraarylporphyrin derivatives of silicon were nonexistent. We now report the synthesis of the first examples of (tetraarylporphyrinato)silicon(IV): (TTP)SiX₂ (TTP = dianion of tetra-*p*-tolylporphyrin; X = Cl (**1**), F (**2**), O₃SCF₃ (**3**)). (TTP)SiCl₂ was prepared by the unprecedented reaction of (TTP)²⁻ with HSiCl₃ or H₂SiCl₂ accompanied by the apparent loss of H⁻ from silicon. The single-crystal X-ray structure of (TTP)Si(O₃SCF₃)₂ is also reported.

Results

Preparation and Characterization of (TTP)SiCl₂ (1). Our initial attempts to prepare **1** followed the method developed by

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Scheme 1. Formation and Reactivity of (Porphyrinato)silicon(IV) Complexes
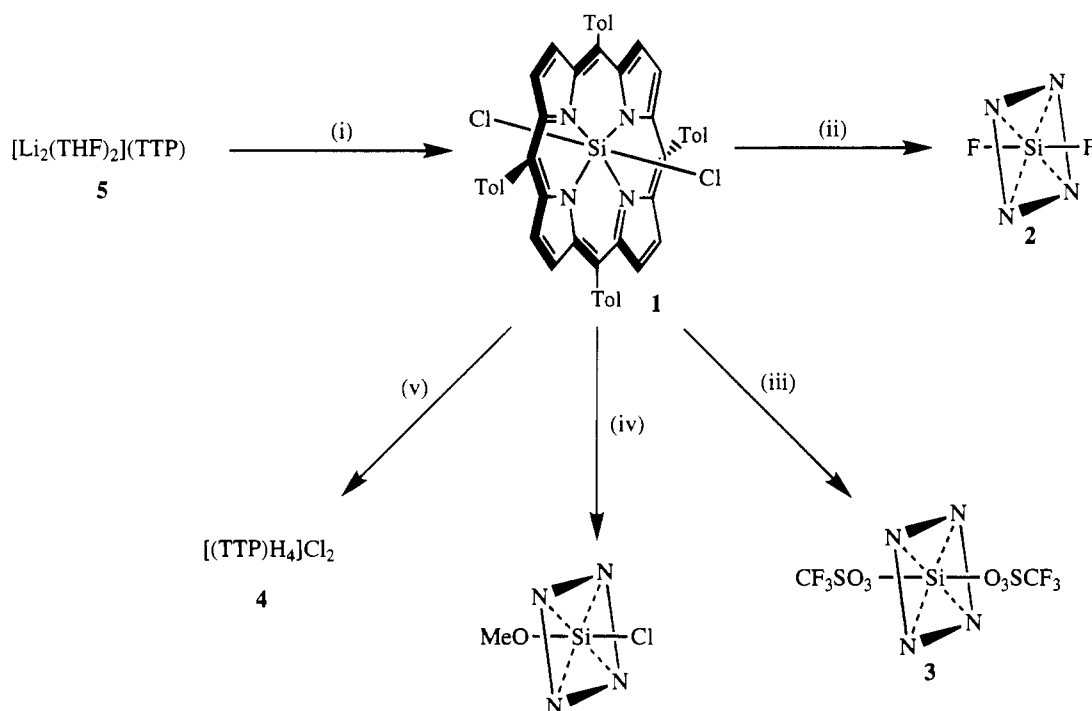
Reaction Conditions: (i) $HSiXCl_2$ (X = H, Cl) in CH_2Cl_2, -LiH, -LiX; (ii) SbF_3 or $AgBF_4$ in CH_2Cl_2; (iii) neat $Me_3SiO_3SCF_3$, or AgO_3SCF_3 in CH_2Cl_2; (iv) neat MeOH; (v) excess H_2O.

Gouterman and co-workers for the preparation of (OEP)$SiCl_2$.[11] The reaction of (TTP)H_2 with $SiCl_4$ in anhydrous pyridine at 170 °C followed by an acidic aqueous workup did not yield **1**; instead the protonated porphyrin [(TTP)H_4]Cl_2 (**4**)[19−21] was isolated (eq 1). Furthermore, attempts to prepare (OEP)$SiCl_2$

$$(TTP)H_2 + SiCl_4 \xrightarrow[\text{2. acidic aqueous workup}]{\text{1. pyridine, 170 °C}} [(TTP)H_4]Cl_2 \quad (1)$$
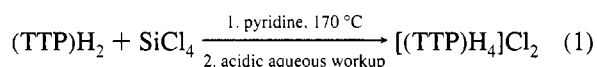
following Gouterman's method were unreliable in our hands and produced considerable amounts of [(OEP)H_4]Cl_2.

It seemed clear that **1** is extremely water sensitive; thus, we sought a synthetic route involving anhydrous conditions. The alkali metal porphyrin complex [Li$_2$(THF)$_2$](TTP) (**5**), recently reported by Arnold and co-workers, offered such a route.[22] The reaction of **5** with $SiCl_4$ in THF or toluene was incomplete, yielding only small amounts of **1**, even under refluxing conditions. Chlorosilanes such as $MeSiCl_3$ and $PhSiCl_3$ were also unreactive with **5**. Surprisingly, the reactions of **5** with the hydrochlorosilanes $HSiCl_3$ and H_2SiCl_2 in CH_2Cl_2 were rapid and complete within minutes and gave exclusively **1** (Scheme 1). We have developed a high-yield, "one-pot" synthetic route toward **1**. Dilithio salt **5** was generated from (TTP)H_2 and LiN-(SiMe$_3$)$_2$ in THF at 60 °C. After removal of THF and HN-(SiMe$_3$)$_2$ under vacuum, CH_2Cl_2 and $HSiCl_3$ were added by vacuum transfer at −78 °C. The lithium salts generated were removed by filtration. The solvent was removed from the filtrate under vacuum, and the residue was vacuum-dried to give **1** as a blue-purple solid in >88% isolated yields. Similarly, reactions

of **5** with $MeSiHCl_2$ and Me_2SiHCl proceeded quickly and gave (TTP)SiMeCl and (TTP)SiMe$_2$, respectively.[23]

In the formation of **1**, 1 equiv each of LiCl and LiH is eliminated. The presence of LiH was suggested by the formation of a basic solution when the isolated lithium salts were dissolved in water. Neither the alkali metal associated with the porphyrin dianion nor the reaction solvent affects the outcome of the reaction described in Scheme 1. Invariably, dichloride **1** was obtained from the reaction of $HSiCl_3$ with **5** in THF or toluene, with [M$_2$(THF)$_n$](TTP) (M = Na and K)[22] in THF or toluene, and with the etherate [Li$_2$(Et$_2$O)$_2$](TTP)[24] in CH_2Cl_2. The base-free Li$_2$(TTP) also gave **1** exclusively when reacted with $HSiCl_3$ in toluene. Moreover, no products other than **1** were isolated when $HSiCl_3$ was reacted with [M$_2$(THF)$_n$](TTP) (M = Na and K) in THF or toluene in the presence of crown ethers.

Porphyrin complex **1** is extremely water sensitive in solution (*vide infra*), but solid **1** may be exposed briefly to atmospheric moisture. The formulation of **1** as the dichloride (TTP)$SiCl_2$ and not the hydridochloro compound (TTP)Si(H)Cl was supported by elemental analysis and NMR spectroscopy. In the ^{1}H NMR spectrum (CD$_2$Cl$_2$) of **1**, only four resonances assignable to the pyrrolic (singlet at 9.03 ppm), aromatic (two doublets at 7.58 and 7.98 ppm), and methyl (singlet at 2.65 ppm) hydrogens were observed. A singlet at δ −217 ppm was observed in the ^{29}Si (^{1}H-coupled) NMR spectrum (CD$_2$Cl$_2$) of **1** with no observable $^1J_{SiH}$. This chemical shift in the ^{29}Si NMR spectrum is consistent with a hexacoordinate silicon complex (−120 to −195 ppm)[6] in the presence of a local shielding field (the porphyrin ring current). The lack of any observable upfield resonance in the ^{1}H NMR spectrum and any J_{SiH} in the ^{29}Si NMR spectrum were consistent with the absence of a Si−H group and the formulation of **1** as the dichloride (TTP)$SiCl_2$ with a *trans* configuration. (In a *cis* configuration, the aromatic

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hydrogens would be diastereotopic and exhibit a more complex pattern in the ¹H NMR spectrum.) The UV—visible spectral data for **1**—**3** are unremarkable and are consistent with absorptions of "normal" metalloporphyrins.[25]

Reactivity of (TTP)SiCl₂ (1). Porphyrin complex **1** is very reactive with protic solvents (Scheme 1). Exposure of a CDCl₃ solution of **1** to a drop of water quantitatively (as determined by ¹H NMR) converted **1** to the protonated porphyrin **4**. This reactivity of **1** toward water is remarkable when compared to that of (OEP)SiCl₂, which was isolated using an acidic aqueous workup. Similarly, (OEP)SiCl₂ is unreactive toward MeOH, yet **1** reacts rapidly with neat MeOH to give the monosubstituted (TTP)Si(OMe)Cl. The methoxy group in (TTP)Si(OMe)Cl was observed upfield at −2.13 ppm in the ¹H NMR (CD₂Cl₂) due to the magnetic field generated by the porphyrin ring current.

Exchange of the chlorides of **1** with anionic groups is facile (Scheme 1). Both AgBF₄ and SbF₃ react with **1** in CH₂Cl₂ to give difluoride **2** in quantitative yields. Similarly, the reaction of **1** either with neat Me₃SiO₃SCF₃ or with AgO₃SCF₃ in CH₂Cl₂, gave bis(triflate) **3** in high yields. Both **2** and **3** are purple solids, but in contrast to **1**, **2** is unreactive to water even in solution and can be handled with impunity on the benchtop. The reaction of a CD₂Cl₂ solution of **3** with water, however, gave a broad singlet at 4.50 ppm in the ¹H NMR spectrum that indicated an equilibrium between triflic acid and a hydroxyl species, formulated as (TTP)Si(OH)₂ (see Discussion). Evaporation of the resultant solution and redissolving in CD₂Cl₂ gave signals corresponding to **3** and another compound, possibly a disiloxane.

The spectroscopic data for **2** and **3** are consistent with the *trans* configuration. The ¹H NMR spectra (CD₂Cl₂) of **2** and **3** are very similar to the spectrum of **1** with the only differences observed in the pyrrolic region. Compared to the resonances of the pyrrolic hydrogens of **1** (9.03 ppm), an upfield shift was observed for **2** (8.99 ppm) while a downfield shift was observed for **3** (9.14 ppm). In the ¹⁹F NMR spectra (CD₂Cl₂), a singlet at δ −45.9 ppm with ²⁹Si satellites (¹J_{SiF} = 203 Hz) was observed for **2**, and a singlet at δ −4.2 ppm was observed for **3**. The ¹J_{SiF} of **2** is within the observed range for fluorosilanes (170—290 Hz). Both **2** and **3** failed to give an observable ²⁹Si NMR resonance in solution. The reason for this remains unclear, and attempts to obtain solid-state ²⁹Si NMR spectra of **2** and **3** are currently in progress. The *trans* configuration of **3** was confirmed by a single-crystal X-ray diffraction study (*vide infra*).

Structure of (TTP)Si(O₃SCF₃)₂ (3). Dark purple crystals of **3** were grown by slow diffusion of Et₂O vapor into a CH₂Cl₂ solution of **3**. Details of the data collection and refinement parameters for the crystallographic study of **3** are given in Table 1. Pertinent bond distances and bond angles for **3** are presented in Table 2, and the atomic coordinates for **3** are listed in Table 3. A perspective view of **3** with the atom-labeling scheme is shown in Figure 1. This crystallographic study confirms the *trans* configuration of **3**. The geometry around the silicon atom is a distorted octahedron, and the porphyrin ring exhibits a distinct saddle shape. One of the triflate groups, composed of atoms O(5), O(6), S(2), C(50), F(4), F(5), and F(6), was disordered. The four pyrrole nitrogens and the silicon are essentially coplanar with perpendicular displacements of +0.013 Å for N(1) and N(3) and −0.013 Å for N(2) and N(4). The O(1)—Si—O(4) moiety is nearly linear (178°), and the Si—O distances of 1.821 and 1.842 Å are significantly longer than the Si—O distances observed for a number of six-coordinate

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Table 1. Crystallographic Data for (TTP)Si(O₃SCF₃)₂ (**3**)

empirical formula	C₅₀H₃₆F₆N₄O₆S₂Si
fw	995.04
crystal system	orthorhombic
space group	$Pca2_1$ (No. 29)
a, Å	24.740(5)
b, Å	11.940(2)
c, Å	15.514(3)
$\alpha = \beta = \gamma$, deg	90
V, Å³	4583(2)
Z	4
ϱ(calcd), g cm⁻³	1.442
radiation (λ, Å)	Mo Kα (0.710 73)
μ, cm⁻¹	2.23
T, K	293(2)
R1ᵃ	0.0414
wR2ᵇ	0.0729

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $[\Sigma(w_i(F_o^2 - F_c^2)^2)/\Sigma(w_i(F_o^2)^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (TTP)Si(O₃SCF₃)₂ (**3**)

Bond Lengths			
Si—O(1)	1.842(4)	Si—O(4)	1.821(4)
Si—N(1)	1.873(4)	Si—N(2)	1.887(4)
Si—N(3)	1.848(5)	Si—N(4)	1.874(4)
O(1)—S(1)	1.505(4)	O(4)—S(2)	1.414(4)
S(1)—O(2)	1.425(4)	S(1)—O(3)	1.407(4)
S(1)—C(49)	1.822(7)	C(49)—F(1)	1.292(8)

Bond Angles			
O(1)—Si—O(4)	178.0(2)	N(1)—Si—N(3)	178.8(2)
N(2)—Si—N(4)	179.1(2)	N(1)—Si—N(2)	89.5(2)
N(1)—Si—N(4)	90.1(2)	N(2)—Si—N(3)	89.6(2)
N(3)—Si—N(4)	90.8(2)	O(1)—Si—N(1)	88.3(2)
O(1)—Si—N(2)	88.8(2)	O(1)—Si—N(3)	92.5(2)
O(1)—Si—N(4)	90.4(2)	O(1)—S(1)—C(49)	98.9(3)
O(1)—S(1)—O(2)	110.8(2)	O(1)—S(1)—O(3)	114.4(2)

silicon complexes: 1.813, 1.765, and 1.775 Å for [Si-(catecholate)₃]²⁻;[26] 1.779 and 1.785 Å for [(*o*-(Me₂NCH₂)C₆H₄)-Si(catecholate)₂]⁻;[27] 1.763 and 1.766 Å for MeSi(Cl)(8-quinolate)₂.[28] The average Si—N distance of 1.870 Å in **3** is shorter than distances observed in [(*o*-(Me₂NCH₂)C₆H₄)Si(catecholate)₂]⁻ (2.157 Å)[27] and MeSi(Cl)(8-quinolate)₂ (2.015 Å)[28] and is slightly longer than the average Si—N bond distance of 1.820 Å in (Me₃SiO)₂Si(phthalocyanine).[29]

The porphyrin ring adopts a ruffled geometry to accommodate the small silicon atom. This ruffling is most apparent in the displacement of the meso carbons, and the dihedral angles between the pyrrole rings and the pyrrole nitrogen plane. The meso carbons C(5), C(10), C(15), and C(20) are displaced +0.839, −0.824, +0.714, and −0.776 Å, respectively, with respect to the pyrrole nitrogen plane. The acute dihedral angles between the pyrrole rings and the plane of pyrrole nitrogens are 26.2° (N(1)—C(4)), 26.7° (N(2)—C(9)), 24.5° (N(3)—C(14)), and 23.1° (N(4)—C(19)), respectively. Whereas the point group of the molecule approaches C_{2v}, the porphyrin ring has a localized symmetry of D_{2d}, consistent with Hoard's treatment for a contracted macrocycle accommodating a small central atom.[30] This alternating displacement of the meso carbons resulting from the "twist" of the pyrroles is characteristic of a

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for (TTP)Si(O$_3SCF_3$)$_2$ (3)

atom	x	y	z	U(eq)^a	atom	x	y	z	U(eq)^a
Si	3835(1)	11710(1)	7500	38(1)	C(27)	7002(3)	14040(7)	9852(6)	119(3)
S(1)	3640(1)	9569(1)	6394(1)	55(1)	C(28)	4399(2)	11945(5)	4553(4)	50(2)
F(1)	3961(2)	7952(3)	7399(3)	105(2)	C(29)	4186(3)	10073(6)	4096(4)	60(2)
F(2)	3139(2)	8422(3)	7582(3)	88(1)	C(30)	4328(3)	10904(6)	3237(5)	75(2)
F(3)	3360(2)	7493(3)	6466(3)	106(2)	C(31)	4675(3)	11604(7)	2831(4)	69(2)
O(1)	3897(1)	10268(3)	7090(2)	42(1)	C(32)	4877(3)	12490(6)	3278(4)	73(2)
O(2)	4027(2)	9272(4)	5754(3)	82(2)	C(33)	4738(2)	12679(5)	4141(4)	60(2)
O(3)	3123(2)	9934(3)	6140(3)	79(2)	C(34)	4821(3)	11376(8)	1894(4)	101(3)
N(1)	4193(2)	11247(4)	8502(3)	38(1)	C(35)	2009(2)	12915(5)	6921(5)	55(2)
N(2)	4509(2)	12044(4)	6991(3)	39(1)	C(36)	1794(2)	13623(5)	7562(5)	66(2)
N(3)	3492(2)	12194(3)	6510(3)	43(1)	C(37)	1288(2)	14116(5)	7437(7)	89(3)
N(4)	3169(2)	11355(3)	8006(3)	40(1)	C(38)	993(3)	13946(6)	6701(7)	92(3)
C(1)	4014(2)	10514(5)	9121(4)	42(2)	C(39)	1195(3)	13205(6)	6114(6)	84(3)
C(2)	4400(2)	10385(5)	9763(4)	49(2)	C(40)	1697(3)	12689(5)	6206(5)	74(2)
C(3)	4807(2)	11102(5)	9595(4)	51(2)	C(41)	460(3)	14519(7)	6570(8)	153(5)
C(4)	4691(2)	11614(4)	8786(4)	40(2)	C(42)	3359(2)	9217(5)	9799(4)	46(2)
C(5)	5058(2)	12204(4)	8297(4)	44(2)	C(43)	3549(3)	8143(5)	9677(4)	61(2)
C(6)	4987(2)	12264(4)	7410(4)	44(2)	C(44)	3450(3)	7308(5)	10277(5)	75(2)
C(7)	5396(2)	12428(5)	6800(4)	52(2)	C(45)	3170(3)	7516(6)	11025(5)	68(2)
C(8)	5194(2)	12219(5)	6018(4)	55(2)	C(46)	3005(3)	8585(6)	11158(5)	82(2)
C(9)	4625(2)	12031(4)	6119(4)	43(2)	C(47)	3087(3)	9429(5)	10546(5)	70(2)
C(10)	4248(2)	12063(4)	5480(4)	40(2)	C(48)	3055(3)	6592(6)	11658(5)	100(3)
C(11)	3711(2)	12269(5)	5683(4)	43(2)	C(49)	3530(3)	8287(6)	7006(5)	70(2)
C(12)	3320(2)	12736(5)	5115(4)	61(2)	O(4)	3798(1)	13132(3)	7919(3)	50(1)
C(13)	2876(2)	12976(5)	5583(4)	60(2)	S(2)	3654(1)	13899(2)	8575(2)	56(1)
C(14)	2961(2)	12594(4)	6425(4)	45(2)	O(5)	4099(4)	14200(10)	9088(6)	99(4)
C(15)	2565(2)	12431(4)	7056(4)	47(2)	O(6)	3183(4)	13583(9)	8994(6)	110(4)
C(16)	2664(2)	11769(4)	7766(4)	45(2)	C(50)	3556(7)	15132(12)	7922(11)	129(9)
C(17)	2258(2)	11228(5)	8280(4)	56(2)	F(4)	3172(8)	14959(14)	7389(12)	210(10)
C(18)	2507(2)	10493(5)	8803(5)	57(2)	F(5)	3491(8)	15922(12)	8487(12)	223(10)
C(19)	3081(2)	10593(5)	8861(4)	46(2)	F(6)	3972(5)	15443(9)	7470(9)	167(5)
C(20)	3486(2)	10109(4)	9157(4)	44(2)	S(2′)	3965(2)	14295(3)	7874(3)	74(2)
C(21)	5567(2)	12640(5)	8693(4)	50(2)	O(5′)	4049(7)	14558(12)	6984(8)	150(7)
C(22)	6049(3)	12142(6)	8607(5)	85(2)	O(6′)	4398(5)	14620(12)	8431(13)	154(7)
C(23)	6515(3)	12595(6)	8998(5)	91(3)	C(50′)	3372(7)	15019(13)	8214(12)	98(9)
C(24)	6490(3)	13546(6)	9468(5)	68(2)	F(4′)	3259(7)	14634(14)	8996(11)	202(8)
C(25)	5998(3)	13991(7)	9575(6)	111(3)	F(5′)	3377(5)	16093(10)	8301(12)	93(5)
C(26)	5536(3)	13545(7)	9206(6)	100(3)	F(6′)	2995(6)	14680(13)	7640(14)	144(8)

^{a} U(eq) defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.
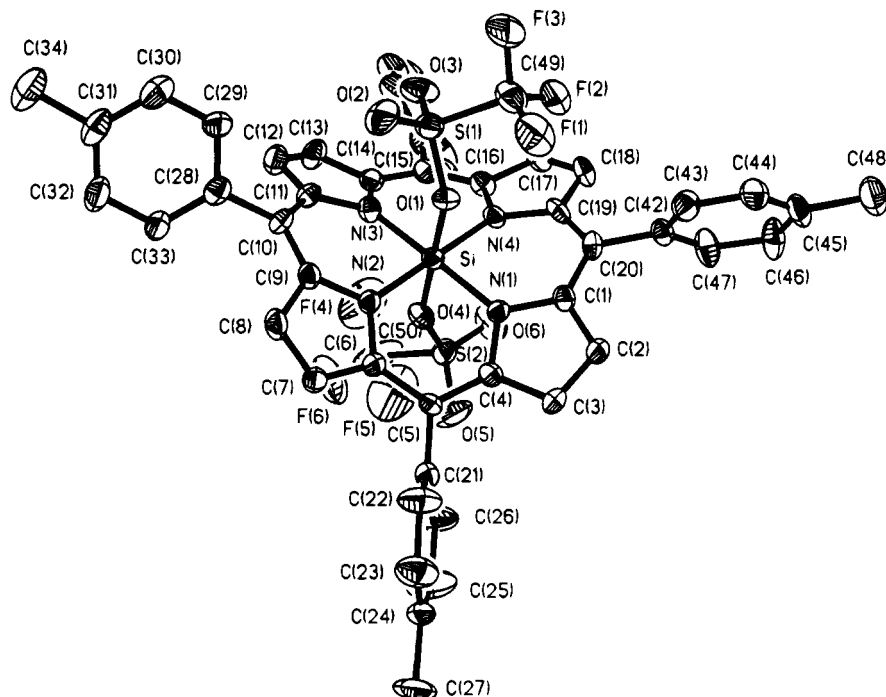

Figure 1. Perspective view of the molecular structure of **3** with atom labels provided for all non-hydrogen atoms except those of the p-tolyl substituent that contains carbon atoms C(35)−C(41). The thermal ellipsoids are scaled to enclose 30% probability.

ruf nonplanar porphyrin, according to Scheidt's formalism.[31] Further evidence for the severe porphyrin ring contraction in **3**

is the angles centered on the meso carbons, which average 120.1°. For comparison, the average meso carbon angles in

the planar porphyrin complex (TPP)SnCl₂[32] and the two ruffled porphyrin complexes (OEP)Ni[33,34] and [(TPP)P(OH)₂]OH[35] are 126.9, 124.1, and 120.5°, respectively. In the case of **3**, the ruffling is restricted to distortions at the meso carbons, as the pyrrole rings are planar.

Discussion

Preparation of (TTP)SiX₂ (X = Cl, F, O₃SCF₃). Treatment of (TTP)²⁻ with HSiXCl₂ (X = Cl, H) proves to be a facile method for forming the previously unknown (porphyrinato)-silicon(IV) complex **1**. The spectroscopic and elemental analyses strongly suggest that LiH and LiX are the byproducts of this salt-elimination reaction. Use of other hydrochlorosilanes, such as MeSiHCl₂ and Me₂SiHCl, yields the corresponding (porphyrinato)silicon(IV) complexes: (TTP)SiMeCl and (TTP)SiMe₂.[23] Chlorosilanes (*e.g.* SiCl₄, MeSiCl₃, Me₂SiCl₂, PhSiCl₃), on the other hand, exhibit very little reactivity with (TTP)²⁻. This observed difference in reactivities between chlorosilanes and the corresponding hydrochlorosilanes (*i.e.* SiCl₄ and HSiCl₃) is consistent with other reports. Cowley *et al.* reported that Cp*SiHCl₂ reacted completely with Me₂NH to yield Cp*SiH(NMe₂)₂, whereas under similar conditions Cp*SiCl₃ was only partially aminated.[36] Recently, we reported that the relative reactivity of Cp(PMe₃)₂RuH with hydrosilanes is greater than its reactivity with the corresponding chlorosilane; observed reactivity ratios were (HSiCl₃):(SiCl₄) = 3 and (MeSiHCl₂):(MeSiCl₃) = 100.[37] This increase in reactivity for the hydrochlorosilanes has been attributed to a decrease in sterics around silicon. However, since hydride is the preferred leaving group in the reaction of (TTP)²⁻ with hydrochlorosilanes, sterics may not be the only controlling factor. This preference for LiH elimination is currently under investigation, and a mechanism for the formation of **1** from (TTP)²⁻ and HSiXCl₂ (X = H, Cl) will be described in a forthcoming publication.

Complex **1** readily undergoes halogen exchange reactions with SbF₃ (or AgBF₄) and Me₃SiO₃SCF₃ (or AgO₃SCF₃) to give difluoride **2** and bis(triflate) **3**, respectively. The difference in reactivity of **1** compared to **2** and (OEP)SiCl₂ is noteworthy. Compound **2** is unreactive with water, whereas **1** is very sensitive to water and readily forms protonated porphyrin **4** (Scheme 1). This reactivity is consistent with the silicon—element bond strengths where Si—Cl is the weakest and Si—F the strongest: Si—Cl (109 kcal/mol) and Si—F (129 kcal/mol).[38] (OEP)SiCl₂ has been reported to be stable to hydrolysis.[11] The difference in hydrolytic stability between **1** and (OEP)SiCl₂ is attributed to an electronic difference between the (OEP)²⁻ and (TTP)²⁻ ligands as opposed to a structural difference. The possibility of (OEP)²⁻ adopting a different structural configuration around silicon compared to (TTP)²⁻ is not reasonable, given that the structural parameters of (TPP)SnCl₂[32] and (OEP)-SnCl₂[39] are virtually identical. On the other hand, the greater

electron-donating ability of (OEP)²⁻ over (TTP)²⁻ has been documented[40,41] and would render the silicon atom in (OEP)-SiCl₂ less electrophilic. The structure and reactivity of (OEP)-SiCl₂ and its derivatives are currently under investigation.

Bis(triflate) **3** is also water-sensitive, but present data indicate that Si—OH species are generated instead of [(TTP)H₄]²⁺. The broad resonance observed at 4.50 ppm in the ¹H NMR spectrum of a CD₂Cl₂ solution of **3** and excess water is assigned to an equilibrium between triflic acid (8.92 ppm) and (TTP)Si(OH)₂. The ¹⁹F NMR spectrum of this mixture showed two signals at −2.67 and −3.93 ppm (2:3 ratio) that became a single resonance at −2.96 ppm upon addition of excess Et₃N. After removing the volatiles and redissolving in CD₂Cl₂, we observed only a singlet at −2.96 ppm (assigned to [Et₃NH][OTf], confirmed with an authentic sample). The ¹H NMR showed signals assigned to [Et₃NH][OTf] and a new porphyrin species with a sharp singlet at −2.99 ppm that we formulate as (TTP)Si(OH)₂.[23]

Comparison of (TTP)Si(O₃SCF₃)₂ (3) with Other Main-Group Porphyrin Complexes. Although few crystal structures of main-group metalloporphyrins have been reported, it is still possible to compare the structure of **3** with analogous group 14 and second-row element porphyrin complexes. Tin(IV) met-alloporphyrins are invariably planar molecules; despite the large size of the metal atom, it is still small enough to fit in the core of the porphyrin. On the other hand, structural studies of germanium porphyrins have revealed that both planar and nonplanar conformations exist, as germanium is small enough to induce deformation of the macrocycle, but the steric and electronic requirements of the axial ligands may limit this ruffling. Nonplanar porphyrins have been the subject of increasing study[42-45] because of the effects on the reactivity of the central atom and the porphyrin that these distortions cause. It is clear that the porphyrin moiety is a rather flexible ligand, and the ability to present nonplanar conformations has been attributed to the catalytic activity[46] of some metalloporphyrins.

Table 4 presents selected bond distance and bond angle data for **3** and several main-group metalloporphyrins.[13,15,35,47] It is immediately clear from the data that the size of the central atom has a significant effect on the planarity of the porphyrin ligand. Silicon and phosphorus have similar M—N distances, and these metalloporphyrins exhibit a highly ruffled shape because of the small size of the central atom. A recent report on the X-ray structural characterization of the (porphyrinato)phosphorus complex [(TPP)P(OCH₂CH₂CH₂OH)₂]OH also showed that the porphyrin has a ruffled conformation.[48]

Within group 14, an increase in the size of the metal decreases the ruffling of the porphyrin with respect to the N₄ plane. Since the pyrroles remain essentially unchanged (planar), deformation of the porphyrin occurs at the meso carbons. The most noticeable changes are seen in the *trans* N—N, M—Cₘ, and *trans*

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Table 4. Selected Structural Data for Main-Group Metalloporphyrins

	3	[(TPP)P(OH)₂]⁺ ᵃ	(OEP)GeF₂ ᵇ	(Porph)Ge(OMe)₂ ᶜ	[(TPP)Sn(H₂O)₂]²⁺ ᵈ
		*Average Distances*ᵉ (Å)			
M−N	1.87	1.89	1.97	2.01	2.06
M−C_m	3.32	3.32	3.38	3.41	3.41
M−L	1.83	1.64, 1.55	1.79	1.82	2.16
N−N (*trans*)	3.74	3.78	3.97	4.03	4.24
C_m−C_m (*trans*)	6.46	6.44	6.70	6.82	6.82
dev of C_m from N₄ plane	±0.79	±0.83	±0.44	planar	planar
		*Average Bond Angles*ᵉ (deg)			
N−M−N	90.0	89.8	90.0	92.8	90.0
C_α−C_m−C_α	120.1	120.5	125.5	126.3	130.3
C_α−N−C_α	106.0	107.5	106.3	106.6	107.0
dihedral angle of pyrroles	25.1	26.6	19.8	planar	planar

ᵃ As the hydroxide salt; ref 36. ᵇ Reference 13. ᶜ Reference 15. ᵈ As the triflate salt; ref 45. ᵉ L = axial ligand; C_m = meso carbon; C_α = pyrrole α carbon.

C_m−C_m distances, which all gradually increase to a maximum in the planar germanium and tin porphyrins. In addition, as the metal size is increased, the axial displacements of the pyrrolic nitrogens decrease, as do the dihedral angles of the pyrroles with respect to the N₄ plane.

Evidence that germanium is "on the cusp'" in terms of planarity of metalloporphyrins is apparent when the planar (Porph)Ge(OMe)₂ and the nonplanar (OEP)GeF₂ are compared. Of the structural parameters listed in Table 4, the greatest difference is seen in the *trans* C_m−C_m distances of the two compounds. The planar germanium porphyrin has a C_m−C_m distance equal to that of the tin complex (6.82 Å) whereas the nonplanar (OEP)GeF₂ has a C_m−C_m distance of 6.70 Å. Moreover, the angle at the meso carbon (C_α−C_m−C_α) of all of the complexes gradually increases from 120 to 130° as the central atom becomes larger and the metalloporphyrin becomes planar.

Finally, the comparison of the structure of **3** to that of (TPP)-Sn(OTf)₂ is noteworthy. Arnold and co-workers reported that this compound was actually the diaquo complex [(TPP)Sn-(OH₂)₂](OTf)₂ and that the triflates were disordered in the unit cell with reasonably close O−O contacts.⁴⁷ Ostensibly, [(TPP)-Sn(OH₂)₂](OTf)₂ is a stannyl (2+) cationic complex. Given the disorder observed for one of the triflates in the structure of **3** and the ease with which triflate is displaced when **3** is reacted with water, there exists the possibility of generating silyl cations from (porphyrinato)silicon compounds. Investigations into (porphyrinato)silicon cation formation are currently underway.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive compounds were carried out either under an atmosphere of argon by using Schlenk or vacuum-line techniques or under a helium/argon atmosphere in a Vacuum Atmospheres drybox.⁴⁹ ¹H NMR (400 and 250 MHz) and ¹⁹F NMR (376 and 235 MHz) spectra were recorded on a Varian VXR 400S and a Bruker AC-250 spectrometer, respectively, at 295 K. ²⁹Si NMR (79.5 MHz) spectra were recorded on a Varian VXR 400S spectrometer at 295 K. The ¹H chemical shifts were referenced to the residual proton peak of the solvent: C₆D₅H, δ 7.15; CDHCl₂, δ 5.32. The ¹⁹F chemical shifts were referenced to external CF₃CO₂H (δ 0.00). The ²⁹Si chemical shifts were referenced to external SiMe₄ (δ 0.00). Infrared spectra were recorded on a Perkin Elmer FT1600 spectrophotometer. UV−vis spectra were recorded on a Cary 16 spectrophotometer controlled using OLIS software. Elemental analyses were carried out by Oneida Research Services or Galbraith Laboratory.

Materials. Tetra-*p*-tolylporphyrin, (TTP)H₂, was prepared according to the literature method⁵⁰ and purified prior to use.⁵¹ Anhydrous diethyl ether was stored over [Cp₂TiCl]₂ZnCl₂⁵² and vacuum-transferred immediately prior to use. Dichloromethane was distilled from and stored over CaH₂ and vacuum-transferred immediately prior to use. Tetrahydrofuran was distilled from and stored over potassium/benzophenone and vacuum-transferred immediately prior to use. Toluene was distilled from potassium/benzophenone and stored over [Cp₂-TiCl]₂ZnCl₂ *in vacuo*. Methanol was dried and stored over fresh magnesium turnings and vacuum-transferred immediately prior to use. Benzene-*d₆* was dried over NaK and stored over [Cp₂TiCl]₂ZnCl₂. Dichloromethane-*d₂* was dried over P₂O₅ and stored over CaH₂. Lithium bis(trimethylsilyl)amide was sublimed prior to use. Silanes were stirred for 24 h with K₂CO₃, transferred to bulbs containing fresh K₂CO₃, and degassed with at least three freeze−pump−thaw cycles. Trimethylsilyl triflate was stored and transferred under vacuum. All other materials were used as received.

(TTP)SiCl₂ (1). Tetrahydrofuran (50 mL) was condensed into an evacuated flask containing (TTP)H₂ (0.50 g, 0.75 mmol), LiN(SiMe₃)₂ (0.29 g, 1.73 mmol), and a stirbar. The flask was sealed, and the mixture was heated to 60 °C for 12 h to yield a green solution, which was then evaporated to dryness. Methylene chloride (20 mL) was condensed into the flask (−78 °C), followed by HSiCl₃ (0.15 g, 1.12 mmol). The mixture was stirred and allowed to warm slowly to room temperature. The solution was heated at 40 °C for 30 min and then evaporated to dryness. The solid was extracted with methylene chloride (50 mL), and the extract was filtered through Celite to yield a dark, blue-green filtrate. Evaporation of the filtrate followed by drying under vacuum gave **1** as an analytically pure, powdery purple solid (0.57 g, 99%). ¹H NMR (CD₂Cl₂): δ 9.03 (s, 8H, pyrrole β), 7.98 (d, 8H, *J*_HH = 8.0 Hz, C₆H₄CH₃), 7.56 (d, 8H, *J*_HH = 8.0 Hz, C₆H₄CH₃), 2.65 (s, 12H, C₆H₄C*H₃*). ²⁹Si NMR (CD₂Cl₂): δ −217 (s). UV−vis (CH₂-Cl₂; λ_max (log ε)): 420 (5.53), 508 (3.46), 550 (4.04), 591 (3.66) nm. Anal. Calcd for C₄₈H₃₆N₄Cl₂Si: C, 75.09; H, 4.73; N, 7.30. Found: C, 74.59; H, 4.83; N, 7.30.

Miscellaneous Methods. Compound **1** was also prepared in identical fashion by the reaction of HSiCl₃ with the Na and K salts of (TTP)²⁻, which were prepared according to published procedures.²² Reactions employing crown ethers were also similar in technique; an example is as follows: To a solution of **5** (207 mg, 0.25 mmol) was added 12-crown-4 (100 μL, 0.83 mmol), and the mixture was stirred for 15 min and then cooled to −78 °C. The flask was evacuated, HSiCl₃ (0.34 mmol) was added under vacuum, and the mixture was stirred for another 20 min. After warming to room temperature and removal of the volatiles, the reaction mixture was worked up as before. Yield: 175 mg of **1** (90%).

(TTP)SiF₂ (2). Method A. Methylene chloride (20 mL) was condensed into an evacuated flask containing **1** (100 mg, 0.13 mmol) and SbF₃ (50 mg, 0.28 mmol). The mixture was heated at 50 °C for 6 h, cooled, and then filtered through Celite. The wine-red filtrate

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was evaporated to dryness to yield **2** as a powdery purple solid (75 mg, 82% yield). Analytically pure **2** was obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution; the resulting iridescent prisms crumbled upon drying.

Method B. Methylene chloride (25 mL) was added to a flask containing (TTP)SiCl₂ (100 mg, 0.13 mmol) and AgBF₄ (52 mg, 0.27 mmol). The mixture was stirred for 2 h at room temperature the filtered through Celite. The wine-colored filtrate was evaporated to dryness to yield **2** (68 mg, 60% yield). ¹H NMR (CD₂Cl₂): δ 8.99 (s, 8H, pyrrole β), 7.99 (d, 8H, J_{HH} = 8.4 Hz, C₆H₄CH₃), 7.56 (d, 8H, J_{HH} = 8.4 Hz, C₆H₄CH₃), 2.66 (s, 12H, C₆H₄C*H*₃). ¹⁹F NMR (CD₂Cl₂): δ − 45.1 (s, J_{SiF} = 203 Hz). UV−vis (CH₂Cl₂; λ_{max} (log ϵ)): 412 (5.51), 447 (3.91), 546 (4.14), 587 (3.60) nm. Anal. Calcd for C₄₈H₃₆N₄F₂-Si: C, 78.45; H, 4.94; N, 7.62; F, 5.17. Found: C, 78.34; H, 4.58; N, 7.19; F, 4.92.

(TTP)Si(O₃SCF₃)₂ (3). Method A. Trimethylsilyl triflate (5 mL) was condensed into an evacuated flask containing **1** (0.30 g, 0.40 mmol). The flask was sealed and heated at 65 °C for 4 h. The reaction volatiles were removed under vacuum, and the solid was vacuum-dried. The solid was then rinsed with pentane on a glass frit and vacuum-dried to yield **3** as a purple crystalline solid (0.38 g, 98%).

Method B. Methylene chloride (35 mL) was added to a flask containing (TTP)SiCl₂ (250 mg, 0.33 mmol) and AgO₃SCF₃ (210 mg, 0.81 mmol). The mixture was stirred for 2 h and then filtered through Celite. The deep red filtrate was evaporated to dryness to yield **3** (271 mg, 82%). ¹H NMR (CD₂Cl₂): δ 9.14 (s, 8H, pyrrole β), 8.00 (d, 8H, J_{HH} = 8.0 Hz, C₆H₄CH₃), 7.57 (d, 8H, J_{HH} = 8.0 Hz, C₆H₄CH₃), 2.65 (s, 12H, C₆H₄C*H*₃). ¹⁹F NMR (CD₂Cl₂): δ − 4.2 (s). IR (KBr): ν-(S−O) 1361 cm⁻¹. UV−vis (CH₂Cl₂; λ_{max} (log ϵ)): 420 (5.74), 546 (4.32), 591 (3.82) nm.

[(OEP)H₄]Cl₂. According to the method of Gouterman *et al.* for the preparation of (OEP)SiCl₂,[11] (OEP)H₂ (534 mg, 1.0 mmol) and pyridine (30 mL) were placed in a reaction bulb, frozen, and degassed twice. Silicon tetrachloride (1.5 mL, 12.6 mmol) was added by vacuum transfer, and the mixture was warmed and then heated to 180 °C under stirring for 25 h. After cooling, the contents were poured into 500 mL of water with vigorous stirring. The mixture was extracted with CH₂-Cl₂ (3 × 150 mL), and the combined extracts were washed with 1 M HCl until no odor of pyridine was detected. The solution was evaporated to dryness, the solid was redissolved in 25 mL of boiling CH₂Cl₂, and the solution was cooled, and covered with 10 mL of dry hexanes. Yield: 410 mg (67%) of shiny purple microcrystals. ¹H NMR (CDCl₃): δ 10.51 (s, 4H, CH), 4.05 (q, 16H, $^3J_{HH}$ = 7.8 Hz, CH₂), 2.04 (t, 24H, $^3J_{HH}$ = 7.8 Hz, CH₃), −1.90 (br s, 4 H, NH). Anal. Calcd for C₃₆H₄₈N₄Cl₂: C, 71.15; H, 7.96; N, 9.22. Found: C, 70.99; H, 7.84; N 9.23.

X-ray Crystallographic Analysis of (TTP)Si(O₃SCF₃)₂ (3). Crystals of **3** were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution. A dark purple crystal of approximate dimensions of 0.18 × 0.30 × 0.40 mm was sealed in a glass capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The corresponding lattice parameters and orientation matrix for the orthorhombic unit cell were determined from a least-squares fit of the orientation angles of 32 reflections at 22 °C. The systematic absences of {0*kl*}, *l* = 2*n* + 1, and {*h*0*l*}, *h* = 2*n* + 1, are consistent with the noncentrosymmetric space group *Pca*2₁ (No. 29) and with *Pcam*, a nonstandard setting of the centrosymmetric space group *Pbcm* (No. 57). The former was determined to be correct on the basis of the structure solution and refinement.

Intensity data were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and variable ω scans. Background counts

were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections. A total of 6856 reflections were collected (−1 ≤ *h* ≤ 26, −12 ≤ *k* ≤ 12, −1 ≤ *l* ≤ 16) in the range 1.65° < θ < 22.49° with 3390 being unique (R_{int} = 4.67%). No evidence of crystal decay was observed. The data were corrected for Lorentz−polarization effects. An empirical absorption correction (μ = 2.23 cm⁻¹) was based upon the ψ scans of eight reflections with χ ∼ 90°.

The structure solution was accomplished using the direct methods program available with the SHELXTL structure solution software. The initial *E* map revealed the positions of nearly all of the non-hydrogen atoms, with the exception of those of one of the triflate ligands which was determined to be disordered. This disorder was refined by using a two-site model with atoms O(5), O(6), S, C(50), F(4), F(5), and F(6) assigned to one site and O(5′), O(6′), S′, C(50′), F(4′), F(5′), and F(6′) to the other. During the subsequent refinement cycles the S=O, S−C, and C−F bond distances of the disordered fragment were restrained to 1.43 ± 0.02, 1.80 ± 0.02, and 1.32 ± 0.02 Å, respectively. The occupancy factor was refined to a value of 0.566(3) for the site containing the unprimed atoms O(5), O(6), S, C(50), F(4), F(5), and F(6). Idealized positions for all of the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i |F_o^2 − F_c^2|^2$, with w_i^{-1} = $[\sigma^2(F_o^2) + (0.062P)^2]$ where P = (Max(F_o^2,0) + 2F_c^2)/3, was performed with SHELXL-93[53] operating on a Silicon Graphics IRIS Indigo workstation. After convergence, the final discrepancy indices[54] were R1 = 0.0414, wR2 = 0.0729, and GOF = 1.044 for 2358 reflections with $I > 2\sigma(I)$. A final difference electron density map did not reveal any significant residuals of electron density.

Supporting Information Available: Complete listings of crystallographic data, bond lengths and angles, thermal parameters, and atomic parameters of hydrogen atoms for **3** (8 pages). Ordering information is given on any current masthead page.

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(53) SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077 Göttingen, Germany) for single-crystal X-ray structural analyses.

(54) The discrepancy indices were calculated from the expressions R1 = $\sum ||F_o| − |F_c||/\sum |F_o|$ and wR2 = $[\sum (w_i(F_o^2 − F_c^2)^2)/\sum (w_i(F_o^2)^2)]^{1/2}$, and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum (w_i(F_o^2 − F_c^2)^2)/(n − p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.