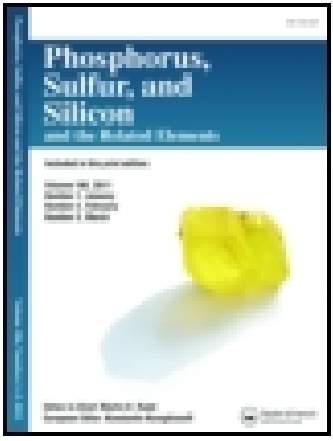

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Discrete Spirobicyclic Silicate Anions with SiO_2N_2C, SiN_2S_2C and SiO_4C Frameworks

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*Bis(2-aminobenzoato)phenylsilicate (**1**), bis(2-aminothiophenoxy)phenylsilicate (**2**), and bis(2-hydroxybenzoato) phenylsilicate (**3**) anions were obtained as their triethylammonium salts from the reactions of phenylsilane with appropriate ligands in the presence of triethylamine. The compounds were characterized by IR, multinuclear (^1H, ^{13}C, and ^{29}Si) NMR, and FAB mass spectral data. Th X-ray crystal structure of **1**.CH_2Cl_2 revealed slightly distorted trigonal bipyramidal geometry around silicon. The spirobicyclic silicate anions are the first examples with silicon-heteroatom linkages having six-membered (**1**) and five-membered (**2**) rings on silicon.*

Keywords Discrete silicate; heteroatom; spirobicyclic

INTRODUCTION

Ionic complexes have assumed a special place among hypervalent silicon compounds. Besides unique chemical features,[1] developments relating to new structural varieties of these silicates have also come to light.[2–5] Cationic complexes were known for a long time,[6] although

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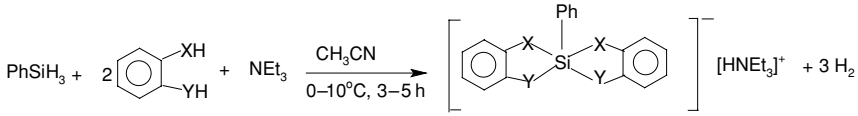
the authors have demonstrated their use as precursors to hexacoordinate bicyclic silicate dianions.[7] The authors have reported earlier penta and hexacoordinate silicate anions with SiO_4N and SiO_4N_2 skeletons, respectively, where silicon–nitrogen linkage was derived from acyclic substituent(s).[8] Although Pframmer and Tacke,[9] Bertermann et al.,[10] and Seiler et al.[11] have reported many zwitterionic silicates with nitrogen and sulfur atoms in a spirosilicate framework, discrete silicate anions with silicon-heteroatom linkages are not known. The present communication reports the preparation and structure elucidation of pentacoordinate silicates with a SiO_2N_2C, SiS_2N_2C, and SiO_4C framework. These complexes incorporate six-membered (1, 3) and five-membered (2) ring systems on silicon atoms. The details are reported in this article.

RESULTS AND DISCUSSION

Compounds **1–3** were prepared by a single step reaction between phenylsilane and an appropriate ligand in the presence of triethyl amine at 0 to 10°C (Scheme 1).



Y= NH, X= C(O)O (**1**)
Y= NH, X= S (**2**)
Y= O, X= C(O)O (**3**)

SCHEME 1

Effervescence on the addition of phenylsilane to the other reactants indicated progress of the reaction and the evolution of hydrogen. **1** was precipitated out from the reaction mixture, while **2** and **3** were isolated after work-up of the reaction mixture using diethyl ether. All these complexes were soluble in dichloromethane, chloroform, methanol, and DMSO. Elemental analyses and molar conductance (see the Experimental section) of these compounds suggest the composition and formula as assigned.

Spectral Studies

IR spectra of **1** and **3** revealed νCO (carboxylate) absorptions due to benzoate groups at 1641 and 1634 cm^{-1}, respectively. These absorptions were shifted by 40–50 cm^{-1} toward lower frequency compared to those

of free acids, suggesting attachment of the ligands to silicon. νNH vibrations were observed at 3110 cm^{-1} in spectra of **1** and **2**. νSi-Ph absorption was identified at 1119–1130 cm^{-1} in the spectra of all three complexes. Absorption bands at 2703–2657 cm^{-1} were due to quarternization of nitrogen in a triethyl ammonium cation.

^{1}H NMR spectra of **1–3** depicted signals for aromatic and triethyl ammonium protons in a desired intensity ratioed as expected for the composition assigned (see the Experimental section). ^{13}C NMR spectra revealed signals due to phenyl and bidentate ligands besides those due to the cation (see the Experimental section). Only one set of signals was observed for the two substituents (C_6H_4XY) forming the spirocyclic framework around silicon, thus suggesting their equivalent position. ^{29}Si NMR spectra revealed a sharp single peak in each case at −112.5, −49.8, and −121.0 ppm for **1**, **2**, and **3**, respectively, and are suggestive of pentacoordination around the silicon atom. These chemical shift values are within the range for the respective complexes.

Attempts to obtain good quality crystals for **1** were successful, while for **2** and **3**, attempts failed. FAB mass spectral data have been frequently used for the elucidation of bonding in ionic compounds. Selected FAB mass spectral data of **1–3** are given in Table I. The anion of **1** was identified from a peak at m/z 375 in the negative ion mode. Similarly, the spectra of **2** and **3** exhibited peaks in the negative ion mode corresponding to an anion/anionic cluster/fragmented anion. The spectra of **1–3** in positive ion mode depicted a peak at m/z 102, thus identifying cation $[HNEt_3]^+$ in each case.

X-ray Crystal Structure of 1.CH_2Cl_2

X-ray quality crystals were grown by refrigerating a solution of **1** in dry CH_2Cl_2. The atomic coordinates, selected bond lengths, and bond angles are recorded in Tables II and III, respectively. The crystal system

TABLE I Selected FAB Mass Spectral Data (in 3-nitrobenzyl alcohol [NBA]) of 1–3

	Positive Ion Mode		Negative Ion Mode	
Compound	(m/z)	Assignment	(m/z)	Assignment
1	102	$[HNEt_3]^+$	375	$[(C_6H_4(COO)NH)_2SiPh]^-$
	255	$[HNEt_3]^+$. NBA	528	$[(C_6H_4(COO)NH)_2SiPh]^-$.NBA
	102	$[HNEt_3]^+$	351	$[(C_6H_4(S)NH)_2SiPh]^-$
2	228	$[HNEt_3]^+.C_6H_4NH_2SH$	459	$[(C_6H_4(S)NH)_2SiPh]^-.C_6H_5CH_2OH$
			504	$[(C_6H_4(S)NH)_2SiPh]^-$.NBA
3	102	$[HNEt_3]^+$	581	$[(C_6H_4(COO)O)_2SiPh]^-$.2NBA

TABLE II Crystal Data and Structure Refinement

Empirical formula	$C_{27}H_{33}Cl_2N_3O_4Si$
Formula weight	562.55
Temperature	173 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$(No. 2, Ci^1)
Unit cell dimensions	a = 11.259 (2) Å; alpha = 77.506 (4)°;
	b = 11.473 (2) Å; beta = 76.646 (4)°;
	c = 23.589 (5) Å; gamma = 70.883 (4)°;
Volume, z	2768.3 (10) $Å^3$, 4
Density (calculated)	1.350 Mg/m^3
Absorption coefficient	0.316 mm^{-1}
F (000)	1184
Crystal size	0.36 × 0.32 × 0.24 mm
θ range for data collection	0.90–25.00°
Limiting indices	$-13 \le h \le 13$, $-13 \le k \le 13$, $-28 \le l \le 27$
Reflections collected	20,545
Independent reflections	9717 (R_{int} = 0.0364)
Completeness to θ = 25.000	99.5%
Absorption correction	Empirical
Max. and min. transmission	0.9280 and 0.8948
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9717/0/740
Goodness-of-fit on F^2	1.126
Final R indices [1 > 2σ(I)]	R l = 0.0630, wR2 = 0.1472
R indices (all data)	R l = 0.0788, wR2 = 0.1551
Largest diff. peak and hole	0.415 and -0.317 e $Å^{-3}$

R l = (Σ ‖‖F_o ‖ − ‖ F_c ‖ ‖ / Σ ‖ Fo‖), wR2 = Σw (F_0^2 -F_c^2)^2 / Σw[(F_0^2)^2]$^{1/2}$, s = [Σw(F_0^2 -F_c^2)^2 / (n-p)]$^{1/2}$

is triclinic with the $P\bar{1}$($2Ci^1$) space group. The unit cell dimensions are a = 11.259 (2), b = 11.473 (2), c = 23.589 (2) Å, and α = 77.506°, β = 76.646(4)°, γ =70.883 (4)° with Z = 4. The atomic labeling scheme is shown in the ORTEP plot (Figure 1).

Figure 1 clearly depicts the presence of two similar but crystallographically independent anions with their cations Et_3NH^+ and a solvent molecule (CH_2Cl_2) each in a unit cell. Thus, the compound seems to exist as solvate **1**.CH_2Cl_2 in the crystal. (For the sake of clarity, the anions have been designated as A and B in the figure and data for both the molecules that are given. A marginal difference in the bond parameters of the two anions was observed, thus giving them a separate identity [Table III]). A silicon coordination polyhedron was observed as a slightly distorted trigonal bipyramid with each of the axial positions occupied by oxygen atoms. The two nitrogen atoms and the phenyl group were at equatorial positions. Si—N bond lengths in both

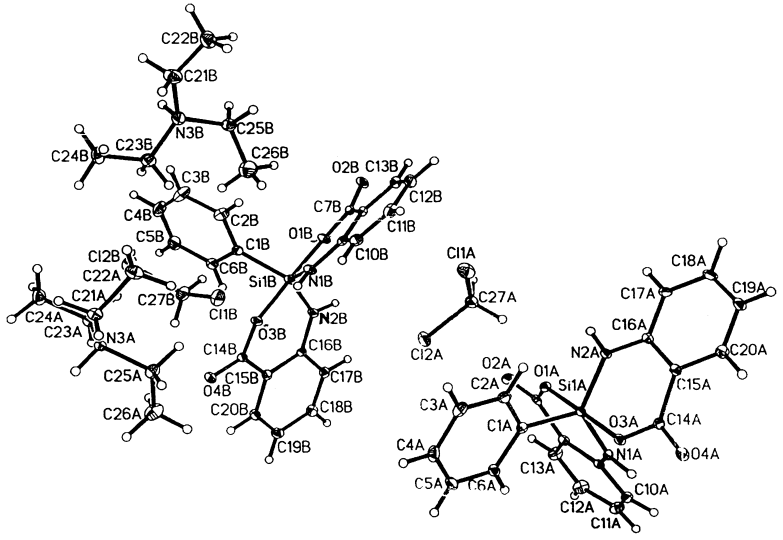


FIGURE 1 Crystal structure of $1.CH_2Cl_2$ (ORTEP plot with probability level 30%), showing atomic labeling scheme. The two crystallographically independent molecules presented in a single crystal are shown with the solvent (CH_2Cl_2) molecules.

anions fell in the range 1.730(3)–1.744(3) Å, and all Si—O bond lengths were observed between 1.796(2) and 1.838(2) Å. ∠NSiN were 122.44(13)° and 125.24(15)°, and ∠NSiO fell in the range 85.71(12)°–92.71(11)°, while ∠OSiO were 179.05(11)° and 176.73(12)° (Table III). The bond parameters are comparable to similar zwitterionic silicates incorporating five-membered rings around silicon.[4] In spite of the presence

TABLE III Selected Bond Lengths (Å) and Bond Angles (°) of 1

Si (1A)-N (1A)	1.730 (3)	Si (1B)-N (1B)	1.742 (3)
Si (1A)-N (2A)	1.744 (3)	Si (1B)-N (2B)	1.732 (3)
Si (1A)-O (1A)	1.796 (2)	Si (1B)-O (1B)	1.809 (2)
Si (1A)-O (3A)	1.838 (2)	Si (1B)-O (3B)	1.804 (2)
Si (1A)-C (1A)	1.875 (3)	Si (1B)-C (1B)	1.876 (4)
N (1A)-Si (1A)-N (2A)	122.44 (13)	N (1B)-Si (1B)-N (2B)	125.24 (15)
N (1A)-Si (1A)-O (1A)	92.71 (11)	N (1B)-Si (1B)-O (1B)	91.59 (12)
N (1A)-Si (1A)-O (3A)	86.47 (12)	N (1B)-Si (1B)-O (3B)	85.71 (12)
N (2A)-Si (1A)-O (1A)	88.39 (12)	N (2B)-Si (1B)-O (1B)	88.06 (12)
N (2A)-Si (1A)-O (3A)	91.64 (11)	N (2B)-Si (1B)-O (3B)	91.99 (12)
N (1A)-Si (1A)-C (1A)	120.18 (14)	N (1B)-Si (1B)-C (1B)	116.58 (15)
N (2A)-Si (1A)-C (1A)	117.29 (14)	N (2B)-Si (1B)-C (1B)	118.17 (15)
O (1A)-Si (1A)-O (3A)	179.05 (11)	O (1B)-Si (1B)-O (3B)	176.73 (12)
O (1A)-Si (1A)-C (1A)	91.73 (12)	O (1B)-Si (1B)-C (1B)	91.42 (13)
O (3A)-Si (1A)-C (1A)	89.10 (12)	O (3B)-Si (1B)-C (1B)	91.44 (13)

TABLE IV Analysis of Potential Hydrogen Bonds

No.	Donor···H...Acceptor	(ARU)	D—H	H···A	D···A	D—H···A
1	N(1A)—H(1A)···O(3B)	(2666.02)	0.7961	2.3962	3.1627	161.95
2	N(1B)—H(1B)···O(4B)	(2775.02)	0.8065	2.2553	3.0321	161.86
3	N(2A)—H(2A)···O(3B)	(2566.01)	0.8600	2.4614	3.2284	148.87
4	C(6A)—H(6A)···O(3B)	(2666.02)	0.9300	2.5853	3.3901	145.10
5	C(21A)—H(21A)···O(2B)	(2666.01)	0.9700	2.3650	3.2324	148.57
6	C(21B)—H(21C)···O(1B)	(Intra)	0.9700	2.3939	3.0088	120.85
7	C(21B)—H(21D)···O(3B)	(Intra)	0.9700	2.5440	3.3076	135.63

Equivalent position code: (2556) = −x, 1−y, 1−z; (2666) = 1−x, 1−y, 1−z; (2775) = 2−x, 2−y, −z;

For C—H···acceptor interactions, see: Th. Steiner, *Cryst. Rev.*, **6,** 1 (1996).

For H-bond classification, see G. A. Jeffery, H. Maluszynska, and J. Mitra, *Int. J. Biol. Macromol.*, **7,** 336 (1985).

of six-membered rings around silicon in **1**, bond angles were more toward those for ideal trigonal bipyramidal (tbp) geometry [∠N—Si—O 91.64(11), ∠N—Si—C 120.18(14), ∠O—Si—O 179.05 (11), ∠O—Si—C 91.73 (12), ∠O—Si—C 89.10 (12)]. The widest ∠O—Si—O reported for such zwitterions was 177.01°.[4] Bond lengths represented five normal covalent bonds thus justifying the formation of a stable discrete pentacoordinate anion with SiO_2N_2C framework incorporating six-membered rings around silicon. Additional geometric data revealed the involvement of all the oxygen atoms of anion B in inter- and intramolecular hydrogen bonding (Table IV).

Conclusion

The X-ray crystal structure of **1** and spectral data of **1**, **2**, and **3** established the formation of new discrete silicate anions incorporating unsymmetrical ligands with different heteroatoms and ring sizes around a silicon atom.

EXPERIMENTAL

Materials and Analyses

All operations were carried out under a dry nitrogen atmosphere using an all-glass vacuum line. Solvents were dried by refluxing over P_2O_5 (acetonitrile, dichloromethane) or sodium metal (diethyl ether) and were freshly distilled prior to use. Triethyl amine (Merck) was purified by being refluxed over KOH pallets followed by distillation under nitrogen. $PhSiCl_3$ (Aldrich) and $LiAlH_4$(Aldrich) were used as received. $PhSiH_3$ was prepared by the reaction of $PhSiCl_3$ with

$LiAlH_4$in diethylether. o-aminobenzoic acid, o-aminothiophenol, and salicylic acid (o-hydroxybenzoic acid) (Qualigens) were purified by conventional procedures.

Infrared spectra were routinely obtained as thin films or Nujol mulls using KBr plates on FTIR model RX-I. ^{1}H and ^{13}C NMR were recorded on a Bruker 300 Mz instrument, while ^{29}Si NMR spectra were taken on a Bruker (AMX 500) or Jeol 300 MHz instrument. FAB mass spectra were obtained on MAT 95 of a finniganan MAT spectrometer using a 3-nitrobenzyl alcohol (NBA) matrix. C, H, and N analyses were carried out on a Perkin-Elmer Model 2400 CHN elemental analyzer, while Si content was estimated gravimetrically.

X-ray Crystallography

A colorless, block-shaped crystal (0.24 × 0.32 × 0.36 mm) was mounted with the largest dimension, and data were collected with a Bruker SMART APEX diffractometer equipped with a molybdenum sealed tube and a highly oriented graphite monochromator. Frame data were acquired with SMART software using a three-axis stage. The chi axis on this stage was fixed at 54.74°, and the CCD detector was maintained at −40°C. Cell constants were determined from 1200 10s frames at the detector resolution of 512 × 512 pixels. A total of 1800 frames were collected in three sets. The frames were then processed on an IBM-compatible PC using SAINT+ software to give an hkl file corrected by Lp/decay and absorption. There were no systematic absences in the data. Therefore, the space group was assumed and later confirmed by successful refinement of the structure. The structure was solved by direct methods using SHELXTL-PC. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were included in the ideal positions with fixed isotropic U values equal to 1.2 times that of the atom they were attached to. There was no evidence of secondary extinction; therefore it was not applied for. All calculations were done using SMART (data collection), SAINT+ (data reduction), SADABS (absorption correction), and SHELTX-PC.[13]

Preparations

Triethylammonium bis(aminobenzoato)phenylsilicate(1)

$PhSiH_3$ (0.7 g, 0.8 mL, 6.4 mmol) was added dropwise to a solution of aminobenzoic acid (1.7 g, 12.8 mmol) and triethyl amine (0.9 mL, 6.4 mmol) in acetonitrile (35 mL) at 0°C. Effervescence started after the complete addition of $PhSiH_3$, and a white solid was precipitated out. The solution was stirred for 3 h while maintaining the temperature of reactants between 0–10°C. The solution was concentrated

to 70% of its volume. The solid was filtered under reduced pressure, washed first with cold acetonitrile and then with diethylether, and dried under vacuum. Yield: 2.0 g (68%). M.p.: 98°C. Λ_M (Ω^{-1} cm^{2}mol^{-1}, CH_3CN): 81.5. Anal. calcd. for $C_{26}H_{31}N_3O_4Si$: C, 65.40; H, 6.49; N, 8.80; Si, 5.87. Found: C, 64.80; H, 6.02; N, 8.59; Si, 5.79. IR (Nujol, KBr, cm^{-1}): 3110 (νNH), 1638 (νC=O, carboxylate), 1120 (νSi-Ph). δ^1H NMR ($CDCl_3$): 0.9 (t, 9H, CH_3), 2.6 (q, 6H, NCH_2), 7.1, 7.2, 7.4 (2H, 1H, 2H, d, t, t, phenyl ring), 6.6, 6.7, 7.2, 7.9 (2H, 2H, 2H, 2H, d, t, d, t, aminobenzoate rings), 4.8 (br, NH). δ^{13}C NMR ($CDCl_3$): 8.2 (CH_3, triethylammonium), 45.4 (NCH_2, triethylammonium), 126.9 (C1 & C3/C5, Ph), 130.8 (C4), 133.6 (C2/C6, Ph), 113.3 (C1, aminobenzoate), 116.3 (C3, aminobenzoate), 118.1 (C5, aminobenzoate), 131.4 (C6, aminobenzoate), 133.6 (C4, aminobenzoate), 150.2 (C2, aminobenzoate), 168.6 (COO, aminobenzoate). δ^{29}Si NMR ($CDCl_3$): −112.5 ppm.

Triethylammonium bis(2-aminothiophenoxy)phenylsilicate (2)

$PhSiH_3$ (0.4 g, 0.5 mL, 4.0 mmol) was added dropwise to a solution of aminothiophenol (1.0 g, 0.8 mL, 8.0 mmol) and triethyl amine (0.5 mL, 4.0 mmol) in acetonitrile (35 mL) at 0°C. Effervescence started after the complete addition of $PhSiH_3$.The solution was stirred for 4 h while maintaining the temperature of reactants between 0–10°C. Thereafter, the solvent was evaporated, and diethyl ether (25 mL) was added. A white solid was precipitated out after stirring the reaction mixture for 5–6 h. The solid was filtered under reduced pressure, washed with diethylether, and dried under vacuum to isolate **2** as a dirty white solid. Yield: 1.08 g (60%). M.p.: 108°C. Λ_M (Ω^{-1} cm^{2}mol^{-1}, CH_3CN): 64.5. Anal. calcd. for $C_{24}H_{31}N_3S_2Si$: C, 63.57; H, 6.84; N, 9.27; S, 14.12; Si, 6.18. Found: C, 63.20; H, 6.82; N, 9.19; S, 14.00; Si, 6.21. IR (Nujol, KBr, cm^{-1}): 3115 (νNH), 1120 (νSi-Ph), 761 (νC—S). δ^1H NMR ($CDCl_3$): 1.3 (t, 9H, CH_3), 2.8 (q, 6H, NCH_2), 7.0, 7.2, 7.5 (d, t, t, 2H, 1H, 2H phenyl ring), 6.8, 7.4, 7.8, 8.1 (2H, 2H, 2H, 2H, d, d, t, t, aminothiophenoxy rings), 4.4 (br, NH). δ^{13}C NMR ($CDCl_3$): 11.1 (CH_3, triethylammonium), 45.6 (NCH_2, triethylammonium), 128.6 (C1, Ph), 128.9 (C3/C5, Ph), 130.8 (C4), 136.1 (C2/C6, Ph), 114.6 (C3, aminothiophenoxy), 116.8 (C4, aminothiophenoxy), 126.6 (C5, aminothiophenoxy), 133.9 (C6, aminothiophenoxy), 135.5 (C1, aminothiophenoxy), 149.2 (C2, aminothiophenoxy). δ^{29}Si NMR ($CDCl_3$): −49.8 ppm.

Triethylammonium bis(2-hydroxybenzoato)phenylsilicate (3)

$PhSiH_3$ (0.5 g, 0.6 mL, 4.8 mmol) was added dropwise to a solution of o-hydroxybenzoic acid (1.3 g, 9.6 mmol) and triethyl amine (0.6 mL, 4.8 mmol) in acetonitrile (40 mL) at 0–10°C. Effervescence started. The solution was stirred for 4 h at r.t. at 25°C. Thereafter, the

solvent was evaporated, and diethyl ether (25 mL) was added. A white solid was precipitated out. The reaction mixture was stirred for 5–6 h. The solid obtained was filtered under reduced pressure, washed with diethylether, and dried under vacuum. Yield: 1.49 g (65%). m.p.: 125°C. Λ_M (Ω^{-1} cm^{2}mol^{-1}, CH_3CN): 110. Anal. calcd. for $C_{26}H_{29}NO_6Si$: C, 65.10; H, 6.05; N, 2.90; Si, 5.84. Found: C, 64.61; H, 6.07; N, 3.13; Si, 6.01. IR (Nujol, KBr, cm^{-1}): 1634 (νC=O), 1113 (νSi-Ph), 1259, 1243 (νC–O aromatic), 877 (νSi–O). δ^1H NMR ($CDCl_3$): 1.1 (t, 9H, CH_3), 3.0 (q, 6H, NCH_2), 7.1, 7.2, 7.4 (d, t, t, 2H, 1H, 2H phenyl ring), 6.9, 7.9, 8.2, 8.4 (2H, 2H, 2H, 2H, t, t, d, d hydroxybenzoate rings), 4.6 (br, NH). δ^{13}C NMR ($CDCl_3$): 8.2 (CH_3, triethylammonium), 45.4 (NCH_2, triethylammonium), 128.0 (C1, Ph), 129.6 (C3/C5, Ph), 130.4 (C4), 136.4 (C2/C6, Ph), 115.2 (C1, hydroxybenzoate), 116.6 (C3, hydroxybenzoate) 119.2 (C5, hydroxybenzoate), 130.1 (C6, hydroxybenzoate), 134.1 (C4, hydroxybenzoate), 161.4 (C2, hydroxybenzoate), 173.1 (COO, hydroxybenzoate). δ^{29}Si NMR ($CDCl_3$): −121.0 ppm.

REFERENCES

[1] C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, *Chem. Rev*., **93,** 1371 (1993).

[2] R. R. Holmes, *Chem. Rev*., **96,** 927 (1996).

[3] D. Kost and I. Kalikhman, In *Chemistry of Organic Silicon Compounds*, Z. Rapport and Y. Apeloig, eds. Vol. 2, p. 1339 (John Wiley & Sons, Chichester, U.K., 1998).

[4] R. Tacke, M. Pulm, and B. Wagner, *Adv. Organomet. Chem*., **44,** 221 (1999).

[5] D. Kost and I. Kalikhman, *Adv. Organomet. Chem*., **50,** 1 (2001).

[6] D. Kummer and T. Seshadri, *Chem. Ber*., **110,** 2355 (1977), and references cited therein.

[7] (a) S. P. Narula, R. Shankar, M. Kumar, and Meenu, *Inorg. Chem*., **33,** 2716 (1994); (b) S. P. Narula, R. Shankar, Meenu, and R. D. Anand, *Polyhedron,* **18,** 2055 (1999); (c) S. P. Narula, M. Puri, N. Garg, and J. K. Puri, *Main Group Metal Chemistry,* **25,** 655 (2001).

[8] (a) S. P. Narula, R. Shankar, M. Puri, and J. K. Puri, *Phosphorus, Sulfur, and Silicon,* **158**, 1 (2000); (b) S. P. Narula, R. Shankar, and Meenu, *Phosphorus, Sulfur, and Silicon*, **113,** 237 (1996); (c) S. P. Narula, R. Shankar, Meenu, J. K. Puri, and R. D. Anand, *Main Gp. Metal Chem*., **23,** 405 (2000).

[9] E. Breitmaier and W. Voelter, *Carbon-13 NMR spectroscopy*, 3rd ed., p. 261, (VCH, Weinheim, Germany, 1987).

[10] (a) B. Pframmer and R. Tacke, *Eu. J. Inorg. Chem*., 415 (1998); [Au – Pls. provide vol. no.] (b) D. Kost, I. Kalikhman, S. Krivonos, R. Bertermann, C. Burschka, R. E. Neugebauer, et al., *Organometallics*, **10,** 1083 (2000).

[11] R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, and R. Tacke, *Organometallics,* **22,** 4104 (2003).

[12] O. Seiler, M. Buttner, M. Penka, and R. Tacke, *Organometallics*, **24,** 6059 (2005).

[13] (a) SMART (Version 5.624), (Bruker X-ray Analytical Instruments, Madison, WI, 1995), (b) SAINT+ (Version 5.6), (Bruker X-ray Analytical Instruments, Madison, WI, 1995); (c) G. M. Sheldrick, SADABS (Version 2.03), (Bruker X-ray Analytical Instruments, Inc. Madison, WI, 1999); (d) G. M. Sheldrick, SHELXTL-PC (Version 6.0), (Bruker X-ray Analytical Instruments, Madison, WI, 1990).

SUPPLEMENTARY TABLE I Torsional Angles [°]

N(1A)-Si(1A)-O(1A)-C(7A)	11.9(3)	N(2A)-Si(1A)-O(1A)-C(7A)	134.3(3)
O(3A)-Si(1A)-O(1A)-C(7A)	43(7)	C(1A)-Si(1A)-O(1A)-C(7A)	−108.4(3)
N(1A)-Si(1A)-O(3A)-C(14A)	113.7(3)	N(2A)-Si(1A)-O(3A)-C(14A)	−8.7(3)
O(1A)-Si(1A)-O(3A)-C(14A)	83(7)	C(1A)-Si(1A)-O(3A)-C(14A)	−126.0(3)
N(2A)-Si(1A)-N(1A)-C(9A)	−94.7(3)	O(1A)-Si(1A)-N(1A)-C(9A)	−4.9(3)
O(3A)-Si(1A)-N(1A)-C(9A)	175.6(3)	C(1A)-Si(1A)-N(1A)-C(9A)	88.7(3)
N(1A)-Si(1A)-N(2A)-C(16A)	−76.1(3)	O(1A)-Si(1A)-N(2A)-C(16A)	−168.3(3)
O(3A)-Si(1A)-N(2A)-C(16A)	10.7(3)	C(1A)-Si(1A)-N(2A)-C(16A)	100.5(3)
N(1A)-Si(1A)-C(1A)-C(2A)	164.1(2)	N(2A)-Si(1A)-C(1A)-C(2A)	−12.7(3)
O(1A)-Si(1A)-C(1A)-C(2A)	−101.8(3)	O(3A)-Si(1A)-C(1A)-C(2A)	78.7(3)
N(1A)-Si(1A)-C(1A)-C(6A)	−13.8(3)	N(2A)-Si(1A)-C(1A)-C(6A)	169.5(3)
O(1A)-Si(1A)-C(1A)-C(6A)	80.4(3)	O(3A)-Si(1A)-C(1A)-C(6A)	−99.2(3)
C(6A)-C(1A)-C(2A)-C(3A)	0.0(5)	Si(1A)-C(1A)-C(2A)-C(3A)	−178.0(3)
C(1A)-C(2A)-C(3A)-C(4A)	0.7(6)	C(2A)-C(3A)-C(4A)-C(5A)	−0.7(6)
C(3A)-C(4A)-C(5A)-C(6A)	−0.1(6)	C(4A)-C(5A)-C(6A)-C(1A)	0.8(6)
C(2A)-C(1A)-C(6A)-C(5A)	−0.8(5)	Si(1A)-C(1A)-C(6A)-C(5A)	177.1(3)
Si(1A)-O(1A)-C(7A)-O(2A)	172.4(2)	Si(1A)-O(1A)-C(7A)-C(8A)	−9.7(4)
O(2A)-C(7A)-C(8A)-C(9A)	176.0(3)	O(1A)-C(7A)-C(8A)-C(9A)	−1.8(4)
O(2A)-C(7A)-C(8A)-C(13A)	−1.4(5)	O(1A)-C(7A)-C(8A)-C(13A)	−179.2(3)
C(13A)-C(8A)-C(9A)-N(1A)	−175.1(3)	C(7A)-C(8A)-C(9A)-N(1A)	7.6(5)
C(13A)-C(8A)-C(9A)-C(10A)	5.7(5)	C(7A)-C(8A)-C(9A)-C(10A)	−171.7(3)
N(1A)-C(9A)-C(10A)-C(11A)	175.6(3)	C(8A)-C(9A)-C(10A)-C(11A)	−5.2(5)
C(9A)-C(10A)-C(11A)-C(12A)	0.8(5)	C(10A)-C(11A)-C(12A)-C(13A)	3.2(6)
C(11A)-C(12A)-C(13A)-C(8A)	−2.6(6)	C(9A)-C(8A)-C(13A)-C(12A)	−1.9(5)
C(7A)-C(8A)-C(13A)-C(12A)	175.5(3)	Si(1A)-O(3A)-C(14A)-O(4A)	−178.5(2)
Si(1A)-O(3A)-C(14A)-C(15A)	3.3(5)	O(4A)-C(14A)-C(15A)-C(20A)	5.6(5)
O(3A)-C(14A)-C(15A)-C(20A)	−176.2(3)	O(4A)-C(14A)-C(15A)-C(16A)	−175.0(3)
O(3A)-C(14A)-C(15A)-C(16A)	3.2(5)	Si(1A)-N(2A)-C(16A)-C(17A)	171.0(3)
Si(1A)-N(2A)-C(16A)-C(15A)	−8.2(5)	C(20A)-C(15A)-C(16A)-N(2A)	178.4(3)
C(14A)-C(15A)-C(16A)-C(2A)	−1.0(5)	C(20A)-C(15A)-C(16A)-C(17A)	−0.8(5)
C(14A)-C(15A)-C(16A)-C(17A)	179.8(3)	N(2A)-C(16A)-C(17A)-C(18A)	−177.7(3)
C(15A)-C(16A)-C(17A)-C(18A)	1.5(5)	C(16A)-C(17A)-C(18A)-C(19A)	−1.6(6)
C(17A)-C(18A)-C(19A)-C(20A)	0.8(6)	C(18A)-C(19A)-C(20A)-C(15A)	−0.1(5)
C(16A)-C(15A)-C(20A)-C(19A)	0.1(5)	C(14A)-O(15A)-C(20A)-O(19A)	179.5(3)
N(2B)-Si(1B)-O(1B)-C(7B)	−130.9(3)	N(1B)-Si(1B)-O(1B)-C(7B)	−5.7(3)
O(3B)-Si(1B)-O(1B)-C(7B)	−40(2)	C(1B)-Si(1B)-O(1B)-C(7B)	111.0(3)
N(2B)-Si(1B)-O(3B)-C(14B)	−24.2(3)	N(1B)-Si(1B)-O(3B)-C(14B)	−149.4(3)
O(1B)-Si(1B)-O(3B)-C(14B)	−115(2)	C(1B)-Si(1B)-O(3B)-C(14B)	94.1(3)
N(2B)-Si(1B)-N(1B)-C(9B)	86.8(3)	O(3B)-Si(1B)-N(1B)-C(9B)	176.2(3)
O(1B)-Si(1B)-N(1B)-C(9B)	−1.9(3)	C(1B)-Si(1B)-N(1B)-C(9B)	−94.3(3)
N(1B)-Si(1B)-N(2B)-C(16B)	98.3(3)	O(3B)-Si(1B)-N(2B)-C(16B)	12.2(3)
O(1B)-Si(1B)-N(2B)-C(16B)	−171.1(3)	C(1B)-Si(1B)-N(2B)-C(16B)	−80.5(3)
N(2B)-Si(1B)-C(1B)-C(6B)	17.8(4)	N(1B)-Si(1B)-C(1B)-C(6B)	−161.2(3)
O(3B)-Si(1B)-C(1B)-C(6B)	−75.2(3)	O(1B)-Si(1B)-C(1B)-C(6B)	106.3(3)
N(2B)-Si(1B)-C(1B)-C(2B)	−163.8(3)	N(1B)-Si(1B)-C(1B)-C(2B)	17.2(4)
O(3B)-Si(1B)-C(1B)-C(2B)	103.1(3)	O(1B)-Si(1B)-C(1B)-C(2B)	−75.3(3)
C(6B)-C(1B)-C(2B)-C(3B)	1.7(6)	Si(1B)-C(1B)-C(2B)-C(3B)	−176.7(3)
C(1B)-C(2B)-C(3B)-C(4B)	−2.9(7)	C(2B)-C(3B)-C(4B)-C(5B)	2.1(7)
C(3B)-C(4B)-C(5B)-C(6B)	−0.4(7)	C(2B)-C(1B)-C(6B)-C(5B)	0.0(6)

SUPPLEMENTARY TABLE I Torsional Angles [°] *(Continued)*

Si(1B)-C(1B)-C(6B)-C(5B)	178.4(3)	C(4B)-C(5B)-C(6B)-C(1B)	−0.7(6)
Si(1B)-O(1B)-C(7B)-O(2B)	−168.0(2)	Si(1B)-O(1B)-C(7B)-C(8B)	10.3(5)
O(2B)-C(7B)-C(8B)-C(13B)	−8.8(5)	O(1B)-C(7B)-C(8B)-C(13B)	173.0(3)
O(2B)-C(7B)-C(8B)-C(9B)	171.1(3)	O(1B)-C(7B)-C(8B)-C(9B)	−7.1(5)
Si(1B)-N(1B)-C(9B)-C(10B)	−176.4(3)	Si(1B)-N(1B)-C(9B)-C(8B)	3.7(5)
C(13B)-C(8B)-C(9B)-C(1B)	−179.2(3)	C(7B)-C(8B)-C(9B)-N(1B)	0.9(5)
C(13B)-C(8B)-C(9B)-C(10B)	0.9(5)	C(7B)-C(8B)-C(9B)-C(10B)	−179.0(3)
N(1B)-C(9B)-C(10B)-C(11B)	178.8(3)	C(8B)-C(9B)-C(10B)-C(11B)	−1.3(5)
C(9B)-C(10B)-C(11B)-C(12B)	0.5(6)	C(10B)-C(11B)-C(12B)-C(13B)	0.8(6)
C(11B)-C(12B)-C(13B)-C(8B)	−1.2(6)	C(9B)-C(8B)-C(13B)-C(12B)	0.3(5)
C(7B)-C(8B)-C(13B)-C(12B)	−179.8(3)	Si(1B)-O(3B)-C(14B)-O(4B)	−161.6(2)
Si(1B)-C(3B)-C(14B)-C(15B)	21.6(5)	O(4B)-C(14B)-C(15B)-C(20B)	−2.2(5)
O(3B)-C(14B)-C(15B)-C(20B)	174.5(3)	O(4B)-C(14B)-C(15B)-C(16B)	−178.9(3)
O(3B)-C(14B)-C(15B)-C(16B)	−2.1(5)	Si(1B)-N(2B)-C(16B)-C(17B)	178.7(3)
Si(1B)-N(2B)-C(16B)-C(15B)	−0.8(5)	C(20B)-C(15B)-C(16B)-N(2B)	176.1(3)
C(14B)-C(15B)-C(16B)-N(2B)	−7.3(5)	C(20B)-C(15B)-C(16B)-C(17B)	−3.4(5)
C(14B)-C(15B)-C(16B)-C(17B)	173.2(3)	N(2B)-C(16B)-C(17B)-C(18B)	−175.5(3)
C(15B)-C(16B)-C(17B)-C(18B)	4.0(5)	C(16B)-C(17B)-C(18B)-C(19B)	−1.9(6)
C(17B)-C(18B)-C(19B)-C(20B)	−1.1(6)	C(18B)-C(19B)-C(20B)-C(15B)	1.7(6)
C(16B)-C(15B)-C(20B)-N(19B)	0.5(5)	C(14B)-C(15B)-C(20B)-C(19B)	−176.1(3)
C(25A)-N(3A)-C(21A)-C(22A)	62.7(4)	C(23A)-N(3A)-C(21A)-C(22A)	−64.8(4)
C(21A)-N(3A)-C(23A)-C(24A)	−54.9(4)	C(25A)-N(3A)-C(23A)-C(24A)	177.5(3)
C(21A)-N(3A)-C(25A)-C(26A)	164.7(3)	C(23A)-N(3A)-C(25A)-C(26A)	−66.7(4)
C(23B)-N(3B)-C(21B)-N(22B)	154.1(9)	C(25B)-N(3B)-C(21B)-C(22B)	5.1(13)
C(21B)-N(3B)-C(23B)-C(24B)	23.7(10)	C(25B)-N(3B)-C(23B)-C(24B)	172.5(7)
C(21B)-N(3B)-C(25B)-C(26B)	146.8(7)	C(23B)-N(3B)-C(25B)-C(26B)	−3.8(10)
C(25B)-N(3B)-C(21B)-C(22B)	171.4(17)	C(23B)-N(3B)-C(21B)-C(22B)	56.5(19)
C(25B)-N(3B)-C(23B)-C(24B)	62.7(15)	C(21B)-N(3B)-C(23B)-C(24B)	177.1(13)
C(21B)-N(3B)-C(25B)-C(26B)	24.1(17)	C(23B)-N(3B)-C(25B)-C(26B)	137.8(13)

SUPPLEMENTARY TABLE II Anisotropic Displacement Parameters [Å2x103]. The Anisotropic Displacement Factor Exponent Takes the Form: −2p2[(h2a* 2U11 + k2b* 2U22 + I2c* 2U33 + 2hka*b*U12 + 2hla*c*U13 + 2klb*c*U23]

	U11	U22	U33	U23	U13	U12
Si(1A)	23(1)	16(1)	17(1)	−2(1)	−4(1)	−5(1)
O(1A)	23(1)	22(1)	21(1)	−6(1)	−4(1)	−4(1)
O(2A)	36(1)	29(1)	20(1)	−8(1)	−5(1)	−7(1)
O(3A)	32(1)	15(1)	21(1)	−3(1)	−4(1)	−4(1)
O(4A)	49(1)	21(1)	22(1)	−7(1)	−5(1)	−7(1)
N(1A)	28(1)	20(1)	18(1)	−7(1)	−5(1)	−7(1)
N(2A)	34(1)	19(1)	16(1)	−3(1)	−6(1)	−6(1)
C(1A)	30(2)	22(2)	14(2)	−5(1)	−2(1)	−10(1)
C(2A)	30(2)	28(2)	29(2)	−5(2)	−10(2)	−6(2)
C(3A)	26(2)	50(2)	34(2)	−11(2)	−6(2)	−14(2)
C(4A)	46(2)	46(2)	30(2)	−6(2)	−1(2)	−31(2)
C(5A)	49(2)	25(2)	33(2)	2(2)	−8(2)	−16(2)
C(6A)	31(2)	22(2)	27(2)	−4(1)	−6(1)	−7(1)
C(7A)	31(2)	16(2)	16(2)	1(1)	−1(1)	−8(1)
C(12A)	25(2)	50(2)	36(2)	−14(2)	3(2)	−1(2)
C(13A)	31(2)	43(2)	25(2)	−12(2)	0(2)	−6(2)
C(14A)	22(2)	20(2)	23(2)	−5(1)	−3(1)	−6(1)
C(15A)	21(2)	19(2)	25(2)	−3(1)	−3(1)	−4(1)
C(16A)	20(2)	19(2)	24(2)	−2(1)	−1(1)	−5(1)
C(17A)	34(2)	24(2)	27(2)	0(1)	−14(2)	−3(2)
C(18A)	41(2)	21(2)	32(2)	5(2)	−13(2)	−3(2)
C(19A)	42(2)	18(2)	33(2)	−5(2)	−9(2)	−3(2)
C(20A)	31(2)	26(2)	24(2)	−7(1)	−2(1)	−6(1)
Si(1B)	26(1)	24(1)	17(1)	1(1)	−3(1)	−8(1)
O(1B)	32(1)	25(1)	21(1)	4(1)	1(1)	−6(1)
O(2B)	47(1)	33(1)	25(1)	9(1)	−4(1)	−18(1)
O(3B)	28(1)	28(1)	20(1)	5(1)	−3(1)	−10(1)
O(4B)	38(1)	32(1)	25(1)	4(1)	−4(1)	−17(1)
N(1B)	31(1)	28(2)	19(1)	3(1)	−1(1)	−8(1)
N(2B)	27(1)	25(1)	22(2)	3(1)	−3(1)	−11(1)
C(1B)	34(2)	33(2)	19(2)	3(1)	−5(1)	−15(2)
C(2B)	40(2)	53(2)	38(2)	−10(2)	−12(2)	−10(2)
C(3B)	42(2)	87(3)	53(3)	−17(3)	−18(2)	−21(2)
C(4B)	71(3)	74(3)	47(3)	−12(2)	−22(2)	−40(3)
C(7B)	27(2)	27(2)	24(2)	3(1)	−8(1)	−14(1)
C(8B)	25(2)	26(2)	29(2)	0(1)	−11(1)	−12(1)
C(9B)	20(2)	34(2)	25(2)	−5(2)	−6(1)	−9(1)
C(10B)	28(2)	38(2)	33(2)	−7(2)	−6(2)	−7(2)
C(11B)	29(2)	39(2)	53(2)	−19(2)	−9(2)	−3(2)
C(12B)	34(2)	25(2)	61(3)	−8(2)	−16(2)	−4(2)
C(13B)	34(2)	32(2)	39(2)	1(2)	−13(2)	−12(2)
C(14B)	33(2)	26(2)	16(2)	−2(1)	−6(1)	−12(1)
C(15B)	33(2)	26(2)	18(2)	−5(1)	−4(1)	−12(1)
C(16B)	30(2)	24(2)	17(2)	−6(1)	−7(1)	−8(1)

SUPPLEMENTARY TABLE II Anisotropic Displacement Parameters [Å2x103]. The Anisotropic Displacement Factor Exponent Takes the Form: −2p2[(h2a* 2U11 + k2b* 2U22 + I2c* 2U33 + 2hka*b*U12 + 2hla*c*U13 + 2klb*c*U23] *(Continued)*

	U11	U22	U33	U23	U13	U12
C(17B)	32(2)	26(2)	26(2)	−5(1)	−4(1)	−11(1)
C(18B)	30(2)	30(2)	37(2)	−9(2)	−5(2)	−5(2)
C(19B)	40(2)	25(2)	36(2)	−4(2)	−13(2)	−2(2)
C(20B)	39(2)	24(2)	29(2)	−1(2)	−8(2)	−11(2)
N(3A)	24(1)	23(1)	20(1)	−1(1)	−3(1)	−7(1)
C(21A)	26(2)	28(2)	30(2)	−4(2)	−1(2)	−2(1)
C(22A)	49(2)	33(2)	42(2)	−3(2)	−11(2)	−4(2)
C(23A)	32(2)	37(2)	21(2)	−9(2)	1(1)	−11(2)
C(24A)	57(2)	45(2)	36(2)	−8(2)	−7(2)	−28(2)
C(25A)	31(2)	40(2)	27(2)	−11(2)	−4(2)	−11(2)
C(21B)	30(3)	47(4)	60(4)	8(3)	−5(3)	−1(3)
C(22B)	48(4)	34(4)	90(7)	−10(4)	−12(5)	−10(3)
C(23B)	48(3)	36(3)	29(3)	−4(3)	−8(3)	−12(3)
C(24B)	58(5)	38(4)	36(5)	−10(4)	−4(4)	−25(4)
C(25B)	28(3)	34(3)	34(3)	−4(3)	−5(2)	−4(2)
C(26B)	44(4)	73(5)	64(5)	1(4)	−5(4)	−21(4)
N(3B)	33(5)	36(5)	1(4)	−15(4)	−4(3)	−9(4)
C(21B)	82(10)	38(7)	42(8)	4(6)	6(7)	−13(7)
C(22B)	19(6)	56(10)	57(10)	−4(7)	−20(6)	−6(6)
C(23B)	59(8)	71(9)	43(7)	−29(7)	5(6)	−32(7)
C(24B)	70(11)	57(12)	61(12)	5(10)	−38(9)	−22(9)
C(25B)	49(7)	71(9)	70(9)	−31(7)	−31(7)	−5(7)
C(26B)	22(5)	49(7)	34(6)	−25(5)	−8(5)	−2(5)
C1(1A)	52(1)	35(1)	51(1)	−12(1)	−7(1)	0(1)
C1(2A)	38(1)	28(1)	58(1)	−3(1)	−6(1)	−11(1)
C(27A)	37(1)	33(2)	52(2)	8(2)	−17(2)	−15(2)
C1(1B)	47(2)	57(1)	42(1)	−15(1)	0(1)	−25(1)
C1(2B)	38(1)	58(1)	40(1)	−13(1)	−6(1)	−20(1)
C(27B)	28(2)	46(2)	51(2)	−11(2)	−8(2)	−11(2)

SUPPLEMENTARY TABLE III Bond Lengths [Å] and Bond Angles [°]

Si(lA)-N(lA)	1.730(3)	Si(lA)-N(2A)	1.744(3)
Si(lA)-O(lA)	1.796(2)	Si(lA)-O(3A)	1.838(2)
Si(lA)-C(lA)	1.875(3)	O(lA)-C(7A)	1.299(4)
O(2A)-C(7A)	1.233(4)	O(3A)-C(14A)	1.297(4)
O(4A)-C(14A)	1.244(4)	N(lA)-C(9A)	1.378(4)
N(2A)-C(16A)	1.377(4)	C(lA)-C(2A)	1.388(4)
C(lA)-C(6A)	1.400(4)	C(2A)-C(3A)	1.390(5)
C(3A)-C(4A)	1.377(5)	C(4A)-C(5A)	1.378(5)
C(5A)-C(6A)	1.384(5)	C(7A)-C(8A)	1.475(5)
C(8A)-C(9A)	1.401(5)	C(8A)-C(13A)	1.402(4)
C(9A)-C(10A)	1.400(5)	C(10A)-C(11A	1.365(5)
C(11A)-C(12A)	1.389(6)	C(12A)-C(13A)	1.370(5)
C(14A)-C(15A)	1.474(4)	C(15A)-C(20A)	1.396(4)
C(15A)-C(16A)	1.412(5)	C(16A)-C(17A)	1.408(4)
C(17A)-C(18A)	1.375(5)	C(18A)-C(19A)	1.391(5)
C(19A)-C(20A)	1.374(5)	Si(lB)-N(2B)	1.732(3)
Si(lB)-N(lB)	1.742(3)	Si(lB)-O(3B)	1.804(2)
Si(lB)-O(lB)	1.809(2)	Si(lB)-C(lB)	1.876(4)
O(lB)-C(7B)	1.298(4)	O(2B)-C(7B)	1.239(4)
O(3B)-C(14B)	1.311(4)	O(4B)-C(14B)	1.229(4)
N(lB)-C(9B)	1.383(4)	N(2B)-C(16B)	1.382(4)
C(1B)-C(6B)	1.384(5)	C(1B)-C(2B)	1.394(5)
C(2B)-C(3B)	1.384(6)	C(3B)-C(4B)	1.360(7)
C(4B)-C(5B)	1.364(6)	C(5B)-C(6B)	1.387(6)
C(7B)-C(8B)	1.472(5)	C(8B)-C(13B)	1.403(5)
C(8B)-C(9B)	1.405(5)	C(9B)-C(10B)	1.403(5)
C(10BC(11B)	1.374(5)	C(11B)-C(12B)	1.397(6)
C(12B)-C(13B)	1.369(5)	C(14B)-C(15B)	1.472(4)
C(15B)-C(20B)	1.388(5)	C(15B)-C(16B)	1.413(5)
C(16B)-C(17B)	1.392(5)	C(17B)-C(18B)	1.385(5)
C(18B)-C(19B)	1.386(5)	C(19B)-C(20B)	1.374(5)
N(3A)-C(21A)	1.493(4)	N(3A)-C(25A)	1.494(4)
N(3A)-C(23A)	1.510(4)	C(21A)-C(22A)	1.509(5)
C(23A)-C(24A)	1.501(5)	C(25A)-C(26A)	1.496(5)
N(3B)-C(21B)	1.425(8)	N(3B)-C(23B)	1.451(8)
N(3B)-C(25B)	1.490(8)	C(21B)-C(22B)	1.392(11)
C(23B)-C(24B)	1.517(12)	C(25B)-C(26B)	1.420(9)
N(3B)-C(25B)	1.526(15)	N(3B)-C(21B)	1.533(15)
N(3B)-C(23B)	1.553(17)	C(21B)-C(22B)	1.323(19)
C(23B)(24B)	1.49(3)	C(25B)-C(26B)	1.478(18)
C1(1A)-C(27A)	1.748(4)	C1(2A)-C(27A)	1.750(4)
Cl(lB)-C(27B)	1.770(4)	C1(2B)-C(27B)	1.752(4)
N(lA)-Si(lA)-N(2A)	122.44(13)	N(1A)-Si(1A) O(lA)	92.71(11)
N(2A)-Si(1A)-O(1A)	88.39(12)	N(1A)-Si(lA)-O(3A)	86.47(12)
N(2A)-Si(lA)-O(3A)	91.64(11)	O(lA)-Si(lA)-O(3A)	179.05(11)
N(lA)-Si(lA)-C(1A)	120.18(14)	N(2A)Si.(lA)-C(lA)	117.29(14)
O(lA)-Si(lA)-C(lA)	91.73(12)	O(3A)-Si(lA)-C(lA)	89.10(12)
C(7A)-O(lA)-Si(lA)	134.8(2)	C(14A)-O(3A)-Si(1A)	134.6(2)
C(9A)-N(1A)-Si(1A)	130.0(2)	C(16A)-N(2A)-Si(1A)	130.5(2)
C(2A)-C(1A)-C(6A)	117.1(3)	C(2A)-C(1A)-Si(1A)	120.6(2)

SUPPLEMENTARY TABLE III Bond Lengths [Å] and Bond Angles [°] ***(Continued)***

C(6A)-C(1A)-Si(1A)	122.3(2)	C(lA)-C(2A)-C(3A)	121.3(3)
C(4A)-C(3A)-C(2A)	120.5(3)	C(5A)-C(4A)-C(3A)	119.3(3)
C(4A)-C(5A)-C(6A)	120.3(3)	C(5A)-C(6A)-C(lA)	121.5(3)
O(2A)-C(7A)-O(lA)	120.6(3)	O(2A)-C(7A)-C(8A)	122.2(3)
O(lA)-C(7A)-C(8A)	117.2(3)	C(9A)-C(8A)-C(13A)	119.9(3)
C(9A)-C(8A)-C(7A)	121.6(3)	C(13A)-C(8A)-C(7A)	118.5(3)
N(lA)-C(9A)-C(8A)	122.5(3)	N(lA)-C(9A)-C(10A)	119.4(3)
C(8A)-C(9A)-C(10A)	118.0(3)	C(11A)-C(10A)-C(9A)	121.2(3)
C(10A)-C(11A)-C(12A)	120.5(3)	C(13A)-C(12A)-C(11A)	119.7(3)
C(12A)-C(13A)-C(8A)	120.4(4)	O(4A)-C(14A)0(3A)	119.8(3)
O(4A)-C(14A)-C(15A)	121.8(3)	O(3A)-C(14A)-C(15A)	118.4(3)
C(20A)-C(15A)-C(16A)	120.0(3)	C(20A)-C(15A)-C(14A)	119.2(3)
C(16A)-C(15A)-C(14A)	120.9(3)	N(2A)-C(16A)-C(17A)	119.4(3)
N(2A)-C(16A)-C(15A)	123.1(3)	C(17A)-C(16A)-C(15A)	117.5(3)
C(18A)-C(17A)-C(16A)	121.2(3)	C(17A)-C(18A)-C(19A)	120.9(3)
C(20A)-C(19A)-C(18A)	118.9(3)	C(19A)-C(20A)-C(15A)	121.5(3)
N(2B)-Si(lB)-N(lB)	125.24(15)	N(2B)-Si(lB)-O(3B)	91.99(12)
N(lB)-Si(lB)-O(3B)	85.71(12)	N(2B)-Si(lB)-O(lB)	88.06(12)
N(lB)-Si(lB)-O(lB)	91.59(12)	O(3B)-Si(lB)-O(lB)	176.73(12)
N(2B)-Si(lB)-C(lB)	118.17(15)	N(lB)-Si(lB)-C(1B)	116.58(15)
O(3B)-Si(lB)-C(lB)	91.44(13)	O(lB)-Si(lB)-C(lB)	91.42(13)
C(7B)-O(lB)-Si(lB)	135.2(2)	C(14B)-O(3B)-Si(lB)	133.5(2)
C(9B)-N(lB)-Si(lB)	131.4(2)	C(16B)-N(2B)-Si(lB)	129.7(2)
C(6B)-C(lB)-C(2B)	116..6(4)	C(6B)-C(lB)-Si(lB)	122.1(3)
C(2B)-C(lB)-Si(lB)	121.3(3)	C(3B)-C(2B)-C(lB)	121.2(4)
C(4B)-C(3B)-C(2B)	120.5(4)	C(3B)-C(4B)-C(5B)	119.9(4)
C(4B)-C(5B)-C(6B)	119.8(4)	C(lB)-C(6B)-C(5B)	122.0(4)
O(2B)-C(7B)-O(lB)	120.3(3)	O(2B)-C(7B)-C(8B)	121.7(3)
O(lB)-C(7B)-C(8B)	118.0(3)	C(13B)-C(8B)-C(9B)	119.4(3)
C(13B)-C(8B)-C(7B)	119.4(3)	C(9B)-C(8B)-C(7B)	121.3(3)
N(lB)-C(,9B)-C(10B)	120.0(3)	N(lB)-C(9B)-C(8B)	121.9(3)
C(10B)-C(9B)-C(8B)	118.1(3)	C(11B)-C(10B)-C(9B)	121.5(4)
C(10B)-C(11B)-C(12B)	120.4(4)	C(13B)-C(12B)-C(11B)	118.9(3)
C(12B)-C(13B)-C(8B)	121.8(4)	O(4B)-C(14B)-O(3B)	120.8(3)
O(4B)-C(14B)-C(15B)	122.0(3)	O(3B)-C(14B)-C(15B)	117.1(3)
C(20B)-C(15B)-C(16B)	120.6(3)	C(20B)-C(15B)-C(14B)	118.5(3)
C(16B)-C(15B)-C(14B)	120.8(3)	N(2B)-C(16B)-C(17B)	119.9(3)
N(2B)-C(16B)-C(15B)	122.9(3)	C(17B)-C(16B)-C(15B)	117.2(3)
C(18B)-C(17B)(16B)	120.9(3)	C(19B)-C(18B)-C(17B)	121.5(3)
C(20B)-C(19B)(18B)	118.1(3)	C(19B)-C(20B)-C(15B)	121.5(3)
C(21A)-N(3A)-C(25A)	111.8(3)	C(21A)-N(3A)-C(23A)	113.6(3)
C(25A)-N(3A)-C(23A)	111.7(3)	N(3A)-C(21A)-C(22A)	114.2(3)
C(24A)-C(23A)-N(3A)	114.2(3)	N(3A)-C(25A)-C(26A)	113.8(3)
C(21B)-N(3B)-C(23B)	121.1(6)	C(21B)-N(3B)-C(25B)	115.6(5)
C(23B)-N(3B)-C(25B)	116.0(5)	C(22B)-C(21B)-N(3B)	130.3(7)
N(3B)-C(23B)-C(24B)	116.5(6)	C(26B)-C(25B)-N(3B)	123.0(6)
C(25B)-N(3B)-C(21B)	107.1(9)	C(25B)-N(3B)-C(23B)	107.8(9)
C(21B)-N(3B)-C(23B)	106.0(10)	C(22B)-C(21B)-N(3B)	127.4(13)
C(24B)-C(23B)-N(3B)	108.7(14)	C(26B)-C(25B)-N(3B)	130.1(12)
C1(lA)-C(27A)-Cl(2A)	112.3(2)	Cl(2B)-C(27B)-Cl(lB)	112.0(2)

SUPPLEMENTARY TABLE IV Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$). U(eq) is Defined as U(eq) = 1/3 $\sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, a_i\, a_j$

	X	Y	Z	U(eq)
Si(1A)	9187(1)	8420(1)	3979(1)	19(1)
O(1A)	9629(2)	7700(2)	3327(1)	22(1)
O(2A)	10653(2)	6486(2)	2655(1)	28(1)
O(3A)	8760(2)	9162(2)	4644(1)	23(1)
O(4A)	8131(2)	10526(2)	5229(1)	31(1)
N(1A)	10750(2)	7988(2)	4089(1)	22(1)
N(2A)	8499(2)	9827(2)	3557(1)	23(1)
C(1A)	8134(3)	7405(3)	4353(1)	22(1)
C(2A)	6819(3)	7868(3)	4390(2)	29(1)
C(3A)	6022(3)	7140(4)	4681(2)	35(1)
C(4A)	6522(4)	5938(4)	4949(2)	37(1)
C(5A)	7825(4)	5457(3)	4919(2)	36(1)
C(6A)	8620(3)	6175(3)	4623(2)	27(1)
C(7A)	10661(3)	6938(3)	3083(1)	22(1)
C(8A)	11932(3)	6682(3)	3325(1)	22(1)
C(9A)	11845(3)	7261(3)	3788(1)	21(1)
C(10A)	13025()	7098(3)	3941(2)	26(1)
C(11A)	14120(3)	6319(4)	3681(2)	36(1)
C(12A)	14090(3)	5678(4)	3251(2)	39(1)
C(13A)	12963(3)	5875(3)	3066(2)	34(1)
C(14A)	8299(3)	10305(3)	4748(1)	22(1)
C(15A)	7953(3)	11307(3)	4253(1)	22(1)
C(16A)	8058(3)	11027(3)	3686(1)	22(1)
C(17A)	7706(3)	12034(3)	3236(2)	29(1)
C(18A)	7303(3)	13247(3)	3342(2)	33(1)
C(19A)	7201(3)	13517(3)	3902(2)	32(1)
C(20A)	7527(3)	12548(3)	4349(2)	28(1)
Si(1B)	8325(1)	3027(1)	969(1)	23(1)
O(1B)	8604(2)	4178(2)	336(1)	29(1)
O(2B)	8383(2)	5903(2)	−308(1)	36(1)
O(3B)	8042(2)	1941(2)	1626(1)	27(1)
O(4B)	8223(2)	145(2)	2224(1)	32(1)
N(1B)	7325(3)	4183(3)	1378(1)	28(1)
N(2B)	9963(2)	2440(3)	929(1)	26(1)
C(1B)	7540(3)	2357(3)	551(2)	29(1)
C(2B)	6306(4)	2969(4)	439(2)	43(1)
C(3B)	5705(4)	2443(5)	156(2)	58(1)
C(4B)	6329(4)	1334(5)	−42(2)	57(1)
C(5B)	7542(4)	714(4)	54(2)	51(1)
C(6B)	8136(4)	1221(3)	351(2)	38(1)
C(7B)	8160(3)	5380(3)	206(2)	25(1)
C(8B)	7363(3)	6085(3)	681(2)	25(1)
C(9B)	6970(3)	5470(3)	1242(2)	25(1)
C(10B)	6194(3)	6202(3)	1671(2)	33(1)

SUPPLEMENTARY TABLE IV Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$). U(eq) is Defined as U(eq) = 1/3 $\sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, a_i\, a_j$ *(Continued)*

	X	Y	Z	U(eq)
C(11B)	5844(3)	7483(4)	1554(2)	40(1)
C(12B)	6249(3)	8094(3)	998(2)	40(1)
C(13B)	6986(3)	7394(3)	571(2)	34(1)
C(14B)	8727(3)	845(3)	1849(1)	24(1)
C(15B)	10120(3)	531(3)	1656(1)	24(1)
C(16B)	10675(3)	1365(3)	1232(1)	23(1)
C(17B)	12002(3)	1061(3)	1119(2)	27(1)
C(18B)	12739(3)	−53(3)	1386(2)	33(1)
C(19B)	12190(3)	−889(3)	1787(2)	35(1)
C(20B)	10881(3)	−574(3)	1922(2)	31(1)
N(3A)	2049(2)	1637(2)	3947(1)	23(1)
C(21A)	769(3)	2573(3)	4054(2)	30(1)
C(22A)	671(4)	3829(4)	3674(2)	43(1)
C(23A)	2406(3)	1275(3)	3338(2)	30(1)
C(24A)	1445(4)	809(4)	3179(2)	42(1)
C(25A)	3067(3)	2040(3)	4090(2)	32(1)
C(26A)	4283(4)	1013(4)	4146(2)	49(1)
N(3B)	1103(5)	5697(5)	1310(3)	46(2)
C(21B)	−125(6)	6593(6)	1323(3)	51(2)
C(22B)	−462(9)	7879(8)	1144(5)	58(3)
C(23B)	1297(6)	4535(5)	1719(3)	38(2)
C(24B)	131(9)	4084(9)	1979(5)	41(3)
C(25B)	2210(5)	6214(5)	1117(3)	34(1)
C(26B)	3369(6)	5665(8)	1341(4)	62(2)
N(3B)	1034(10)	5852(10)	1553(4)	21(2)
C(21B)	831(14)	6882(12)	1018(6)	60(4)
C(22B)	−249(13)	7739(17)	918(8)	44(4)
C(23B)	93(12)	5099(13)	1583(6)	54(4)
C(24B)	290(20)	4030(20)	2077(11)	59(7)
C(25B)	2389(12)	4991(13)	1417(6)	60(4)
C(26B)	3522(9)	5242(11)	1011(5)	33(3)
Cl(1A)	5643(1)	8739(1)	2935(1)	49(1)
Cl(2A)	749(1)	6276(1)	2974(1)	42(1)
C(27A)	7234(3)	7879(3)	2735(2)	40(1)
Cl(1B)	4851(1)	3021(1)	2489(1)	46(1)
Cl(2B)	4041(1)	1559(1)	1862(1)	43(1)
C(27B)	5341(3)	1880(4)	2016(2)	41(1)

Structure occupancy factor is 0.65 and 0.35 respectively for atoms N(3B) to C(26B).

SUPPLEMENTARY TABLE V Coordinates ($\times 10^4$) and isotopic displacement parameters ($\AA^2 \times 10^3$)

	X	Y	Z	U(eq)
H(1AA)	10863	8278	4383	26
H(2AA)	8421	9760	3203	27
H(2AB)	6457	8698	4211	34
H(3AA)	5126	7474	4696	42
H(4AA)	5975	5445	5152	45
H(5AA)	8178	4629	5103	43
H(6AA)	9517	5827	4602	32
H(10A)	13063	7538	4231	31
H(11A)	14909	6215	3795	43
H(12A)	14848	5105	3085	47
H(13A)	12948	5463	2760	40
H(17A)	7747	11873	2853	35
H(18A)	7091	13911	3029	40
H(19A)	6912	14356	3973	38
H(20A)	7460	12726	4732	33
H(1BA)	6986	3897	1734	33
H(2BA)	10409	2895	679	31
H(2BB)	5870	3761	558	52
H(6BA)	8978	776	419	45
H(10B)	5904	5803	2050	40
H(11B)	5323	7957	1853	48
H(12B)	6016	8980	918	48
H(13B)	7250	7806	191	41
H(17B)	12406	1626	856	33
H(18B)	13643	−249	1293	39
H(19B)	12703	−1657	1963	41
H(20B)	10487	−1125	2203	37
H(3AA)	2000	917	4211	28
H(21A)	563	2689	4473	36
H(21B)	120	2236	3983	36
H(22A)	−204	4376	3753	52
H(22B)	896	3724	3257	52
H(22C)	1260	4204	3764	52
H(23A)	2519	2009	3046	36
H(23B)	3237	616	3311	36
H(24A)	1808	450	2813	51
H(24B)	675	1504	3122	51
H(24C)	1225	168	3497	51
H(25A)	2742	2383	4466	38
H(25B)	3252	2718	3778	38
H(26A)	4879	1322	4272	58
H(26B)	4662	728	3763	58
H(26C)	4102	315	4438	58
H(3BA)	1150	5388	969	55
H(21C)	−578	6285	1102	61

SUPPLEMENTARY TABLE V Coordinates ($\times 10^4$) and isotopic displacement parameters ($Å^2 \times 10^3$) *(Continued)*

	X	Y	Z	U(eq)
H(21D)	−550	6483	1740	61
H(22D)	−1250	8147	980	69
H(22E)	224	8097	843	69
H(22F)	−597	8300	1484	69
H(23C)	1648	4635	2048	45
H(23D)	1953	3875	1514	45
H(24D)	393	3241	2200	50
H(24E)	−287	4071	1661	50
H(24F)	−465	4650	2245	50
H(25C)	2437	6252	683	40
H(25D)	1892	7089	1193	40
H(26D)	4052	5955	1069	74
H(26E)	3592	4754	1380	74
H(26F)	3264	5905	1727	74
H(3BA)	898	6177	1899	26
H(21C)	1439	7352	1001	72
H(21D)	1143	6445	670	72
H(22D)	−227	8552	976	52
H(22E)	−967	7514	1191	52
H(22F)	−352	7786	511	52
H(23C)	−797	5644	1649	64
H(23D)	249	4780	1206	64
H(24D)	−399	3648	2149	71
H(24E)	289	4341	2434	71
H(24F)	1112	3415	1973	71
H(25C)	2665	4677	1805	72
H(25D)	2284	4266	1291	72
H(26D)	4270	4878	1206	40
H(26E)	3377	6146	903	40
H(26F)	3670	4869	655	40
H(27A)	7787	8174	2906	48
H(27B)	7478	8029	2300	48
H(27C)	5843	2179	1642	49
H(27D)	5902	1102	2203	49