Copper(I) complexes of sterically-hindered 2-pyridinethione ligands. Crystal structures of $[CuCl(2\text{-}SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3)_2]$ and the disulfide, $[-2\text{-}SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2]_2$

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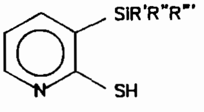
Abstract

The reactions of $Cu(II)X_2$ species ($X=Cl^-$, NO_3^-) with 3-(triorganosilyl)pyridine-2-thiols and 3,6-(triorganosilyl)pyridine-2-thiols were investigated. When the less sterically hindered 3-(triorganosilyl)pyridine-2-thiol ligands were used, Cu(I) species of the type $[Cu(2\text{-}SC_5H_3NH\text{-}3\text{-}SiR_3)_3]^+$ were isolated. In contrast, use of the sterically demanding ligands ($SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3$) and ($SC_5H_2NH\text{-}3,6\text{-}SiMe_2Bu^t$) yielded the Cu(I) species $[Cu(2\text{-}SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3)_2Cl]$ (**2**) and $[Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiMe_3Bu^t)_2Cl]$ (**3**). The sulfur ligands are present as monodentate donors in the neutral thione form, protonated at the pyridine nitrogen. The isolation of 3,3′,6,6′-tetrakis(dimethyl-tert-butylsilyl)pyridyl disulfide (**4**) confirms the role of the thiolates as reductants in the synthesis of the Cu(I) complexes. Crystal data: $[Cu(2\text{-}SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3)_2Cl]$ (**2**), monoclinic $P2_1/c$, $a=16.845(3)$, $b=13.421(2)$, $c=17.288(3)$ Å, $\beta=92.46(1)°$, $V=3904.8$ Å^3, $Z=4$, $D_{calc}=1.18$ g cm^{-3}. Structure refinement and solution based on 1810 reflections converged at 0.065. $C_{34}H_{64}N_2Si_4S_2$ (**4**), orthorhombic $Pbcn$, $a=12.720(2)$, $b=15.521(3)$, $c=21.162(3)$ Å, $V=4177.8(10)$ Å^3, $Z=4$, $D_{calc}=1.07$ g cm^{-3}, 2290 reflections, $R=0.058$.

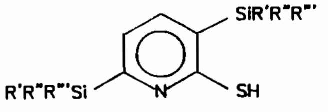
Introduction

Metal complexes of heterocyclic thione donor ligands have received considerable attention as a consequence of the flexibility of bonding modes adopted [1–24] and by virtue of their wide ranging applications [25]. As part of our investigations of the chemistry of sterically-hindered sulfur donor ligands [26–36], we have synthesized a series of 3-(triorganosilyl)pyridine-2-thiols (**A**) and 3,6-bis(triorganosilyl)pyridine-2-thiols (**B**) and described their coordination chemistry with Ag(I), Cu(I), Hg(II) and Mo(III)–Mo(V).

In the course of our investigations of the chemistry of ligand types **A** and **B** with copper, we noted that reactions of **A** with Cu(I) precursors yielded the hexanuclear species $[Cu(2\text{-}SC_5H_3N\text{-}3\text{-}SiR_3)]_6$ with the ligand adopting the μ_3-pyridine-2-thiolate mode. On the other hand, reactions of **B** with both Cu(I) and Cu(II) precursors yielded only Cu(I) mononuclear species of the general types $[Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiR_3)_3](NO_3)$ and $Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiR_3)_2Cl]$. In this paper, we report the structure of the latter compound and that of the disulfide $[-2\text{-}SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2]_2$ which is formed in the reduction of Cu(II) of the starting material.



A



B

Experimental

The ligands $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$, $2\text{-}HSC_5H_3N\text{-}6\text{-}SiMe_2Bu^t$ and $2\text{-}HSC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2$ were prepared as previously described [33]. Dichloromethane was technical grade and was distilled from $CoCl_2$ and P_4O_{10}. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Rigaku AFC-5S four-circle diffractometer.

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Synthesis of $[Cu(2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]NO_3$

The reaction of $Cu(NO_3)_2 \cdot 6H_2O$ (0.296 g, 1 mmol) with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ (0.732 g, 4.0 mmol) in methanol (20 ml) produced a yellow solution upon stirring for 1 h at room temperature. The solution was concentrated to 10 ml and layered with diethyl ether (15 ml). After standing at 4 °C for 5 days, yellow blocks of $[Co(2\text{-}SC_5NH\text{-}3\text{-}SiMe_3)_3]NO_3$ (**1**) were collected in 55% yield. *Anal.* Calc. for $C_{24}H_{39}N_4O_3Si_3Cu$:, C, 43.3; H, 5.87; N, 8.43. Found: C, 43.3; H, 5.83; N, 8.36%. The complex $[Cu(2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]ClO_4$ (**1a**) was prepared analogously from $Cu(ClO_4)_2 \cdot 6H_2O$.

Synthesis of $[Cu(2\text{-}SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3)_2Cl]$

Addition of a solution of $2\text{-}HSC_5H_2N\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3$ (1.188 g, 4 mmol) in methanol (10 ml) to a solution of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) in methanol (15 ml) results in a gradual change of the solution color to yellow–brown. After filtration to remove a small amount of insoluble impurity, the solution was carefully layered with diethyl ether (30 ml). Upon standing at room temperature for 10 days, red–orange crystals of $[Cu(2\text{-}SC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3)_2Cl]$ (**2**) were collected in 65% yield. *Anal.* Calc. for $C_{28}H_{54}N_2Si_4S_2ClCu$: C, 48.5; H, 7.79; N, 4.04; Found: C, 48.2; H, 7.93; N, 4.14%.

Synthesis of $[Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiMe_2Bu^t)_2Cl]$ *and the isolation of 3,3′,6,6′-tetrakis(dimethyl-tert-butylsilyl)-di-2-pyridyl disulfide*

The reaction of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) with $2\text{-}HSC_5H_2N\text{-}3,6\text{-}SiMe_2Bu^t$ (1.356 g, 4 mmol) in methanol (20 ml) yielded a red solution upon stirring for 1 h at room temperature. The solution was evaporated to dryness, and the resultant oil washed with diethyl ether (20 ml). The viscous red residue was dissolved in methylene chloride (10 ml), and the resultant red solution layered with diethyl ether. After standing at 4 °C for 1 week, orange crystals of $[Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiMe_3)_2Cl]$ (**3**) were collected in 40% yield. *Anal.* Calc. for $C_{34}H_{66}N_2Si_4S_2ClCu$: C, 52.5; H, 8.49; N, 3.60. Found: C, 52.2; H, 8.31; N, 3.75%.

The ether washings from the preparation of (**3**) were allowed to evaporate slowly at *c.* 10 °C in a 5 mm diameter test tube of 15 cm length, to give a bright orange crystalline product which was identified as the disulfide, RSSR (**4**) ($R = -C_5H_2N\text{-}3,6\text{-}SiMe_2Bu^t$). *Anal.* Calc. for $C_{34}H_{64}N_2Si_4S_2$: C, 60.4; H, 9.47; N, 4.14. Found: C, 60.0; H, 9.35; N, 4.02%.

X-ray structure determinations

Full details of the crystallographic methods may be found in ref. 37. The crystal data and experimental conditions are summarized in Table 1. In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H distances set at 0.96 Å. All non-hydrogen atoms of both structures were refined anisotropically.

Results and discussion

The 2-pyridinethiol derived ligands of types **A** and **B** react with Cu(II) precursors via a redox process to give mononuclear Cu(I) complexes and derivatized dipyridyl disulfides as products. The identity of the complex product is dependent on the degree of substitution of the 2-pyridinethiol ligand, such that reaction of the monosubstituted $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ yielded complexes of the type $[Cu(2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]X$ ($X = NO_3^-$, ClO_4^-) while the disubstituted ligands $2\text{-}HSC_5H_2NH\text{-}3,6\text{-}SiMe_3$ and $2\text{-}HSC_5H_2NH\text{-}3\text{-}SiMe_3\text{-}6\text{-}SiEt_3$ yielded complexes of the class $[Cu(2\text{-}SC_5H_2NH\text{-}3,6\text{-}SiR_3)_2Cl]$ (**2**) and **3**).

$$CuX_2 + 4HSC_5H_3N\text{-}3\text{-}SiMe_3 \longrightarrow$$

$$[Cu(SC_5H_3NH\text{-}3\text{-}SiMe_3)_3]^+ + \tfrac{1}{2}RSSR + HX + X^-$$

$$(R = -C_5H_3N\text{-}3\text{-}SiMe_3)$$

$$CuCl_2 + 3HSC_5H_2N\text{-}3,6\text{-}SiR'_3 \longrightarrow$$

$$[Cu(SC_5H_2NH\text{-}3,6\text{-}SiR'_3)_2Cl] + \tfrac{1}{2}R'SSR' + Cl^-$$

$$(R' = -C_5H_2N\text{-}3,6\text{-}SiR_3)$$

The increased steric bulk associated with the ligands of type **B** relative to that of ligand **A** may preclude the ligation of three heterocyclic thione ligands to the Cu(I) center. The coordination requirements of the Cu(I) sites of **2** and **3** are satisfied by ligation to the chloride donor.

Reactions of Cu(II) species with the parent 2-pyridinethiol ligand have been shown to yield both the three coordinated species $[Cu(2\text{-}SC_5H_4NH)_3]NO_3$ (**4a**) and the tetrahedral complex $[Cu(2\text{-}SC_5H_4NH)_4]ClO_4$ (**4b**). Complex **1** is mononuclear in solution by osmometry and is most likely structurally analogous to $[Cu(2\text{-}SC_5H_4NH)_3]NO_3$, with the Cu(I) center displaying a distorted trigonal planar geometry.

The IR spectra of the complexes **1**–**3** exhibit bands in the 3100–3400 cm^{-1} region which may be assigned to ν(N–H), confirming that the neutral thione form of the ligand is adopted and that the pyridyl nitrogens are not involved in bonding [38]. Sulfur ligation is indicated by the presence of features at *c.* 350 cm^{-1}, which are assigned to ν(Cu–S) [39]. The most prominent IR absorption bands occur in the 810–860 cm^{-1}

TABLE 1. Summary of crystal data and experimental conditions for the X-ray crystallographic studies of [Cu(2-SC_5H_2NH-3-$SiMe_3$-6-$SiEt_3)_2Cl$] (**2**) and 3,3′,6,6′-tetrakis(dimethyl-tert-butylsilyl)-di-2-pyridyl disulfide (**4**)

	2	**4**
Crystal data		
Empirical formula	$C_{28}H_{54}N_2Si_4S_2ClCu$	$C_{34}H_{64}N_2Si_4S_2$
Color, habit	red, block	orange, needle
Crystal size (mm)	0.25×0.28×0.31	0.22×0.36×0.20
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbcn$
Unit cell dimensions		
a (Å)	16.845(3)	12.720(2)
b (Å)	13.421(2)	15.521(3)
c (Å)	17.288(3)	21.162(3)
α (°)	90.00	90.00
β (°)	92.46(1)	90.00
γ (°)	90.00	90.00
Volume (Å^3)	3904.8(11)	4177.8(10)
Z	4	4
Density (calc.) (g cm^{-3})	1.18	1.07
Density (exp.) (g cm^{-3})	1.16(1)	1.09(10)
Absorption coefficient (cm^{-1})	8.71	4.52
Data collection		
Diffractometer	Rigaku AFC5S	
Radiation	Mo Kα (λ=0.71073 Å)	
Temperature (K)	296	
Monochromator	highly oriented graphite crystal	
2θ range (°)	2.5–45.0	
Scan speed (°/min)	2–6	
Scan range (ω)	1.20° plus Kα separation	
Background measurement	stationary crystal and stationary counter at the beginning and end of each scan	
Standard reflections	3 measured every 200 reflections	
Reflections collected	4325	3697
Observed reflections ($F_o \geq 6\sigma(F_o)$)	1810	2290
Absorption correction	based on Ψ-scans for 5 reflections with χ near 90° or 270°	
Solution and refinement		
System used	MSC TEXSAN solution package	
Solution	Patterson method	
Refinement method	full-matrix least squares	
Quantity minimized	$\Sigma w(F_o - F_c)^2$	
Hydrogen atoms	riding model	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0011F^2$	
Final R indices (obs. data)		
R	0.065	0.058
R_w	0.062	0.062
Goodness of fit	1.65	1.79
Largest and mean Δ/σ	0.22, 0.12	0.14, 0.05
Data to parameter ratio	9.4:1	12:1
Largest difference peak (e Å^{-3})	0.40	0.36
Largest difference hole (e Å^{-3})	0.41	0.24

range and are associated with ν(Si–C) of the ligands. The electronic spectra of the complexes exhibit two intense absorptions with maxima at 360 and 280 nm, assigned as intraligand transitions [40].

The structure of [Cu(2-SC_5H_2NH-3-$SiMe_3$-6-$SiEt_3)_2Cl$] (**2**) is shown in Fig. 1; atomic positional parameters are listed in Table 2, and selected bond lengths and angles in Table 3. The structure consists

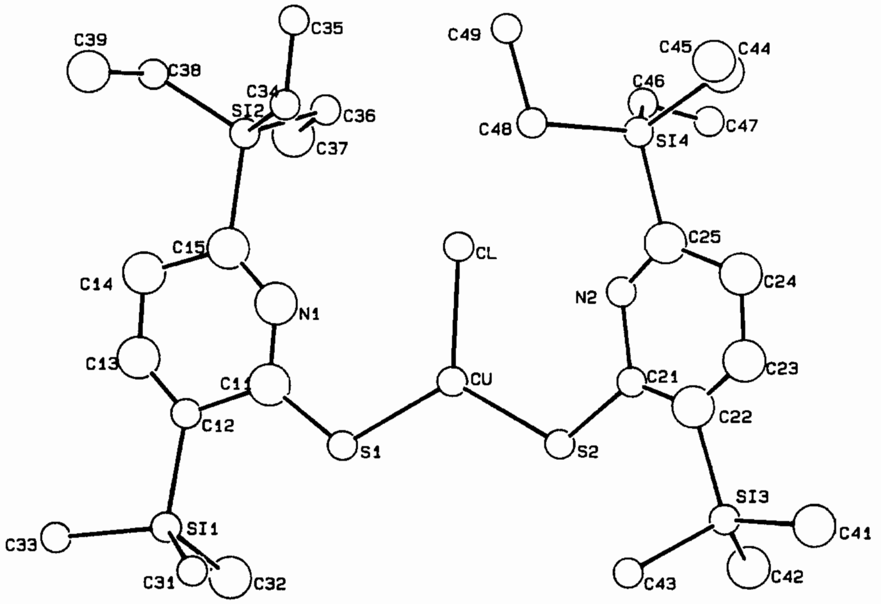


Fig. 1. The structure of [Cu(SC_5H_2NH-3-$SiMe_3$-6-$SiEt_3)_2Cl$], showing the atom-labelling scheme.

of discrete mononuclear units with the Cu(I) center displaying distorted trigonal planar geometry through ligation to two sulfur donors of the neutral 2(1H)-pyridinethione form of the ligands and to the chloride group. In contrast, the Cu(I) complex of the underivatized parent ligand 2-pyridinethiol, SC_5H_4NH, adopts the tris(pyridinethione) geometry $[Cu(SC_5H_4NH)_3]^+$, with trigonal planar coordination to the Cu(I) center [4a]. The presence of two, rather than three, pyridinethione ligands to the Cu(I) center of **2** is a consequence of the steric constraints imposed by the triorganosilyl groups at the 3- and 6-positions of the ligand rings. Since introduction of a single trimethylsilyl group at the 3-position does not preclude isolation of the tris(pryidinethione) complex [Cu(2-SC_5H_4NH-3-$SiMe_3)_3$]Cl (**1**), we conclude that the presence of bulky substituents at both the 3- and 6-positions of the rings are required to provide sufficient steric encumbrance to prevent coordination of the third pyridinethione group. Using MM2 molecular mechanics calculations, minimum energy geometries were determined for [Cu(SC_5H_3NH-3-$SiMe_3)_3]^+$ and $[Cu(SC_5H_4NH)_3]^+$ and for the unrealized 3,6-bis(triorganosilyl)pyridine-2-thiol derivative [Cu(SC_5H_2NH-3,6-$(SiMe_3)_2)_3]^+$. While the former complexes gave reasonable energy minima for trigonal planar geometries, the latter case produced unrealistic bond lengths for Cu–S interactions and necessitated unreasonable C–Si bond lengthening to accommodate the three bulky ligands about the Cu(I) center. Cone angle calculations [33] for the ligands likewise confirmed that three of the 3,6-substituted ligands cannot be accommodated about a trigonal planar Cu(I) center with Cu–S distances of approximately 2.20–2.30 Å without introducing significant non-bonding contacts between the triorganosilyl groups.

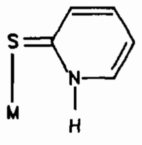
Distorted trigonal planar geometry for Cu(I) coordinated to sulfur ligands has been reported for tris(tetramethylthiourea)Cu(I)tetrafluoroborate [41] and tris(thiophenolato)Cu(I) [42]. The Cu–S bond lengths (2.198(4) and 2.204(4) Å) are unexceptional and fall within the range of values cited in ref. 42 and for other examples of thione coordination to Cu(I), of which $[Cu(SC_5H_4NH)_4]^+$ [4b] and $[Cu(SC_5H_4NH)_2(PPh_3)_2]^+$ [40] are illustrative. The copper atom rests 0.021(1) Å out of the S1–S2–Cl plane. The valence angles at the copper deviate from the trigonal planar idealized value of 120°, principally as a consequence of the steric requirements of the thione ligands which require the expansion of the S1–Cu–S2 angle to 121.5° and the concomitant contraction of the S–Cu–Cl angles to 119.0 and 119.5°.

Although the hydrogen atoms associated with N1 and N2 were located on the final difference Fourier map, the protonated thione form of the ligand was also confirmed by the metrical parameters associated with the (SC_5H_2N-3-$SiMe_3$-6-$SiEt_3$) units. The S1–C11 and S2–C21 distances (1.71(2) Å, av.) are significantly shorter than the corresponding S–C distances for complexes containing the deprotonated

TABLE 2. Atomic positional parameters for [Cu(SC$_5$H$_2$NH-3-SiMe$_3$-SiEt$_3$)$_2$Cl] (**2**)

Atom	*x*	*y*	*z*
Cu	0.0264(1)	0.0742(1)	0.2440(1)
Cl	0.1185(2)	0.0717(3)	0.1513(2)
S(1)	0.0269(2)	−0.0457(3)	0.3306(2)
S(2)	−0.0614(2)	0.1960(3)	0.2448(2)
Si(1)	0.0448(3)	−0.2372(4)	0.4524(3)
Si(2)	0.2640(2)	−0.1760(3)	0.1463(2)
Si(3)	−0.1993(3)	0.3757(4)	0.2158(3)
Si(4)	0.0717(3)	0.2508(3)	−0.0343(2)
N(1)	0.1444(6)	−0.1278(7)	0.2542(5)
N(2)	−0.0106(6)	0.2443(8)	0.1066(6)
C(11)	0.0965(7)	−0.135(1)	0.3158(7)
C(12)	0.1057(7)	−0.218(1)	0.3653(7)
C(13)	0.1646(8)	−0.283(1)	0.3478(7)
C(14)	0.2124(8)	−0.275(1)	0.2827(8)
C(15)	0.2021(7)	−0.196(1)	0.2333(7)
C(21)	−0.0633(8)	0.264(1)	0.1618(7)
C(22)	−0.1208(7)	0.340(1)	0.1462(7)
C(23)	−0.1165(9)	0.390(1)	0.0763(9)
C(24)	−0.058(1)	0.366(1)	0.0239(8)
C(25)	−0.0056(7)	0.292(1)	0.0358(7)
C(31)	−0.057(1)	−0.248(1)	0.425(1)
C(32)	0.066(1)	−0.142(1)	0.527(1)
C(33)	0.073(1)	−0.358(1)	0.495(1)
C(34)	0.1964(9)	−0.158(1)	0.0623(8)
C(35)	0.236(1)	−0.138(1)	−0.013(1)
C(36)	0.327(1)	−0.066(1)	0.1653(9)
C(37)	0.384(1)	−0.074(2)	0.230(1)
C(38)	0.3251(9)	−0.292(1)	0.1339(8)
C(39)	0.279(1)	−0.383(1)	0.105(1)
C(41)	−0.267(1)	0.465(1)	0.1673(9)
C(42)	−0.153(1)	0.435(2)	0.301(1)
C(43)	−0.258(1)	0.269(1)	0.242(1)
C(44)	0.062(1)	0.334(1)	−0.1211(9)
C(45)	−0.005(1)	0.314(1)	−0.176(1)
C(46)	0.171(1)	0.268(1)	0.0124(9)
C(47)	0.191(1)	0.370(1)	0.042(1)
C(48)	0.051(1)	0.118(1)	−0.0583(9)
C(49)	0.107(1)	0.068(1)	−0.106(1)

thiolate ligand form [3, 29, 33], suggesting a significant contribution of the resonance form (C). The pattern of C–C bond distances within the rings likewise conforms to that consistent with the thione geometry.



C

The presence of significant hydrogen bonding is suggested by the orientation of the pyridyl rings relative to the chlorine ligand and confirmed by the Cl–H1 and Cl–H2 distances of 2.34(2) and 2.36(2) Å. This interaction may account in part for the contraction of S–Cu–Cl angles from 120° to an average value of 119.3(4)° which causes the sterically significant triethylsilyl groups to approach contact distances.

TABLE 3. Selected bond lengths (Å) and angles (°) for [Cu(SC$_5$H$_2$NH-3-SiMe$_3$-6-SiEt$_3$)$_2$Cl] (**2**)

Cu–Cl	2.279(4)	C21–N2	1.36(1)
Cu–S1	2.198(4)	N2–C25	1.39(1)
Cu–S2	2.204(4)	C21–C22	1.43(1)
S1–C11	1.71(1)	C22–C23	1.38(1)
S1–C21	1.70(1)	C23–C24	1.40(1)
C11–N1	1.37(1)	C24–C25	1.34(2)
N1–C15	1.39(1)	Si–C(ring), av.	1.89(2)
C11–C12	1.41(1)	Si–C(methyl), av.	1.84(2)
C12–C13	1.37(1)		
C13–C14	1.42(2)		
C14–C15	1.37(1)		
Cl–Cu–S1	119.0(2)	Cu–S1–C11	113.4(5)
Cl–Cu–S2	119.5(2)	Cu–S2–C21	112.3(5)
S1–Cu–S2	121.5(2)		

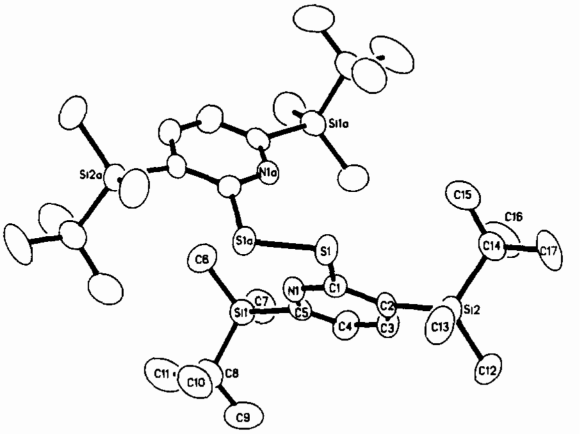


Fig. 2. The structure of 3,3′,6,6′-tetrakis(dimethyl-tert-butylsilyl-2-pyridyl disulfide (**4**).

The structure of 3,3′,6,6′-tetrakis(dimethyl-tert-butylsilyl)-2-pyridyl disulfide (**4**) is illustrated in Fig. 2. Atomic positional parameters and selected bond lengths and angles for **4** are listed in Tables 4 and 5, respectively. The S–S bond length of 2.019(2) Å is similar to those previously reported for the unsubstituted analogue di-2-pyridyl disulfide [43] and the 3,3′-dihydroxydi-2-pyridyl disulfide [44] of 2.0180(2) and 2.016(2) Å, respectively. The N–C–S–S torsion angle of 9.2° indicates that the S–S bond lies approximately in the plane of each pyridine ring. As shown more clearly in Fig. 3, the disulfide adopts the equatorial conformation, rather than the less frequently observed axial conformation which exhibits X–C–S–S torsion angles near 90° [44, 45]. The nitrogen atoms are in the *cis,cis* positions relative to the S–S group, a conformation also observed for the 3,3′-dihydroxydi-2-pyridyl disulfide derivative [44].

The S–S bond length and the equatorial conformation adopted by **4** are consistent with general

TABLE 4. Atomic positional parameters for RSSR, R = $-C_5H_2N$-3,6-$SiMe_2Bu^t$ (**4**)

	x	*y*	*z*
S(1)	−569(1)	−184(1)	2832(1)
Si(1)	1834(1)	2609(1)	3190(1)
Si(2)	−1763(1)	−36(1)	4310(1)
N(1)	520(3)	1208(2)	3169(2)
C(1)	−229(3)	674(3)	3365(2)
C(2)	−798(3)	747(3)	3936(2)
C(3)	−556(4)	1494(3)	4271(2)
C(4)	194(4)	2078(3)	4068(2)
C(5)	737(3)	1915(3)	3513(2)
C(6)	1794(5)	2531(4)	2318(2)
C(7)	1598(5)	3743(3)	3435(3)
C(8)	3123(4)	2199(3)	3507(3)
C(9)	3136(5)	2271(4)	4234(3)
C(10)	3284(5)	1257(4)	3340(3)
C(11)	4011(5)	2743(5)	3243(4)
C(12)	−1645(4)	91(3)	5181(2)
C(13)	−1441(4)	−1181(3)	4139(2)
C(14)	−3146(4)	238(3)	4063(2)
C(15)	−3279(5)	137(4)	3346(3)
C(16)	−3425(5)	1157(4)	4246(3)
C(17)	−3928(5)	−386(5)	4393(3)

TABLE 5. Selected bond lengths (Å) and angles (°) for RSSR, R = $-C_5H_2N$-3,6-$SiMe_2Bu^t$ (**4**)

S1–S1a	2.019(2)	Si1–C5	1.891(4)
S1–C1	1.798(4)	Si1–C6	1.851(5)
C1–N1	1.328(5)	Si1–C7	1.859(5)
N1–C5	1.346(5)	Si–C8	1.883(5)
C1–C2	1.415(6)	Si2–C2	1.900(4)
C2–C3	1.392(6)	Si2–C12	1.860(4)
C3–C4	1.384(6)	Si2–C13	1.860(5)
C4–C5	1.386(6)	Si2–C14	1.883(5)
S1–C1–C2	118.2(3)	N1–C5–Si1	114.9(3)
C2–C1–N1	125.7(4)	C4–C5–Si1	124.8(3)
N1–C1–S1	116.1(3)	C1–C2–Si2	129.4(3)
C1–C2–C3	112.9(4)	C3–C2–Si2	117.6(3)
C2–C3–C4	122.6(4)		
C4–C5–N1	120.3(4)		
C5–N1–C1	119.2(4)		

empirical rules for the geometries of aromatic disulfides [44]. So long as the substituents at the β positions (the 6-$SiMe_2Bu^t$ group on C5) are not strongly electron-donating, the equatorial conformation and concomitant short S–S distances (2.016–2.023 Å) are observed. Substituents more distant from the disulfide group, at δ or γ positions do not affect the S–S bond distance or the X–C–S–S torsion angles. Thus, the 3-$SiMe_2Bu^t$ group of **4** has no influence on the observed geometry.

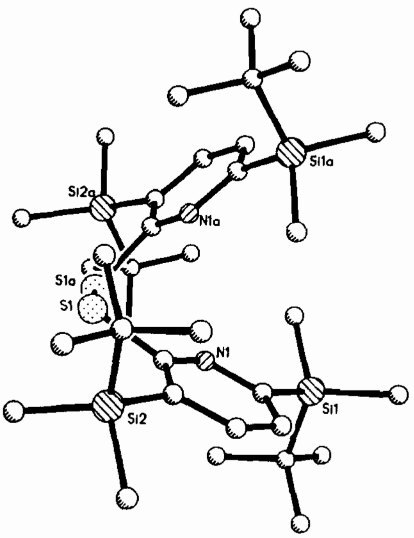


Fig. 3. The structure of **4** viewed down the S1–S1a axis.

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