Hexacoordinate Silicon(IV) Complexes Containing Thiocyanato-*N* Ligands − Syntheses, Structural Characterization, and Computational Studies

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Dedicated to Professor Heinrich Nöth on the Occasion of his 75th Birthday

Abstract. The hexacoordinate silicon(IV) complexes $[NEt_4]_2[Si(NCS)_6]$ (**2**), $[K(18\text{-crown-}6)]_2[Si(NCS)_6]\cdot 2CH_3CN$ (**3**·$2CH_3CN$), and *cis*-$[(acac)_2Si(NCS)_2]$ (*cis*-**4**; acac = acetylacetonato-*O,O*) were synthesized, starting from $Si(NCS)_4$ (**1**). Compounds **1**, **2**, **3**·$2CH_3CN$, and *cis*-**4** were structurally characterized in the solid state (^{13}C, ^{15}N (*cis*-**4** only), and ^{29}Si MAS NMR; crystal structure analyses) and in solution (^{1}H, ^{13}C, and ^{29}Si NMR; *cis*-**4** only). The experimental investigations were complemented by computational studies (RI-MP2 geometry optimizations of **1**, $[Si(NCS)_6]^{2-}$, *cis*-**4**, and *trans*-**4**; calculations of the ^{29}Si NMR chemical shifts using the optimized structures).

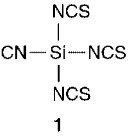
Keywords: Coordination chemistry; Hexacoordinate silicon; Silicon; Solid-state NMR spectroscopy; Thiocyanato-*N* ligand

Hexakoordinierte Silicium(IV)-Komplexe mit Thiocyanato-*N*-Liganden − Synthesen, strukturelle Charakterisierung und theoretische Untersuchungen

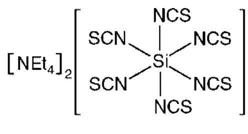
Inhaltsübersicht. Die hexakoordinierten Silicium(IV)-Komplexe $[NEt_4]_2[Si(NCS)_6]$ (**2**), $[K(18\text{-Krone-}6)]_2[Si(NCS)_6]\cdot 2CH_3CN$ (**3**·$2CH_3CN$) und *cis*-$[(acac)_2Si(NCS)_2]$ (*cis*-**4**; acac = Acetylaceton-ato-*O,O*) wurden ausgehend von $Si(NCS)_4$ (**1**) synthetisiert. Die Verbindungen **1**, **2**, **3**·$2CH_3CN$ und *cis*-**4** wurden im festen Zustand (^{13}C-, ^{15}N- (nur *cis*-**4**) und ^{29}Si-MAS-NMR; Kristallstrukturanalysen) und in Lösung (^{1}H-, ^{13}C- und ^{29}Si-NMR; nur *cis*-**4**) strukturell charakterisiert. Die experimentellen Untersuchungen wurden durch theoretische Studien ergänzt (RI-MP2-Geometrieoptimierungen von **1**, $[Si(NCS)_6]^{2-}$, *cis*-**4** und *trans*-**4**; Berechnungen der ^{29}Si-NMR-chemischen Verschiebungen für die geometrieoptimierten Strukturen).

Introduction

Compared to the chemistry of dianionic λ^6Si-silicates with SiO_6 skeletons [1], the chemistry of dianionic hexacoordinate silicon(IV) complexes with SiN_6 frameworks is significantly less explored [2]. Compound **2** represents the first example of this particular formula type that has been structurally characterized by single-crystal X-ray diffraction [2b]. As the quality of this structure analysis is poor and no NMR data of the $Si(NCS)_6^{2-}$ dianion have been reported, compound **2** was resynthesized and studied by single-crystal X-ray diffraction and solid-state NMR spectroscopy. In addition, the related potassium-18-crown-6 salt **3** and the neutral silicon(IV) complex *cis*-**4** (SiO_4N_2 skeleton) were synthesized and structurally characterized. In all cases, the silane **1** [3] served as the starting material. Compound **4** has already been synthesized by an alternative method (starting material: $(RO)_2Si(NCS)_2$ (R = Et, *n*-Pr) [4]), but its stereochemistry has been studied only by solution NMR spectroscopy. We report here on the syntheses of compounds **1**, **2**, **3**·$2CH_3CN$, and *cis*-**4** and their structural characterization in the solid state (single-crystal X-ray diffraction; ^{13}C (except for **1**), ^{15}N (*cis*-**4** only), and ^{29}Si MAS NMR) and in solution (^{1}H, ^{13}C, and ^{29}Si NMR; *cis*-**4** only). These experimental studies were complemented by computational investigations. The studies presented in this paper were carried out as part of our systematic investigations on higher-


$Si(NCS)_4$

1



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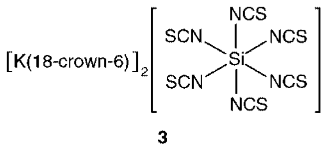

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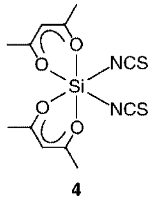

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coordinate silicon compounds (for recent publications, see ref. [5]; for reviews dealing with higher-coordinate silicon compounds, see refs. [1] and [6]). Preliminary results of the studies reported here have already been presented elsewhere [7].

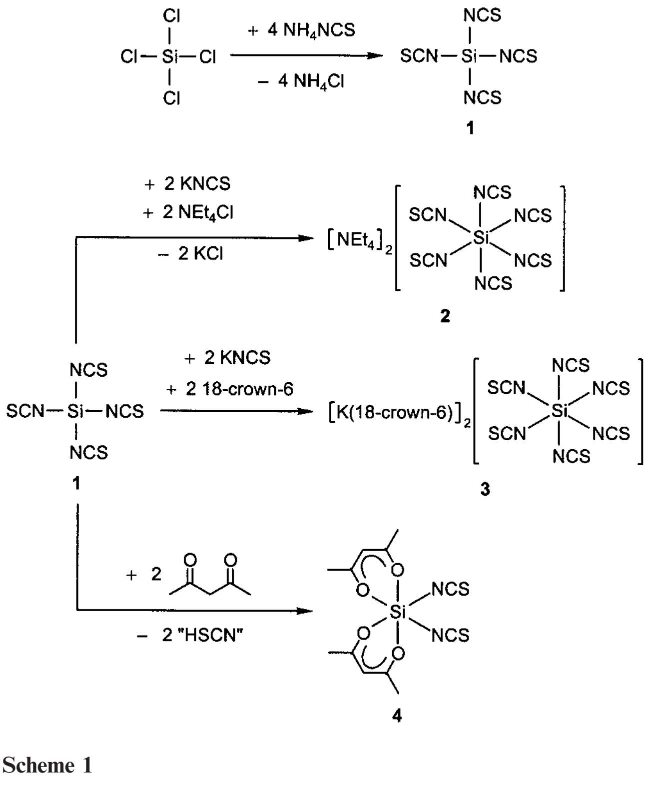
Results and Discussion

Syntheses

Compounds **1**−**4** were synthesized according to Scheme 1. Tetra(thiocyanato-*N*)silane (**1**) [3] was obtained by reaction of tetrachlorosilane with four molar equivalents of ammonium thiocyanate. Tetraethylammonium hexa(thiocyanato-*N*)silicate (**2**) [2b] was synthesized by treatment of **1** with two molar equivalents each of tetraethylammonium chloride and potassium thiocyanate. The related potassium-18-crown-6 salt **3** was obtained by reaction of **1** with two molar equivalents each of potassium thiocyanate and 18-crown-6 and was isolated as the acetonitrile solvate **3**·2CH_3CN. The neutral complex *cis*-bis[acetylacetonato-*O*,*O*]di(thiocyanato-*N*)silicon(IV) (*cis*-**4**) was synthesized by treatment of **1** with two molar equivalents of acetylacetone. Compounds **1**, **2**, **3**·2CH_3CN, and *cis*-**4** were isolated as crystalline solids (yield: **1**, 65 %; **2**, 71 %; **3**·2CH_3CN, 80 %; *cis*-**4**, 77 %). Their identities were established by elemental analyses, NMR studies, and crystal structure analyses.

Crystal Structure Analyses

The crystal structures of compounds **1**, **2**, **3**·2CH_3CN, and *cis*-**4** were determined by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these studies are given in Table 1; selected interatomic distances and angles are listed in Table 2. The structures of the respective molecules (**1**, *cis*-**4**) and dianions (**2**, **3**·2CH_3CN) in the crystal are shown in Figures 1−4.



Scheme 1

The silane **1** crystallizes in the space group $I4_1/a$, with Si−N distances in the range 1.6745(14)−1.6831(15) Å. The Si-coordination polyhedron is an almost ideal tetrahedron, with N−Si−N angles in the range 108.81(7)−109.94(7)°. The Si−N−C angles amount to 174.54(15)−177.12(15)°.

Compounds **2** [8] and **3**·2CH_3CN crystallize in the space groups $P4_2/m$ and $Fdd2$, respectively. The Si-coordination polyhedra of the $[Si(NCS)_6]^{2-}$ dianions are almost ideal octahedra, with N−Si−N angles in the ranges 89.15(10)−90.74(7)° and 179.37(12)−180.0°. The Si−N distances amount to 1.8167(15)−1.8369(17) Å; they are significantly longer than those observed for **1**. The Si−N−C angles are in the range 159.01(16)−180.0°.

The asymmetric unit of **3** contains half an $[Si(NCS)_6]^{2-}$ dianion and one potassium cation that is coordinated by an 18-crown-6 molecule. In addition, there is one acetonitrile molecule completing the coordination sphere of the potassium cation (Figure 5).

The neutral complex *cis*-**4** crystallizes in the space group $P2_1/c$, with Si−O distances in the range 1.7716(13)−1.7843(13) Å and Si−N distances of 1.8093(17) Å and 1.8145(16) Å. The Si-coordination polyhedron is a slightly distorted octahedron, with N−Si−N, N−Si−O, and O−Si−O angles in the ranges 87.13(6)−94.05(6)° and 177.00(7)−178.69(6)°. The Si−N−C angles amount to 167.43(16)° and 173.01(16)°.

Comparison of the bonding situation in the NCS groups of compound **1** (tetracoordination) and compounds **2**, **3**·2CH_3CN, and *cis*-**4** (hexacoordination) reveals significant differences. As can be seen from Table 2, the N−C distances of **1** are longer than those of the hexacoordinate silicon complexes, whereas the C−S distances of **1** are shorter than those of **2**, **3**·2CH_3CN, and *cis*-**4**.

NMR Studies

Compounds **1**, **2**, **3**·2CH_3CN, and *cis*-**4** were characterized by solid-state ^{29}Si NMR spectroscopy (**1**: single pulse MAS NMR; **2**, **3**·2CH_3CN, and *cis*-**4**: VACP/MAS NMR). Compounds **2**, **3**·2CH_3CN, and *cis*-**4** were also studied by solid-state ^{13}C VACP/MAS NMR experiments, and *cis*-**4** was additionally characterized by ^{15}N VACP/MAS NMR spectroscopy. All the NMR experiments were performed at 22 °C. The isotropic ^{29}Si chemical shift of the tetracoordinate silicon compound **1** ($\delta = -143.2$) and of the hexacoordinate silicon compounds **2** ($\delta = -256.5$), **3**·2CH_3CN ($\delta = -253.0$), and *cis*-**4** ($\delta = -210.2$) indicate that the thiocyanato-*N* ligand causes a significant high-field shift of the ^{29}Si resonance. As shown in Figure 6, all solid-state ^{29}Si NMR spectra are characterized by splitted resonance signals due to $^{1}J(^{14}N,^{29}Si)$ couplings.

Table 1 Crystal data and experimental parameters for the crystal structure analyses of **1**, **2**, **3**·2CH$_3$CN, and *cis*-**4**

Compound	**1**	**2**	**3**·2CH$_3$CN	*cis*-**4**
Empirical formula	$C_4N_4S_4Si$	$C_{22}H_{40}N_8S_6Si$	$C_{34}H_{54}K_2N_8O_{12}S_6Si$	$C_{12}H_{14}N_2O_4S_2Si$
Formula mass/g mol^{-1}	260.41	637.07	1065.50	342.46
Collection *T*/K	173(2)	173(2)	173(2)	173(2)
λ(MoKα)/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	orthorhombic	monoclinic
Space group (no.)	$I4_1/a$ (88)	$P4_2/m$ (84)	*Fdd*2 (43)	$P2_1/c$ (14)
a/Å	15.0280(13)	10.3565(15)	25.814(5)	14.463(2)
b/Å	15.0280(13)	10.3565(15)	29.830(6)	8.2446(8)
c/Å	18.634(2)	15.369(3)	13.842(3)	13.785(2)
β/°	90	90	90	98.205(18)
V/Å^3	4208.3(7)	1648.5(5)	10659(4)	1626.9(4)
Z	16	2	8	4
D(calcd)/g cm^{-3}	1.644	1.283	1.328	1.398
μ/mm^{-1}	0.974	0.478	0.493	0.415
F(000)	2080	676	4464	712
Crystal dimensions/mm	0.5 x 0.5 x 0.5	0.5 x 0.4 x 0.3	0.8 x 0.8 x 0.6	0.5 x 0.3 x 0.2
2θ Range/°	5.42−52.76	4.74−49.42	4.18−49.44	5.70−54.00
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-18 \le l \le 18$	$-30 \le h \le 30$, $-35 \le k \le 35$, $-16 \le l \le 16$	$-18 \le h \le 18$, $-10 \le k \le 10$, $-17 \le l \le 17$
Collected reflections	23370	13766	32792	16747
Independent reflections	2148	1467	4536	3514
R_{int}	0.0771	0.0430	0.0513	0.0624
Reflections used	2148	1467	4536	3514
Parameters	118	98	286	194
Restraints	0	0	1	0
S[a)]	1.034	1.013	1.032	1.077
Weight parameters *a*/*b*[b)]	0.0386/2.4795	0.0393/0.1215	0.0375/3.0440	0.0658/0.9351
$R1$[c)] [$I > 2\sigma(I)$]	0.0284	0.0262	0.0228	0.0455
$wR2$[d)] (all data)	0.0779	0.0671	0.0578	0.1259
Max./min. residual electron density/e Å^{-3}	+0.181/−0.266	+0.171/−0.143	+0.142/−0.128	+0.905/−0.717
Absolute structure parameter			0.01(3)	

[a)] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters.
[b)] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$.
[c)] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[d)] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

Compound *cis*-**4** was also studied by ^{1}H, ^{13}C, and ^{29}Si NMR experiments in solution (CDCl$_3$, 22 °C) [9]. The ^{1}H and ^{13}C NMR spectra of a freshly prepared solution are compatible with the *cis*-structure. The ^{13}C and ^{29}Si chemical shifts of *cis*-**4** are very similar to the respective isotropic chemical shifts in the solid-state NMR spectra. Upon dissolution of *cis*-**4** in CDCl$_3$, a *cis*/*trans* isomerization was observed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The kinetics of this process were studied by ^{1}H NMR spectroscopy. As shown in Figure 7, after a period of 20 hours an equilibrium *cis*/*trans* ratio of 1.5:1 was observed. This

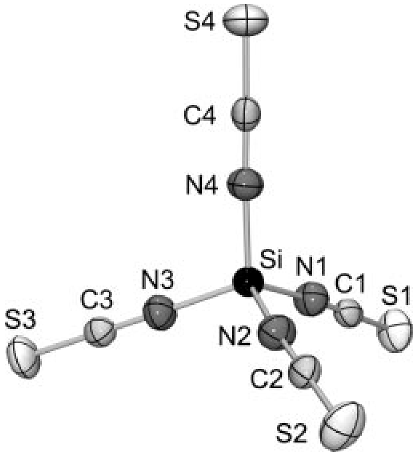


Fig. 1 Molecular structure of **1** in the crystal (probability level of displacement ellipsoids 50 %).

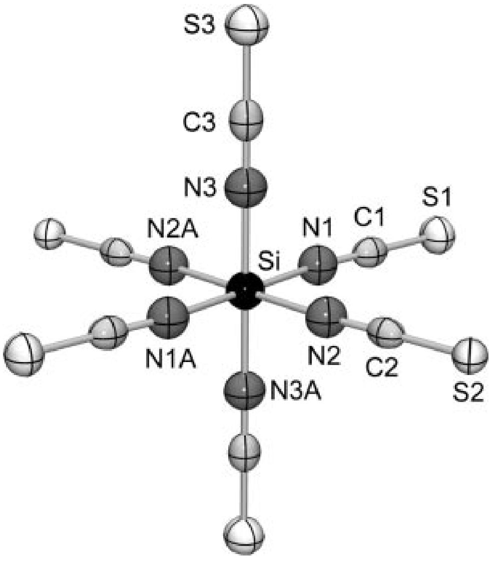


Fig. 2 Structure of the dianion in the crystal of **2** (probability level of displacement ellipsoids 50 %).

Table 2 Selected interatomic distances/Å and angles/° for **1**, **2**, **3**·2CH$_3$CN, and *cis*-**4**

1		**2**		**3**·2CH$_3$CN		*cis*-**4**	
Si−N1	1.6831(15)	Si−N1	1.823(2)	Si−N1	1.8369(17)	Si−O1	1.7816(14)
Si−N2	1.6788(14)	Si−N2	1.822(2)	Si−N2	1.8294(17)	Si−O2	1.7716(13)
Si−N3	1.6779(14)	Si−N3	1.832(2)	Si−N3	1.8167(15)	Si−O3	1.7843(13)
Si−N4	1.6745(14)	N1−C1	1.166(3)	N1−C1	1.165(2)	Si−O4	1.7729(13)
N1−C1	1.182(2)	N2−C2	1.167(3)	N2−C2	1.170(2)	Si−N1	1.8093(17)
N2−C2	1.183(2)	N3−C3	1.166(3)	N3−C3	1.162(2)	Si−N2	1.8145(16)
N3−C3	1.185(2)	C1−S1	1.593(3)	C1−S1	1.6057(19)	N1−C1	1.167(3)
N4−C4	1.183(2)	C2−S2	1.600(3)	C2−S2	1.597(2)	N2−C2	1.168(2)
C1−S1	1.5592(17)	C3−S3	1.602(3)	C3−S3	1.594(2)	C1−S1	1.601(2)
C2−S2	1.5573(16)	N1−Si−N1A	180.0	N1−Si−N1A	89.15(10)	C2−S2	1.6022(19)
C3−S3	1.5576(16)	N1−Si−N2	89.41(9)	N1−Si−N2	90.74(7)	O1−Si−O2	93.30(6)
C4−S4	1.5556(16)	N1−Si−N2A	90.59(9)	N1−Si−N2A	179.61(6)	O1−Si−O3	88.82(6)
N1−Si−N2	109.64(7)	N1−Si−N3	90.0	N1−Si−N3	90.40(7)	O1−Si−O4	87.28(6)
N1−Si−N3	108.81(7)	N1−Si−N3A	90.0	N1−Si−N3A	90.05(7)	O2−Si−O3	87.13(6)
N1−Si−N4	109.42(7)	N1A−Si−N2	90.59(9)	N1A−Si−N2	179.61(8)	O2−Si−O4	178.69(6)
N2−Si−N3	109.34(7)	N1A−Si−N2A	89.41(9)	N1A−Si−N2A	90.74(7)	O3−Si−O4	94.05(6)
N2−Si−N4	109.94(7)	N1A−Si−N3	90.0	N1A−Si−N3	90.05(7)	O1−Si−N1	177.54(7)
N3−Si−N4	109.67(7)	N1A−Si−N3A	90.0	N1A−Si−N3A	90.40(7)	O1−Si−N2	89.99(7)
Si−N1−C1	174.74(15)	N2−Si−N2A	180.0	N2−Si−N2A	89.36(11)	O2−Si−N1	88.96(7)
Si−N2−C2	174.54(15)	N2−Si−N3	90.0	N2−Si−N3	89.57(7)	O2−Si−N2	90.18(7)
Si−N3−C3	176.22(14)	N2−Si−N3A	90.0	N2−Si−N3A	89.97(7)	O3−Si−N1	90.34(7)
Si−N4−C4	177.12(15)	N2A−Si−N3	90.0	N2A−Si−N3	89.97(7)	O3−Si−N2	177.00(7)
N1−C1−S1	179.77(18)	N2A−Si−N3A	90.0	N2A−Si−N3A	89.57(7)	O4−Si−N1	90.47(7)
N2−C2−S2	179.15(16)	N3−Si−N3A	180.0	N3−Si−N3A	179.37(12)	O4−Si−N2	88.64(7)
N3−C3−S3	179.17(16)	Si−N1−C1	170.2(2)	Si−N1−C1	171.34(15)	N1−Si−N2	90.97(8)
N4−C4−S4	178.98(16)	Si−N2−C2	173.40(19)	Si−N2−C2	160.34(15)	Si−N1−C1	167.43(16)
		Si−N3−C3	180.0	Si−N3−C3	159.01(16)	Si−N2−C2	173.01(16)
		N1−C1−S1	178.8(2)	N1−C1−S1	179.62(16)	N1−C1−S1	178.34(18)
		N2−C2−S2	178.5(2)	N2−C2−S2	177.58(17)	N2−C2−S2	178.71(17)
		N3−C3−S3	180.0	N3−C3−S3	177.30(17)		

isomerization was also described in ref. [4]; however, some of our NMR data differ significantly from those reported in ref. [4]. One of the most striking differences concerns the ^{29}Si NMR data of the *cis*/*trans* mixture (this study: *cis*-**4**: $\delta = -208.7$; *trans*-**4**: $\delta = -208.2$ (Figure 8); ref. [4]: $\delta = -199.3$ and -214.0). Furthermore, separated resonance signals for the NCS groups of both isomers (*cis*-**4**: $\delta = 133.0$, $^1J(^{13}C,^{14}N) = 26.3$ Hz; *trans*-**4**: $\delta = 134.7$; $^1J(^{13}C,^{14}N) = 24.9$ Hz; Figure 9) were observed in the ^{13}C NMR spectrum of the *cis*/*trans* mixture (ref. [4]: one signal for both isomers at $\delta = 133.5$).

Computational Studies

Geometry optimizations for **1**, $[Si(NCS)_6]^{2-}$, *cis*-**4**, and *trans*-**4** were performed at the RI-MP2 level [10] using a

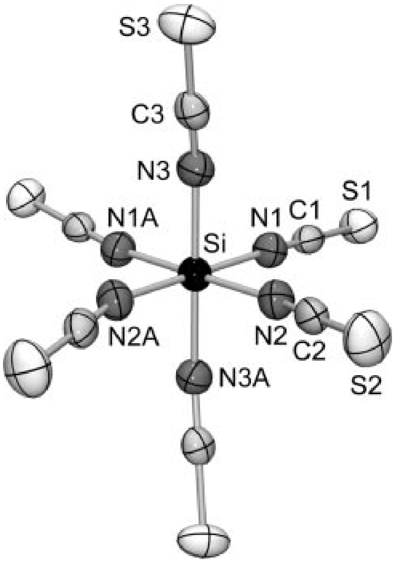


Fig. 3 Structure of the dianion in the crystal of **3**·2CH$_3$CN (probability level of displacement ellipsoids 50 %).

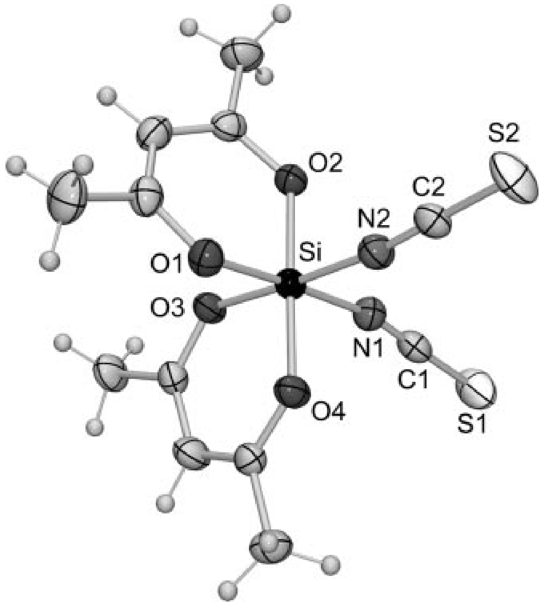


Fig. 4 Molecular structure of *cis*-**4** in the crystal (probability level of displacement ellipsoids 50 %).

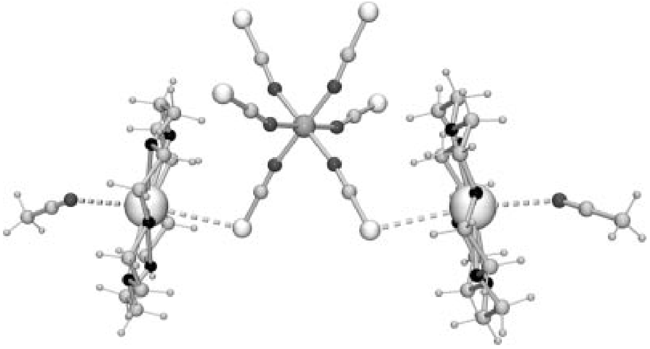


Fig. 5 Interaction of the [K(18-crown-6)] cations with the $[Si(NCS)_6]^{2-}$ dianion and the CH_3CN molecules in the crystal of **3**·$2CH_3CN$.

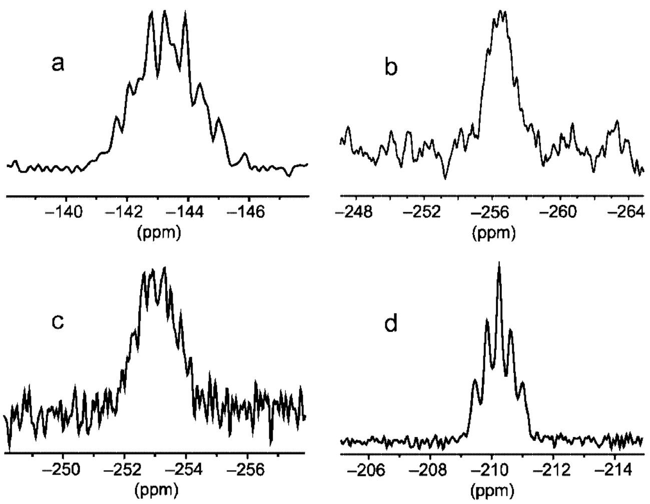


Fig. 6 Solid-state ^{29}Si MAS NMR spectra of **1** (a), **2** (b), **3**·$2CH_3CN$ (c), and *cis*-**4** (d) showing the splittings due to the $^1J(^{14}N,^{29}Si)$ couplings.

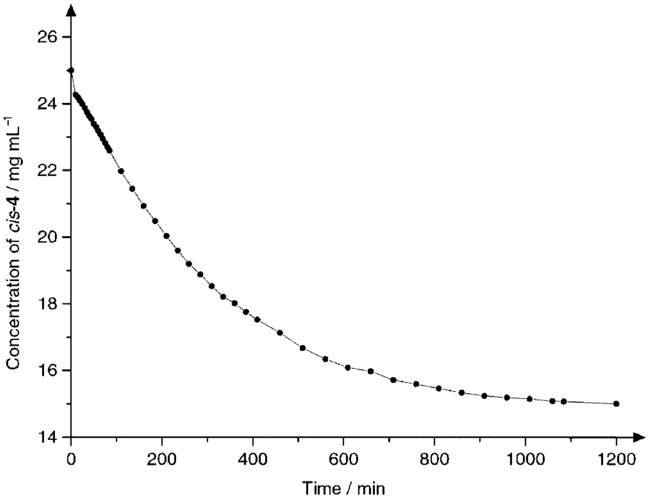


Fig. 7 Kinetics of the *cis*/*trans* isomerization of **4**, starting from a solution of *cis*-**4** in $CDCl_3$ (25 mg mL^{-1}). The kinetics were monitored at 22 °C by ^1H NMR spectroscopy, using the methyl resonance signals of *cis*-**4** and *trans*-**4** as the probe. After a period of 20 h, an equilibrium *cis*/*trans* ratio of 1.5 : 1 was observed.

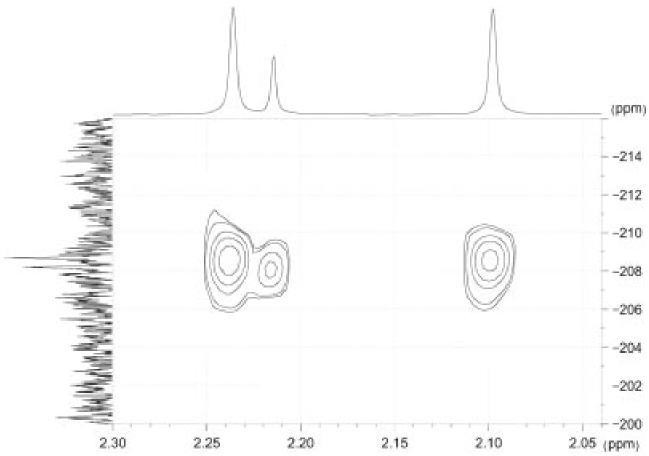


Fig. 8 Partial $^1H,^{29}Si$ COSY NMR spectrum of a mixture of *cis*-**4** and *trans*-**4** in $CDCl_3$ at 22 °C, showing the correlating ^1H signals (CH_3 groups) and ^{29}Si signals of *cis*-**4** and *trans*-**4**.

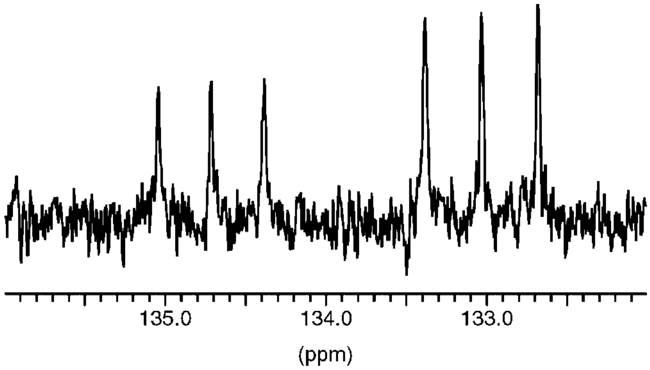


Fig. 9 Partial ^{13}C NMR spectrum of a mixture of *cis*-**4** and *trans*-**4** in $CDCl_3$ at 22 °C, showing the N*C*S resonance signals of *cis*-**4** (higher field) and *trans*-**4** (lower field) as tripletts due to the $^1J(^{13}C,^{14}N)$ couplings.

TZP basis set [11] and a TZVP auxiliary basis for the fit of the charge density [12]. The calculations were performed starting from T_d symmetry (**1**), O_h symmetry ($[Si(NCS)]_6^{2-}$), C_2 symmetry (*cis*-**4**), or C_i symmetry (*trans*-**4**) using the TURBOMOLE program system [13]. The structures of the respective calculated minima are shown in Figures 10−13, with selected calculated distances and angles in the respective figure captions. As can be seen from Figures 10−12, the calculated and experimentally established structures are in reasonable agreement [14]. The experimental Si−N−C angles vary from 180° (symmetry axis in the case of **2**) to 159.01(16)° (Si−N3−C3 for **3**·$2CH_3CN$). As shown by additional computational studies of the $[Si(NCS)_6]^{2-}$ dianion (geometry optimization for C_S symmetry; Figure 14), this variability of the Si−N−C angle can be explained by intermolecular interactions in the crystal: when all six Si−N−C angles are artificially bent to 160° (the resulting structure does not represent a local minimum), an energy increase of only 8.8 kJ mol^{-1} arises which

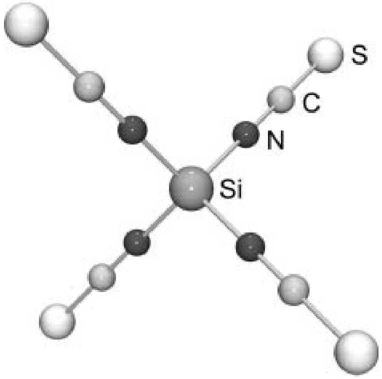


Fig. 10 Calculated structure of **1** (T_d symmetry); selected bond lengths/Å and angles/°:

Si−N 1.698, N−C 1.204, C−S 1.569, N−Si−N 109.5, Si−N−C 180.0, N−C−S 180.0. Calculated ^{29}Si NMR shift for this structure: $\delta = -141$.

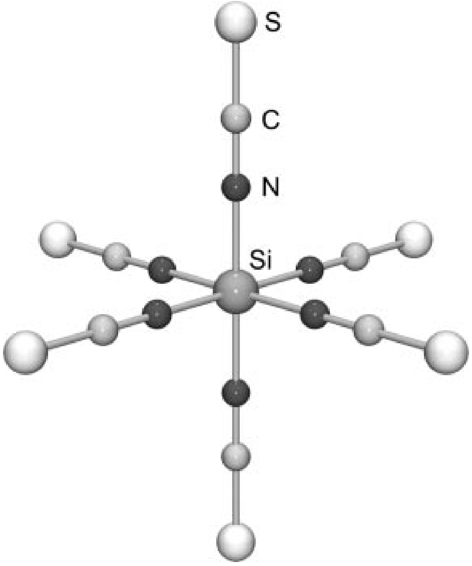


Fig. 11 Calculated structure of the $[Si(NCS)_6]^{2-}$ dianion (O_h symmetry); selected bond lengths/Å and angles/°:

Si−N 1.833, N−C 1.187, C−S 1.613, N−Si−N 90.0/180.0, Si−N−C 180.0, N−C−S 180.0. Calculated ^{29}Si NMR shift for this structure: $\delta = -251$.

can be easily compensated by packing effects in the crystal.

The isotropic ^{29}Si chemical shifts determined experimentally for **1**, **2**, **3**·2CH$_3$CN, *cis*-**4**, and *trans*-**4** were also accurately reproduced by quantum-chemical calculations (see captions of Figures 10−13). These studies were carried out at the HF/TZP level.

The calculated relative energies of the *cis*- and *trans*-isomers of **4** differ only by 1.8 kJ mol^{-1}, the *cis*-isomer being energetically more stable than the *trans*-isomer. The molar equilibrium ratio determined by NMR spectroscopy (*cis*/*trans* ratio in CDCl$_3$ at 22 °C ca. 1.5:1) is in good agreement with the calculated energy difference between *cis*-**4** and *trans*-**4**.

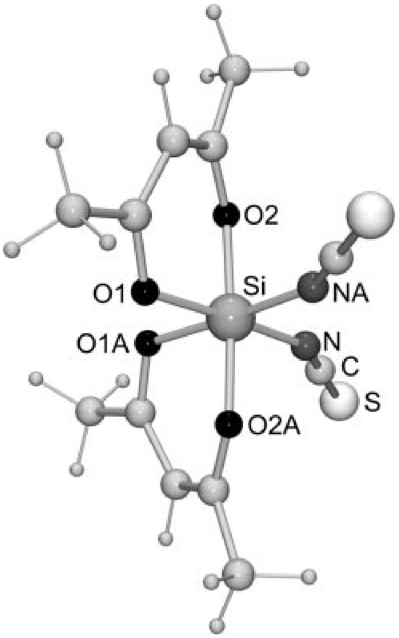


Fig. 12 Calculated structure of *cis*-**4** (C_2 symmetry); selected bond lengths/Å and angles/°:

Si−O1 1.822, Si−O2 1.802, Si−N 1.800, N−C 1.197, C−S 1.593, O1−Si−O2 91.4, O1−Si−O1A 86.3, O1−Si−O2A 86.4, O1−Si−N 176.3, O1−Si−NA 90.2, O2−Si−O2A 176.9, O2−Si−N 89.6, O2−Si−NA 92.5, N−Si−NA 93.3, Si−N−C 150.7, N−C−S 179.2. Calculated ^{29}Si NMR shift for this structure: $\delta = -199$.

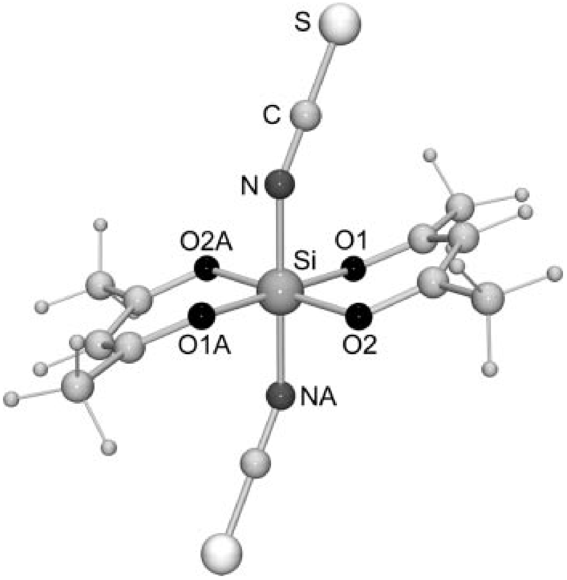


Fig. 13 Calculated structure of *trans*-**4** (C_i symmetry); selected bond lengths/Å and angles/°:

Si−O1 1.804, Si−O2 1.801, Si−N 1.815, N−C 1.198, C−S 1.594, O1−Si−O2 93.3, O1−Si−O1A 180.0, O1−Si−O2A 86.7, O1−Si−N 90.3, O1−Si−NA 89.7, O2−Si−O2A 180.0, O2−Si−N 90.4, O2−Si−NA 89.6, N−Si−NA 180.0, Si−N−C 150.0, N−C−S 179.2. Calculated ^{29}Si NMR shift for this structure: $\delta = -201$.

Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according

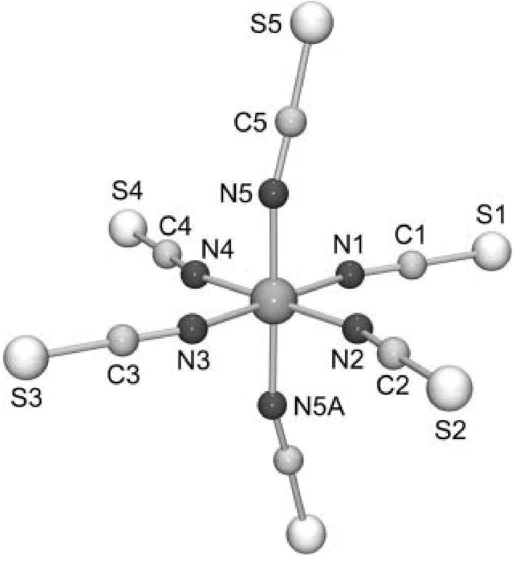


Fig. 14 Calculated structure of the "bent" $[Si(NCS)_6]^{2-}$ dianion (C_s symmetry); selected bond lengths/Å and angles/°: Si−N 1.836−1.844, N−C 1.188−1.190, C−S 1.610−1.614, N−Si−N 89.3−90.7/178.6−179.9, Si−N−C 160.0, N−C−S 177.5−177.9. Calculated ^{29}Si NMR shift for this structure: $\delta = -246$.

to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) using $CDCl_3$ as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, $\delta = 7.24$), internal $CDCl_3$ (^{13}C, $\delta = 77.00$), or external TMS (^{29}Si, $\delta = 0$). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Assignment of the ^{29}Si NMR data of *cis*-**4** and *trans*-**4** was supported by ^{1}H,^{29}Si COSY experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (^{13}C, ^{29}Si; $\delta = 0$) or glycine (^{15}N, $\delta = -342.0$); spinning rate, 5−7 kHz; contact time, 1−8 ms (^{13}C), 3 ms (^{15}N), or 5−8 ms (^{29}Si); 90° ^{1}H transmitter pulse length, 3.6 µs; repetition time, 4 s). Solid-state ^{29}Si single-pulse MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample (79.5 MHz; external standard, TMS ($\delta = 0$); spinning rate, 5 kHz; ^{29}Si transmitter pulse length, 4 µs; repetition time, 120 s).

*Tetra(thiocyanato-*N*)silane (1).* The synthesis of **1** was carried out analogously to ref. [3] by reaction of tetrachlorosilane (8.37 g, 49.3 mmol) with ammonium thiocyanate (15.0 g, 197 mmol), using toluene instead of benzene as the solvent. Yield: 8.32 g (65 %) of a colorless crystalline solid. Mp. 145 °C.

$C_4N_4S_4Si$ (260.4 g mol^{-1})
Analyses: C 18.8 (calc. 18.45); N 21.1 (21.51) %.

^{29}Si MAS NMR: $\delta = -143.2$.

*Tetraethylammonium Hexa(thiocyanato-*N*)silicate (2).* A mixture of **1** (750 mg, 2.88 mmol), tetraethylammonium chloride (954 mg, 5.76 mmol), potassium thiocyanate (560 mg, 5.76 mmol), and tetrahydrofuran (20 mL) was heated under reflux for 3 h. After the mixture was cooled to 20 °C, the precipitate was filtered off and discarded, and the filtrate was concentrated to ca. 5 mL and then kept at −20 °C for 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 1.30 g (yield: 71 %) of a colorless crystalline product. Mp. 76 °C

$C_{22}H_{40}N_8S_6Si$ (637.1 g mol^{-1})
Analyses: C 41.6 (calc. 41.48); H 6.3 (6.33); N 17.8 (17.59); S 29.9 (30.20) %.

^{13}C VACP/MAS NMR: δ = 8.7 (NCH_2CH_3), 52.5 (NCH_2CH_3), 127.3−131.5 (NCS) [15]. − ^{29}Si VACP/MAS NMR: $\delta = -256.5$.

*Potassium-18-crown-6 Hexa(thiocyanato-*N*)silicate-Diacetonitrile (3).* A mixture of **1** (938 mg, 3.60 mmol), potassium thiocyanate (700 mg, 7.20 mmol), 18-crown-6 (1.90 g, 7.19 mmol), and acetonitrile (20 mL) was heated under reflux for 3 h. After the mixture was cooled to 20 °C, the precipitate was filtered off and discarded, and the filtrate was kept at −20 °C for 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 3.08 g (yield 80 %) of a colorless crystalline product. Mp. 232 °C (dec.)

$C_{34}H_{54}K_2N_8O_{12}S_6Si$ (1065.5 g mol^{-1})
Analyses: C 38.5 (calc. 38.33); H 5.0 (5.11); N 10.4 (10.52); S 17.9 (18.06) %.

^{13}C VACP/MAS NMR: δ = 2.1 (CH_3CN), 71.2 (OCH_2C), 117.3 (CH_3CN), 126.7 (NCS), 131.1 (NCS), 132.1 (NCS) [15]. − ^{29}Si VACP/MAS NMR: $\delta = -253.0$.

cis-*Bis[acetylacetonato-*O,O*]di(thiocyanato-N)silicon(IV)* (cis-**4**). Acetylacetone (1.37 g, 13.7 mmol) was added at 20 °C to a stirred solution of **1** (1.79 g, 6.87 mmol) in tetrahydrofuran (20 mL). After the mixture was stirred at 20 °C for 1 h, *n*-pentane (20 mL) was added, and the resulting mixture was kept undisturbed at 20 °C for 2 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 1.82 g (yield 77 %) of a colorless crystalline product. Mp. 180 °C (dec.)

$C_{12}H_{14}N_2O_4S_2Si$ (342.5)
Analyses: C 42.1 (calc. 42.09); H 4.2 (4.12); N 8.2 (8.18); S 18.4 (18.73) %.

^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 6 H, CH_3), 2.24 (s, 6 H, CH_3), 5.86 (s, 2 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 25.7 (CH_3), 25.9 (CH_3), 102.89 (CH), 133.0 (t, $^{1}J(^{13}C,^{14}N)$ = 26.3 Hz , NCS), 191.9 (CO), 193.1 (CO). − ^{29}Si NMR ($CDCl_3$): $\delta = -208.7$. − ^{13}C VACP/MAS NMR: δ = 26.3 (CH_3), 27.1 (CH_3), 27.3 (CH_3), 103.2 (CH), 106.0 (CH), 131.4 (NCS), 132.8 (NCS) [15], 193.0 (CO), 194.3 (CO), 194.9 (CO). − ^{15}N VACP/MAS NMR: $\delta = -233.5$ and −230.8. − ^{29}Si VACP/MAS NMR: $\delta = -210.2$ (quint., $^{1}J(^{14}N,^{29}Si)$ = 29.3 and 32.4 Hz).

Solution NMR data of *trans*-**4**: ^{1}H NMR ($CDCl_3$): δ = 2.21 (s, 12 H, CH_3), 5.86 (s, 2 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 25.8 (CH_3), 102.93 (CH), 134.7 (t, $^{1}J(^{13}C,^{14}N)$ = 24.9 Hz , NCS), 192.8 (CO). − ^{29}Si NMR ($CDCl_3$): $\delta = -208.2$.

Single-Crystal X-Ray Diffraction Studies. A suitable single crystal of **1** was obtained directly from the reaction mixture. Suitable single crystals of **2**, **3**·$2CH_3CN$, and *cis*-**4** were obtained as follows: **2**, crystallization from THF at −20 °C; **3**·$2CH_3CN$, crystallization from acetonitrile (cooling of a saturated solution from 20 °C to

−20 °C); *cis*-**4**, crystallization from THF/*n*-pentane (1:1 (v:v)) at 20 °C. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS diffractometer; graphite-monochromated MoK_α radiation, λ = 0.71073 Å). The structures were solved by direct methods (**1**, ref. [16a]; **2**, **3**·2CH$_3$CN, and *cis*-**4**, ref. [16b]). The non-hydrogen atoms were refined anisotropically [17]. A riding model was employed in the refinement of the C*H* hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-206855 (**1**), CCDC-206856 (**2**), CCDC-206857 (**3**·2CH$_3$CN), and CCDC-206858 (*cis*-**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Studies. RI-MP2 [10] geometry optimizations of **1**, [Si(NCS)$_6$]$^{2-}$, *cis*-**4**, and *trans*-**4** were carried out at the TZP level (with a TZVP auxiliary basis for the fit of the charge density) [11,12] using the TURBOMOLE program system [13]. The calculations were performed starting from the following symmetries: T_d (**1**), O_h ([Si(NCS)$_6$]$^{2-}$), C_s ("bent" [Si(NCS)$_6$]$^{2-}$), C_2 (*cis*-**4**), and C_i (*trans*-**4**). The optimized structures were characterized as minima (the "bent" [Si(NCS)$_6$]$^{2-}$ dianion is not a minimum because the Si−N−C angles were fixed during the optimization) on the potential energy surfaces by harmonic vibrational frequency analysis. The calculations of the ^{29}Si NMR chemical shifts for the optimized structures of **1**, [Si(NCS)$_6$]$^{2-}$, *cis*-**4**, and *trans*-**4** were carried out at the HF/TZP level using the module mpshift implemented in TURBOMOLE. Computed absolute shieldings (σ) were converted to relative shifts (δ) using the shielding of TMS (399.4 ppm), computed at the same theoretical level. The reported energy differences include the MP2 and zero-point vibrational energies obtained by HF calculations.

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References and Notes

[1] Recent review dealing with penta- and hexacoordinate silicon(IV) complexes with *Si*O$_5$ and *Si*O$_6$ skeletons: R. Tacke, O. Seiler, in: *Silicon Chemistry: From Molecules to Extended Systems*, P. Jutzi, U. Schubert (eds.), Wiley-VCH, Weinheim, in press.

[2] Publications dealing with hexacoordinate silicon(IV) complexes with *Si*N$_6$ skeletons: (a) E. Bär, W. P. Fehlhammer, D. K. Breitinger, J. Mink, *Inorg. Chim. Acta* **1984**, *82*, L17. (b) W. Heininger, R. Stucka, G. Nagorsen, *Z. Naturforsch.* **1986**, *41b*, 702. (c) W. Heininger, K. Polborn, G. Nagorsen, *Z. Naturforsch.* **1988**, *43b*, 857. (d) M. Fritz, D. Rieger, E. Bär, G. Beck, J. Fuchs, G. Holzmann, W. P. Fehlhammer, *Inorg. Chim Acta* **1992**, *198−200*, 513. (e) A. C. Filippou, P. Portius, G. Schnakenburg, *J. Am. Chem. Soc.* **2002**, *124*, 12396.

[3] Synthesis of **1**: R. G. Neville, J. J. McGee, in: *Inorganic Syntheses, Vol. VIII,* H. F. Holtzclaw, Jr. (ed.), McGraw-Hill, New York, 1966, pp. 27−31.

[4] Alternative synthesis and solution NMR studies of **4**: S. P. Narula, R. Shankar, B. Kaur, S. Soni, *Polyhedron* **1991**, *10*, 2463.

[5] Recent publications dealing with compounds of higher-coordinate silicon: (a) R. Tacke, M. Penka, F. Popp, I. Richter, *Eur. J. Inorg. Chem.* **2002**, 1025. (b) A. Biller, C. Burschka, M. Penka, R. Tacke, *Inorg. Chem.* **2002**, *41*, 3901. (c) I. Richter, M. Penka, R. Tacke, *Inorg. Chem.* **2002**, *41*, 3950. (d) I. Richter, M. Penka, R. Tacke, *Organometallics* **2002**, *21*, 3050. (e) O. Seiler, C. Burschka, M. Penka, R. Tacke, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2427. (f) O. Seiler, C. Burschka, M. Penka, R. Tacke, *Silicon Chemistry*, in press. (g) R. Tacke, R. Bertermann, A. Biller, C. Burschka, M. Penka, *Can. J. Chem.*, submitted. (h) R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics*, submitted.

[6] Selected reviews dealing with compounds of higher-coordinate silicon: (a) S. N. Tandura, M. G. Voronkov, N. V. Alekseev, *Top. Curr. Chem.* **1986**, *131*, 99. (b) W. S. Sheldrick, in: *The Chemistry of Organic Silicon Compounds, Part 1*, S. Patai, Z. Rappoport (eds.), Wiley, Chichester, U.K., 1989, pp. 227−303. (c) A. R. Bassindale, P. G. Taylor, in: *The Chemistry of Organic Silicon Compounds, Part 1*, S. Patai, Z. Rappoport (eds.), Wiley, Chichester, U.K., 1989, pp. 839−892. (d) R. J. P. Corriu, J. C. Young, in: *The Chemistry of Organic Silicon Compounds, Part 2*, S. Patai, Z. Rappoport (eds.), Wiley, Chichester, U.K., 1989, pp. 1241−1288. (e) R. R. Holmes, *Chem. Rev.* **1990**, *90*, 17. (f) C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371. (g) R. Tacke, J. Becht, A. Lopez-Mras, J. Sperlich, *J. Organomet. Chem.* **1993**, *446*, 1. (h) J. G. Verkade, *Coord. Chem. Rev.* **1994**, *137*, 233. (i) R. Tacke, O. Dannappel, in: *Tailor-made Silicon-Oxygen Compounds − From Molecules to Materials*, R. Corriu, P. Jutzi (eds.), Vieweg, Braunschweig-Wiesbaden, Germany, 1996, pp. 75−86. (j) E. Lukevics, O. A. Pudova, *Chem. Heterocycl. Compd. (Engl. Transl.)* **1996**, *32*, 1381. (k) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927. (l) D. Kost, I. Kalikhman, in: *The Chemistry of Organic Silicon Compounds, Vol. 2, Part 2*, Z. Rappoport, Y. Apeloig (eds.), Wiley, Chichester, U.K., 1998, pp. 1339−1445. (m) V. Pestunovich, S. Kirpichenko, M. Voronkov, in: *The Chemistry of Organic Silicon Compounds, Vol. 2, Part 2*, Z. Rappoport, Y. Apeloig (eds.), Wiley, Chichester, U.K., 1998, pp. 1447−1537. (n) C. Chuit, R. J. P Corriu, C. Reye, in: *Chemistry of Hypervalent Compounds*, K. Akiba (ed.), Wiley-VCH, New York, 1999, pp. 81−146. (o) R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221. (p) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, 2000, pp. 97−114.

[7] O. Seiler, N. Buggisch, M. Penka, R. Tacke, *XIII International Symposium on Organosilicon Chemistry − 35th Organosilicon Symposium*, Guanajuato, Mexico, August 25−30, 2002, Abstracts Book, Abstract P2-45, p. 161.

[8] The quality of the crystal structure analysis described in this paper is significantly better than that reported in ref. [2b].

[9] Attempts to obtain solution NMR spectra of **1** and the [Si(NCS)$_6$]$^{2-}$ dianion of **2** and **3**·2CH$_3$CN were unsuccessful.

[10] (a) F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331. (b) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143.

[11] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.

[12] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[13] Program system TURBOMOLE: R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.

[14] A perfect agreement between the calculated and experimentally established structures of **1**, [Si(NCS)$_6$]$^{2-}$, and *cis*-**4** cannot

be expected since the latter are influenced by intermolecular interactions in the crystal.

[15] The expected splittings due to the $^{1}J(^{13}C,^{14}N)$ coupling of the N*C*S carbon atoms were only poorly resolved because of the low signal to noise ratio of the respective signals and the large chemical shift anisotropy (CSA) of the N*C*S carbon atoms.

[16] (a) A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR97, University of Bari, Bari, Italy, 1997. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435. (b) G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen, Germany, 1997. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[17] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.