1282 *Organometallics* **2001,** *20,* 1282−1284

Synthesis and Structure of a S_4Si_4 Cage Compound[†]

Carsten Ackerhans, Herbert W. Roesky,* and Mathias Noltemeyer

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

Received October 20, 2000

Summary: The reaction of the tetraaminodisilane $R_2Si_2(NH_2)_4$ ($R = CH(SiMe_3)_2$) with liquid H_2S at −70 °C resulted in the formation of a $R_4S_4Si_4$ cage. The core of the molecule consists of four five-membered rings. Two disilane units are bridged cross over by four sulfur atoms. This is a new structural type in the group of silicon−sulfur ring and cluster compounds.

Compounds of the N_4S_4 type[1] have been known for a long time. Mostly they are formed by the elements of groups 15 and 16 of the periodic table: for example, As_4S_4, α-P_4S_4, $P_4(NR)_4$ ($R = t$Bu), and the $S_4Te_4^{2+}$ cation.[2−5] The compound $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{Se}_4\mathrm{Sn}_4$ (groups 14 and 16) has also a similar structure.[6] Furthermore, $R_4Ga_4Cl_4$ ($R = Si(SiMe_3)_3$) is formed from elements of groups 13 and 17[7] (Chart 1).

Subsequently we succeeded in preparing a comparable compound by combining elements of groups 14 and 16 and obtaining the crystal structural analysis. This compound shows a new structural type in a series of other silicon−sulfur ring and cluster compounds[8] (Chart 2).

Chart 1. Structures of the Previously Reported As_4S_4 and $R_4As_4Cl_4$ Cages[2,7]

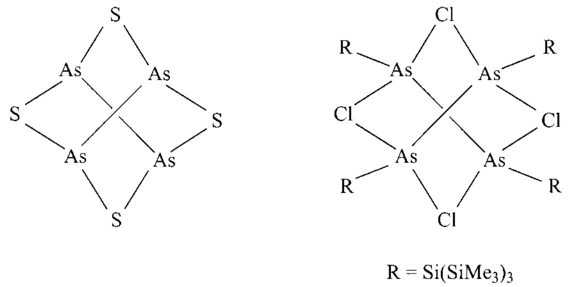
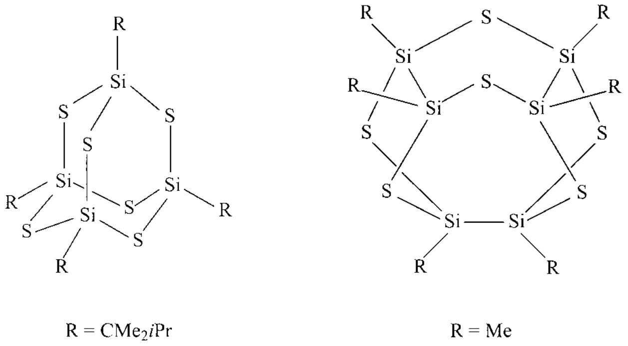
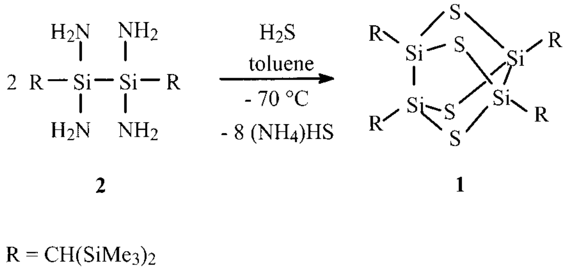


Chart 2. Examples of Previously Reported S_xSi_y Cage Structures[8]



Scheme 1



2,3a,5,6a-Tetrakis(bis(trimethylsilyl)methyl)tetrahydro-1,3,4,6-tetrathia-2,3a,5,6a-tetrasila-2,5-cyclopentalene (**1**) consists of two disilane units which are crossover-bridged by four sulfur atoms (Scheme 1). Compound **1** possesses the same cage structure as the aforementioned compounds, and the coordination number 4 at all silicon atoms is completed by a bis(trimethylsilyl)methyl group. The driving force for the crossover arrangement of the sulfur atoms is most likely the formation of the four five-membered rings. The starting material for the synthesis of this cage compound is the tetraaminodisilane $R_2Si_2(NH_2)_4$ (**2**; $R = CH(SiMe_3)_2$).[9]

Compound **2** reacts with liquid H_2S at −70 °C.[10] The resulting crude product was crystallized from benzene after workup and contained, in addition to **1**, some other uncharacterizable byproducts. Colorless benzene-containing crystals were obtained. Compound **1** reacts with moisture under formation of H_2S. The crystals were fully characterized by IR, MS (EI), and multinuclear NMR[11] and a single-crystal X-ray structural analysis.[12]

---

* To whom correspondence should be addressed. Fax: +49 (0)551/39 3373. E-mail: hroesky@gwdg.de.

[†] Dedicated to Professor Ulrich Müller on the occasion of his 60th birthday.

(1) (a) Sharma, B. D.; Donohue, J. *Acta Crystallogr., Sect. B* **1963**, *16*, 891−897. (b) Roesky, H. W. *Angew. Chem.* **1979**, *91*, 112−118; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 91−97.

(2) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347−1349.

(3) Chang, C.-C.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1978**, *17*, 2056−2062.

(4) DuBois, D.; Duesler, E. N.; Paine, R. T. *J. Chem. Soc., Chem. Commun.* **1984**, 488−489.

(5) Faggiani, R.; Gillespie, R. J.; Vekris, J. E. *J. Chem. Soc., Chem. Commun.* **1988**, 902−904.

(6) Weidenbruch, M.; Stilter, A.; Marsmann, H.; Peters, K.; von Schnering, H. G. *Eur. J. Inorg. Chem.* **1998**, 1333−1336.

(7) Linti, G.; Köstler, W. *Angew. Chem.* **1996**, *108*, 593−595; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 550−552.

(8) (a) Herzog, U.; Böhme, U.; Roewer, G.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **2000**, *602*, 193−207. (b) Rangan, K. K.; Trikalitis, P. N.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 10230−10231. (c) Unno, M.; Ishii, D.; Matusmoto, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2469−2473. (d) Unno, M.; Kawai, Y.; Shioyama, H.; Matsumoto, H. *Organometallics* **1997**, *16*, 4428−4434. (e) Ando, W.; Kadowaki, T.; Kabe, Y.; Ishii, M. *Angew. Chem.* **1992**, *104*, 84−85; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 59−60.

(9) Ackerhans, C.; Böttcher, P.; Krätzner, R.; Müller, P.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.*, in press.

10.1021/om000899t CCC: $20.00
Publication on Web 03/07/2001

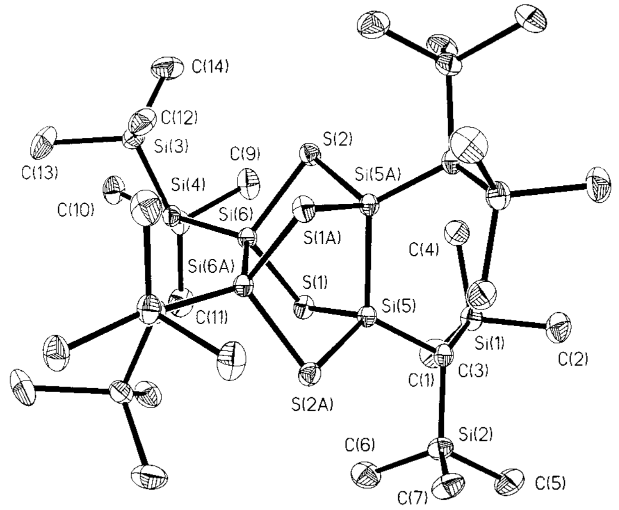


Figure 1. Molecular structure of **1** in the crystal state. Selected bond lengths (Å) and angles (deg): S(1)−Si(5) = 2.1461(10), S(2)−Si(5A) = 2.1506(10), S(1)−Si(6) = 2.1535(10), S(2)−Si(6) = 2.1510(10), Si(5)−Si(5A) = 2.414(2), Si(6)−Si(6A) = 2.3988(14), Si(5)−C(1) = 1.857(3), Si(6)−C(8) = 1.854(3); Si(5)−S(1)−Si(6) = 87.85(4), Si(5A)−S(2)−Si(6) = 87.74(4), S(1)−Si(5)−S(2A) = 104.40(4), S(1)−Si(6)−S(2) = 104.01(4), S(1)−Si(5)−Si(5A) = 104.84(4), S(2)−Si(6)−Si(6A) = 105.19(4). Symmetry transformations for the equivalent atoms: (A) $-x + 1, y, -z + {}^1/_2$.

The ^{1}H NMR spectrum of **1** shows a signal for the protons of the methyl groups (0.38 ppm). The resonance of the CH protons was not observed, but this behavior is known for other compounds with this ligand.[13] In the ^{13}C NMR spectrum two signals are found; the first (3.5 ppm) can be assigned to the carbon atoms of the methyl groups and the second (5.3 ppm) to the CH groups. The ^{29}Si NMR spectrum also shows two resonances as expected, one for the trimethylsilyl groups (1.6 ppm) and one for the silicon atoms of the central S_4Si_4 cage (19.6 ppm). In the EI mass spectrum the molecular ion peak is clearly identified at *m*/*e* 877.

Table 1. Crystallographic Data for 1

empirical formula	$C_{28}H_{76}S_4Si_{12}\cdot 3C_6H_6$
fw	1112.53
cryst size (mm)	0.60 × 0.40 × 0.40
cryst syst	monoclinic
space group	*P*2/*c*
unit cell dimens	
a (Å)	12.690(3)
b (Å)	11.954(2)
c (Å)	21.283(4)
α (deg)	90
β (deg)	93.90(3)
γ (deg)	90
cell vol (Å^3)	3221.1(11)
Z	2
calcd density (g/cm^3)	1.147
μ(Mo Kα) (mm^{-1})	0.400
θ range for data collecn (deg)	2.34−27.91
limiting indices	$-16 \le h \le 16$ $0 \le k \le 15$ $0 \le l \le 27$
no. of rflns collected	50 690
no. of indep rflns	7618 (R_{int} = 0.0780)
no. of data/restraints/params	7618/0/292
goodness of fit on F^2	S^a = 1.120
final *R* indices ($I > 2\sigma(I)$)	R1^b = 0.0508 wR2^c = 0.1156
R indices (all data)	R1 = 0.0700 wR2 = 0.1233
largest diff peak and hole (e Å^{-3})	0.808 and −0.322

^{a} $S = [\sum w(F_o^2 - F_c^2)^2/\sum(n - p)]^{1/2}$. ^{b} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

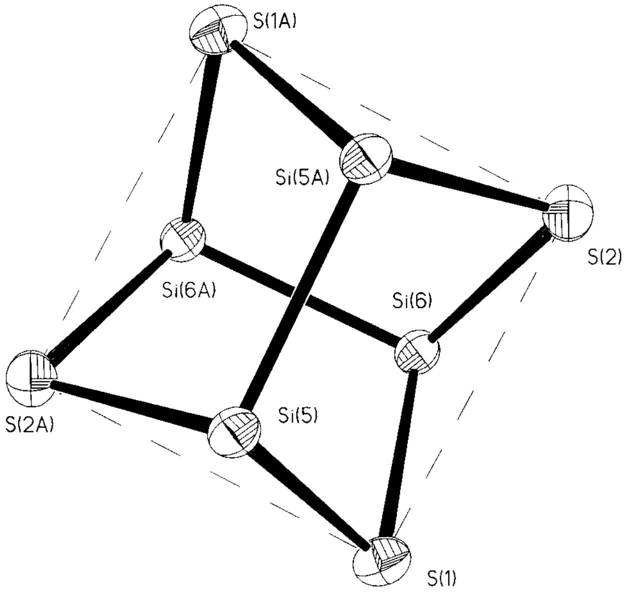


Figure 2. Structure of the central S_4Si_4 cage.

The single-crystal structural analysis of **1** shows a central eight-atom S_4Si_4 core structure. The coordination sphere of the silicon atom is completed by a bis(trimethylsilyl)methyl group (Figure 1). The average Si−Si bond length of the disilanes is 2.406 Å. Similar Si−Si bond lengths are found in $R_2Si_2Cl_4$ (R = *i*Pr$_2$N, 2.336 Å; R = CH(SiMe$_3$)$_2$, 2.380 Å) and in RSi(NH$_2$)-NHTiMe(Cp*)NHSi(NH$_2$)R (R = PhNSiMe$_3$, 2.356

---

(10) Synthesis of **1**: In a Schlenk flask (100 mL) H_2S (5 mL) was condensed at −70 °C and a cold solution (−70 °C) of **2** (0.53 g, 1.2 mmol) in toluene (50 mL) was added dropwise. After it was stirred at this temperature for 1 h, the mixture was warmed slowly to room temperature, whereupon the remaining H_2S vaporized. The solid that formed was filtered, and the solvent was removed under vacuum. Benzene (10 mL) was added to the crude product. After a second filtration and slow crystallization at room temperature **1** (0.14 g, 0.16 mmol, 27%) was obtained as colorless crystals, suitable for an X-ray crystal structural analysis. For the other analytical investigation the crystals were ground and stored under vacuum for 5 h to remove the benzene.

(11) Characterization data for **1** are as follows. Mp: 261 °C. ^{1}H NMR (500 MHz, C_6D_6, TMS): δ 0.38 (Si(CH$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6, TMS): δ 3.5 (Si(CH$_3$)$_3$), 5.3 (CH(SiMe$_3$)$_2$). ^{29}Si NMR (100 MHz, C_6D_6, TMS): δ 1.6 (SiMe$_3$), 19.6 (Si_4S_4). IR (KBr, Nujol): $\tilde{\nu}$ 1303, 1253, 1097, 1007, 840, 771, 722, 680, 560, 519, 498, 477 cm^{-1}. MS (EI): *m*/*e* (%) 877 (24) [M$^+$], 862 (10) [M$^+$ − Me], 219 (100) [(SiMe$_3$)$_2$CHSiS$^+$]. Anal. Calcd for $C_{28}H_{76}S_4Si_{12}$ (878.20): C, 38.3; H, 8.7. Found: C, 37.5; H, 8.8.

(12) X-ray structure determination of **1**: A crystal of **1** was mounted on a glass fiber in a rapidly cooled perfluoropolyether.[20] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), performing φ and ω scans. The structure was solved by direct methods using SHELXS-97[21] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Other details of the data collection, structure solution, and refinement are listed in Table 1.

(13) Ackerhans, C.; Räke, B.; Krätzner, R.; Müller, P.; Roesky, H. W.; Usón, I. *Eur. J. Inorg. Chem.* **2000**, 827−830.

(14) Schuh, H.; Schlosser, T.; Bissinger, P.; Schmidbaur, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1347−1352.

(15) Ackerhans, C. Diplomarbeit, Universität Göttingen, 1998.

(16) Böttcher, P.; Wraage, K.; Roesky, H. W.; Lanfranchi, M.; Tiripicchio, A. *Chem. Ber.* **1997**, *130*, 1787−1790.

Å).[14−16] The four sulfur atoms are arranged in a nearly square-planar geometry with an average side length of 3.39 Å (Figure 2.). The van der Waals distance for an S−S contact was calculated to be 3.60 Å,[17] while in As_4S_4 an S−S bond length of 3.285 Å was found.[2] At the sulfur atoms of **1** an average bond angle of 87.8° was found, and the mean Si−S bond length amounts to 2.150 Å. This is comparable with the Si−S bond length in bis(triphenylsilyl) sulfide (2.153 Å) and only marginally shorter than the bond length in decamethyl-7-thiahexasilanorbornane (2.169 Å).[18,19] The angles between the two Si−S bonds at the silicon atoms average to 104.2°. In contrast to N_4S_4, where the electropositive sulfur atoms have a tetrahedral symmetry and the electronegative nitrogen atoms form a square plane, in compound **1** the inverse arrangement is found with the sulfur atoms in a plane like that in As_4S_4. This structural arrangement is understandable, because in the S_4Si_4 cage as well as in the As_4S_4 molecule the sulfur atoms are the electronegative partners.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000899T

---

(17) Huheey, J. E. *Anorganische Chemie, Prinzipien von Struktur und Reaktivität*; Walter de Gruyter: Berlin, New York, 1988; p 278.

(18) Wojnowski, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1985**, *525*, 121−126.

(19) Wojnowski, W.; Dreczewski, B.; Herman, A.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem.* **1985**, *97*, 978−979; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 992−993.

(20) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615−619.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(22) Sheldrick, G. M. SHELX-93; Universität Göttingen, 1993.