

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243816690>

Crystal and Molecular Structure of $\text{NH}_4[\text{S}_4\text{N}_5\text{O}]$ – A New Sulfur–Nitrogen Cage

ARTICLE in ANGEWANDTE CHEMIE INTERNATIONAL EDITION · APRIL 1973

Impact Factor: 11.26 · DOI: 10.1002/anie.197303162

CITATIONS

10

READS

18

3 AUTHORS, INCLUDING:



Ralf Steudel

Technische Universität Berlin

357 PUBLICATIONS 4,586 CITATIONS

SEE PROFILE



Hans Bradaczek

EFG GmbH Berlin former Freie Universität ...

122 PUBLICATIONS 1,273 CITATIONS

SEE PROFILE

are added dropwise from two dropping funnels during 3 h into vigorously stirred anhydrous benzene (1000 ml) at 5°C. LiCl is removed from the reaction mixture by filtration at room temperature. The benzene solution is concentrated and the product (2) is then precipitated by cyclohexane at 5°C. All operations are effected under N₂. Crude yield 37%; after six-fold recrystallization from dry cyclohexane 26%.

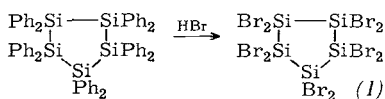
Received: November 27, 1972 [Z 774 a IE]
German version: Angew. Chem. 85, 304 (1973)

Cyclopentasilane, the First Unsubstituted Cyclic Silicon Hydride

By Edwin Hengge and Günther Bauer^(*)

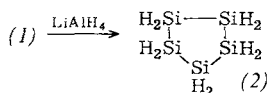
Only a few derivatives of cyclosilanes have previously been known and, except for a single chloro-derivative of uncertain structure^[2], these all contained alkyl or aryl substituents^[1]. Cyclic silanes containing functional groups were first obtained by removing phenyl groups from perphenylated cyclosilanes by means of HI^[3], but this is not generally possible and led, for example, only to derivatives of pentaphenylcyclopentasilane Si₅(C₆H₅)₅X₅^[4].

We have now found that decaphenylcyclopentasilane is converted quantitatively into decabromocyclopentasilane (1) by anhydrous HBr in a bomb tube at room temperature:



Compound (1), easily prepared in this way and the first bromocyclosilane to be known, forms colorless crystals melting at 195°C and extremely sensitive to moisture. The relative molecular masses (ebullioscopically, in benzene; mean of several measurements) are 939 (calc. 939.5). The Raman and IR spectra have very few lines, as expected; a Raman-active breathing vibration of the ring is observed at 510 cm⁻¹ as well as the Si—Br bands.

As regards the reactions of (1) we were naturally most interested in the possibility of hydrogenation to the unsubstituted cyclosilane. This can be done by using very pure ethereal LiAlH₄ solution which should be added slowly to a benzene solution of the bromocyclosilane. After removal of the solvent a product could be isolated from the residue under reduced pressure (yield 80%); this proved to be the long sought cyclopentasilane (2):



Si₅H₁₀ is a colorless liquid with an extrapolated boiling point of ≈ 130°C. Elemental analysis shows only silicon and hydrogen in the correct proportions. The ¹H-NMR spectrum (in benzene, internal standard benzene) shows a single sharp singlet at 6.57 ppm with a coupling constant *J*²⁹SiH of 195 Hz. The vibration spectra show few lines: IR: νSiH 2130, δSiH₂ 865, 890 cm⁻¹; Raman: νSiH 2135,

δSiH₂ 891, 924, ring pulsation (ν_sSiSi) 382, ν_{as}SiSi 463, δ_{ring} 175 cm⁻¹. A theoretical estimate of the pulsation frequency, on the assumption that the ring is planar and with the nuclear separations and force constants of disilane, gave a value of 373 cm⁻¹^[5].

The mass spectrum of (2) contains lines in the region of *m/e* 150 (molecular ion), 118 (Si₄ units with varying proportions of hydrogen), 88 (Si₃ units with varying proportions of hydrogen) and 60 (Si₂ units with varying proportions of hydrogen). The individual groups were split by isotope effects, as expected.

The existence of the cyclic silane C₅H₁₀ can be regarded as proved by the findings described above.

Received: December 8, 1972 [Z 774 b IE]
German version: Angew. Chem. 85, 304 (1973)

[1] Previous reviews in H. Gilman and G. L. Schwebke, *Advan. Organometal. Chem.* 1, 89 (1964); see also R. West and A. Indriksons, *J. Amer. Chem. Soc.* 94, 6110 (1972); E. Hengge and F. Lunzer, *Syn. Inorg. Metallorg. Chem.* 2, 93 (1972).

[2] R. Schwarz and A. Köster, *Z. Naturforsch.* 7b, 57 (1952); E. Bonitz, *Angew. Chem.* 78, 475 (1966); *Angew. Chem. internat. Edit.* 5, 462 (1966).

[3] E. Hengge and H. Marketz, *Monatsh. Chem.* 100, 890 (1969).

[4] E. Hengge and H. Marketz, *Monatsh. Chem.* 101, 528 (1970).

[5] We thank Dr. F. Höfler for calculating the pulsation frequency and for the vibration spectroscopic studies.

Crystal and Molecular Structure of NH₄[S₄N₅O]—A New Sulfur-Nitrogen Cage^[1]

By Ralf Steudel, Peter Luger, and Hans Bradaczek^[*]

NH₄[S₄N₅O] (1) is obtained as yellow water-soluble crystals on reaction of SOCl₂ with liquid NH₃ and subsequent hydrolysis of the reaction products^[2]. As the IR and mass spectrum of this compound indicate an unusual cage structure of the anion S₄N₅O⁻, we have carried out a single-crystal X-ray structure analysis of (1).

The compound crystallizes in the monoclinic space group *C* 2/*m* with *a* = 17.848, *b* = 6.232, *c* = 7.095 Å; β = 104.83°; *Z* = 4; *d*_{exp.} = 1.96, *d*_{calc.} = 2.01 g/cm³. 1207 reflections were measured on an automatic Siemens single-crystal diffractometer with θ between 2.4° and 30°. 82 reflections whose intensities were less than twice the statistical error were treated as unobserved. The structure was solved by the multisolution method and refined by the method of least squares. Temperature factors of the atoms S, N and O were anisotropic, but that of the H atom was isotropically refined. Because the linear absorption coefficient was small and the crystal form was nearly that of a cube, we did not apply an absorption correction. After convergence of the refinements the final *R* value amounted to 5.1%. Figure 1 shows the result of the analysis; Table 1 lists the most important intramolecular distances and angles. Two neighboring ions NH₄⁺ and S₄N₅O⁻, joined by an O—H hydrogen bridge are placed on a common mirror plane. Both ions have C_s symmetry; moreover, the NH₄⁺ ion is bonded to the N² atoms of two further anions by way of two N—H hydrogen bridges. Only one of the four H atoms of NH₄⁺ does not take part in an H bridge.

[*] Prof. Dr. R. Steudel
Institut für Anorganische und Analytische Chemie der
Technischen Universität
1 Berlin 12, Strasse des 17. Juni 135 (Germany)

Prof. Dr. H. Bradaczek and Dr. P. Luger
Institut für Kristallographie der Freien Universität
1 Berlin 33, Takustrasse 6 (Germany)

[*] Prof. Dr. E. Hengge and Dipl.-Ing. G. Bauer
Anorganisch-chemisches Institut der Technischen Hochschule
A-8010 Graz, Stremayrgasse 16 (Austria)

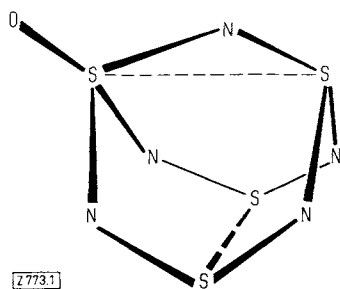
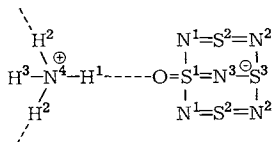


Fig. 1. Structure of the anion $S_4N_5O^-$.

Thus the cation is not tetrahedral but instead is strongly deformed (three different N—H nuclear separations, HNH angles between 82 and 128°).



The structure of the anion can be formally derived from the cage of S_4N_4 ^[3], one S atom (S^1) carrying an O atom and bridged to a neighboring S atom (S^3) through an N atom. This oxidized S atom is almost tetrahedrally coordinated. The S=O nuclear separation, 1.433 Å, corresponds to that in other molecules with S=O double bonds (SO_3 1.42 Å; SOF_4 1.42 Å).

Table 1. Bond lengths and angles in $NH_4[S_4N_5O]$ (1). Standard deviations in parenthesis.

Bond lengths [Å]					
N^4-H^1	1.03 (0.06)	S^1-O	1.433 (0.004)	S^2-S^2	2.633 (0.001)
N^4-H^2	0.98 (0.06)	S^1-N^3	1.580 (0.004)	S^1-S^3	2.717 (0.002)
N^4-H^3	0.93 (0.12)	S^1-N^1	1.591 (0.003)	S^1-S^2	2.658 (0.001)
$N^2 \cdots H^2$	2.00 (0.06)	S^2-N^1	1.631 (0.004)	S^2-S^3	2.741 (0.001)
$O \cdots H^1$	1.95 (0.06)	S^2-N^2	1.603 (0.003)	N^1-N^2	2.676 (0.004)
		S^3-N^2	1.651 (0.004)	N^1-N^1	2.524 (0.004)
		S^3-N^3	1.658 (0.005)	N^2-N^2	2.506 (0.005)
Bond angles [°]					
OS^1N^3	108.7 (0.2)	$N^1S^2N^2$	111.7 (0.2)	$H^1N^4H^2$	119 (5)
OS^1N^1	110.4 (0.2)	$S^2N^2S^3$	114.8 (0.2)	$H^1N^4H^3$	85 (7)
$N^1S^1N^3$	111.2 (0.1)	$S^1N^3S^3$	114.1 (0.3)	$H^2N^4H^2$	82 (5)
$N^1S^1N^1$	105.0 (0.2)	$N^3S^3N^2$	107.5 (0.2)	$H^2N^4H^3$	128 (5)
$S^1N^1S^2$	111.2 (0.2)	$N^2S^3N^2$	98.8 (0.2)		

The S—N nuclear separations in $S_4N_5O^-$ are somewhat more strongly differentiated than in S_4N_4 , where they vary only between 1.596 and 1.634 Å. Nevertheless one must assume largely delocalized π -bonds within the S_4N_5 skeleton. The structural formula above can therefore be described only as a limiting structure.

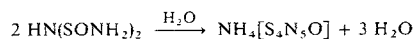
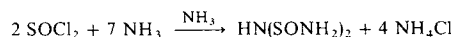
As in S_4N_4 , the contacts between the S atoms of one cage, being 2.7 Å, are appreciably smaller than the van der Waals S—S separations which are 3.7 Å. The smallest distances between different anions are practically in agreement with the van der Waals distances.

[1] Part 19 of Sulfur-Oxygen Compounds.—Part 18: R. Steudel and M. Rebsch, *Angew. Chem.* 84, 344 (1972); *Angew. Chem. internat. Edit.* 11, 302 (1972).

[2] R. Steudel, *Z. Naturforsch.* 24b, 934 (1969).

[3] B. D. Sharma and J. Donohue, *Acta Crystallogr.* 16, 891 (1963).

The formation of (1) from $SOCl_2$ and NH_3 can be interpreted by a series of successive condensations with elimination of HCl, H_2O and NH_3 :



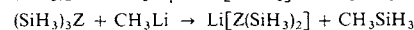
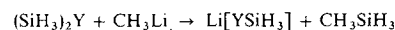
Received: November 21, 1972 [Z 773 IE]
German version: *Angew. Chem.* 85, 307 (1973)

Lithium Derivatives of Silanol and Related Compounds

By Stephen Cradock, Evelyn A. V. Ebsworth,
Hans Moretto, David W. H. Rankin, and
W. John Savage^[*]

Although disilylphosphane is relatively stable *in vacuo*, silanethiol and silaneselenol are not, while silanol is not known^[1]. Alkali metal derivatives of these compounds are therefore difficult to obtain directly.

We find that methyllithium reacts smoothly in diethyl ether over a period of minutes at 227 K with $(SiH_3)_2Y$ ($Y=O, S, Se$)^[2] or $(SiH_3)_3Z$ ($Z=P, As$); methylsilane is evolved in about 90% of the amount required by the equations:



The lithium derivatives may be isolated as white crystalline solids by evaporation of the solvent. They have been characterized by their Raman spectra (obtained from solids and from solutions—Tables 1 and 2).

Table 1. Raman spectra (cm^{-1}) of lithium silyl sulfide and lithium silyl selenide $Li[YSiH_3]$ in diethyl ether.

Y=S	Y=Se	Assignment
2130 m, p	2118 m, p	ν, SiH
945 w (br), dp	940 w (br), dp	δSiH_3
655 vw (br), dp	624 vw (br), dp	ρSiH_3
565 s, p	429 vs, p	$\nu Si-Y$

[*] Prof. Dr. E. A. V. Ebsworth, Dr. S. Cradock, Dr. H. Moretto, Dr. D. W. H. Rankin, and Dr. W. J. Savage
Department of Chemistry, Edinburgh University
West Mains Road, Edinburgh EH9 3JJ (Scotland)