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From Aminosilanoles to Homo- and Heterocyclic SiOSiN-Rings and Cages

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Alkaline derivates of aminosilanoles are isolated as rings, cubanes and prisms. They react stepwisely with element halides to give four-, six-, and eight-membered ring molecules. The smallest two silicon atoms containing four-membered rings were formed in these reactions. Reactions and structures are discussed.

Keywords: Aminosilanoles; (SiNSiO)-rings; Lithium derivatives

The lithium derivative of the aminosilanol crystallizes as LiO-cubane^[1], the sodium derivate as hexagonalic prism^[2], and the potassium derivative as polymer.^[2] In reactions with halosilanes 1-amino-1,3-disiloxanes are formed.

$$\begin{pmatrix} \times & & \\ \times & & \\ \times & & \\ N & & \\ H_2 & & \\ N & & \\$$

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$$Me_{2}HC CHMe_{2}$$

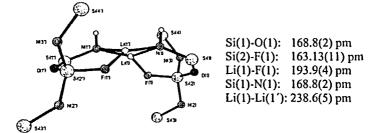
$$CMe_{3} N CHMe_{2}$$

$$Me_{3}C - Si - O - Si - N CHMe_{2}$$

$$O - Si - N CHMe_{2}$$

Usually the lithium derivatives of these aminosiloxanes are isolated as 1,3-disilazane-1-olates (A), that means a 1,3-(O-N)-silyl group migration has occurred. This rearrangement can be prevented by bulky substituents (B).

e.g. type B



In fluorine containing compounds often lithium is coordinated to the fluorine atom. Six-membered (Si-O-Si-N-Li-F)- or four-membered (Si-O-Li-N)-rings are obtained. LiF-elimination leads to the formation of (SiNSiO)_n-rings (n = 1,2). Eight-membered rings are isolated by using smaller ligands.

Four-membered rings are isolated by using bulky substituents,

e.g

The C(1)-atom has a non planar environment (Σ° C(1) = 355.7°). The Si-O bonds are larger than the Si-N bonds.

The lithium derivative of this ring crystallizes from n-hexane as a dimer.

The crystal structure shows some irregularities. The dimer is formed via a four-membered (Li-N)₂-ring, which is not entirely planar but folded by 10.7° across the Li-Li line. The (Si-O-Si-N)-rings have an angle of 86° on the central (LiN)₂-ring and of 5.8° to each other. As far as we know this is the smallest two Si-atoms containing four-membered ring.

The transannular Si...Si distance is found to be 237.2 pm.

The lithium atom can be substituated by other groups, e.g. the SiMe₃-group^[2]:

Si(1)-O 167.56 (12) pm
Si(2)-O 165.32 (12) pm
Si(1)-N 177.41 (14) pm
Si(2)-N 175.26 (14) pm
O-Si(1)-N 88.07 (6)°
O-Si(2)-N 89.51 (6)°
Si(1)-O-Si(2) 94.54 (6)°
Si(1)-N-Si(2) 87.79 (6)°

$$\Sigma^{\circ}$$
 (N) = 353.39°

The ring angles at the Si-atoms are smaller than 90° and the angles at the N- and O-atom are larger. The transannular Si....Si-distance measures 244.5 pm. The (OSiNSi) four-membered ring is planar. The sum of the angles around the N-atom is 353.39°, indicating a slightly trigonal environment.

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