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Masafumi Unno; Hiroaki Shioyama; Hideyuki Matsumoto

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Synthesis and Structures of Tetrasilsesquisulfides: Tetrakis(*tert*-butylsilsesquisulfide) and Tetrakis((1,1,2-trimethylpropyl)silsesquisulfide)

MASAFUMI UNNO, HIROAKI SHIOYAMA, AND HIDEYUKI MATSUMOTO*
*Department of Applied Chemistry, Faculty of Engineering,
Gunma University, Kiryu, Gunma 376, JAPAN*

Two tetra(alkylsilsesquisulfides) ($R_4Si_4S_6$, $R = t\text{-Bu}$, 1,1,2-trimethylpropyl) were synthesized. The structures were determined by X-ray crystallography and novel "double decker"-type structure was revealed for tetrakis((1,1,2-trimethylpropyl)silsesquisulfide).

INTRODUCTION

Cage silsesquioxanes are basically stable and various compounds with different sizes ($R_6Si_6O_9$, $R_8Si_8O_{12}$, $R_{10}Si_{10}O_{15}$) and with different substituents (H, alkyl, aryl, alkoxy) have been synthesized and characterized.¹ However, the chemistry of silicon-sulfur cage compounds are relatively much less known due to their susceptibility to hydrolysis. By introducing bulky groups, we have synthesized octasilacubane and related compounds and studied their unique reactions.² Here we report the synthesis and structures of silicon-sulfur cage compounds, tetrasilsesquisulfides.

RESULTS AND DISCUSSION

Until now, some tetrasilathianes were reported ($R_4Si_4S_6$, $R = H$, Me, Et, Ph, *t*-Bu) and all are known to possess adamantane-type structure.^{3,4b} On the other hand, two structures are known in $R_4Ge_4S_6$. When R is methyl or mesityl, the structure is adamantane-type, but when R is *tert*-butyl, the structure is "double decker"-type.⁴ For organic tetrasilathianes, no "double decker"-type structure has been reported.⁵ In this paper, synthesis and structures of tetra(alkylsilsesquisulfides), ($R_4Si_4S_6$, **1**: $R = t\text{-Bu}$, **2**: $R = 1,1,2\text{-trimethylpropyl}$) are described.

Silsesquisulfides **1** or **2** was prepared by the reaction of trichlorosilane with Na_2S or Li_2S . The compounds are both remarkably stable and no decomposition was observed in the air at room temperature. The structures of **1** and **2** were determined by X-ray crystallography (Figure 1). The result revealed that **2** possesses novel "double decker"-type structure. The formation of this unique structure is thought to be due to

the bulkiness of the 1,1,2-trimethylpropyl groups, which makes smaller ring more favorable. Also unsymmetrical structure of the substituents may give contribution to the generation of **2**. Average Si-S bond lengths were similar for both structures (2.132 Å for **1** and 2.133 Å for **2**), and interestingly, the distance of two silicon atoms of the four-membered ring in **2** was 2.82 Å. This unusual short distance can be a result of the relief of the strain around silicon atoms.

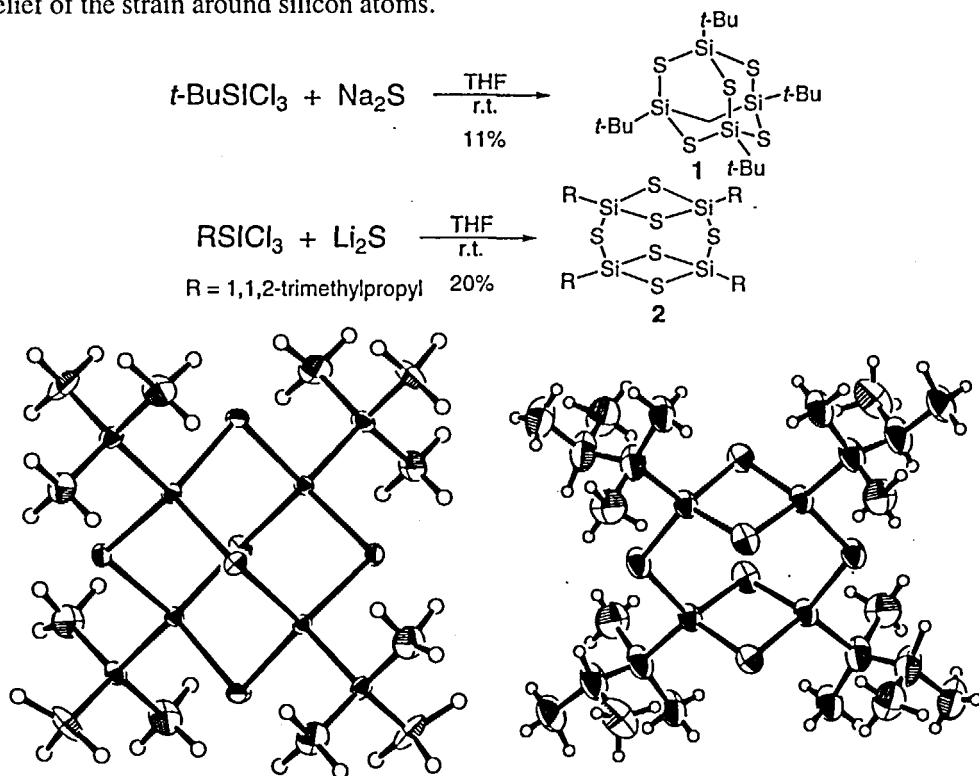


FIGURE 1 Thermal ellipsoids are drawn at the 30% probability level.

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