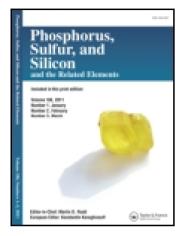
This article was downloaded by: [University of Toronto Libraries] On: 30 December 2014, At: 06:21 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

# The Preparation of 1, 5- $Se_2S_2N_4$

Arto Maaninen , Jari Siivari , Risto S. Laitinen & Tristram Chivers

<sup>a</sup> Departments of Chemistry , University of Oulu , FIN-90570 Oulu, Finland

<sup>b</sup> Departments of Chemistry, University of Oulu, FIN-90570 Oulu, Finland

 $^{\rm c}$  Departments of Chemistry , University of Oulu , FIN-90570 Oulu, Finland

<sup>d</sup> Departments of Chemistry, University of Calgary, 2500 University Dr. N.W., Calgary, Alberta, Canada T2N 1N4 Published online: 02 Apr 2008.

To cite this article: Arto Maaninen , Jari Siivari , Risto S. Laitinen & Tristram Chivers (1997) The Preparation of 1,  $5-Se_2S_2N_4$ , Phosphorus, Sulfur, and Silicon and the Related Elements, 124:1, 457-460, DOI: <u>10.1080/10426509708545658</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426509708545658</u>

# PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

#### THE PREPARATION OF 1, 5-Se<sub>2</sub>S<sub>2</sub>N<sub>4</sub>

## ARTO MAANINEN,<sup>a</sup> JARI SIIVARI,<sup>a</sup> RISTO S. LAITINEN,<sup>a</sup> and TRISTRAM CHIVERS<sup>b</sup> Departments of Chemistry, <sup>a</sup> University of Oulu, FIN-90570 Oulu, Finland, and <sup>b</sup> University of Calgary, 2500 University Dr. N.W., Calgary, Alberta, Canada T2N 1N4

The reaction of  $[(Me_3Si)_2N]_2S$  with an equimolar amount of SeCl<sub>4</sub> or the reaction of  $[(Me_3Si)_2N]_2Se$  with 1:1 mixture of SCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub> produces 1,5-Se<sub>2</sub>S<sub>2</sub>N<sub>4</sub> in good yields. The product is identified and characterized using X-Ray diffraction, vibrational analysis, mass spectroscopy, and NMR-spectroscopy.

Keywords: Chalcogen-nitrogen-compounds; Raman spectroscopy; NMR spectroscopy; crystal structure

#### INTRODUCTION

The chemistry of selenium-nitrogen compounds is a relatively limited but a rapidly growing field.<sup>[1,2]</sup>We report here a convenient synthesis of 1,5-Se<sub>2</sub>S<sub>2</sub>N<sub>4</sub> from [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>S and SeCl<sub>4</sub>, or from [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Se and SCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub>. Both reactions afford the same product that is identified using X-ray diffraction, vibrational analysis, as well as NMR and mass spectroscopy.

#### EXPERIMENTAL SECTION

All reactions were carried under an argon atmosphere. The solvents were dried by freshly distilling under a nitrogen atmosphere.

**Caution!** The eight-membered  $Se_2S_2N_4$  ring molecule is explosive when heated or subjected to mechanical stress.

#### Reaction of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>S with SeCl<sub>4</sub>

A solution of  $[(Me_3Si)_2N]_2S$  in CS<sub>2</sub> was added dropwise to a slurry of SeCl<sub>4</sub> in CS<sub>2</sub> at -78° C. The reaction mixture was allowed to warm slowly to room temperature with stirring for 12 hours. The yield was 70 mol % based on the initial amount of  $[(Me_3Si)_2N]_2S$ .

### Reaction of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Se with SCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub>

 $[(Me_3Si)_2N]_2Se$  was dissolved in CS<sub>2</sub>, and a mixture of SCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub> in CS<sub>2</sub> was added dropwise at -78° C. The yield was 73 mol % based on the initial amount of  $[(Me_3Si)_2N]_2Se$ .

#### **RESULTS AND DISCUSSION**

 $Se_2S_2N_4$  can be prepared in good yields according to the following reactions.

 $[(Me_3Si)_2N]_2S + SeCl_4 \rightarrow \frac{1}{2} Se_2S_2N_4 + 4 Me_3SiCl$  $[(Me_3Si)_2N]_2Se + SCl_2 + SO_2Cl_2 \rightarrow \frac{1}{2} Se_2S_2N_4 + 4 Me_3SiCl_2N_4 + 4 Me_3SiCl_2N_4$ 

The resulting dark brown-red material was almost insoluble in organic solvents and precipitated during the reaction. The elemental analysis of

the solid product can be inferred in terms of a mixture containing 91 mol % of  $Se_2S_2N_4$  and 9 mol % of  $Se_8$  (Anal. calcd for  $Se_2S_2N_4$ : N, 20.1; S, 23.0; Se 56.9. Found: N, 16.5. The <sup>77</sup>Se NMR spectrum of the product indicates a mixture of 90-95 %  $Se_2S_2N_4$  and 5-10 %  $Se_8$ ).

Se<sub>2</sub>S<sub>2</sub>N<sub>4</sub> crystallizes in a monoclinic space group  $P2_1/c$ , Z = 4, with the unit cell dimensions a = 8.818(2), b = 7.387(1), c = 8.981(2)Å,  $\beta = 93.14(3)$  ° (T = 298 K); R = 0.0545. The compound is isostructural with S<sub>4</sub>N<sub>4</sub> <sup>[3]</sup> and  $\beta$ -Se<sub>4</sub>N<sub>4</sub>.<sup>[4]</sup> The structure is disordered with sulfur and selenium statistically distributed over chalcogen atom sites (site occupation factors of selenium in every position *ca*. 50 %).

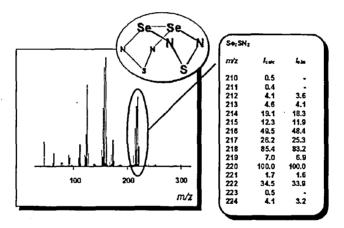


FIGURE 1 12 eV EI mass spectrum of 1,5-Se<sub>2</sub>S<sub>2</sub>N<sub>4</sub>.

The 12 eV mass spectrum of the product showed  $Se_2SN_2$  as the largest fragment. It can be inferred as a part of the  $1,5-Se_2S_2N_4$  ring (see Fig. 1). The <sup>14</sup>N NMR spectrum of the crude reaction mixture showed two resonances at -46 and -238 ppm. The resonance at -238 ppm is assigned to  $Se_2S_2N_4$  (*c.f.* -256 ppm for  $S_4N_4$  <sup>[5]</sup>). The resonance

at -46 ppm is due to an unknown species that is removed during the purification of the product by distillation. The <sup>77</sup>Se NMR spectrum showed two resonances at 1418 ppm and 620 ppm that are assigned to  $1,5-Se_2S_2N_4$  and  $Se_8$ ,<sup>[6]</sup> respectively. The single <sup>14</sup>N resonance also indicates that the product is the 1,5-isomer.

The observed Raman lines are in a good agreement with the fundamental vibrations calculated for  $Se_2S_2N_4$  by using the general valence force field approach. The calculations also yield reasonable force constants.

#### Acknowledgments

The financial support from the Academy of Finland is gratefully acknowledged.

#### References

- T. Klapötke, In *The Chemistry of Inorganic Ring Systems*, ed. Steudel, R. (Elsevier Science Publishers, Amsterdam, 1992), pp 409-427.
- [2.] (a) E. G. Awere, J. Passmore, P. S. White, and T. Klapötke, J. Chem. Soc., Chem. Commun., 1415 (1989). (b) E. G. Awere, J. Passmore, and P. S. White, J. Chem. Soc., Dalton Trans., 299 (1993). (c) P. F. Kelly, M. Z. Slawin, D. J. Williams, and J. D. Woollins, J. Chem. Soc., Chem. Commun., 408 (1989).
- [3.] M.L. DeLucia and P. Coppens, Inorg. Chem., 17, 2336 (1978).
- [4.] H. Folkerts, B. Neumuller and K. Dehnicke, Z. anorg. allg. Chem. 620, 1011 (1994).
- [5.] T. Chivers, R.T. Oakley, O.J. Scherer, and G. Wolmershäuser, *Inorg. Chem.*, 20, 914 (1981).
- [6.] R.S. Laitinen and T.A. Pakkanen, *Inorg. Chem.*, 26, 2598 (1987).