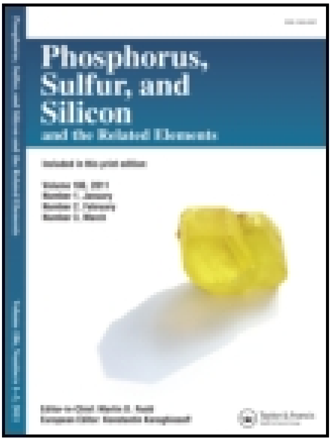

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The Preparation of 1, 5-$Se_2S_2N_4$

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THE PREPARATION OF 1, 5-$Se_2S_2N_4$

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The reaction of $[(Me_3Si)_2N]_2S$ with an equimolar amount of $SeCl_4$ or the reaction of $[(Me_3Si)_2N]_2Se$ with 1:1 mixture of SCl_2 and SO_2Cl_2 produces 1,5-$Se_2S_2N_4$ 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.[1,2] We report here a convenient synthesis of 1,5-$Se_2S_2N_4$ from $[(Me_3Si)_2N]_2S$ and $SeCl_4$, or from $[(Me_3Si)_2N]_2Se$ and SCl_2 and SO_2Cl_2. 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 $[(Me_3Si)_2N]_2S$ with $SeCl_4$

A solution of $[(Me_3Si)_2N]_2S$ in CS_2 was added dropwise to a slurry of $SeCl_4$ in CS_2 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 $[(Me_3Si)_2N]_2Se$ with SCl_2 and SO_2Cl_2

$[(Me_3Si)_2N]_2Se$ was dissolved in CS_2, and a mixture of SCl_2 and SO_2Cl_2 in CS_2 was added dropwise at -78° C. The yield was 73 mol % based on the initial amount of $[(Me_3Si)_2N]_2Se$.

RESULTS AND DISCUSSION

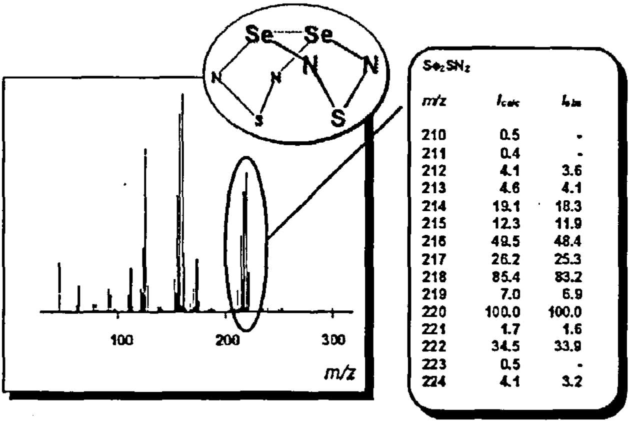
$Se_2S_2N_4$ can be prepared in good yields according to the following reactions.

$$[(Me_3Si)_2N]_2S + SeCl_4 \rightarrow \tfrac{1}{2}\, Se_2S_2N_4 + 4\, Me_3SiCl$$

$$[(Me_3Si)_2N]_2Se + SCl_2 + SO_2Cl_2 \rightarrow \tfrac{1}{2}\, Se_2S_2N_4 + 4\, Me_3SiCl$$

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 ^{77}Se NMR spectrum of the product indicates a mixture of 90-95 % $Se_2S_2N_4$ and 5-10 % Se_8).

$Se_2S_2N_4$ 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_4N_4 [3] and β-Se_4N_4.[4] The structure is disordered with sulfur and selenium statistically distributed over chalcogen atom sites (site occupation factors of selenium in every position *ca.* 50 %).



Se_2SN_2

m/z	I_{calc}	I_{obs}
210	0.5	-
211	0.4	-
212	4.1	3.6
213	4.6	4.1
214	19.1	18.3
215	12.3	11.9
216	48.5	48.4
217	26.2	25.3
218	85.4	83.2
219	7.0	6.9
220	100.0	100.0
221	1.7	1.6
222	34.5	33.9
223	0.5	-
224	4.1	3.2

FIGURE 1 12 eV EI mass spectrum of 1,5-$Se_2S_2N_4$.

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 ^{14}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 [5]). The resonance at –46 ppm is due to an unknown species that is removed during the purification of the product by distillation. The ^{77}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,[6] respectively. The single ^{14}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

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