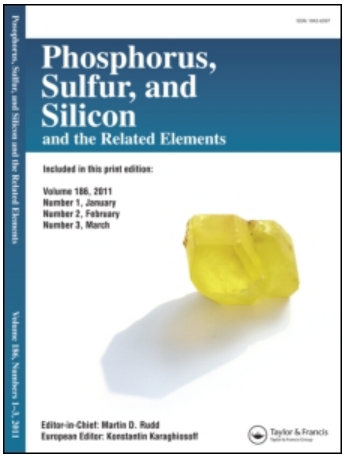

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The Pathway of the Reaction between $[(Me_3Si)_2N]_2S$ and $SeCl_4$

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The reaction of $[(Me_3Si)_2N]_2S$ with an equimolar amount of $SeCl_4$ in CS_2 or CH_2Cl_2 at −70°C provides a route to 1,5-$Se_2S_2N_4$ in a good yield. When the reaction is carried out in dioxane at +50°C five membered heterocycle $(SSe_2N_2Cl)_2$ is formed. The product is identified and characterized using X-Ray diffraction, Raman spectroscopy, mass spectroscopy and NMR spectroscopy. ^{77}Se MAS NMR study of the 1,5-$Se_2S_2N_4$ is reported.

Keywords: Chalcogen-nitrogen-compounds; Raman spectroscopy; NMR spectroscopy; 77Se MAS NMR; crystal structure

INTRODUCTION

We have recently prepared 1,5-$Se_2S_2N_4$ from equimolar amounts of $[(Me_3Si)_2N]_2S$ and $SeCl_4$.[1] The analoguous reaction in dioxane at 50°C has been reported to produce a six-membered ring species, $Se_2S_2N_2Cl_2$.[2] The reinvestigation of the reaction shows that the product is in fact $(Se_2SN_2Cl)_2$. It is identified using X-ray diffraction, Raman spectroscopy, NMR spectroscopy and mass spectroscopy.

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$(Se_2SN_2Cl)_2$ can also be obtained by the reaction of $[(Me_3Si)_2N]_2S$ with 2:1 mixture of $SeCl_4$ and Se_2Cl_2.[3]

EXPERIMENTAL SECTION

All reactions were carried under an argon atmosphere. The solvents were dried by freshly distilling under a nitrogen atmosphere. 1,5-$Se_2S_2N_4$ was prepared by literature procedures.[1]

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

Preparation of $(Se_2SN_2Cl)_2$

A solution of $[(Me_3Si)_2N]_2S$ (0.704 g, 2 mmol) in dioxane was added to a solution of $SeCl_4$ (0.442 g, 2 mmol) in dioxane at +50°C. The reaction mixture was stirred for 7 hours at +50°C.

RESULTS AND DISCUSSION

$(Se_2SN_2Cl)_2$ is obtained as golden brown microcrystalline solid that is almost insoluble in organic solvents. Single crystals suitable for X-ray crystallography were grown from dioxane at r.t.

Crystal data: $(Se_2SN_2Cl)_2$, orthorhombic, P_{bca}, $Z = 8$, $a = 8.5721(7)$, $b = 7.8336(6)$, $c = 15.228(1)$ Å, $V = 1022.55(13)$ Å^3; $R = 0.0323$. Data were collected on a Nonius Kappa CCD diffractometer at 173 K using graphite monochromated MoK_α radiation by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$). The molecular structure of $(Se_2SN_2Cl)_2$ is dimeric, which consists of two Se_2SN_2Cl five membered rings (see Figure 1). Intermolecular Se···Se distances are 3.07 Å.

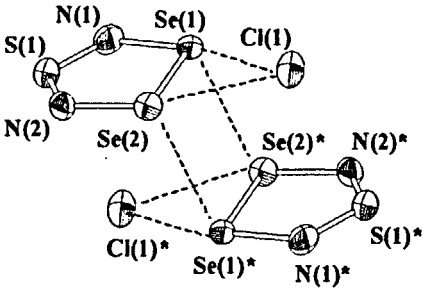

FIGURE 1 The molecular structure of $(Se_2SN_2Cl)_2$.

The 12 eV mass spectrum of the product showed Se_2SN_2 (m/z 220) as the most abundant fragment. The ^{14}N NMR spectrum of the crude reaction mixture showed a single resonance at –52 ppm. The ^{77}Se NMR spectrum showed two resonances at 1394 ppm and 1407 ppm that are assigned to $(Se_2SN_2Cl)_2$ and 1,5-$Se_2S_2N_4$ (*c. f.* 1418 ppm in CS_2)[1] respectively.

The characteristic Raman vibrations of $(Se_2SN_2Cl)_2$ occur at 980w, 951w, 627m, 470m, 359vw, 269vs, 240vw, 155w, 119vs. The Raman spectrum is in good agreement with that reported previously.[3]

A. Haas *et al.* have proposed a reaction pathway to formation of Se_2SN_2-ring from 1,5-$Se_2S_2N_4$.[4] This route seems likely in a view of this work.

The ^{77}Se MAS NMR spectrum of 1,5-$Se_2S_2N_4$ shows two series of spinning sideband patterns with isotropic chemical shifts at 1455 ppm and 1409 ppm. Isotropic shifts were confirmed also in experiments with different spinning rates.

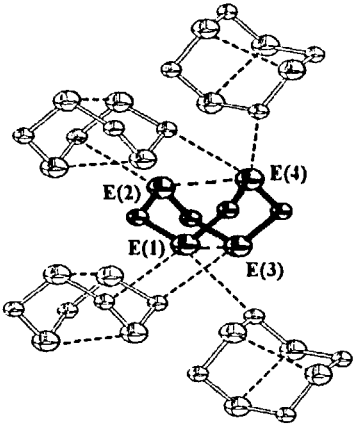

FIGURE 2 The molecular structure of 1,5-$Se_2S_2N_4$ showing intermolecular chalcogen···N secondary interactions. E(1), E(3): sof(Se) = 52 %; E(2), E(4): sof(Se) = 48 %. Sof(S_i) = 1 - sof(Se_i).

Observation of two signal series in ^{77}Se MAS spectrum is in agreement with the crystal structure. Chalcogen atom positions are not equivalent because of the secondary chalcogen···N interactions to neigbouring molecules (see Fig. 2).

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