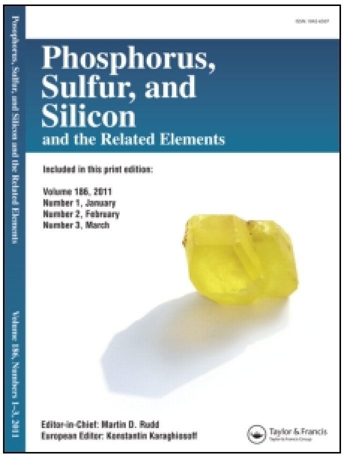

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CHLORINATION OF THE HETEROCYCLE 1,2-Se_2S_5 TO GIVE $Se_2S_5Cl_2$[1]

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Abstract Careful chlorination of 1,2-Se_2S_5 with Cl_2 in CS_2 mainly yields Cl-Se-S_5-Se-Cl which reacts with $(\eta^5\text{-}CH_3C_5H_4)_2TiS_5$ to give the heterocycle 1,7-Se_2S_{10}. $ClSeS_5SeCl$ was characterized by Raman, mass and ^{77}Se NMR spectroscopy.

INTRODUCTION

1,2-Se_2S_5 is available from reaction (1):[2]

$$(C_5H_5)_2TiS_5 + Se_2Cl_2 \longrightarrow 1,2\text{-}Se_2S_5 + (C_5H_5)_2TiCl_2 \qquad (1)$$

The orange crystalline Se_2S_5 is unstable at 20 °C and DSC measurements show an exothermic polymerization at 51 °C resulting in an unsoluble solid. This material slowly depolymerizes on treatment with liquid carbon disulfide with reformation of 1,2-Se_2S_5 as can be observed by HPLC analysis. This indicates the connectivity $(\text{-}SeS_5Se\text{-})_n$ for the polymer.[3]

On stretching of the polymer followed by CS_2 extraction a partly crystalline but still polymeric material is obtained . The powder x-ray diffraction pattern of this polymer indicates the space group P2/m which is known from polymeric sulfur, S_∞. Therefore, helical chain-like molecules as in S_∞ can be assumed for $(1,2\text{-}Se_2S_5)_n$.[3]

Careful chlorination of 1,2-Se_2S_5 with Cl_2 in CS_2 yields mainly Cl-Se-S_5-Se-Cl under specific cleavage of the Se-Se bond[3], equation (2).

$$1,2\text{-}Se_2S_5 + Cl_2 \longrightarrow ClSeS_5SeCl\ (\mathbf{1}) \qquad (2)$$

EXPERIMENTAL

Within 4 min 1.1 ml of a solution of Cl_2 (7.5 mg Cl_2/ml CCl_4) were added to the stirred solution of 208 µmol (66.3 mg) 1,2-Se_2S_5 in 15 ml of dry CS_2 at 0 °C. The reaction mixture was stirred for 10 min at 4 °C and further 10 min at 24 °C. After filtration the solvent was removed at 4 °C in a vacuum. The yield of the dark red oil obtained was 78% based on equ. (2). All operations were carried out with exclusion of light. Solutions of $ClSeS_5SeCl$ in carbon disulfide mostly decompose within a few hours at 4 °C in the dark. The neat oil is stable for some days at -78 °C with exclusion of light and moisture.

CHARACTERIZATION

$ClSeS_5SeCl$ reacts with titanocene pentasulfide according to equation (3):

$$(CH_3C_5H_4)_2TiS_5 + ClSeS_5SeCl \longrightarrow 1,7\text{-}Se_2S_{10} + (CH_3C_5H_4)_2TiCl_2 \qquad (3)$$

The reaction was followed by reversed phase HPLC. All signals could be assigned by reference compounds and using RS values.[4,5] After 12 min the following compounds ordered by increasing retention time could be detected: $(CH_3Cp)_2TiCl_2$, CS_2, $(CH_3Cp)_2TiS_5$, SeS_5, 1,2-Se_2S_5, 1,2,3-Se_3S_5, 1,7-Se_2S_{10} and 1,2-Se_2S_{10}. The twelve membered rings were isolated and identified by Raman spectroscopy. The formation of SeS_5 and 1,2,3-Se_3S_5 results from decomposition of the educt:[2]

$$1,2\text{-}Se_2S_5 \longrightarrow SeS_5 + 1,2,3\text{-}Se_3S_5 \qquad (4)$$

The presence of 1,2-Se_2S_{10} is likely due to the following equilibrium:

$$1,2\text{-}Se_2S_{10} \rightleftharpoons 2\,SeS_5 \rightleftharpoons 1,7\text{-}Se_2S_{10} \qquad (5)$$

Raman spectroscopy

The Raman spectrum of the solution of **1** in carbon disulfide is shown in FIGURE 1. The lines at 646 and 655 cm^{-1} can be assigned to CS_2. The wavenumbers of all other lines are listed in TABLE 1. The stretching vibrations clearly indicate the presence of Se-Cl, Se-S and S-S bonds. Typical signals for SCl_2[6], S_2Cl_2[7], S_xCl_2 with x=3-5[8], S_6Cl_2, S_7Cl_2 and S_8Cl_2[9] have not been observed. No S-Cl stretching vibrations are present at all.

^{77}Se NMR spectroscopy

The ^{77}Se NMR spectrum at 24 °C of a solution of **1** in carbon disulfide shows a dominant singlet at 1267 ppm (70%) for **1**. The other singlets at 1293 (11%), 1318 (3%), 1319 (7%), 1339 (3%) and 1359 (6%) ppm may be assigned to other, unknown compounds of type $Se_xS_yCl_2$. The chemical shifts of these compounds strongly depend on the concentration and the solvent.[10] Therefore, further investigations are necessary for a definite assignment. C_6D_6/CS_2 was used as an external reference referred to neat Me_2Se. After 10 hours 2 signals between 400 and 1000 ppm indicated the presence of SeS_5 (632 ppm, 53%) and SeS_7 (698 ppm, 47%) in the solution. Latter compounds were not present in the original reaction mixture. They probably indicate the way of decomposition of **1**. The mass spectrum of **1** supports this assumption.

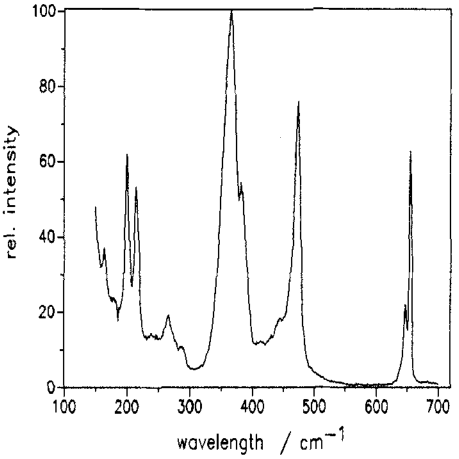

FIGURE 7 Raman spectrum of $ClSeS_5SeCl$ in CS_2.

TABLE 1 Raman spectrum of $ClSeS_5SeCl$.

Wavenumber cm^{-1}	intensity	assignment
164	w	bending mode
200	s	bending mode
215	s	bending mode
266	w	bending mode
289	vw	bending mode
365	vs	ν Se-Cl ν Se-S
382	s	ν Se-Cl ν Se-S
431	vw	ν S-S
444	sh	ν S-S
474	s	ν S-S

Mass spectrum

The 70 eV (EI) mass spectrum of neat **1** at 30 °C shows signals for the following ions: HCl (36, 63%), S_2 (64, 86%), SeCl (115, 29%), S_4 (128, 31%), Se_2 and S_5 (160, 100%), Se_2Cl (195, 98%), Se_2Cl_2 (230, 87%), S_8 (256, 33%), SeS_7 (304, 19%), S_{10} (320, 2%) and Se_2S_6 (350, 2%). At 90 °C the following ions were detected: S_x (x= 1-6, 8, 10), SeS_3, SeS_4, SeS_5, SeS_7 and Se_2S_6. No chlorine-containing fragments were present. **1** probably decomposes on heating in the vacuum with formation of selenosulfides Se_xS_y and volatile Se_2Cl_2. But there is no evidence for fragments like $S_x\text{-Cl}]^{+\cdot}$.

RESULTS AND DISCUSSION

To check the presence of Se_2Cl_2 which can hardly be detected by Raman spectroscopy in the presence of a large excess of **1**, we investigated the reaction of **1** with Cp_2TiSe_5:

$$Cp_2TiSe_5 + Se_2Cl_2 \longrightarrow Se_7 + Cp_2TiCl_2 \qquad (6)$$

If there were any Se_2Cl_2 present the formation of Se_7 were to be observed.[11] However, no Se_7 was detected by HPLC after 15 min. The formation of Cp_2TiCl_2 and other products could be observed, no HPLC signals for the expected 1,2,3,4,5-Se_7S_5 have been found because of the low solubility of Se_7S_5 in CH_3OH.

Our measurements give evidence for the specific chlorination of the Se-Se-bond of 1,2-Se_2S_5. Neither chlorosulfanes nor Se_2Cl_2 are formed, and the Raman spectrum indicates the presence of Se-S, S-S and Se-Cl bonds. The formation of the chain like molecule **1** is likely. This is supported by the formation of the derivative 1,7-Se_2S_{10}. The main signal in the ^{77}Se NMR spectrum of **1** is in the typical range for the sequence -S-Se-Cl.[12]

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