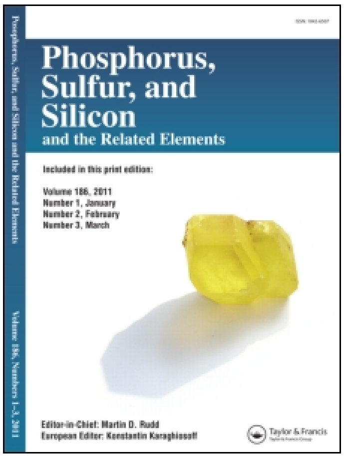

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Small Chalcogen Rings

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SMALL CHALCOGEN RINGS

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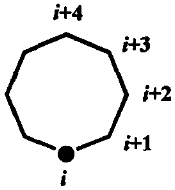
Abstract The reaction of $[Ti(C_5Me_5)_2S_3]$ with Se_2Cl_2 produces 1,5-Se_2S_5, 1,2,3,4,5-Se_5S_3, and 1,2-Se_2S_6 as the main end products. This implies the existence of 1,2-Se_2S_3 as an initial reaction product the decomposition of which proceeds with parallel selenium atom transfer and dimerization reactions.

Bis(cyclopentadienyl)titanium chalcogenides of the types $[TiCp_2E_5]$ and $[TiCp_2(E_2)_2TiCp_2]$ (E = S, Se, Te) are well known to be good precursors for heterocyclic chalcogen rings.[1] In the present work we report the reaction of $[Ti(C_5Me_5)_2S_3]$ with Se_2Cl_2 that should initially form a five-membered 1,2-Se_2S_3. It is, however, unstable and decomposes rapidly to larger ring molecules. The nature of the final products should give information about the transient existence of 1,2-Se_2S_3.

The composition of the reaction mixture was monitored as a function of time with ^{77}Se NMR spectroscopy. The first signals to appear are those at 683, 653, 593, and 587 ppm with a later appearance of a signals at 629 and 610 ppm. The five latter resonances can be assigned to 1,2,3,4,5-Se_5S_3, 1,2-Se_2S_6, and Se8 based on previous information.[2] The assignment of the signal at 683 ppm to 1,5-Se_2S_6 requires refinement in our earlier deductions.[2] In the study of ^{77}Se-enriched selenium sulfide mixtures (enrichment 92 %) the singlets at 729, 717, and 687 ppm were assigned to 1,3-, 1,5-, and 1,4-isomers, respectively with a provision that the assignment can also be interchanged. With the accumulation of definite ^{77}Se chemical shift data of the eight-membered selenium sulfide rings, a quantitative dependence of the chemical shift with the nature and location of the ring atoms can now be made and these singlets definitely assigned. The least-squares fit of the chemical shift data resulted the following equation:

$$\delta = -66.6\, n_1 + 14.2\, n_2 + 19.7\, n_3 - 6.0\, n_4 + 699.0$$



where n_1 is the number of Se atoms adjacent to the active Se nucleus (i), n_2, n_3, and n_4 the number of Se atoms in the i+2, i+3, and i+4 positions, respectively. The calculated chemical shifts of the four isomers of Se_2S_6 are thus: 1,2-Se_2S_6 632 ppm, 1,3-Se_2S_6 713 ppm, 1,4-Se_2S_6 719 ppm, and 1,5-Se_2S_6 693 ppm. The earlier assignment must thus be modified and the signal at 683 ppm of the present work assigned to 1,5-Se_2S_6.

The appearance of 1,5-Se_2S_6, 1,2,3,4,5-Se_5S_3, and 1,2-Se_2S_6 as the main end products in the reaction of $[Ti(C_5Me_5)_2S_3]$ and Se_2Cl_2 implies the formation of 1,2-Se_2S_3 with rapid decomposition involving parallel selenium atom transfer reactions and dimerization (see Fig. 1).

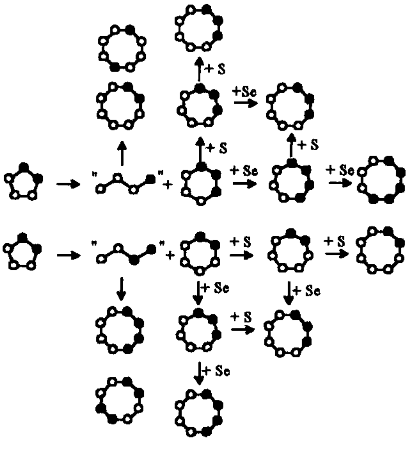


FIGURE 1 The decomposition of 1,2-Se_2S_3 involving both selenium and sulfur atoms transfer reactions as well as dimerization. It can be seen that sulfur atoms transfer does not lead to the observed end products.

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