to an energy (32 800 cm^{-1} or 4.07 eV) much higher than those calculated by Xα, which suggests that there may be a systematic underestimation in the calculation.

With respect to the transition of lowest energy (907 nm or 11 030 cm^{-1}), we recall that a similar one in the triazeno complex was initially assigned as a $\pi^* \rightarrow \sigma^*$(Ru–N) transition.[5] From the above discussion of the electronic structures, it is clear that the lowest energy transition should be $\pi^* \rightarrow \delta^*$ (i.e. HOMO $\rightarrow$ LUMO) transition instead. There are two possible absorptions related to this transition, i.e., ${}^1A_{1g} \rightarrow {}^1E_u$ and ${}^1A_{1g} \rightarrow {}^3E_u$, and the latter is spin-forbidden and of lower energy. However, the strong spin–orbit coupling that prevails among the second and third transition series elements can induce substantial intensity for such a normally spin-forbidden transition. In the cases of both $Pt(CN)_4{}^{2-}$[24] and $Ir(CN\text{-}t\text{-}Bu)_4{}^+$,[25] the singlet–triplet (${}^1A_{1g} \rightarrow {}^3E_u$) transition of metal-localized $d_\pi(d_{xz,yz}) \rightarrow \pi^*(pz)$ character was observed with an ϵ_{max} as high as one-third that of the corresponding singlet–singlet (${}^1A_{1g} \rightarrow {}^1E_u$) transition; the separations between ${}^1E_u$ and ${}^3E_u$ were determined as 6820 and 8600 cm^{-1} for Pt and Ir complexes, respectively. Considering the possible underestimation previously mentioned and the relative intensities of the peaks, we assign the absorptions at 905 and 492 nm as ${}^{3,1}(\pi^* \rightarrow \delta^*)$ (${}^1A_{1g} \rightarrow {}^{3,1}E_u$), respectively. The ratio $\epsilon_{max}(904)/\epsilon_{max}(492)$ is also about one-third. According to the relative order given by the calculation the weaker peak next to ${}^1(\pi^* \rightarrow \delta^*)$ at 434 nm can be attributed to the ${}^1(\pi^* \rightarrow \sigma^*)$ (${}^1A_{1g} \rightarrow {}^1E_u$) transition. The intensity of this transition is smaller than that of ${}^1(\pi^* \rightarrow \delta^*)$ perhaps because there is less ligand mixing in the σ^* orbital. Its singlet–triplet counterpart ${}^3(\pi^* \rightarrow \sigma^*)$ is not obvious in the spectrum, probably because it is covered by the high-energy tail of the ${}^3(\pi^* \rightarrow \delta^*)$ transition. It is now not difficult to locate the ${}^1(\delta \rightarrow \delta^*)$ (${}^1A_{1g} \rightarrow {}^1A_{2u}$) transition at 396 nm, in accord with the order from Xα calculation. While the intensity of a purely metal-based $\delta \rightarrow \delta^*$ transition is known to be inherently low,[26,27] this transition is very intense due to the appreciable ligand character in both the δ and δ^* orbitals. The ${}^3(\delta \rightarrow \delta^*)$ (${}^1A_{1g} \rightarrow {}^3A_{2u}$) transition is assigned to the shoulder around 540 nm.

From the above assignment the singlet–triplet separation for the metal-based excited configurations can be estimated in the range 7000–9000 cm^{-1}, which is in good agreement with the estimation we suggested in the discussion of the magnetic structure.[2,8]

Acknowledgment. We thank the National Science Foundation for support. Dr. X. Feng is acknowledged for sharing his expertise in SCF–Xα calculations.

Supplementary Material Available: Complete tables of crystal data, bond distances and angles, and anisotropic displacement parameters and a full list of the valence molecular orbitals (8 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Chalcogen Ring Interconversion Pathways. ^{77}Se NMR Spectroscopic Study of the Decomposition of 1,2,3,4,5-Se_5S_2 to 1,2,3,4,5,6-Se_6S_2 and 1,2,3,4-Se_4S_2

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The decomposition of both natural-abundance and ^{77}Se-enriched 1,2,3,4,5-Se_5S_2 in CS_2 solution has been monitored with ^{77}Se NMR spectroscopy. The freshly prepared samples showed only signals due to 1,2,3,4,5-Se_5S_2. When samples are allowed to stand in the CS_2 solution, additional resonances are observed. Comparison of the natural-abundance spectrum with that from the enriched sample enabled the assignment of these additional resonances to 1,2,3,4-Se_4S_2 and 1,2,3,4,5,6-Se_6S_2 to be made. The simulation of the enriched spectrum yielded the ^{77}Se–^{77}Se coupling constants. All transitions could be assigned with an excellent fit. The NMR results show that the decomposition of 1,2,3,4,5-Se_5S_2 proceeds with a selenium atom transfer from one seven-membered ring molecule to another.

Introduction

Compounds containing cumulated S–S bonds are known to undergo interconversion reactions. Typical examples are the decomposition of thermodynamically unstable sulfur molecules with the formation of stable S_8,[2] the decomposition of S_8 in the molten state or in organic solvents,[3] the polymerization and depolymerization of liquid sulfur,[2] the decomposition of organic polysulfanes R_2S_n on heating,[4] and the vulcanization of rubber.[5] Similar interconversion reactions have also been observed for selenium. When Se_8 is dissolved in CS_2, an equilibrium between Se_6, Se_7, and Se_8 is rapidly set up.[6] Analogous decomposition of S_8 is much slower in CS_2 and requires heating.[7] In acetonitrile, however, the equilibrium is instantaneously established.[8]

The mechanism of such interconversion reactions is not known. Though several alternative pathways have been suggested (for a review, see ref 9), the lack of rigorous experimental evidence

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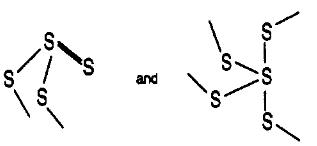
renders them all speculative. Recently, the geometries and the energetics of formation of the different types of interconversion intermediates were studied with ab initio MO techniques.[10] These calculations suggest that hypervalent species of the types



are energetically reasonable alternatives to homolytic cleavage of the S–S bond. These kinds of intermediates have often been proposed to effect a sulfur atom transfer in the reactions of compounds containing cumulated S–S bonds.[9,11]

Heterocyclic selenium sulfides provide a means to gain more experimental insight into these interconversion reactions. The structural characteristics as well as the electronic structures of the Se–S bonds are similar to those of S–S and Se–Se bonds (for a recent review on the preparation and characterization of selenium sulfides, see ref 12). Furthermore, various molecular species can conveniently be identified by ^{77}Se NMR spectroscopy even in complicated mixtures.[13] The interconversion pathways of compounds containing S–S bonds can thus be studied by using selenium as a chemical label in the molecules.

Seven-membered selenium sulfide ring molecules Se_nS_{7-n} are particularly useful for the investigation of the interconversion pathways. Bis(cyclopentadienyl)titanium pentasulfide $[Ti(C_5H_5)_2S_5]$ reacts with Se_2Cl_2 to produce stoichiometrically pure 1,2-Se_2S_5.[14] The product is unstable both in solid state and in solution. It has been shown by vibrational analysis and by natural-abundance ^{77}Se NMR spectroscopy that in CS_2 solution at ambient temperature 1,2-Se_2S_5 decomposes rapidly to form SeS_5 and 1,2,3-Se_3S_5.[15] Stoichiometrically pure 1,2,3,4,5-Se_5S_2, and Se_7 can be produced by analogous reactions treating $[Ti(C_5H_5)_2Se_5]$ with either S_2Cl_2 or Se_2Cl_2, respectively.[16] In the solid state the selenium-rich Se_nS_{7-n} molecules are much more stable than the sulfur-rich species, but in CS_2 solution they also decompose readily. For example, Se_7 is shown by HPLC to form an equilibrium mixture with Se_6 and Se_8.[6a]

The present study was undertaken to establish the decomposition pathway of 1,2,3,4,5-Se_5S_2. The species is well characterized by vibrational analysis[15b,16] and ^{77}Se NMR spectroscopy.[13c,17] By analogy to the decomposition of 1,2-Se_2S_5, which proceeds by a selenium atom transfer from one seven-membered ring molecule to another,[15] the decomposition of 1,2,3,4,5-Se_5S_2 can be expected to involve either a selenium or a sulfur atom transfer. The different alternative pathways are shown in Figure 1. It is interesting to note that all reaction pathways involving the selenium atom transfer produce a six-membered 1,2,3,4-Se_4S_2 ring molecule whereas in the case of the sulfur atom transfer Se_5S is formed.

It has been deduced by Raman spectroscopy[16] that in CS_2 solution 1,2,3,4,5-Se_5S_2 decomposes via the selenium atom transfer. However, the Raman spectroscopic characterization has been based on the crystallization of all relevant reaction components and on their identification in the solid state. Since ^{77}Se NMR spectroscopy provides the means to identify all heterocyclic selenium sulfides directly from the reaction solution, it can be used to determine unambiguously the decomposition pathway.

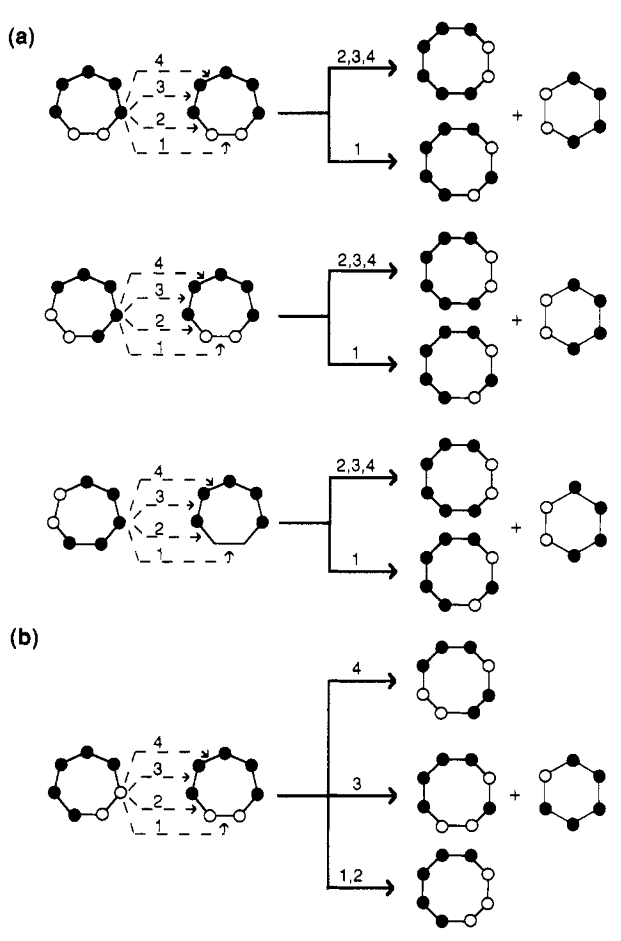
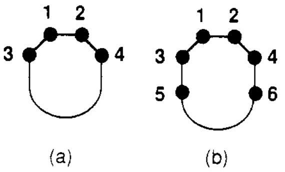


Figure 1. Possible interconversion pathways involving (a) selenium atom transfer and (b) sulfur atom transfer. The closed circles denote selenium atoms and the open ones sulfur atoms.



(a) (b)

Figure 2. Numbering of selenium atoms in (a) four-spin and (b) six-spin selenium sulfide with adjacent selenium atoms. The molecular symmetry in each case is C_2.

Experimental Section

Two types of samples of 1,2,3,4,5-Se_5S_2 were prepared from $[Ti(C_5H_5)_2Se_5]$ and S_2Cl_2: one using natural-abundance selenium (E. Merck GmbH), and the other involving selenium enriched in the ^{77}Se isotope (enrichment 92%, Techsnabexport). The synthetic procedure has been described earlier.[13c,16]

The decomposition of the samples in CS_2 solution[18] was monitored at 300 K by ^{77}Se NMR spectroscopy using a Jeol JNM-GX400 spectrometer. For the recording of the natural-abundance spectrum the spectrometer was operating at 76.31 MHz, the spectral width was 100.00 kHz, and the resolution was 1.54 Hz/data point. The pulse width was 7.0 μs, corresponding to the nuclide tip angle of 35°, and the pulse delay was 1.7 s. The corresponding spectrum of the ^{77}Se-enriched sample was recorded in two spectral windows. For the region containing the reso-

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(18) The preparation involved 50 mg of elemental selenium. The volume of the CS_2 solution was 3 mL. Therefore the initial concentration of 1,2,3,4,5-Se_5S_2 prior to the decomposition was ca. 0.04 M in all samples studied in this work.

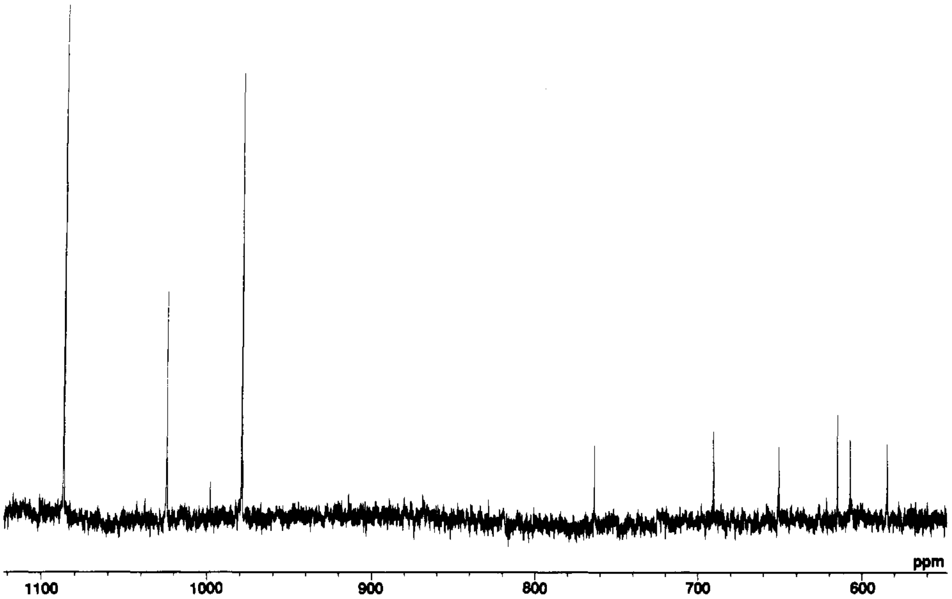

Figure 3. Natural-abundance ^{77}Se NMR spectrum of the CS_2 solution of 1,2,3,4,5-Se_5S_2 after 1 day of decomposition.

nances of the seven-membered heterocyclic selenium sulfides (1370–950 ppm) the spectrometer was operating at 76.33 MHz, and for the region containing the resonances of the eight- and six-membered selenium sulfides (840–540 ppm), at 76.29 MHz. In both windows, the spectral width was 35.21 kHz and the resolution 0.27 Hz/data point. The pulse width was 9.0 μs, corresponding to a nuclide tip angle of 45°, and the pulse delay was 2.4 s.

In all samples, the transients were cumulatively stored at intervals of 30 min.[19] D_2O was used as an external ^{2}H lock, and the saturated solution of SeO_2, as an external reference. The chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. The simulations of the spectra have been carried out with the program MAOCON.[20] The numbering of the atoms in 1,2,3,4,5,6-Se_6S_2 and 1,2,3,4-Se_4S_2 is shown in Figure 2.

Results and Discussion

The natural-abundance ^{77}Se NMR spectrum of the CS_2 solution of 1,2,3,4,5-Se_5S_2 after 24 h of decomposition is shown in Figure 3. Initially (i.e. during the first 2 h of accumulation), only three signals at 1087.3, 1025.0, and 979.5 ppm with an intensity ratio of 2:1:2 were observed. These signals have previously been assigned to 1,2,3,4,5-Se_5S_2.[13c,17] It has also been inferred that the NMR spectrum is consistent with the concept of a fluxional seven-membered chalcogen ring molecule. The relative values of $^1J_{SeSe}$ and $^2J_{SeSe}$ coupling constants indicate that all possible isomers with both the chair and boat conformation coexist together in the sample solution.[13c]

As 1,2,3,4,5-Se_5S_2 decomposes in the CS_2 solution, additional signals at 998.6, 764.2, 695.1, 651.2, 615.0, 607.8, and 584.8 ppm appear in the NMR spectrum (see Figure 3).[21] These resonances can be assigned as follows: The signal at 615.0 ppm is due to Se_8[6b,13a] and that at 998.6 ppm is due to Se_7.[17] The three signals of equal intensity at 695.1, 607.8, and 584.8 ppm have earlier been given a tentative assignment to 1,2,3,4,5,6-Se_6S_2.[13a] The ^{77}Se NMR spectrum of the decomposition products of the ^{77}Se-enriched 1,2,3,4,5-Se_5S_2 yields the coupling information for all signals and can be used to verify this assignment. As seen from Figure 4, the resonances at 695.1, 607.8, and 584.8 ppm all appear as complicated second-order multiplets in the spectrum of the enriched material. The signals were simulated as a six-spin (AA′BB′MM′) system. The simulation enabled the assignment of all transitions and yielded refined ^{77}Se–^{77}Se coupling constants, which are in good agreement with corresponding coupling constants calculated for other eight-membered heterocyclic selenium sulfides[13a] (see Table I).

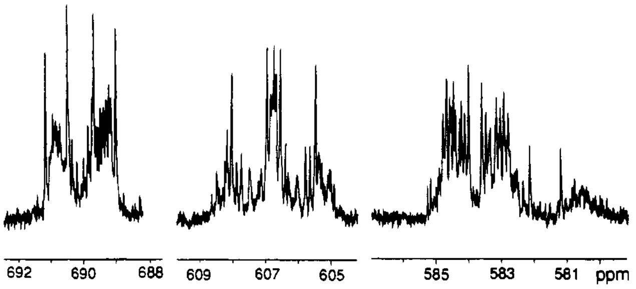

Figure 4. ^{77}Se NMR resonances of the ^{77}Se-enriched 1,2,3,4,5,6-Se_6S_2. There is a partial overlap of the signal at 584.8 ppm with a multiplet due to 1,2,3,4-Se_4S_4 (581.6 ppm).[13a] It is, however, possible to resolve and assign all transitions.

Table I. ^{77}Se–^{77}Se Coupling Constants (Hz) of 1,2,3,4,5,6-Se_6S_2, 1,2,3,4-Se_4S_4, and 1,2,3,4-Se_4S_2

J_{SeSe}[a]	1,2,3,4,5,6-Se_6S_2	1,2,3,4-Se_4S_4[b]	1,2,3,4-Se_4S_2
$^1J_{12}$	−29	−17	0
$^1J_{13}$, $^1J_{24}$	−23	−39	−73
$^1J_{35}$, $^1J_{46}$	−46		
$^2J_{14}$, $^2J_{23}$	105	112	115
$^2J_{15}$, $^2J_{26}$	107		
$^3J_{34}$	7	3	0
$^3J_{16}$, $^3J_{25}$	6		
$^3J_{56}$	16		

[a] For numbering of the atoms in the four-spin and six-spin systems, see Figure 2. [b] Reference 13a.

The two signals of equal intensity at 764.2 and 651.2 ppm are assigned to 1,2,3,4-Se_4S_2. The molecule is expected to have a chair conformation similar to S_6[23] or Se_6.[24] With four adjacent selenium atoms, it has a molecular symmetry of C_2. Therefore, it should show two signals of identical intensity in the ^{77}Se NMR spectrum. The only known chemical shift for the six-membered selenium

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[19] Each stored data set contains transients from the start of the experiment until the moment of storage. This method, while not providing kinetic information on the process, balances the need for a sufficient signal-to-noise ratio in the spectrum with a qualitative description of the decomposition reaction.

[20] Laatikainen, R. *J. Magn. Reson.* **1988**, *78*, 127.

[21] It should be noted that it is not self-evident that all the new signals have appeared because of the decomposition of 1,2,3,4,5-Se_5S_2. It could be that as weak signals they are initially lost in the background and only appear as the signal-to-noise ratio improves due to the increasing number of transients. This is specially the case with the signals due to Se_8 and Se_7. It has been shown earlier that the CS_2 solution of freshly prepared [$Ti(C_5H_5)_2Se_5$] contains homocyclic selenium impurities.[22]

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sulfide ring is that for SeS_5, which lies at 786 ppm.[15c] It is well established for neutral heterocyclic selenium sulfides[13a] that the selenium atoms with two sulfur neighbors show the NMR signals at the lowest field, with one sulfur and one selenium neighbor at higher field, and with two selenium neighbors at the highest field. In the light of this trend and the known chemical shift for SeS_5 (two sulfur neighbors), the chemical shifts of 764.2 and 651.2 ppm are reasonable for 1,2,3,4-Se_4S_2, since the former lies in the region expected for selenium with one sulfur and one selenium neighbor and the latter in the region typical for two selenium neighbors.

In contrast to the ^{77}Se-enriched eight-membered 1,2,3,4-Se_4S_4 ring, which shows a second-order (AA′BB′) four-spin system,[13a] the two signals due to 1,2,3,4-Se_4S_2 at 764.2 and 651.2 ppm appear surprisingly as almost pure first-order quartets (i.e. doublets of doublets) in the enriched spectrum. The simulation of the resonances yielded the refined coupling constants shown in Table I. The one-bond coupling over the end bond of the four-atomic selenium chain ($^1J_{13}$ and $^1J_{24}$) shows a larger value than the corresponding coupling in the eight-membered rings.[25] This can be explained by the dependence of the one-bond coupling on the torsion angle.[26] It is also interesting that the coupling over the symmetry element ($^1J_{12}$ and $^3J_{34}$) is almost zero probably due to the mutual canceling of the different components forming these two coupling constants.

Further indications on the correct assignment of the signals at 764.2 and 651.2 ppm can be deduced from the stoichiometry of the decomposition reaction. The two signals have approximately the same intensity as the three signals assigned to 1,2,3,4,5,6-Se_6S_2, implying that the two products are formed in the reaction in equal amounts, as expected from Figure 1. The appearance of 1,2,3,4,5,6-Se_6S_2 must imply selenium atom transfer from one 1,2,3,4,5-Se_5Se_2 molecule to another, and therefore the six-membered 1,2,3,4-Se_4S_2 is the other required product. In the case of the sulfur atom transfer, Se_5S should be formed together with 1,2,3,4,5-Se_5S_3 and/or 1,2,3,5,6-Se_5S_3. However, resonances that could be assigned to the three latter species are not observed in the NMR spectra.

Because only 1,2,3,4-Se_4S_2 and 1,2,3,4,5,6-Se_6S_2 are observed as initial decomposition products, it is evident from Figure 1 that the selenium atom from one 1,2,3,4,5-Se_5S_2 molecule does not insert itself into the S–S bond of another molecule, since this would necessitate the presence of 1,2,3,4,5,7-Se_6S_2 and no resonances are observed that could be assigned to this species. It is not, however, possible to make a distinction on the insertion of the selenium atom into other bonds, since the reaction products in all cases are identical. Likewise, it is not possible to deduce whether any one of the five selenium atoms in 1,2,3,4,5-Se_5S_2 is more favorable for selenium atom transfer than the other four. In the light of the fluxionality of the seven-membered starting material, it is possible that any one selenium atom can act as the transfer agent.

When the CS_2 solution is allowed to stand for a prolonged time, further interconversion reactions are observed to take place with the formation of several additional heterocyclic six-, seven-, and eight-membered selenium sulfides. The characterization of these mixtures is currently in progress.

Conclusions

In this work, we have reported the ^{77}Se NMR spectroscopic study of the decomposition of 1,2,3,4,5-Se_5S_2 in CS_2. The comparison of the natural-abundance spectrum of the reaction mixture with that from the ^{77}Se-enriched sample (enrichment 92%) has enabled the identification of the decomposition products as 1,2,3,4,5,6-Se_6S_2 and 1,2,3,4-Se_4S_4. Thus the NMR results imply that the reaction involves a selenium atom transfer from one seven-membered molecule to another. Since no intermediate has been observed in the spectra, a more detailed description of the reaction mechanism is not possible at present. In the light of the reported absence of free chalcogen radicals in organic solutions,[28] the homolytic cleavage of the chalcogen–chalcogen bonds in the starting 1,2,3,4,5-Se_5S_2 is not probable. The desired selenium atom transfer may well proceed via hypervalent intermediates, which do not require radical formation.

Acknowledgment. Financial support from the Academy of Finland, Emil Aaltonen Foundation, Finnish Academy of Science, and Finnish Cultural Foundation (Fund for Northern Finland) is gratefully acknowledged.

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(25) See Table I for coupling constants in 1,2,3,4,5,6-Se_6S_2 and 1,2,3,4-Se_4S_4. More examples on the coupling in eight-membered selenium sulfides are found in ref 13a.

(26) According to Eggert et al. the magnitude of the coupling constant depends on the degree of overlap of the p lone-pair orbitals of the two selenium atoms involved in the coupling. According to this scheme the absolute value $^1J_{SeSe}$ coupling constant is smallest when the torsion angle of the Se–Se bond is ca. 90°, since the overlap between the p lone-pair orbitals of the adjacent selenium atoms is minimized. As the torsion angle gets smaller or larger, the value of the coupling constant gets larger.[27]

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(28) (a) Koningsberger, D. C.; Neef, T. *Chem. Phys. Lett.* **1970**, *4*, 615. (b) Koningsberger, D. C.; Neef, T. *Chem. Phys. Lett.* **1972**, *14*, 453. (c) Gardner, D. M.; Fraenkel, G. F. *J. Am. Chem. Soc.* **1956**, *78*, 3279.