Selenium-77 Nuclear Magnetic Resonance Identification of Seven-membered Selenium Sulfide Ring Molecules

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Seven-membered heterocyclic selenium sulfides were prepared from a mixture of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species (Se:S = 3:2) **1** upon treatment with S_2Cl_2 and Se_2Cl_2, and the products identified with ^{77}Se NMR spectroscopy. The assignment of the spectra was based on the known chemical shifts, and on the well established trends in the chemical shifts. The reaction of **1** with S_2Cl_2 produced 1,2,3,4,5-Se_5S_2, 1,2,3,4-Se_4S_3, 1,2,3-Se_3S_4 and 1,2-Se_2S_5, and that with Se_2Cl_2 produced Se_7, 1,2,3,4,5,6-Se_6S, 1,2,3,4,5-Se_5S_2, 1,2,3,5,6-Se_5S_2 and 1,2,4,5-Se_4S_3. A comparison of the predicted product distribution from the known composition of the starting $[Ti(C_5H_5)_2Se_xS_{5-x}]$ mixture to that determined semiquantitatively from the peak intensities supports the spectral assignment.

Binary heterocyclic selenium sulfides can be prepared by a variety of synthetic routes, but in most cases the product is a complicated mixture of several molecular species (for a recent review see ref. 1). The identification of individual selenium sulfides from these mixtures is rather difficult and can best be performed by using ^{77}Se NMR spectroscopy.[2] A successful preparation of pure stoichiometric selenium sulfide ring molecules or their simple mixtures has only been achieved utilizing bis(cyclopentadienyl)titanium chalcogenides of the types $[Ti(C_5H_5)_2E_5]$[3] and $[Ti(C_5H_5)_2(\mu\text{-}E_2)_2Ti(C_5H_5)]$[4] (E = S or Se). The products have been characterized by Raman spectroscopy, X-ray crystallography, and ^{77}Se NMR spectroscopy.[5]

The most interesting class of molecular species formed in the reactions of $[Ti(C_5H_5)_2E_5]$ (E = S or Se) with dichlorodisulfane or -diselane are the seven-membered chalcogen ring molecules for which structural information is rather sparse. The crystal structure determinations of S_7[6] and 1,2,3,4,5-Se_5S_2[3c] have shown that in the solid state they contain a fragment of four approximately coplanar atoms resulting in significant alternation in the bond lengths. The Raman spectrum of Se_7[3c] is also consistent with this structure. Theoretical considerations[7] as well as Raman and ^{77}Se NMR spectroscopic evidence[4a,5] have indicated that the seven-membered chalcogen rings are fluxional undergoing rapid pseudo-rotation in solution. Because of the fluxionality, all atomic positions in the seven-membered ring are averaged on the NMR time-scale and thus the chemical shift is only dependent on the chemical nature of the neighbours of the selenium nuclei. For example, solid-state Se_7 assumes a chair conformation with four inequivalent selenium atoms, but in the ^{77}Se NMR spectrum of the molecule in CS_2 solution only one signal is observed.[3c]

We have recently reported that mixtures of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species can be prepared by treating $[Ti(C_5H_5)_2Cl_2]$ with a nearly equimolar mixture of lithium polyselenides and polysulfides.[8] The ^{77}Se NMR spectroscopic identification of the different molecular species was based on the observed trends in the chemical shifts of $[Ti(C_5H_5)_2Se_5]$[9] and Se_nS_{8-n}.[2b] A typical reaction product (initial Se:S = 3:2) contained 25% $[Ti(C_5H_5)_2Se_5]$, 26% $[Ti(C_5H_5)_2Se_4S]$, 8% $[Ti(C_5H_5)_2Se_3S_2]$, 14% $[Ti(C_5H_5)_2SSe_3S]$, 9% $[Ti(C_5H_5)_2Se_2S_3]$ and 18% $[Ti(C_5H_5)_2S_5]$. The reactions of this $[Ti(C_5H_5)_2Se_xS_{5-x}]$ **1** mixture with S_2Cl_2 and Se_2Cl_2 should produce heterocyclic selenium sulfides in predictable relative amounts. The expected quantitative relationships between the different product molecules assists in the ^{77}Se NMR spectroscopic identification of thus far unknown seven-membered heterocyclic selenium sulfides.

Experimental

Syntheses.—The mixtures of lithium polysulfides and polyselenides were prepared by mixing 18–25 mmol of a mixture of elemental selenium and sulfur with dried and degassed tetrahydrofuran (thf, J. T. Baker Chemicals) (50 cm^3) and by reducing the resulting suspensions with a 1 mol dm^{-3} thf solution of $LiBHEt_3$ ('Super-hydride', Aldrich) (7.5–10.0 cm^3) in a nitrogen atmosphere as described by Gladysz *et al.*[10] Mixed-chalcogen $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species were prepared by treating these lithium polyselenide–polysulfide mixtures with $[Ti(C_5H_5)_2Cl_2]$ (Fluka Chemie) as described earlier.[8] Two samples (100 mg, 0.21 mmol) of the product from the reaction with an initial molar ratio of selenium and sulfur of 3:2 were subjected to further study. They were both dissolved in CS_2 (E. Merck) (20 cm^3). One sample was treated with 5 cm^3 of a solution containing S_2Cl_2 (Fluka Chemie) (286 mg) in CS_2 (50 cm^3) (0.21 mmol of S_2Cl_2), and the other with 5 cm^3 of a solution containing Se_2Cl_2 (232 mg) (prepared according to Fehér[11]) in CS_2 (25 cm^3) (0.20 mmol of Se_2Cl_2). These reactions were analogous to those described previously for $[Ti(C_5H_5)_2S_5]$ with Se_2Cl_2[3a,b] and $[Ti(C_5H_5)_2Se_5]$ with S_2Cl_2.[3c,5b,c] The resulting solutions were filtered to remove $[Ti(C_5H_5)_2Cl_2]$ which was regenerated during the reaction. The ^{77}Se NMR spectra were recorded immediately from the solutions thus obtained.

Spectroscopic Measurements.—The ^{77}Se NMR spectra were recorded with a JEOL JNM-GX400 spectrometer operating at 76.33 MHz. The spectral width was 151.52 kHz and the resolution 2.3 Hz per data point. The pulse width was 5.0 μs corresponding to a nuclide tip angle of 25°, and the pulse delay 1.0 s. The accumulations contained 47 000 and 126 000 transients. Deuterium oxide was used as an external ^2H lock and a saturated solution of SeO_2 as an external reference. The chemical shifts (ppm) are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

The Raman spectra of the $[Ti(C_5H_5)_2Se_xS_{5-x}]$ (x = 0–5) samples were recorded using a Perkin-Elmer 1760X FTIR spectrometer equipped with a Raman module and a Nd:YAG laser.

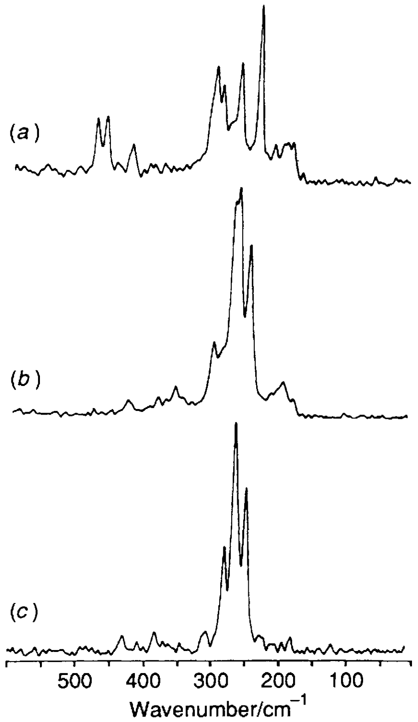

Fig. 1 Fourier-transform Raman spectra of (*a*) [Ti(C_5H_5)$_2$$S_5$], (*b*) [Ti($C_5H_5$)$_2$$Se_xS_{5-x}$] (Se:S = 3:2) and (*c*) [Ti(C_5H_5)$_2$$Se_5$]

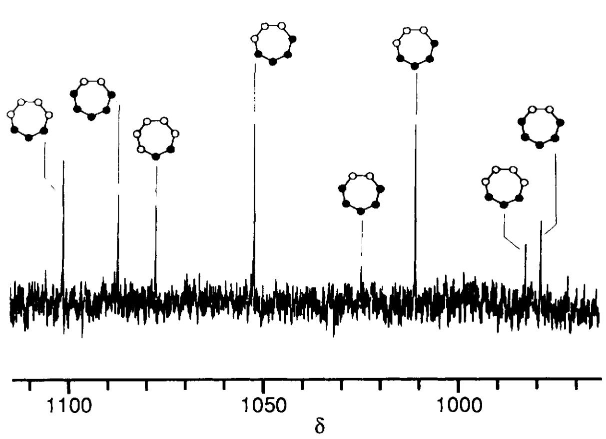

Fig. 2 The ^{77}Se NMR spectrum of seven-membered heterocyclic selenium sulfides obtained from the reaction of [Ti(C_5H_5)$_2$$Se_xS_{5-x}$] with S_2Cl_2. The spectral assignment to individual selenium atoms of the different molecular species is also indicated. Closed circles denote selenium atoms and open ones sulfur atoms

Results and Discussion

General.—The composition of the starting [Ti(C_5H_5)$_2$$Se_xS_{5-x}$] was inferred utilizing ^{77}Se NMR spectroscopy and X-ray crystallography.[8] The assignment of the ^{77}Se NMR spectra of the different samples was based on the trends of the chemical shifts as well as on the constant intensity ratios between some resonances. Since [Ti(C_5H_5)$_2$$S_5$] is unobservable by ^{77}Se NMR spectroscopy, its presence was deduced by X-ray crystallography on the basis of the disorder scheme in the chalcogen atom positions. In this work we utilized Raman spectroscopy to gain qualitative information about the sulfur-rich [Ti(C_5H_5)$_2$$Se_xS_{5-x}$] molecules.

The Raman spectrum of [Ti(C_5H_5)$_2$$Se_xS_{5-x}$] (Se:S = 3:2) together with those of [Ti(C_5H_5)$_2$$S_5$] and [Ti($C_5H_5$)$_2$$Se_5$] is shown in Fig. 1. The general features of these three spectra in the region below 400 cm^{-1} are rather similar. An important observation can be made by comparing the spectrum of [Ti(C_5H_5)$_2$$S_5$] with that of [Ti($C_5H_5$)$_2$$Se_xS_{5-x}$] (Se:S = 3:2).

While the former molecule clearly shows SS stretching modes at 477 and 462 cm^{-1}, the mixed-chalcogen species shows no or very little evidence of the corresponding modes. Its Raman spectrum is rather similar to that of [Ti(C_5H_5)$_2$$Se_5$]. The present sample seems to contain little or no [Ti(C_5H_5)$_2$$S_5$]. According to our earlier ^{77}Se NMR study[8] only small amounts of [Ti(C_5H_5)$_2$$Se_3S_2$] and [Ti($C_5H_5$)$_2$$SSe_2S_2$] are expected.

[Ti(C_5H_5)$_2$$Se_xS_{5-x}$] + S_2Cl_2.—The ^{77}Se NMR spectrum of the selenium sulfides produced in the reaction of [Ti(C_5H_5)$_2$$Se_xS_{5-x}$] with S_2Cl_2 is shown in Fig. 2. On the basis of the reported composition of the starting bis(cyclopentadienyl)titanium selenide sulfide mixture,[8] the reaction is expected to produce the following seven-membered selenium sulfide ring molecules: 1,2,3,4,5-Se_5S_2, 1,2,3,4-Se_4S_3, 1,2,3-Se_3S_4, 1,2-Se_2S_5 and S_7. The last species is unobservable by ^{77}Se NMR spectroscopy. In the light of the Raman spectroscopic results described above S_7 might not be produced in the present reaction.

The assignment of the spectrum to these species is based on the known chemical shifts of 1,2,3,4,5-Se_5S_2 and 1,2-Se_2S_5, on the trends in the selenium chemical shift,[2b] as well as on the constant intensity ratios between some signals.

The signal at δ 1078 has previously been assigned to 1,2-Se_2S_5.[5a] Similarly, the three resonances at δ 1087, 1025 and 979 with an intensity ratio of 2:1:2 have been assigned to 1,2,3,4,5-Se_5S_2.[5b,c] It has also been previously deduced that in structurally analogous selenium sulfides the ^{77}Se resonances of selenium atoms with two sulfur neighbours appear at the lowest field, those for selenium atoms with one selenium and one sulfur neighbour lie at a higher field and those for selenium atoms with two selenium neighbours at the highest field.[2b]

From the above-mentioned assignments and from these known trends in the chemical shifts of Se_nS_{8-n} it can be deduced that the resonances at δ *ca.* 1100–1050 imply selenium atoms with one selenium and one sulfur neighbour, and those at δ *ca.* 1050–980 indicate selenium atoms with two selenium neighbours. The chemical shifts of the isolated selenium atoms (*i.e.* those with two sulfur neighbours) are expected to lie well downfield from δ 1100 and therefore the spectrum in Fig. 2 does not indicate molecular species with a structural unit –S–Se–S–. The ^{77}Se NMR spectrum of 1,2,5-Se_3S_4 furnishes further evidence on the correctness of the trends described above.[4a] The molecule shows two signals at δ 1155 and 1080 with the intensity ratio of 1:2. The former resonance was assigned to an isolated selenium atom and the latter to a selenium atom with one sulfur and one selenium neighbour.

The two signals at δ 1101 and 983 with an intensity ratio of 2:1 are assigned to 1,2,3-Se_3S_4 and those of equal intensity at δ 1052 and 1011 are assigned to 1,2,3,4-Se_4S_3.

[Ti(C_5H_5)$_2$$Se_xS_{5-x}$] + Se_2Cl_2.—The ^{77}Se NMR spectrum of the heterocyclic chalcogen rings produced in the reaction of bis(cyclopentadienyl)titanium selenide sulfide mixture with dichlorodiselane is shown in Fig. 3. The predicted products are Se_7, 1,2,3,4,5,6-Se_6S, 1,2,3,4,5-Se_5S_2, 1,2,3,5,6-Se_5S_2 and 1,2,4,5-Se_4S_3. According to the Raman spectroscopic evidence the formation of 1,2-Se_2S_5 is not expected in appreciable amounts.

The signals at δ 1087, 1025 and 980 again imply 1,2,3,4,5-Se_5S_2,[5b,c] and a strong resonance at δ 998 is due to Se_7.[5b] There are three resonances of equal intensity at δ 1053, 1005 and 999. The first one is in the region implying one selenium and one sulfur neighbour and the last two in the region implying two selenium neighbours. These signals are assigned to 1,2,3,4,5,6-Se_6S.

The signals at δ 1065, 1061 and 1003 with the intensity ratio of 2:2:1 are assigned to 1,2,3,5,6-Se_5S_2. The first two chemical shifts are typical for selenium with one selenium and one sulfur neighbour and the last one is typical for selenium with two

Table 1 The relative abundance (in mol %) of the seven-membered selenium sulfide ring molecules prepared from $[Ti(C_5H_5)_2Se_xS_{5-x}]$ and E_2Cl_2 (E = S or Se)

	S_2Cl_2			Se_2Cl_2		
$[Ti(cp)_2Se_xS_{5-x}]$*	Product	Predicted	Obs.	Product	Predicted	Obs.
$[Ti(cp)_2Se_5]$ (30%)	1,2,3,4,5-Se_5S_2	30	21	Se_7	30	34
$[Ti(cp)_2Se_4S]$ (32%)	1,2,3,4-Se_4S_3	32	33	1,2,3,4,5,6-Se_6S	32	22
$[Ti(cp)_2Se_3S_2]$ (10%)	1,2,3-Se_3S_4	10	27	1,2,3,4,5-Se_5S_2	10	10
$[Ti(cp)_2SSe_3S]$ (17%)	1,2,3-Se_3S_4	17		1,2,3,5,6-Se_5S_2	17	18
$[Ti(cp)_2SSe_2S_2]$ (11%)	1,2-Se_2S_5	11	18	1,2,4,5-Se_4S_3	11	17

* The content of the selenium-containing $[Ti(C_5H_5)_2Se_xS_{5-x}]$ in the starting material has previously been determined by ^{77}Se NMR spectroscopy.[8] cp = C_5H_5.

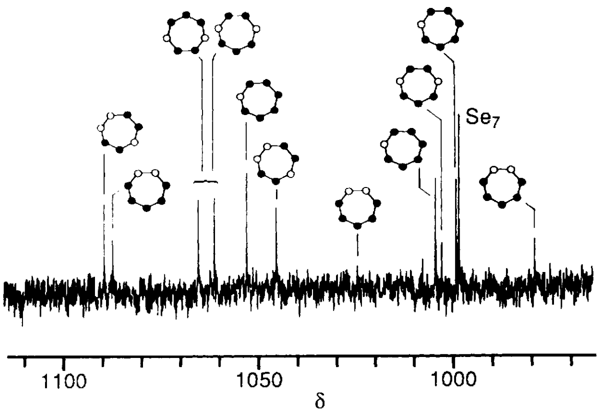

Fig. 3 The ^{77}Se NMR spectrum of seven-membered heterocyclic selenium sulfides obtained from the reaction of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ with Se_2Cl_2. Details as in Fig. 2

selenium neighbours. With similar arguments the two signals of equal intensity at δ 1089 and 1045 are assigned to 1,2,4,5-Se_4S_3.

The assignment of the signals to individual selenium atoms in various molecular species is also indicated in Figs. 2 and 3. While this can be done unambiguously for the products in the reaction of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ with S_2Cl_2 by considering the trends described above (see Fig. 2), the situation is not so straightforward in the case of the products from the reaction of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ with Se_2Cl_2. One possible assignment is shown in Fig. 3. However, the assignment of the two signals of 1,2,3,5,6-Se_5S_3 at δ 1065 and 1061 can equally well be interchanged. The same ambiguity applies to the two signals of 1,2,3,4,5,6-Se_6S at δ 1005 and 999 and to the two signals of 1,2,4,5-Se_4S_3 at δ 1089 and 1045. The present assignment, however, provides more consistent trends in the chemical shifts than the alternative scheme. In any case the interchanging of the signals for different selenium atoms within the given molecular species does not change the conclusions about the composition of the product mixture as discussed below.

Product Distribution.—The assignment of the spectra in Figs. 2 and 3 finds support when comparing the distribution of the selenium-containing products as measured semiquantitatively from the peak intensities to that predicted from the composition of the starting material as determined previously[8] (see Table 1). In general, the predicted and observed relative abundances of the different components are in reasonable agreement with each other. When the sample solutions are allowed to stand for a prolonged time, the interconversion of the seven-membered molecules leads to the formation of eight- and six-membered selenium sulfide rings Se_nS_{8-n}, as reported earlier.[2d]

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