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^{77}Se NMR Spectroscopic and X-ray Crystallographic Characterization of Bis(cyclopentadienyl)titanium Selenide Sulfide Mixtures, $[Ti(C_5H_5)_2Se_xS_{5-x}]$

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Mixed crystals of bis(cyclopentadienyl)titanium selenide sulfides, $[Ti(C_5H_5)_2Se_xS_{5-x}]$, have been prepared by reacting $[Ti(C_5H_5)_2Cl_2]$ with a series of lithium polyselenide and polysulfide mixtures at different molar ratios. The reaction products were studied with ^{77}Se NMR spectroscopy and X-ray crystallography. When the initial lithium polyselenide/polysulfide mixture was either sulfur-rich or selenium-rich, mainly $[Ti(C_5H_5)_2S_5]$ or $[Ti(C_5H_5)_2Se_5]$ were formed, respectively. However, when the initial molar ratio of selenium and sulfur was near unity, several different $[Ti(C_5H_5)_2Se_xSe_{5-x}]$ species were formed. The product from the reaction with initial molar ratio of selenium and sulfur of 3:2 was subjected to a more detailed study. A typical crystal was isomorphic with $[Zr(C_5H_5)_2Se_5]$ with the monoclinic space group $P2_1/c$ (No. 14) and $a = 13.143$ (1) Å, $b = 8.051$ (1) Å, $c = 14.417$ (1) Å, $\beta = 114.86$ (1)°, and $Z = 4$. The structure was refined to $R = 0.034$ ($R_w = 0.028$). The molecular structure is expectedly analogous with $[Ti(C_5H_5)_2S_5]$ and $[Ti(C_5H_5)_2Se_5]$, comprising two η^5-cyclopentadienyl rings and a chain of five chalcogen atoms, which form a didentate chelate ring with titanium. The crystal structure is disordered with all chalcogen atom positions partially occupied by both sulfur and selenium. According to the ^{77}Se NMR spectrum the main selenium-containing components in the product are $[Ti(C_5H_5)_2Se_5]$, $[Ti(C_5H_5)_2Se_4S]$, $[Ti(C_5H_5)_2Se_3S_2]$, $[Ti(C_5H_5)_2SSe_3S]$, and $[Ti(C_5H_5)_2Se_2S_3]$. The product also contains $[Ti(C_5H_5)_2S_5]$. The refined occupation factors of sulfur and selenium from the crystal structure determination agree well with the relative abundance of the different molecular species as calculated from the NMR spectrum.

Introduction

Bis(cyclopentadienyl)titanium chalcogenides of the types $[Ti(C_5H_5)_2E_5]$ and $[Ti(C_5H_5)_2(\mu\text{-}E_2)_2Ti(C_5H_5)_2]$ (E = S or Se) are attractive starting materials for the synthesis of pure stoichiometric heterocyclic selenium sulfides,[2] which are generally produced only as complicated mixtures. The characterization of these mixtures has proved to be rather difficult (for a recent review, see ref 4). It is only with the advent of ^{77}Se NMR spectroscopy that it has been possible to identify individual molecular species.[5,6] Supporting evidence for the spectral assignment of the selenium sulfide mixtures has been obtained from the ^{77}Se NMR spectra of pure stoichiometric six- and seven-membered selenium sulfide ring molecules.[7]

The present study of the preparation of bis(cyclopentadienyl)titanium selenide sulfides was initiated in order to get starting materials for the synthesis of new stoichiometric selenium sulfides. It has also been suggested that the mononuclear $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species are intermediates in the reactions of the dinuclear $[Ti(C_5H_5)_2(\mu\text{-}E_2)_2Ti(C_5H_5)_2]$ (E = S, Se) complexes with chlorosulfanes or chloroselanes.[3d] The ^{77}Se NMR data of $[Ti(C_5H_5)_2Se_5]$[8] together with those for heterocyclic selenium sulfides[6,7] provide a good basis for the identification of the different $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species.

Table I. Crystal Data for $[Ti(C_5H_5)_2Se_xS_{5-x}]$ (Se:S = 3:2)

formula	$[Ti(C_5H_5)_2Se_xS_{5-x}]^a$
fw	478.9
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
T, K	293
a, Å	13.143 (1)
b, Å	8.051 (1)
c, Å	14.417 (1)
β, deg	114.86 (1)
V, Å^3	1384.0 (3)
Z	4
d_c, g cm^{-3}	2.298
$F(000)$	904
λ, Å	0.71073
μ(Mo Kα), cm^{-1}	86.9
min and max abs cor	0.849, 0.999
$R(F_o)^b$	0.034
$R_w(F_c)^c$	0.028

[a] The molecular formula used for the calculations of the physical constants was estimated from the initial Se:S ratio of 3:2, since the final refinement indicates that this is very near the actual composition of the mixture. [b] $R(F_o) = \sum||F_o| - |F_c||/|F_o|$. [c] $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Experimental Section

Preparation of $[Ti(C_5H_5)_2Se_xS_{5-x}]$. A series of reactions was carried out by mixing elemental selenium (E. Merck GmbH) and elemental sulfur (E. Merck GmbH) at molar ratios of 1:4, 2:3, 3:2, and 4:1[9] with 50 mL of dried and degassed tetrahydrofuran (thf, J. T. Baker Chemicals) and by reducing the resulting suspensions with 7.5–10.0 mL of 1 M thf solution of $LiBHEt_3$ ("Super-hydride", Aldrich) in N_2 atmosphere applying the method described by Gladysz et al.[10]

In each synthesis 100 mL of the thf solution of $[Ti(C_5H_5)_2Cl_2]$ (Fluka Chemie AG) was slowly added into the hot suspension of lithium polychalcogenide mixture with subsequent refluxing under N_2 atmosphere.[11] The solvent was evaporated, and the crude product was extracted with

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(2) The reaction of $[Ti(C_5H_5)_2S_5$ with Se_2Cl_2 produces 1,2-Se_2S_5, which decomposes to SeS_5 and 1,2,3-Se_3S_5.[3a,b] The reactions of $[Ti(C_5H_5)_2Se_5$ with S_2Cl_2, SCl_2, or Se_2Cl_2 produce 1,2,3,4,5-Se_5S_2, 1,2,3,4,5-Se_5S, or Se_7, respectively.[3c] $[Ti(C_5H_5)_2(\mu\text{-}Se_2)_2Ti(C_5H_5)_2]$ reacts with SCl_2 to form 1,4-Se_4S_2.[3d] With S_2Cl_2 it forms 1,2,5-Se_3S_4 and 1,2,5,6-Se_4S_4. It is interesting to note that the reaction of $[Ti(C_5H_5)_2(\mu\text{-}S_2)_2Ti(C_5H_5)_2]$ with Se_2Cl_2 also results in the formation 1,2,5-Se_3S_4 and 1,2,5,6-Se_4S_4.[3d,3e] The reaction of $[Ti(C_5H_5)_2S_5]$ with selenium dibromide gives several heterocyclic selenium sulfides with ring sizes of 6, 7, 8, and 12.[3f]

(3) (a) Laitinen, R.; Rautenberg, N.; Steidel, J.; Steudel, R. *Z. Anorg. Allg. Chem.* **1982**, *486*, 116. (b) Steudel, R.; Strauss, E.-M. *Angew. Chem.* **1984**, *96*, 356; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 362. (c) Steudel, R.; Papavassiliou, M.; Strauss, E.-M.; Laitinen, R. *Angew. Chem.* **1986**, *98*, 81; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 99. (d) Steudel, R.; Jensen, D.; Papavassiliou, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 349. (e) Giolando, D. M.; Papavassiliou, M.; Pickardt, J.; Rauchfuss, T. B. *Inorg. Chem.* **1988**, *27*, 2596. (f) Steudel, R.; Jensen, D.; Baumgart, F. *Polyhedron* **1990**, *9*, 1199.

(4) Laitinen, R. S. *Acta Chem. Scand.* **1987**, *A41*, 361.

(5) The spectral analysis has been based on the combined information obtained from the ^{77}Se spectra of the samples containing natural-abundance selenium and from those of the ^{77}Se-enriched samples (94% enrichment) of the same chemical composition.[6a]

(6) (a) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598. (b) Laitinen, R. S.; Pekonen, P.; Hiltunen, Y.; Pakkanen, T. A. *Acta Chem. Scand.* **1989**, *43*, 436.

(7) (a) Steudel, R.; Papavassiliou, M.; Jensen, D.; Seppelt, K. *Z. Naturforsch.* **1988**, *43b*, 245. (b) Steudel, R.; Papavassiliou, M.; Krampe, W. *Polyhedron* **1988**, *7*, 581. (c) Pekonen, P.; Hiltunen, Y.; Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1990**, *29*, 2770.

(8) Pekonen, P.; Hiltunen, Y.; Laitinen, R. S. *Acta Chem. Scand.* **1989**, *43*, 914.

(9) The total amount of selenium and sulfur was in the range 18–25 mmol depending on the synthesis.

(10) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204.

(11) The syntheses were carried out by applying the method of Shaver and McCall.[12] In each preparation the molar ratio of $[Ti(C_5H_5)_2Cl_2]$, $LiBHEt_3$, and Se + S was constrained to 1:2:5.

(12) Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823.

0020-1669/91/1330-1874$02.50/0

200 mL of methylene chloride (E. Merck GmbH). The solution was concentrated to ca. 50 mL. Upon cooling, well-defined deep red rod-shaped crystals were formed.

NMR Spectroscopy. The ^{77}Se NMR spectra of all products were recorded for carbon disulfide solutions with a JEOL JNM-GX400 spectrometer operating at 76.31 MHz. The spectral width was 200.00 kHz, and the resolution, 3.1 Hz/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 50 000–115 000 transients. D_2O 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 [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

X-ray Crystallography. A crystal from the product with initial molar ratio of selenium and sulfur of 3:2 was selected for X-ray crystallographic study.[13] The crystal data and some details of the structure determination are given in Table I.[14] Full information about the intensity collection and structure refinement is available as supplementary material. An Enraf-Nonius CAD-4 diffractometer was used in the X-ray measurements using Mo Kα radiation (0.71073 Å). The unit cell parameters were determined by least-squares refinement of 25 randomly searched reflections having the θ range 7.8–13.9°. Two reference reflections were used to monitor the stability of the crystal. Their intensities were measured periodically every 60 min and showed no significant variation during the data collection. An empirical absorption correction was made from the ψ-scan data, after which the net intensities were corrected for Lorentz and polarization effects. Of the 3242 reflections collected, those with $I \geq 3\sigma(I)$ (1401 unique reflections) were considered observed.

Direct methods combined with subsequent difference Fourier synthesis utilizing the SDP program package supplied by Enraf-Nonius provided the positions of all non-hydrogen atoms.[15] It was apparent early in the refinement that the chalcogen atom positions were disordered with sulfur and selenium statistically distributed over the atomic sites. Therefore the least-squares refinement of the structure was carried out by using the program SHELX 76,[17] since this program facilitates the refinement of the occupation factors of sulfur and selenium in the disordered atomic sites. Because of the correlation between the thermal parameters and the occupation factors, the following constraints had to be applied:

$$\mathrm{of}_{Se(i)} + \mathrm{of}_{S(i)} = 1$$

$$U_{Se(i)} = U_{S(i)}$$

where $\mathrm{of}_{Se(i)}$, $\mathrm{of}_{S(i)}$, $U_{Se(i)}$, and $U_{S(i)}$ are the occupation factors and isotropic thermal parameters of selenium and sulfur atoms at the *i*'th atomic position. Since the selenium atom is slightly larger than the sulfur atom, the fractional coordinates of the chalcogen atom at the given atomic site vary slightly depending not only on its chemical identity but also on that of its neighbors. However, because of the statistical distribution of sulfur and selenium, this variation is undetectable in the electron density map. Therefore the estimation of the electron density, and thus the occupation factors of sulfur and selenium, at the given chalcogen atom position necessitates the constraining of corresponding sulfur and selenium atoms in the same atomic position. While information about the physically meaningful bond lengths and bond angles is therefore lost, the method enables the reliable refinement of the occupation factors of selenium and sulfur at the disordered chalcogen atom sites.

The refinement with isotropic thermal parameters was carried out in stages. At first, occupation parameters were refined and the common isotropic thermal parameters of each sulfur/selenium atom were kept constant. Convergence was achieved in five cycles of full-matrix refinement. Subsequently, the thermal parameters were refined by keeping the occupation factors constant. All other atoms were refined normally with isotropic thermal parameters. This stepwise refinement was continued until no further changes were obtained.[18] Occupation factors of sulfur and selenium were not refined during the anisotropic refinement.

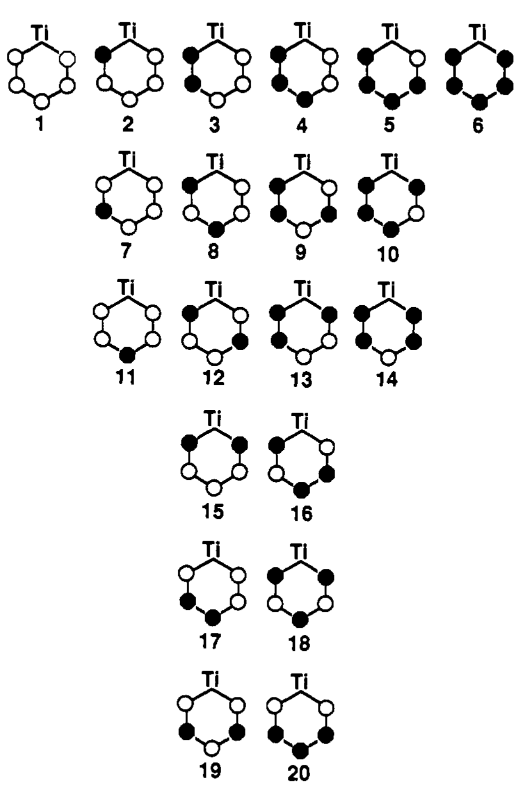

Figure 1. All possible [$Ti(C_5H_5)_2Se_xS_{5-x}$] (x = 0–5) species that could be formed in the reaction of Li_2Se_x/Li_2S_y mixtures with [$Ti(C_5H_5)_2Cl_2$].

In the final stages of the refinement, the cyclopentadienyl rings were refined as rigid pentagons (C–C 1.420 Å, C–C–C 108°). Hydrogen atom positions were calculated and refined as part of the rigid group (C–H 1.080 Å, C–C–H 126.0°). All hydrogen atoms were given a common isotropic thermal parameter, which was refined along with other parameters. The function minimized was $\sum w\Delta F^2$ with $w = 1.7029[\sigma^2(F_o) - 0.000092F_o]^{-1}$. An empirical extinction correction $F_c(\mathrm{corr}) = F_c(1 - \epsilon F_{c2}/\sin\theta)$ was applied in the last cycles of refinement with ϵ refined along with other variables [final value of $\epsilon = 9\ (7) \times 10^{-5}$].

Results and Discussion

Assignment of ^{77}Se Spectrum. All possible [$Ti(C_5H_5)_2Se_xS_{5-x}$] species that could be formed in the reaction of lithium polychalcogenide mixtures with [$Ti(C_5H_5)_2Cl_2$] are shown in Figure 1. The natural-abundance ^{77}Se NMR spectrum of the product from the Se:S = 3:2 preparation is shown in Figure 2. The assignment of the spectrum is based on the observed trends in the chemical shifts in related systems and can be deduced as follows.

It has been shown earlier that [$Ti(C_5H_5)_2Se_5$] has three signals in an intensity ratio of 2:2:1 at 1237.9, 728.3, and 654.0 ppm, respectively.[8] The spectral analysis indicated that the chemical shift of the selenium nuclei is strongly dependent on the position of the atom with respect to titanium in the six-membered chelate ring. Selenium atoms bonded to titanium (position a; see Figure 3) show the signal at the lowest field (1237.9 ppm), the next atoms (position b) resonate at significantly higher field (728.3 ppm), and the selenium atom furthest removed from titanium (position c) produces a signal at the highest field (654.0 ppm). A similar trend has also been reported for mono- and oligomeric molybdenum and tungsten polyselenide anions.[19]

The ^{77}Se NMR spectroscopic study of heterocyclic selenium sulfides Se_nS_{8-n} has shown the presence of another trend.[6a] The selenium atoms with two sulfur neighbors show the NMR signals at the lowest field, with one sulfur and one selenium neighbor show

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(13) When the lithium selenide sulfide mixture was either selenium-rich or sulfur-rich, mainly [$Ti(C_5H_5)_2Se_5$] or [$Ti(C_5H_5)_2S_5$] was formed, respectively. Mixtures of several [$Ti(C_5H_5)_2Se_xS_{5-x}$] species were formed only when the molar ratio of selenium and sulfur was near unity. A crystal from Se:S = 3:2 preparation was selected for the crystal structure determination as a typical example for the mixed product.

(14) In order to check the homogeneity of the bulk material, the unit cell parameters of 10 different crystals were determined. All unit cells were identical within the experimental errors.

(15) Neutral-atom scattering factors were used and corrected for anomalous dispersion in the case of non-hydrogen atoms.[16]

(16) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2B. (b) Cromer, D. T. *Ibid.*, Table 2.3.1.

(17) Sheldrick, G. M. SHELX 76. Program for Crystal Structure Determinations. University of Cambridge, 1976.

(18) The sums of the occupation factors of sulfur and selenium in the five chalcogen atom sites converged to a values near the initial molar ratio Se:S = 3:2.

(19) (a) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747. (b) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790.

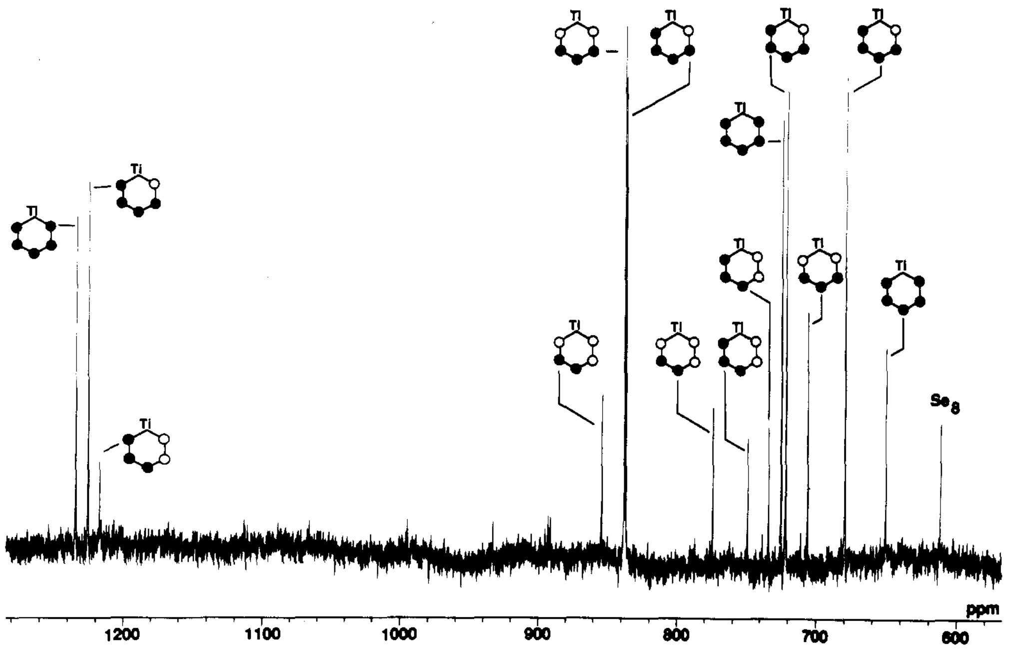

Figure 2. Natural-abundance ^{77}Se NMR spectrum of the $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species in CS_2 solution. The initial molar ratio of selenium and sulfur in the preparation was 3:2. The assignment of the signals to individual selenium atoms in various molecular species is also indicated in the spectrum.

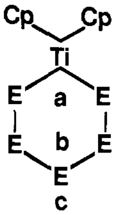

Figure 3. Three possible locations for the selenium atoms in the six-membered $TiSe_xS_{5-x}$ chelate ring.

signals at higher field, and with two selenium neighbors show signals at the highest field.

By consideration of the two trends described above, it can be concluded that in the mixed $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species the selenium atoms in position a should show NMR signals above 1200 ppm, in position b in the range 950–720 ppm, and in position c in the range 800–650 ppm. In each region the signal is shifted downfield with the increasing number of sulfur neighbors.

The signals at 1238, 728, and 654 ppm are assigned to $[Ti(C_5H_5)_2Se_5]$, since the three chemical shifts and their intensity ratio of 2:2:1 agree with those reported earlier for the pure compound.[8,20] The signal at 615 ppm is due to Se_8 (see ref 6) that is formed as a decomposition product.[21]

Since the signal at 1238 ppm is due to $[Ti(C_5H_5)_2Se_5]$, the two additional signals at 1229 and 1221 ppm must also imply a structural unit Ti–Se–Se, since the Se signal of the structural unit Ti–Se–S should appear at significantly lower field. The spectrum of Figure 2 therefore indicates the absence of the molecular species **2**, **8**, **10**, **12**, **13**, **15**, **16**, and **18**.

The four signals at 1229, 840, 725, and 680 ppm have an intensity ratio 1:1:1:1[22] and are assigned to $[Ti(C_5H_5)_2Se_4S]$ (**5**). As described above, the signal at 1229 ppm is typical for selenium bonded to titanium and selenium. The signal at 840 ppm implies a selenium atom in position b (see Figure 3) with one selenium and one sulfur neighbor, that at 725 ppm is reasonable for a selenium atom in position b with two selenium neighbors, and that at 680 ppm indicates position c with two selenium neighbors.

The three signals at 1221, 752, and 737 ppm also show equal intensities in all spectra. They are assigned to $[Ti(C_5H_5)_2Se_3S_2]$ (**4**). The signal at 752 ppm indicates a position b selenium with two selenium neighbors, and that at 737 ppm, a position c selenium with one sulfur and one selenium neighbor.

There are two signals at 841 and 710 ppm with an intensity ratio of 2:1. These chemical shifts are typical for position b having one sulfur and one selenium neighbor and for position c with two selenium neighbors, respectively, and are therefore assigned to $[Ti(C_5H_5)_2SSe_3S]$ (**20**).

The two signals of equal intensities at 858 and 778 ppm are assigned to $[Ti(C_5H_5)_2SSe_2S_2]$ (**17**). The detailed assignment of all chemical shifts to different molecular species is shown in Figure 2.

The main features of the spectrum of the more sulfur-rich product (initial molar ratio Se:S = 2:3) are similar to those discussed above. The spectrum of the product from the Se:S = 2:3 preparation showed one additional signal of low intensity at 936 ppm.[23] This chemical shift implies a position b selenium with two sulfur neighbors. The signal can be assigned to either $[Ti(C_5H_5)_2SSeS_3]$ (**7**) or $[Ti(C_5H_5)_2SSeSSeS]$ (**19**). ^{77}Se NMR spectroscopy does not provide the means to distinguish between these two molecular species.

There are some very weak signals apparent in the spectrum of Figure 2. Because of the low signal-to-noise ratio it is not possible to discuss their exact assignment. Furthermore, the emphasis in the present work is in the identification of the main products in the reaction of $[Ti(C_5H_5)_2Cl_2]$ with mixtures of lithium polysulfides and polyselenides, and thus the low concentration of these species in all sample solutions renders them less interesting within the scope of this study.

Composition of the Samples. The ^{77}Se NMR spectra of the products can be used for the semiquantitative determination of the main selenium-containing molecular species in the sample solutions. The NMR spectrum of the product from the Se:S = 1:4 preparation showed only weak signals of $[Ti(C_5H_5)_2SSe_2S_2]$ (**17**). Thin-layer chromatographic results[24] indicated that the

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(20) A partial separation of the molecular species using column chromatography [silica gel 60 (E. Merck GmbH) with a 60:40% (v/v) mixture of CS_2 and CH_2Cl_2 as an eluant] was used as a test to see which signals are due to the same molecular species. Though significant changes in the intensities of some signals were observed in different fractions collected, the relative intensities of the signals at 1238, 728, and 654 ppm always remained constant at 2:2:1, those at 1229, 840, 725, and 680 ppm at 1:1:1:1, those at 1221, 752, and 737 ppm at 1:1:1, and those at 841 and 710 ppm at 2:1.

(21) The Se_8 signal was also observed in the solution containing pure $[Ti(C_5H_5)_2Se_5]$.

(22) The three signals at ca. 1230 ppm are broader than the signals at higher field owing to the coupling to the cyclopentadienyl hydrogens.[8]

(23) A weak signal at 936 ppm is also observed in the spectrum of the product with Se:S = 3:2 (see Figure 2).

Table II. Relative Abundance (mol %) of Selenium-Containing $[Ti(C_5H_5)_2Se_xSe_{5-x}]$ Species in the Products from the Se:S = 2:3 and Se:S = 3:2 Preparations[a]

component	Se:S = 2:3	Se:S = 3.2
$[Ti(C_5H_5)_2Se_5]$ (**6**)	5	30
$[Ti(C_5H_5)_2Se_4S]$ (**5**)	32	32
$[Ti(C_5H_5)_2Se_3S_2]$ (**4**)	12	10
$[Ti(C_5H_5)_2SSe_3S]$ (**20**)	25	17
$[Ti(C_5H_5)_2SSe_2S_2]$ (**17**)	18	11
$[Ti(C_5H_5)_2SSeS_3]$ (**7**)[b]	8	

[a] The ^{77}Se NMR spectrum indicates that both samples contain about 10% of Se_8. $[Ti(C_5H_5)_2S_5]$ (**1**) is present in both samples. The crystal structure determination of the sample crystal from the Se:S = 3:2 preparation indicates that there is ca. 18% of **1** in the lattice (see Table V). [b] The low intensity signal at 936 ppm could equally well be assigned to $[Ti(C_5H_5)_2SSeSSeS]$.

Table III. Atomic Coordinates for $[Ti(C_5H_5)_2Se_xS_{5-x}]$ (Se:S = 3:2 Preparation) with Estimated Standard Deviations Given in Parentheses

atom[a]	x	y	z	U_{eq},[b] Å^2
Ti(1)	0.7303 (1)	0.6809 (2)	0.4590 (1)	3.43 (8)
E(1)	0.9253 (1)	0.6204 (1)	0.5804 (1)	4.22 (7)
E(2)	0.9411 (1)	0.3437 (1)	0.6121 (1)	5.20 (6)
E(3)	0.8479 (1)	0.3161 (1)	0.7162 (1)	5.08 (6)
E(4)	0.6597 (1)	0.3385 (1)	0.6079 (1)	4.91 (6)
E(5)	0.6423 (1)	0.6115 (2)	0.5753 (1)	4.28 (8)
C(1)	0.6069 (5)	0.6188 (6)	0.2888 (4)	5.2 (6)
C(2)	0.5948 (5)	0.4891 (6)	0.3501 (4)	5.1 (5)
C(3)	0.6981 (5)	0.4018 (6)	0.3946 (4)	4.6 (5)
C(4)	0.7741 (5)	0.4775 (6)	0.3607 (4)	5.4 (6)
C(5)	0.7177 (5)	0.6116 (6)	0.2954 (4)	6.1 (6)
C(6)	0.7171 (9)	0.9431 (7)	0.3802 (5)	8.6 (7)
C(7)	0.6316 (9)	0.9386 (7)	0.4160 (5)	7.6 (7)
C(8)	0.6841 (9)	0.9317 (7)	0.5244 (5)	8.2 (7)
C(9)	0.8020 (9)	0.9318 (7)	0.5556 (5)	7.4 (7)
C(10)	0.8223 (9)	0.9389 (7)	0.4665 (5)	9.7 (9)

[a] For the occupation factors of Se in the disordered positions E(1)–E(5), see Figure 4. [b] U_{eq} is given as one-third of the trace of the orthogonalized U_{ij} tensor. The numerical values have been multiplied by 10^2.

product contained mainly $[Ti(C_5H_5)_2S_5]$ (**1**). Similarly, the ^{77}Se NMR spectrum and the thin-layer chromatogram of the selenium-rich preparation Se:S = 4:1 only indicated the presence of $[Ti(C_5H_5)_2Se_5]$ (**6**).

The relative abundance of the selenium-containing $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species in the Se:S = 2:3 and 3:2 preparations is presented in Table II. As expected, the concentration of the selenium-rich molecular species increases as the selenium content of the starting mixture increases.

It is interesting to note that the main components in the $[Ti(C_5H_5)_2Se_xS_{5-x}]$ mixtures have preferably the selenium atoms adjacent to each other, maximizing the number of homopolar bonds. This phenomenom has also been observed for binary selenium sulfides[2,6a] and seems to be a typical feature of the structural chemistry of sulfur–selenium mixed systems.

Crystal Structure. The crystal from the Se:S = 3:2 preparation is isostructural with $[Zr(C_5H_5)_2Se_5]$.[25] The atomic coordinates of the non-hydrogen atoms are given in Table III, and the selected bond parameters, in Table IV. The molecular structure indicating the numbering of the atoms is shown in Figure 4.

Table IV. Selected Bond Lengths, Bond Angles, and Dihedral Angles in $[Ti(C_5H_5)_2Se_xS_{5-x}]$ (Se:S = 3:2 Preparation)

(a) Bond Lengths (Å)

Ti(1)–E(1)	2.469 (2)	Ti(1)–C(1)	2.357 (5)	Ti(1)–C(6)	2.369 (6)
Ti(1)–E(5)	2.469 (2)	Ti(1)–C(2)	2.381 (5)	Ti(1)–C(7)	2.386 (7)
E(1)–E(2)	2.266 (2)	Ti(1)–C(3)	2.400 (5)	Ti(1)–C(8)	2.412 (8)
E(2)–E(3)	2.312 (1)	Ti(1)–C(4)	2.389 (6)	Ti(1)–C(9)	2.409 (6)
E(3)–E(4)	2.311 (1)	Ti(1)–C(5)	2.361 (6)	Ti(1)–C(10)	2.383 (8)
E(4)–E(5)	2.239 (2)	Ti(1)–Cp(1)[a]	2.048 (5)	Ti(1)–Cp(2)[a]	2.064 (5)

(b) Bond Angles (deg)

E(1)–Ti(1)–E(5)	96.71 (7)	Ti(1)–E(5)–E(4)	109.21 (9)
Ti(1)–E(1)–E(2)	108.46 (6)	C(i)–Ti(1)–C(i + 1)[b]	34.3 (4)–35.0 (2)
E(3)–E(2)–E(1)	101.34 (7)	C(i)–Ti(1)–C(i + 2)[b]	57.2 (4)–57.9 (2)
E(4)–E(3)–E(2)	105.22 (7)	Cp(1)–Ti(1)–Cp(2)[a]	130.3 (2)
E(5)–E(4)–E(3)	101.78 (5)		

(c) Dihedral Angles (deg)

Ti(1)–E(1)–E(2)–E(3)	−73.87 (8)	E(3)–E(4)–E(5)–Ti(1)	73.36 (8)
E(1)–E(2)–E(3)–E(4)	74.93 (6)	E(4)–E(5)–Ti(1)–E(1)	−67.10 (7)
E(2)–E(3)–E(4)–E(5)	−74.72 (8)	E(5)–Ti(1)–E(1)–E(2)	67.06 (9)

[a] Cp(1) is the cyclopentadienyl ring comprising carbon atoms C(1)–C(5). Cp(2) comprises the carbon atoms C(6)–C(10). [b] Carbon atoms i, i + 1, and i + 2 are adjacent in the given cyclopentadienyl ring.

Table V. Disorder Scheme in $[Ti(C_5H_5)_2Se_xSe_{5-x}]$ (Se:S = 3:2 Preparation) Derived by Using the ^{77}Se NMR Spectroscopic Results

molecule	E(1)	E(2)	E(3)	E(4)	E(5)	abundance, %[a]
$[Ti(C_5H_5)_2Se_5]$	Se	Se	Se	Se	Se	25
$[Ti(C_5H_5)_2Se_4S]$	Se	Se	Se	Se	S	19
	S	Se	Se	Se	Se	7
$[Ti(C_5H_5)_2Se_3S_2]$	Se	Se	Se	S	S	8
$[Ti(C_5H_5)_2SSe_3S]$	S	Se	Se	Se	S	14
$[Ti(C_5H_5)_2SSe_2S_2]$	S	Se	Se	S	S	9
$[Ti(C_5H_5)_2S_5]$	S	S	S	S	S	18
Se (%) in atomic sites	52	82	82	65	32	

[a] The relative abundance of the selenium-containing molecular species shown in Table II was modified due to the presence of $[Ti(C_5H_5)_2S_5]$ in the sample. Its content was estimated from the Se occupation factors of E(2) and E(3) as ca. 18%.

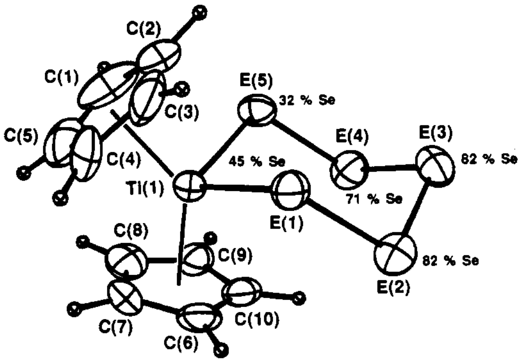

Figure 4. ORTEP drawing of the molecular structure of $[Ti(C_5H_5)_2Se_xS_{5-x}]$ (Se:S = 3:2 preparation). The occupation factors of selenium at the disordered chalcogen atom sites are indicated in the figure. The thermal ellipsoids represent the 50% probability surfaces.

The two cyclopentadienyl rings bond to titanium via their π electrons as in **1**,[26] **6**, and $[Zr(C_5H_5)_2Se_5]$.[25] The Ti–C distances range 2.357 (5)–2.412 (6) Å and are in agreement with those in **1**[26] and **6**.[25] Because of the disorder in the chalcogen atom positions, the bond parameters involving these atoms do not have actual physical significance but rather reflect the composition of the atomic positions. It can, however, be seen that the six-membered chelate ring assumes a chair conformation as in $[Ti(C_5H_5)_2S_5]$ (**1**)[26] and $[Ti(C_5H_5)_2Se_5]$ (**6**).[25]

Both Ti–E (E = S and Se) distances in the present structure are 2.469 (2) Å (see Table IV). In contrast, the two Ti–S distances in **1** are unequal [2.422 (1) and 2.448 (1) Å].[26b] This is also the case in **6** [2.564 (2) and 2.588 (2) Å] and to a lesser extent in $[Zr(C_5H_5)_2Se_5]$ [2.654 (2) and 2.659 (2) Å].[25] When comparing the present structure to that of the isostructural $[Zr(C_5H_5)_2Se_5]$, it can be noted that the chalcogen atom position E(5), which is nearer to the transition metal in the zirconium compound, corresponds to a position with a smaller occupation factor of selenium (see Figure 4).

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(24) Silica gel 60 F_{254} plates (E. Merck GmbH) with a 60:40% (v/v) mixture of CS_2 and CH_2Cl_2 as an eluant.

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The disorder in the chalcogen atom positions can be resolved by using the relative composition of the $[Ti(C_5H_5)_2Se_xS_{5-x}]$ species as determined from the ^{77}Se NMR spectrum of the Se:S = 3:2 product (see Table III). The numerical details are presented in Table V.

The asymmetrical distribution of the occupation factors of selenium in the chalcogen atom positions E(1)-E(5) implies that the chiral molecular species $[Ti(C_5H_5)_2Se_3S_2]$ (**4**), $[Ti(C_5H_5)_2Se_4S]$ (**5**), and $[Ti(SSe_2S_2]$ (**17**) may have preferable orientations in the lattice. Since in the present structure the chalcogen atom position E(5) (see Figure 4 and Table III) is richer in sulfur and in the related structures it is nearer to the transition metal than E(1) it was assumed that the asymmetric molecular species **4** or **5** (see Figure 1) will mainly have the orientation with the three- or four-atom selenium fragment starting from E(1) rather than E(5). In fact, since the occupation factors of selenium in E(2) and E(3) are equal, $[Ti(C_5H_5)_2Se_3S_2]$ (**4**) and $[Ti(C_5H_5)_2SSe_2S_2]$ (**17**) can only assume one orientation. It is also known that the crystal contains $[Ti(C_5H_5)_2S_5]$ (**1**), even though it cannot be observed by ^{77}Se NMR spectroscopy. Without the presence of **1**, the occupation factors of selenium in E(2) and E(3) should be 100%. Therefore the relative amount of **1** in the crystal was estimated by scaling the occupation factors of selenium in these two atomic positions to the observed 82%. Finally, the relative amount of the chiral molecule **5** in the two alternative positions was adjusted by using the refined occupation factors of selenium in E(5). As a test of the disorder scheme, it can be noted that the occupation factors of selenium in E(1) and E(4) that have not been used to resolve of the disorder are reasonably well reproduced by this scheme.

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Supplementary Material Available: Details of structure determination (Table 1S), anisotropic thermal parameters of non-hydrogen atoms (Table 2S), calculated hydrogen atom positions (Table 3S), and bond angles (Table 4S) (7 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Hydrogen Bonding in Alkylammonium Chlorometalates of the First Transition Metals

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A study of hydrogen bonding in alkylammonium chlorometalates has been carried out by using the Cambridge Structural Database as a source of data and a search tool. The results support a range of bonded H··Cl distances from 2.1 to 2.8 Å and indicate that the N-H···Cl angle should be 120-180° when significant H bonding is present. Hydrogen bonding by alkyl hydrogens to chloride ions is not supported by the data. The outer end of the range of H··Cl distances is a little longer than has been commonly used in the recent literature in analyzing hydrogen bonding in such structures. Bifurcated hydrogen bonds from a single hydrogen to two neighboring chlorides are possible, but hydrogen bonds from two different hydrogens on a single nitrogen to the same chloride ion are not observed. Inferring hydrogen bonding from N···Cl distances in the absence of hydrogen positions will give erroneous false positive results in a significant fraction of cases.

The existence of hydrogen bonds of the type N-H··X, where X = Cl or Br, is now well-known, and an array of structure determinations on alkylammonium halometalates attests to the importance of this bond in stabilizing a variety of structures.[2-5] However there occur in the literature many cases in which such bonds have been indicated or suggested when the hydrogen positions were unknown, by using the N··X distance as a guide to the existence or nonexistence of the bond. Inability to determine hydrogen positions is common in such structures and cannot always be overcome.[6] This study was undertaken to see whether such assignments from the N··Cl distance alone were or were not a good indication of hydrogen bonding. We have taken as a point of departure the view that if the sum of the two van der Waals radii for Cl and H is greater than the observed distance, then it is reasonable to call the interaction a hydrogen bond. To two significant figures, these numbers are usually quoted as 1.8 and 1.2 Å,[7-9] giving 2.9-3.0 Å as a maximum distance to be acceptable as a possible bond. Very early work[10] had suggested a range considerably longer than this for such hydrogen bonds, from 3.10 to 3.45 Å. Results presented here support a shorter upper limit than either of these suggestions, about 2.10-2.85 Å. However, this suggested range is still somewhat wider at the upper end than seems to have been common practice in interpreting such structures in recent papers.

In the last decade X-ray determinations of the structures of several hundred compounds of the general form $C_nM_zX_y$ (C = a stable organic cation with some N-H hydrogen-bonding capacity; M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd; and M_zY_y may be a simple complex ion, a layer, a chain, or an oligomeric anion) have been reported and these structures are now part of the Cambridge Structural Database (CSD). This database was taken as the starting point for this study. The selected database is also a good one for examining the possibility of C-H··X hydrogen bonds. The existence of C-H··O and C-H··N hydrogen bonds is well established in several cases,[11,12] and Taylor and

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