Sulfur Compounds, 187[◇]

Synthesis of Bis(trichloromethyl)tetra- and -heptasulfane from Titanocene Polysulfide Complexes and Structure of $(CCl_3)_2S_7$

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CCl_3SCl reacts with $(C_5H_5)_2TiS_5$ to give the heptasulfane $(CCl_3)_2S_7$ which forms colorless crystals of m.p. 38 °C. An X-ray structural analysis revealed that the $C-S_7-C$ chain is helical but the CCl_3 groups are slightly tilted. In the triclinic crystals the molecules are arranged parallel to each other. Decomposition of $(CCl_3)_2S_7$ provides other members of the homologous series with 4–12 sulfur atoms as shown by HPLC analysis. The reaction of CCl_3SCl with $(C_5H_4CH_3)_4Ti_2S_4$ yields colorless crystals of $(CCl_3)_2S_4$, demonstrating the usefulness also of dinuclear titanocene polysulfide complexes for the synthesis of organic polysulfanes. Infrared, Raman, and ^{13}C-NMR spectra of $(CCl_3)_2S_4$ and $(CCl_3)S_7$ are reported.

The synthesis of sulfur-rich organic polysulfanes R_2S_n ($n > 3$) has always been a challenge since the classical preparation methods[1] usually result in mixtures of homologous compounds which are not easy to separate on a preparative scale. We therefore have explored the use of sulfur-transfer reagents for the synthesis of cyclic and acyclic organic polysulfanes. The reaction of titanocene pentasulfide $(\eta^5\text{-}C_5H_5)_2TiS_5$ with certain organic halides RCl, sulfenyl chlorides RSCl, or bissulfenyl chlorides like $R'(SCl)_2$, $R'(SCl)(S_2Cl)$, or $R'(S_2Cl)_2$ allowed the preparation of chain-like penta-, hepta-, octa-, and nonasulfanes as well as cyclic heptasulfanes[2]; eqs. (1) to (3).

$$2\,RCl + Cp_2TiS_5 \rightarrow R_2S_5 + Cp_2TiCl_2 \qquad (1)$$

$$2\,RSCl + Cp_2TiS_5 \rightarrow R_2S_7 + Cp_2TiCl_2 \qquad (2)$$

$$R'(SCl)_2 + Cp_2TiS_5 \rightarrow R'S_7 + Cp_2TiCl_2 \qquad (3)$$

Various groups R (triphenylmethyl) and R′ (norbornyl, ethylenyl, tolyl) were used.

Results and Discussion

In this paper we report on the properties of two trichloromethyl-substituted polysulfanes obtained by reaction of CCl_3SCl with Cp_2TiS_5 and with the dinuclear complex $Cp'_4Ti_2S_4$ ($Cp' = \eta^5\text{-}C_5H_4CH_3$)[3] to give $(CCl_3)_2S_7$ (**1**) and $(CCl_3)_2S_4$ (**2**), respectively; eqs. (4) and (5).

$$2\,CCl_3SCl + Cp_2TiS_5 \rightarrow (CCl_3)_2S_7 + Cp_2TiCl_2 \qquad (4)$$

$$4\,CCl_3SCl + Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2 \rightarrow 2\,(CCl_3)_2S_4 + 2\,Cp'_2TiCl_2 \qquad (5)$$

The X-ray structural analysis of $(CCl_3)_2S_7$ provided the first structural information on a chain-like organic heptasulfane. $(CCl_3)_2S_4$ has been prepared before by condensation of CCl_3SCl with H_2S_2[4]; eq. (6).

$$2\,CCl_3SCl + H_2S_2 \rightarrow (CCl_3)_2S_4 + 2\,HCl \qquad (6)$$

The preparation according to eq. (5) demonstrates that the dinuclear titanocene polysulfide complex $Cp_2Ti_2S_4$ can also be successfully applied in the synthesis of organic polysulfanes.

The Heptasulfane $(CCl_3)_2S_7$

CCl_3SCl reacts with Cp_2TiS_5 at 20 °C in CS_2 within 12–15 h according to eq. (4). After removal of the by-product Cp_2TiCl_2 the heptasulfane was recrystallized from dichloromethane/ethanol mixture to afford colorless crystals of m.p. 38 °C in 50% yield. The rather low melting point of a compound of that molar mass (461) indicates that the heptasulfane adopts a large number of different conformations in the liquid state while in the solid state only one conformation exists (see below). Obviously, the entropy increases considerably on melting ($\Delta S_m \gg 0$) which lowers the melting temperature T_m since $T_m = \Delta H_m/\Delta S_m$ (ΔH_m enthalpy of fusion). Similar observations were made with the nonasulfane $S_9(CN)_2$[5].

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$(CCl_3)_2S_7$ melts reversibly although crystallization of the melt requires cooling to temperatures well below T_m. At 4 °C the compound is stable for weeks. However, heating to 40 °C or above for extended periods of time results in an equilibration reaction according to eq. (7).

$$2\,(CCl_3)_2S_7 \rightleftharpoons (CCl_3)_2S_{7-x} + (CCl_3)_2S_{7+x} \qquad (7)$$

This reaction was followed by reversed-phase HPLC analysis and all members of the series with 4–12 sulfur atoms were observed. Their retention times (t_{br}) increase systematically with the chain length n. The function ln k′ = a · n + b showed a correlation coefficient of 0.9999 (k′ = t_{br}-t_0/t_0; t_0 = dead time); see Table 1. Interestingly, no elemental sulfur molecules like S_6, S_7, or S_8 were observed as decomposition products of $(CCl_3)_2S_7$ despite the formation of very long sulfur chains as in $(CCl_3)_2S_{12}$. The retention indices[6] (RS) of S_6, S_7, and S_8 are, by definition, 600, 700, and 800, and the data in Table 1 show that at least the signals of S_7 and S_8, if they were present, would not overlap with those of any bistrichloromethylpolysulfane. No $(CCl_3)_2S_n$ molecules with $n > 4$ have previously been observed.

Table 1. Retention data of bis(trichloromethyl)polysulfanes R_2S_n containing 4 to 12 sulfur atoms (in contrast to the retention time t_{br} the retention index RS[6] is independent of the apparatus used)

n	t_{br} (min)	ln k'	RS
4	2.408	0.540	612
5	2.806	0.772	680
6	3.342	1.019	751
7	4.020	1.263	821
8	4.853	1.498	889
9	6.024	1.757	964
10	7.478	2.006	1036
11	9.305	2.251	1107
12	11.718	2.503	1180

The considerable stability of $(CCl_3)_2S_7$ is also observed in the EI mass spectrum which shows the molecular ion at m/z = 460 and shorter chains as obtained by extrusion of S_2, S_3, or S_4 (see Experimental).

Structural Analysis

A single crystal of $(CCl_3)_2S_7$, obtained from MTB (MeO*t*Bu), was subjected to an X-ray structural analysis at −70 °C. The molecules (Figure 1) contain a nine-atomic helical chain C–S_7–C; the four SSSS torsional angles are found in the narrow range of 80–84° while the two CSSS torsional angles amount to 91° (Table 2). All torsional angles at SS bonds have the same sign. As expected, the terminal SS bonds (202 pm) are shorter than the remaining SS bonds (204–206 pm) since electron-withdrawing substituents increase the bond order of neighboring SS bonds[7]. The SS single bond value in H_2S_2 and in S_8 is 205 pm[7a]. To a first approximation the CS_7C chain of the heptasulfane exhibits C_2 symmetry but when the chlorine atoms are taken into account the symmetry is only C_1.

Figure 1. Structure of $(CCl_3)_2S_7$ in the crystal and numbering of atoms

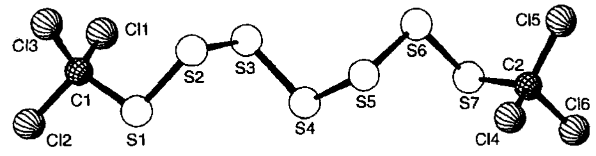


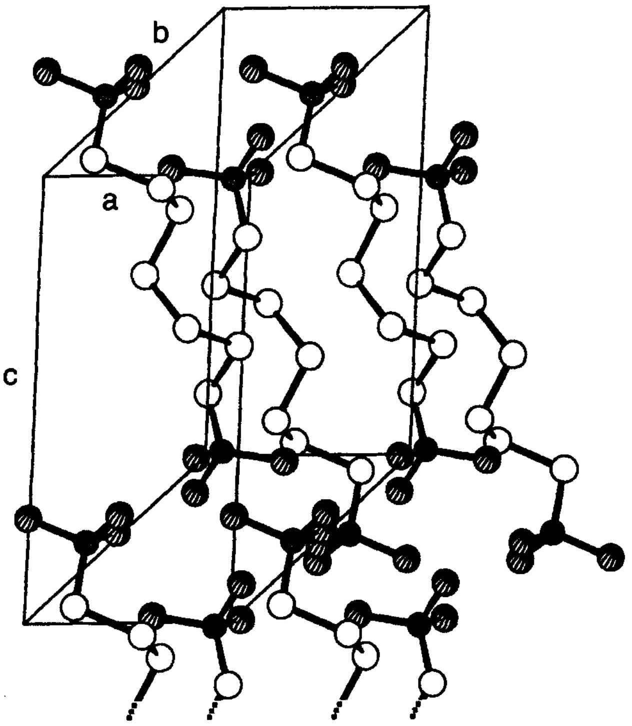
Table 2. Internuclear distances, bond angles, and selected torsional angles of $(CCl_3)_2S_7$ (standard deviations in brackets); for numbering of atoms see Figure 1

Internuclear distances (pm)			
S1-C1	181.8 (6)	S1-S2	201.8 (2)
S2-S3	205.9 (3)	S3-S4	203.7 (3)
S4-S5	203.7 (2)	S5-S6	205.3 (3)
S6-S7	202.3 (3)	S7-C2	182.5 (6)
C1-Cl1	176.9 (6)	C1-Cl2	176.9 (6)
C1-Cl3	174.4 (6)	C2-Cl4	175.9 (6)
C2-Cl5	176.2 (6)	C2-Cl6	175.8 (6)
Bond angles (°)			
C1-S1-S2	102.5 (2)	S1-S2-S3	105.9 (1)
S4-S3-S2	105.6 (1)	S3-S4-S5	107.1 (1)
S4-S5-S6	106.0 (1)	S5-S6-S7	106.3 (1)
C2-S6-S7	103.6 (2)	C1-Cl1-Cl2	109.7 (3)
C1-Cl1-Cl3	108.7 (3)	C1-Cl2-Cl3	110.4 (3)
C1-S1-Cl1	112.7 (3)	C1-S1-Cl2	102.7 (3)
C1-S1-Cl3	112.6 (3)	C2-Cl4-Cl5	109.1 (3)
C2-Cl4-Cl6	110.4 (3)	C2-Cl5-Cl6	109.5 (3)
C2-S7-Cl4	112.6 (3)	C2-S7-Cl5	112.1 (3)
C2-S7-Cl6	103.0 (3)		
Torsion angles (°)			
C1-S1-S2-S3	-90.8 (2)	S1-S2-S3-S4	-81.8 (1)
S2-S3-S4-S5	-83.8 (1)	S3-S4-S5-S6	-81.4 (1)
S4-S5-S6-S7	-79.7 (1)	S5-S6-S7-C2	-91.1 (2)
S2-S1-C1-Cl3	-60.7 (3)	S2-S1-C1-Cl2	-179.4 (2)
S2-S1-C1-Cl1	62.7 (3)	S6-S7-C2-Cl4	62.8 (3)
S6-S7-C2-Cl5	-60.6 (3)	S6-S7-C2-Cl6	-178.2 (2)

The CCl bonds are of almost identical length (174.4–176.9 pm) and the ClCCl angles are also almost identical (108.7–110.4°). However, the ClCS angles differ considerably reducing the ideal local C_{3v} symmetry of the $SCCl_3$ group to C_s. The terminal SS units are approximately in a plane with one CCl unit each: the torsional angles S2–S1–C1–Cl2 (−179.4°) and S6–S7–C2–Cl6 (−178.2°) are close to 180°. In other words, the $SSCCl_3$ units display C_s symmetry. But there is a tilt of the CCl_3 groups with respect to the CS bonds so that the nonbonded contacts between S2 and S6, respectively, and the neighboring chlorine atoms (Cl1/Cl3 and Cl4/Cl5) are increased. Consequently, the angles Cl2–C1–S1 (102.7°) and

S7–C2–Cl6 (103.0°) are much smaller than the remaining four S–C–Cl angles (average: 112.5°).

Figure 2. Unit cell of $(CCl_3)_3S_7$ showing the parallel arrangement of the molecules



In the unit cell the molecules are packed in a parallel manner (Figure 2). The shortest intermolecular SS distances are 343.2 pm (S3···S7) and 343.6 pm (S1···S5); from these values the van der Waals radius of the sulfane sulfur atoms can be derived as 172 pm. The shortest intermolecular Cl···Cl contacts (342.0 pm) are also of van der Waals type.

The Tetrasulfane $(CCl_3)_2S_4$

The tetrasulfane $(CCl_3)_2S_4$ was obtained according to reaction (5) and isolated in 20% yield as colorless crystals of m.p. 38 °C. The molecular ion in the EI-mass spectrum and a single peak in the HPLC analysis at the expected retention time proved the identity and the purity of the compound. The chemical shift in the ^{13}C NMR spectrum obviously depends only slightly on the sulfur chain length as the following values show: $(CCl_3)_2S_4$ 100.17, $(CCl_3)_2S_7$ 100.07 ppm (in C_6D_6; for comparison: CCl_3SCl 97.8 ppm). The tetrasulfane synthesis reported here is much simpler than the literature method according to eq. (6) which requires distillation of this labile compound in a special vacuum apparatus[4].

Vibrational Spectra

The vibrational spectra of polysulfanes are of particular interest since under suitable conditions they allow the estimation of the sulfur chain length from the number of SS stretching and SSS bending vibrations observed in particular in the Raman spectrum. The vibrational spectra of the bistrichloromethyldi-, tri-, and tetrasulfanes had already been studied by Fehér and Berthold[4] who investigated the molten substances using a mercury discharge lamp (blue, green, and yellow lines). Because of the light sensitivity of all polysulfanes we measured the Raman spectra of the tetra- and heptasulfanes at −80 °C using the red line of a krypton ion laser. The results are given in Table 3 together with the IR spectra of both compounds.

The assignments given in Table 3 are based on the comparison with the IR and Raman spectra of the starting compound, CCl_3SCl[8]. As was to be expected the spectra are dominated by the signals arising from the vibrations of the $SCCl_3$ unit. This group may be compared to the CCl_4 molecule. However, since CCl_3SCl will be of C_s symmetry as is the CCl_3SS group in **1**, all vibrations degenerate in CCl_4 are split into their components. Our results support the recent assignment of the CCl_3SCl spectra which have been disputed many times. The three SS stretching modes of **2** give rise to two Raman lines while the six SS modes of **1** result in only three Raman signals in the region 420–510 cm^{-1}.

Incidental degeneracies and the presence of the very strong symmetrical $SCCl_3$ stretching vibration (**1**: 447 cm^{-1}; **2**: 436 cm^{-1}) in this region explain these discrepancies. Comparison of our Raman spectrum of **2** with the literature data[4] obtained with the mercury lamp shows considerable differences: the reported lines[4] at 857, 183, and 112 cm^{-1} cannot be seen in our spectra and for all other lines considerable wavenumber differences (up to 7 cm^{-1}) are observed. No IR spectra of **2** have been reported before.

In summary, it can be stated that titanocene polysulfide chelate complexes, mononuclear and dinuclear, provide access to organic polysulfanes which hitherto could be prepared only with difficulties or not at all. The high purity of the heptasulfane **1** obtained in this work was certainly the prerequisite for its crystallization. The structural analysis revealed a perfectly helical molecule – the largest sulfur helix observed so far in a non-polymeric compound. The simplicity of the Raman spectrum of **1** in the SS stretching region – only three lines assigned to $\tilde{\nu}(SS)$ are observed – reflects the symmetrical arrangement of the SS bonds in the helix.

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Experimental[9]

Methods: HPLC analyses by liquid chromatograph consisting of Perkin Elmer Serie 2 pump, Rheodyne syringe loading injector (10 μl loop), Perkin Elmer variable wavelength detector LC75 (operated at 254 nm), Hewlett-Packard 3390A integrator, Waters 990 diode array detector for recording of UV-VIS spectra. Column: Waters Radial Pack (l = 10 cm, *i.d.* = 8 mm, particle size 10 or 5 μm). Eluent: methanol (distilled from $MgSO_4$ and degassed). Column, eluent, and capillary (1 m) between pump and injector were thermostated to 21.0(2)°C. – MS: Varian MAT 311A (EI). – Raman: Jobin Yvon U1000 double monochromator, Hamatsu GaAs photomultiplier, MAC 80A computer with spectra control software by Spectradata, Spectra Physics krypton laser (674.1 nm), sample temperature: −80 °C. – IR: Nicolet Magna 750 FT spectrometer. – ^{13}C-NMR: Bruker ARX200.

Table 3. Infrared and Raman spectra of $(CCl_3)_2S_4$, $(CCl_3)_2S_7$ and, for comparison, of CCl_3SCl in the region 280–820 cm^{-1}; for data below 280 cm^{-1} see Experimental

CCl_3SCl[8]		$(CCl_3)_2S_4$		$(CCl_3)_2S_7$		Assignment
Ra	IR	Ra	IR	Ra	IR	
807 w	807 vs					$\nu(SCCl_3)$ (ν_3 of CCl_4)
		780 w	787 s	779 w	786 s	
755 m	760 vs		765 s	754 vw	764 s	
743 m	740 vs	739 w	740 vs	740 w	742 vs	
538 s	536 w					$\nu(SCl)$
		500 m	511 m	505 m	503 w	$\nu(SS)$
		446 m		469 s		$\nu(SS)$
453 vs	452 s	436 vs	441 m	447 vs	444 m	$\nu_s(SCCl_3)$
				426 w		$\nu(SS)$
337 s		344 w		338 w		$\delta(SCCl_3)$ (ν_4 of CCl_4)
299 m		305 m		311 m		
287 m		286 w		291 w		

Bis(trichloromethyl)tetrasulfane (**2**): To 2.0 g of $Cp'_4Ti_2S_4$ (3.7 mmol) in 180 ml of CS_2 was added 2.75 g of CCl_3SCl (14.8 mmol; Merck, 96%) with stirring. After 12–15 h the Cp'_2TiCl_2 was removed by filtration through a 8 cm long column filled with silica gel 40 (Merck). After washing of the SiO_2 with CS_2 the solvent was evaporated in vacuo, the residue dissolved in little CH_2Cl_2 and the solution cooled to −50°C whereupon **2** crystallized out. Recrystallization from CH_2Cl_2 by covering with a layer of ethanol. Yield of **2** 2.70 g (20%); m.p. 38°C. – Raman (solid; see also Table 3): $\tilde{\nu}$ = 246 (w), 217 (m), 165 (m), 106 (s), 78 (m), 48 (m), 38 (m) cm^{-1}. – IR (KBr): s. Table 3. – MS (60 eV; T_p = 25°C); m/z (%): 364 (7) $[M^+]$, 329 (5) $[M^+ - Cl]$, 265 (14) $[M^+ - S_2Cl]$, 215 (10) $[M^+ - SCCl_3]$, 146 (9), 131 (15), 117 (100) $[CCl_3^+]$. – UV (methanol): λ_{max} = 221 (100), 383 (25) nm. – $C_2Cl_6S_4$ (365.0): calcd. C 6.58; found C 6.99.

Bis(trichloromethyl)heptasulfane (**1**): To 3.80 g of Cp_2TiS_5 (11.2 mmol) in 180 ml of CS_2 was added 4.18 g of CCl_3SCl (22.5 mmol) with stirring. After 12–15 h the precipitated Cp_2TiCl_2 was filtered off and 10 g of silica gel 40 (Merck) was added to adsorb dissolved Cp_2TiCl_2. After filtration and washing of the gel with CS_2 the solvent was evaporated in vacuo, the residue dissolved in 10 ml of CH_2Cl_2 and the solution cooled to −50°C. The crystals obtained were recrystallized from CH_2Cl_2 by covering with a layer of ethanol. Yield of **1** 5.18 g (56%); m.p. 38°C. – Raman (solid; see also Table 3): $\tilde{\nu}$ = 270 (w), 266 (m), 247 (m), 240 (w), 219 (w), 212 (w), 189 (m), 147 (m), 105 (w), 101 (w), 95 (w), 76 (vs), 66 (vs), 58 (s), 45 (vs), 36 (vs) cm^{-1}. – IR (KBr): see Table 3. – MS (EI, 60 eV, T_p = 100°C); m/z (%): 460 (5) $[M^+]$, 428 (1) $[M^+ - S]$, 396 (3) $[M^+ - S_2]$, 311 (6) $[M^+ - SCCl_3]$, 297 (4) $[M^+ - S_4Cl]$, 279 (53) $[M^+ - CCl_3S_2]$, 247 (3), 227 (3) $[S_6Cl]$, 117 (100) $[CCl_3^+]$. – UV (methanol): λ_{max} = 228, 280 (sh) nm. – $C_2Cl_6S_7$ (461.2): calcd. C 5.21, S 48.67; found C 5.14, S 48.68.

Crystal Structure Analysis of **1**: Single crystals with dimensions 0.50 × 0.40 × 0.25 mm were obtained from methyl *tert*-butyl ether and measured at −70°C to prevent decomposition of the sample: triclinic, space group $P\bar{1}$; $Z = 2$; a = 570.0(3), b = 1180.8(5), c = 1255.5(7) pm, α = 104.23(4), β = 93.06(4), γ = 67.26(4)°; V = 7.546(7) · 10^8 pm^3; ρ_{calcd} = 2.030 g cm^{-3}; μ (Mo-K_α) = 2.071 mm^{-1}, M = 461.14. The measurement of the X-ray reflection intensities was carried out in the 2Θ-ω scan mode keeping the sample crystal at a constant temperature of −70°C with an LN_2 gas stream apparatus[10]. The reflection intensities were Lorentz polarization-corrected. The structure was solved by direct methods[11]. The coefficients for anomalous atomic scattering[12] were included in the structure factor calculation for the least-squares refinement. For visualization SCHAKAL[13] plots were drawn[14].

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