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NMR Spectroscopic Evidence for the Existence of Tellurium-Containing Chalcogen Rings and Polymers in Sulfur–Tellurium and Sulfur–Selenium–Tellurium Melts

Tristram Chivers,[*,1a] **Risto S. Laitinen,**[*,1b] **Kenneth J. Schmidt,**[1a] **and Jari Taavitsainen**[1b]

Departments of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary,
Alberta, Canada T2N 1N4, and University of Oulu, Linnanmaa, SF-90570 Oulu, Finland

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The composition of sulfur-rich molten mixtures of sulfur, selenium, and tellurium has been studied by using ^{125}Te and ^{77}Se NMR spectroscopy at 145 °C. The spectral assignments and the identification of the molecular species were made on the basis of combined information from the natural abundance and from the ^{77}Se- and ^{125}Te-enriched samples (enrichment in both cases 92%), taking the known trends in the ^{77}Se and ^{125}Te chemical shifts into account. The melts were found to contain cyclic chalcogen molecules in equilibrium with polymeric chains. The main tellurium-containing chalcogen ring in the binary sulfur–tellurium melts was TeS_7 [δ(Te) = 1316 ppm]. The presence of small amounts of 1,2-Te_2S_6 [δ(Te) = 1126 ppm] and its other isomers could also be inferred. The ternary sulfur–selenium–tellurium mixtures contained binary heterocycles SeS_7, all isomers of Se_2S_6, TeS_7, and 1,2-Te_2S_6 as well as its other isomers. The presence of 1,2-$TeSeS_6$ [δ(Te) = 1148 ppm; δ(Se) = 493 ppm, $^1J_{TeSe}$ = 50 Hz] and 1,3-$TeSeS_6$ [δ(Te) = 1364 ppm, $^2J_{TeSe}$ = 220 Hz] was indicated by the ^{77}Se and ^{125}Te NMR spectroscopic data of the enriched sample. The presence of 1,4- and 1,5-isomers of $TeSeS_6$ could also be inferred from the ^{125}Te spectrum of the enriched samples. The NMR signals of the sulfur–tellurium and sulfur–selenium–tellurium polymeric material can be interpreted in terms of the statistical distribution of –S–Te–S–, –Te–Te–S–, and –Te–Te–Te– fragments. The ternary melts also show the resonances due to –Se–Te–S– in the ^{125}Te spectrum and those due to –Te–Se–S– in the ^{77}Se spectrum. All samples studied in this work also contain both homocyclic and polymeric sulfur species.

Introduction

Whereas sulfur and selenium are known to form a complex binary system with a wide variety of heterocyclic selenium sulfides with ring sizes of 6–8 and 12 (for a recent review, see ref 2), the existence of tellurium sulfide ring molecules is not so well established. Cooper and Culka[3] deduced the existence of the TeS_7 fragment in the mass spectrum of a sample obtained from the quenched molten mixture of the elements. Pupp and Weiss[4] reported a single-crystal X-ray diffraction study of the phase prepared from H_2S and $TeCl_4$. They concluded that the product is a mixture of S_8, TeS_7, and Te_2S_6. An eight-membered crown-shaped tellurium-containing ring is also found in TeS_7X_2 (X = Br, Cl) with the two halogen atoms bound to tellurium.[5] Nagata et al.[6] have reported crystal structure determinations of the seven- and eight-membered selenium-rich tellurium selenide heterocycles. Their conformations are expectedly similar to the analogous sulfur, selenium, and selenium sulfide ring molecules.[2,7]

We have recently reported a ^{77}Se NMR study of the molten mixtures of sulfur and selenium at varying molar ratios of the elements.[8] The equilibrium melt was found to contain both heterocyclic and polymeric molecular forms. The distribution of the heterocyclic Se_nS_{8-n} molecules was very similar to that obtained previously in the CS_2 solutions of the quenched sulfur–selenium melts.[9]

Tellurium has two NMR-active, spin $^1/_2$ nuclei: ^{125}Te and ^{123}Te. The former isotope has a natural abundance of 6.99% and a sensitivity of 12.2 relative to ^{13}C. ^{125}Te NMR spectroscopy should therefore be an attractive tool to identify individual molecular species in mixtures of tellurium-containing compounds. Several organic and transition metal tellurides, polytelluride anions, and tellurium-containing cations (for two recent reviews, see ref 10) have been characterized by ^{125}Te NMR spectroscopy and provide background information for this study.

We describe here a ^{125}Te and ^{77}Se NMR spectroscopic study of sulfur–tellurium and sulfur–selenium–tellurium melts at 145 °C, which, on the basis of information from sulfur–selenium systems,[8,9] provides direct evidence for the formation of binary sulfur–tellurium and ternary sulfur–selenium–tellurium ring molecules in equilibrium with polymeric chalcogen chains.

The phase diagram of the sulfur–tellurium system[11] indicates that there is a eutectic point at 105–110 °C with the composition of ca. 2 mol % of tellurium. With higher tellurium content the liquidus, however, rises very rapidly in temperature. At 10 mol % of tellurium it is already above 300 °C, and the content of the molten material in this mixture is too low to obtain a reasonable NMR spectrum even at 145 °C. Since the phase diagram also indicates that the composition of the liquid does not vary significantly below 10 mol % of tellurium, this study was limited to tellurium contents below 7.5 mol %.

Experimental Section

Materials. Two analogous series of both binary sulfur–tellurium and ternary sulfur–selenium–tellurium samples were prepared; one series contained selenium and tellurium enriched in the ^{77}Se- and ^{125}Te-isotope

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(1) (a) The University of Calgary. (b) University of Oulu.

(2) Laitinen, R. S. *Acta Chem. Scand., Ser. A* **1987**, *41*, 361.

(3) Cooper, R.; Culka, J. V. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1877.

(4) Pupp, M.; Weiss, J. *Z. Anorg. Allg. Chem.* **1978**, *440*, 31.

(5) (a) Weiss, J.; Pupp, M. *Angew. Chem.* **1970**, *82*, 447. (b) Weiss, J.; Pupp, M. *Acta Crystallogr., Sect. B* **1972**, *28*, 3653.

(6) (a) Nagata, K.; Hayashi, H.; Miyamoto, Y. *Fukuoka Univ. Sci. Rep.* **1988**, *18*, 23. (b) Nagata, K.; Hayashi, H.; Miyamoto, Y. *Fukuoka Univ. Sci. Rep.* **1988**, *18*, 35.

(7) (a) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F.; Reinhardt, R. *Z. Naturforsch.* **1980**, *35b*, 1378. (b) Steudel, R.; Papavassiliou, M.; Strauss, E.-M.; Laitinen, R. *Angew. Chem.* **1986**, *98*, 81; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 99.

(8) Chivers, T.; Laitinen, R. S.; Schmidt, K. J. *Can. J. Chem.* **1992**, *70*, 719.

(9) (a) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381. (b) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598.

(10) (a) McFarlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 15, pp 417–435. (b) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.

(11) (a) Losana, L. *Gazz. Chim. Ital.* **1923**, *53*, 396. (b) Hansen, M.; Anderko, K. *Constitution of Binary Alloys*; McGraw-Hill: New York, 1958; p 1165.

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(enrichment 92%, Techsnabexport), and the other contained natural abundance selenium and tellurium (E. Merck GmbH). Natural abundance sulfur (E. Merck GmbH) was used throughout. The mass of each sample was adjusted to 3.0 g.

Binary Sulfur–Tellurium Mixtures. The ^{125}Te-enriched sulfur–tellurium mixture contained 1.5 mol % of tellurium. The three natural abundance samples contained 2.5, 5.0, and 7.5 mol % of tellurium.

Ternary Sulfur–Selenium–Tellurium Mixtures. The ^{77}Se- and ^{125}Te-enriched sulfur–selenium–tellurium mixture contained 1.5 mol % of both selenium and tellurium. The four ternary natural abundance mixtures all had a constant tellurium content of 2.5 mol %, but the selenium content was adjusted to 2.5, 5.0, 7.5, and 10.0 mol %.

Sample Preparation. Each sample was sealed in an evacuated ampule with an external diameter of 8 mm and heated at ca. 450 °C for 4 h. The ampules were allowed to cool to 145 °C and were subsequently inserted in 10-mm NMR tubes for the NMR measurements. They were immediately lowered into the NMR probe, which was kept at 145 °C throughout the accumulation.[12]

NMR Spectroscopy. The NMR spectra of the enriched samples were recorded on a Bruker AM-400 spectrometer operating at 126.3 MHz for ^{125}Te and at 76.3 MHz for ^{77}Se.[13] The ^{125}Te data were accumulated in 64 K of memory, and that for ^{77}Se, in 32 K. The spectral widths were 100.0 kHz for the ^{125}Te spectra and 83.3 kHz for the ^{77}Se spectra yielding resolutions of 3.1 and 3.8 Hz/data point, respectively. The ^{125}Te and ^{77}Se pulse widths were 10.0 and 6.0 μs, respectively, corresponding to a nuclide tip angle of ca. 24° in both cases. The relaxation delay for tellurium was 0.1 s, and that for selenium, 2.8 s. The ^{125}Te accumulations contained ca. 300 000 transients, and the ^{77}Se accumulation, ca. 25 000 transients. The saturated solutions of H_6TeO_6(aq) and SeO_2(aq) at room temperature were used as external standards. The spectra of the enriched samples were recorded unlocked. No significant field drift was observed during the accumulations. The chemical shifts (ppm) are reported relative to neat Me_2Te and Me_2Se at room temperature [$\delta(Me_2Te) = \delta(H_6TeO_6) + 712$; $\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. The assignment of the NMR signals to discrete molecular species is summarized in Table I.

Results and Discussion

Binary Sulfur–Tellurium Melts. In the tellurium range 2.5–7.5 mol % the equilibrium sulfur–tellurium melt showed the major resonances at 1827, 1778, 1589, and 1316 ppm and some very weak signals at 1457, 1438, 1428, 1321, 1126, and 848 ppm, as exemplified by the NMR spectrum of the binary sulfur–tellurium melt containing 1.5 mol % of tellurium enriched in the ^{125}Te isotope (see Figure 1). All major resonances appear as singlets. The absence of ^{125}Te–^{125}Te coupling implies the chemical and magnetic equivalence of all tellurium atoms in each molecular species.

It has previously been shown that in analogous compounds ^{125}Te chemical shifts bear an almost linear relationship with the ^{77}Se chemical shifts [$\delta(\mathrm{Te}) \sim 1.8\delta(\mathrm{Se})$].[14] Thus, the NMR spectroscopic data obtained from the sulfur–selenium melts[8] can be utilized in the identification of the tellurium sulfides. It can initially be inferred that the resonances below 1500 ppm are caused by heterocyclic tellurium sulfides and those above 1500 ppm by polymeric species.

The major signal at 1316 ppm is assigned to TeS_7. In the sulfur–selenium melt SeS_7 shows a ^{77}Se chemical shift at 705 ppm.[8] These two values are in accord with the reported relationship of the tellurium and selenium chemical shifts.[14] Furthermore, it is reasonable that TeS_7, which is the most sulfur-rich heterocyclic tellurium sulfide, is the main tellurium-containing component in these sulfur-rich melts.

Table I. Assignment of the ^{125}Te and ^{77}Se NMR Spectra of the Sulfur–Tellurium and Sulfur–Selenium–Tellurium Melts

chem shift (ppm)			
^{125}Te[a]	^{77}Se[b]	coupling const (Hz)	assgnt
		(a) Heterocyclic Molecules	
1368		$^3J_{TeSe} = 27$	1,4-$TeSeS_6$[c]
1364		$^2J_{TeSe} = 220$	1,3-$TeSeS_6$
1316			TeS_7
1282		broad	1,5-$TeSeS_6$[c]
1148	493	$^1J_{TeSe} = 50$	1,2-$TeSeS_6$
1126			1,2-Te_2S_6
848			Te_8[d]
	1150, 1080[e]		1,2,3,4,5-Se_5S_2[f]
	734		1,3-Se_2S_6[g]
	722		1,5-Se_2S_6[g]
	705		SeS_7[g]
	693		1,4-Se_2S_6[g]
	644		1,2-Se_2S_6[g]
		(b) Polymeric Material	
1827			–S–Te–S–
1778			–Te–Te–S–
1650			–Se–Te–S–
1590			–Te–Te–Te–
	1020		–S–Se–S–[g]
	930		–Se–Se–S–[g]
	780		–Te–Se–S–[g]

[a] See Figures 1 and 2. [b] See Figures 3. [c] The assignment of the signals at 1368 and 1282 ppm can equally well be interchanged. [d] The assignment of this signal to Te_8 does not quite fit in the expected linear relationship[14] between ^{125}Te and ^{77}Se chemical shifts. (The ^{77}Se chemical shift of Se_8 in the sulfur–selenium melt is 621 ppm.[8]) [e] These two resonances have an intensity ratio of 2:1 in the natural abundance spectrum. The third resonance expected for 1,2,3,4,5-Se_5S_2 is obscured by the polymer signal at 1020 ppm. [f] Reference 20. [g] Reference 8.

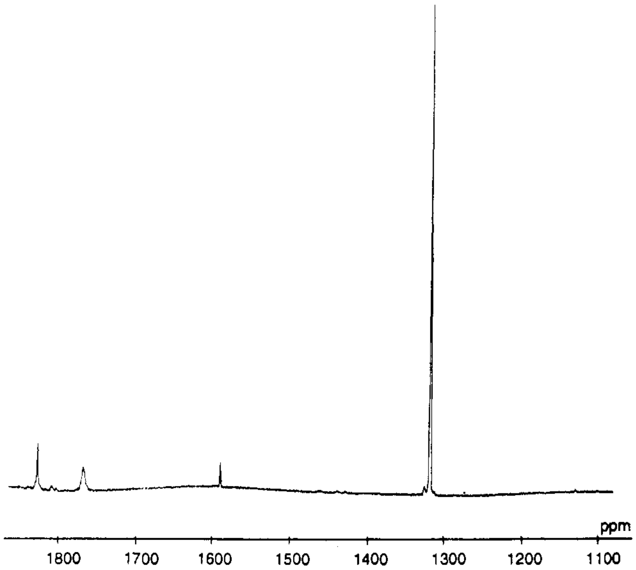

Figure 1. ^{125}Te NMR spectrum of the sulfur–tellurium melt containing 1.5 mol % of tellurium enriched in the ^{125}Te isotope (enrichment 92%). The very weak resonance at 848 ppm is not shown.

The very weak resonance at 1126 ppm is assigned to 1,2-Te_2S_6, since it is consistent with the ^{77}Se chemical shift of 1,2-Se_2S_6 in the sulfur–selenium melt (644 ppm).[8] It is not so straightforward, however, to assign the other weak resonances found in the region for cyclic species. The signals at 1457, 1438, 1428, and 1321 ppm suggest tellurium atoms surrounded by two sulfur atoms thus implying 1,3-, 1,4-, and 1,5-isomers of Te_2S_6 or heterocyclic species of other ring sizes containing isolated tellurium atoms (for instance, TeS_5 could be expected to show a chemical shift at ca. 1430 ppm, since the ^{77}Se resonance of SeS_5 appears at 765

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(12) One sample of a natural abundance ternary melt containing 2.5 mol % of both selenium and tellurium was quenched at liquid nitrogen temperature and extracted with carbon disulfide. The ^{125}Te spectrum of the resulting solution was recorded at 25 °C.

(13) All natural abundance spectra were recorded on a Jeol JNM-GX400 spectrometer at 165 °C. The data were accumulated in 32 K of memory. The spectral widths were 151.5 and 96.2 kHz yielding the resolutions of 4.6 and 2.9 Hz/data point for ^{125}Te and ^{77}Se, respectively. The Jeol pulse widths for tellurium and selenium were 8.0 and 6.0 μs, both corresponding to the nuclide tip angle of ca. 24°. The tellurium relaxation delay was in the range 0.01–0.04 s, and that for selenium was 2.8 s. The ^{125}Te accumulations contained ca. 500 000 transients, and the ^{77}Se accumulations, ca. 25 000 transients. d_5-Nitrobenzene (Aldrich) was used as an external ^{2}H lock for all natural abundance spectra.

(14) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1973**, 2416.

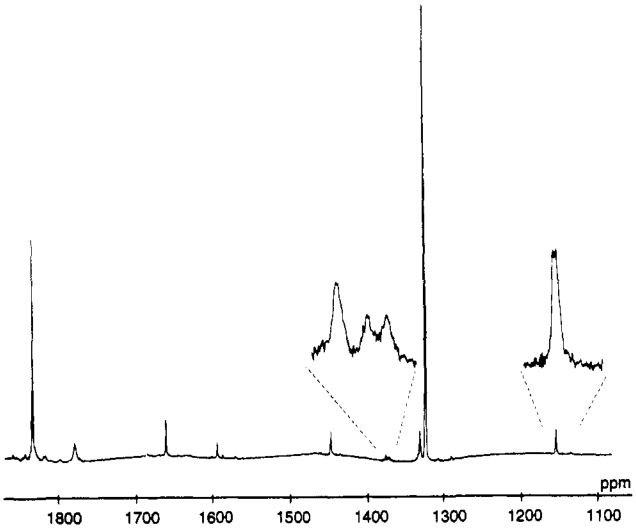

Figure 2. ^{125}Te NMR spectrum of the ternary sulfur–selenium–tellurium melt containing 1.5 mol % of both ^{77}Se-enriched selenium and ^{125}Te-enriched tellurium. The very weak resonance at 848 ppm is not shown.

ppm[15]). The ^{125}Te resonance at 848 ppm may possibly be due to Te_8, even though it does not quite fit in the above-mentioned linear relationship between the ^{125}Te and ^{77}Se chemical shifts.

Like molten mixtures of sulfur and selenium,[8] the equilibrium sulfur–tellurium melt is also expected to contain polymeric material. The three signals at ca. 1830, 1780, and 1590 ppm are assigned to tellurium atoms in the polymer. On the basis of the above-mentioned relationship between the ^{125}Te and ^{77}Se chemical shifts, the resonance at ca. 1830 ppm is probably due to a structural unit –S–Te–S– (the ^{77}Se chemical shifts of the –S–Se–S– unit in the polymeric material are 1050–980 ppm), that at 1780 ppm is due to the unit –Te–Te–S– (the chemical shifts of the unit –Se–Se–S– are 970–920 ppm), and that at 1590 ppm is due to –Te–Te–Te– (the chemical shifts of the unit –Se–Se–Se– are 890–850 ppm). The small satellites around the main resonances are consistent with the random distribution of these structural units (for a qualitative discussion on the distribution of the satellite intensities in sulfur–selenium polymers, see ref 8).

The main features of the ^{125}Te spectra of the sulfur–tellurium melt remain virtually unchanged in the whole concentration range of tellurium, which was studied in this work (1.5–7.5 mol %). This is consistent with the observations made from the phase diagram of the sulfur–tellurium system.[11]

Ternary Sulfur–Selenium–Tellurium Melts. The ^{125}Te spectrum of a sample containing 1.5 mol % of both enriched selenium and tellurium illustrates typical features in the spectra of the ternary sulfur–selenium–tellurium melts (see Figure 2).[16] New resonances can be seen to appear as compared to the spectrum of the binary melts (see Figure 1). The assignment of the main signals is discussed below.

Because of the assignment of the signals at 1316 and 1126 ppm to TeS_7 and 1,2-Te_2S_6, respectively, the resonance at 1148 ppm can also be attributed to an eight-membered tellurium-containing ring molecule. In the ^{125}Te NMR spectrum of the ternary melt containing enriched ^{77}Se and ^{125}Te this signal appears as a doublet as shown in Figure 2. The resonance at 1148 ppm is therefore assigned to 1,2-$TeSeS_6$. The $^{1}J_{TeSe}$ coupling constant is 50 Hz and is of the same order of magnitude as the $^{1}J_{SeSe}$ coupling constants (23–56 Hz) reported previously for the binary selenium sulfides.[9] It should be noted that in general the ^{1}J coupling constants involving ^{125}Te seem to be larger and of the opposite sign than those involving ^{77}Se in corresponding situations. McFarlane and McFarlane[10a] have attributed this as a consequence of tellurium having a higher electron density at the nucleus than selenium and of the magnetogyric ratio of ^{125}Te being -1.65 times that of ^{77}Se. The range of coupling constants, however, is rather large for both nuclei in question, and thus the $^{1}J_{TeSe}$-coupling of 50 Hz can be thought to be quite reasonable for 1,2-$TeSeS_6$.

The assignment of the resonance at 1148 ppm to 1,2-$TeSeS_6$ finds support from the observation that the relative intensity of this resonance grows with increasing selenium content. Also, there is no evidence of this signal in any recorded spectra of the binary melts. It is well established that the ^{77}Se chemical shift of the selenium atoms with two sulfur neighbors lies at the highest frequency. The shielding increases as the electronegativity of the neighboring atoms decreases. Thus selenium with one selenium and one sulfur neighbor resonates at the lower frequency and that with two selenium neighbors at the lowest frequency.[9] A similar dependence of the chemical shifts on the electronegativity of neighboring atoms can also be expected to apply for the resonances in the ^{125}Te spectra. Thus the resonance at 1148 ppm appearing upfield from that assigned to TeS_7 (1316 ppm) is quite reasonable for 1,2-$TeSeS_6$.

The weak ^{125}Te resonances at 1368, 1364, and 1282 ppm may be attributed to the 1,3-, 1,4-, or 1,5-isomers of $TeSeS_6$. The two first signals appear as doublets (see Figure 2), but the last resonance is too weak for the observation of coupling. It has previously been found that the $^{2}J_{SeSe}$ (96–114 Hz) coupling constants are significantly larger than $^{1}J_{SeSe}$.[9] Eggert et al.[17] have suggested that the magnitude of the ^{77}Se–^{77}Se coupling constants depends on the extent of interaction between the p lone-pairs of the selenium atoms in question. This scheme explains why $^{1}J_{SeSe} < ^{2}J_{SeSe}$ and why longer range coupling can be expected to be relatively small.[18]

The resonance at 1368 ppm shows a coupling constant of 27 Hz, and that at 1364 ppm shows a coupling constant of 220 Hz.[19] It can be inferred from the trends deduced for the ^{77}Se–^{77}Se coupling in the heterocyclic selenium sulfides that the latter coupling implies $^{2}J_{TeSe}$ and therefore the resonance at 1364 ppm is assigned 1,3-$TeSeS_6$. The larger value of $^{2}J_{TeSe}$ relative to $^{2}J_{SeSe}$ can be explained by the concept of mutual p lone-pair orbital interaction as the means to transfer coupling information.[17] The i to $i + 2$ distance in the –Te–S–Se– unit is not significantly longer than that in the –Se–S–Se– unit. The 5p lone-pair of tellurium, however, is radially more diffuse than the 4p lone-pair of selenium. Therefore the 5p(Te)···4p(Se) interaction can be expected to be greater than the 4p(Se)···4p(Se) interaction resulting in a larger coupling constant.

It is not possible to make an unambiguous assignment for the resonance at 1368 ppm from the coupling constant of 27 Hz, since according to the NMR spectroscopic data from the selenium sulfides[9] both $^{3}J_{TeSe}$ and $^{4}J_{TeSe}$ can be expected to be of this order of magnitude. The signal at 1368 ppm can be assigned to either the 1,4- or the 1,5-isomer of $TeSeS_6$. The very weak signal at 1282 ppm is probably the other isomer. Even though no multiplets are resolved for this signal, it seems to be rather broad implying small coupling.

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(15) Steudel, R.; Papavassiliou, M.; Jensen, D.; Seppelt, D. *Z. Naturforsch.* **1988**, *43B*, 245.

(16) The room-temperature ^{125}Te NMR spectrum of the CS_2 solution from the quenched ternary sulfur–selenium–tellurium melt (2.5 mol % of both natural abundance selenium and tellurium)[12] shows two signals: A strong resonance at 1301 ppm and a weaker one at 1128 ppm. Their intensity ratio corresponds approximately to that observed for the signals at 1316 and 1148 ppm of the ternary melt shown in Figure 2. Since no resonances are observed at 1850–1500 ppm in this CS_2 solution, it is reasonable to assign the melt resonances in this region to polymeric material (see Figures 1 and 2). It is unlikely that a tellurium-containing polymer is soluble in CS_2.

(17) Eggert, H.; Nielsen, O.; Henriksen, L. *J. Am. Chem. Soc.* **1986**, *108*, 1725.

(18) Since the dihedral angles in the eight-membered crown-shaped chalcogen rings are close to 90°, the p lone-pair overlap between the adjacent selenium atoms is minimized. The corresponding lone-pair orbitals in the selenium atoms i and $i + 2$ are directed to the same region of space and therefore have a possibility to overlap and transfer coupling information.

(19) Upon comparison of the natural abundance ^{125}Te spectrum to that recorded from the enriched sample, it can be seen that the four multiplet components in the enriched spectrum indeed arise from two signals in the natural abundance spectrum.

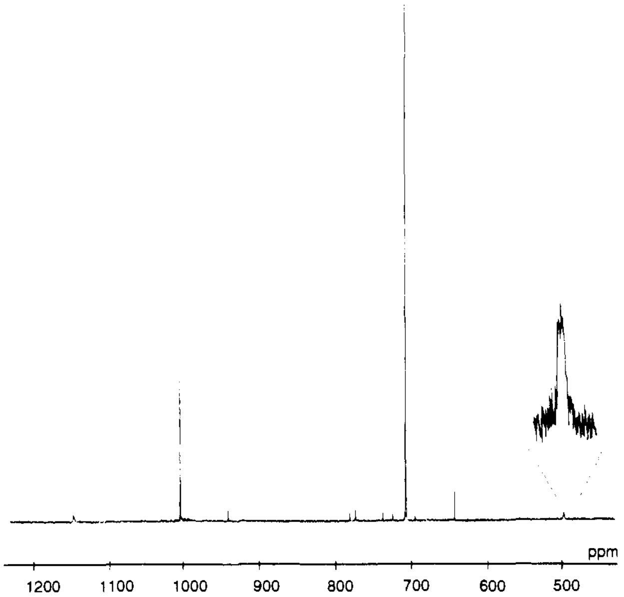

Figure 3. ^{77}Se NMR spectrum of the ternary sulfur–selenium–tellurium melt containing 1.5 mol % of both ^{77}Se-enriched selenium and ^{125}Te-enriched tellurium.

The spectra of the ternary sulfur–selenium–tellurium melts (Figure 2) also show additional features in the region of polymeric material (1850–1500 ppm) compared to the spectra of the binary sulfur–tellurium melts (see Figure 1). In addition to the signals observed in the binary melts, a new resonance at 1650 ppm appears upon introduction of selenium. It is assigned to the structural unit –Se–Te–S–. This signal gains in intensity with increasing selenium content of the melt. Small satellites can also be observed to appear around the polymer resonances. These observations can be interpreted analogously to the polymer signals in the sulfur–selenium melts[8] as a consequence of the random distribution of the above-mentioned structural units.

The resonances at 1830 and 1457 ppm are seen to gain in intensity upon introduction of selenium in the chalcogen mixture (see Figure 2). As these signals are observed already in the binary melt, they cannot be assigned to species containing selenium. The assignment of these resonances has been discussed above.

It is interesting to compare the differences in the chemical shifts between the different chemical environments of the observed tellurium atoms. In TeS_7 the tellurium atom has two sulfur neighbors and in 1,2-$TeSeS_6$ one selenium and one sulfur neighbor. The difference in the ^{125}Te chemical shifts between these two molecular species is 168 ppm with the latter upfield from the former. In the region of the polymeric material the difference in the ^{125}Te chemical shifts between the structural unit –S–Te–S– (two sulfur neighbors) and the structural unit –Se–Te–S– (one selenium and one sulfur neighbor) is virtually identical (170 ppm). This is of course to be expected because of the similar differences in chemical environments between TeS_7 and 1,2-$TeSeS_6$ on one hand and between –S–Te–S– and –Se–Te–S– on the other and serves as an indirect verification of the above assignments.

Further support for the assignments of the ^{125}Te NMR spectra comes from the ^{77}Se NMR spectra of the ternary mixtures (see Figure 3). The main features of all selenium spectra are much like those observed for binary sulfur–selenium melts[8] implying that the major selenium-containing species in the ternary sulfur–selenium–tellurium mixtures are binary selenium sulfides (for the interpretation of the ^{77}Se spectrum, see Table I). SeS_7 is expectedly the most abundant species for this sulfur-rich system. There are, however, a few resonances in these ternary melts that are not observed in the spectra of the binary sulfur–selenium mixtures.

There is a weak signal at 493 ppm relative to Me_2Se the intensity of which grows with increasing selenium content of the melt. In the ^{77}Se spectrum of the sample containing 1.5 mol % of both ^{77}Se and ^{125}Te this resonance appears as a doublet ($^1J_{TeSe} = 50$ Hz; see Figure 3). This resonance can therefore be assigned to 1,2-$TeSeS_6$. The low intensity of this ^{77}Se signal, while the ^{125}Te resonance of the same molecular species in the same sample has a relatively high intensity, can be understood in terms of the low concentration of 1,2-$TeSeS_6$ *relative to binary selenium sulfides*, whereas the concentration of this heterocycle *relative to other tellurium-containing species* is higher. Because of this intensity difference in the ^{125}Te and ^{77}Se spectra, it is clear why no ^{77}Se resonances are observed for 1,3-, 1,4-, and 1,5-$TeSeS_6$, which show only a very weak signals in the ^{125}Te spectra.

Another set of resonances found in the selenium spectra of the ternary melts but not in those of the binary sulfur–selenium melts lies at ca. 780 ppm. Applying yet again the trends in the chemical shifts,[9] these signals are assigned to the polymeric fragment –Te–Se–S–. The difference in ^{77}Se chemical shifts between SeS_7 (two sulfur neighbors) and 1,2-$TeSeS_6$ (one tellurium and one sulfur neighbor) of 212 ppm is virtually identical with the chemical shift difference of ca. 220 ppm between the polymeric fraction –S–Se–S– (ca. 1000 ppm) and –Te–Se–S– (ca. 780 ppm) indicating the internal consistency of the assignments.

One interesting feature in the natural abundance ^{77}Se spectra of the ternary sulfur–selenium–tellurium melts is the appearance of two weak resonances at ca. 1150 and 1080 ppm with a rough intensity ratio of 2:1. Their positions and intensity ratios correspond closely to those observed for the seven-membered selenium sulfide ring molecule 1,2,3,4,5-Se_5S_2.[20] In the spectrum of the enriched sample these signals appear very broad indicating coupling. Because the intensities of both resonances are very small, the expected second-order coupling patterns[20b] are not resolved. The third resonance expected for this molecular species should lie at ca. 990 ppm, but it is obscured by the strong polymer signals attributed to –S–Se–S– fragments.

Conclusions

This ^{125}Te and ^{77}Se NMR spectroscopic study of binary sulfur–tellurium and ternary sulfur–selenium–tellurium melts has revealed the existence of heterocyclic tellurium sulfides, selenium sulfides, and tellurium selenium sulfides in equilibrium with polymeric material. The main tellurium heterocycle in the binary melts is TeS_7 with only traces of 1,2-Te_2S_6 and its other isomers as well as Te_8 present. The principal heterocycles in the ternary sulfur–selenium–tellurium melts are the binary selenium sulfides (mainly SeS_7 and the different isomers of Se_2S_6). The most abundant tellurium-containing ring molecules are TeS_7 and 1,2-$TeSeS_6$. They show an isolated tellurium atom, surrounded either by two sulfur atoms or by one sulfur and one selenium atom. All cyclic species containing Te–Te bonds seem to have only very small concentrations in the melts. The composition of the polymeric material can best be understood in terms of the statistical distribution of various chalcogen fragments governed by the overall elemental composition. These sulfur-rich melts also contain several homocyclic and polymeric sulfur species, but they are unobservable by ^{77}Se and ^{125}Te NMR spectroscopy.

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(20) (a) Steudel, R.; Papavassiliou, M.; Krampe, W. *Polyhedron* **1988**, *7*, 581. (b) Pekonen, P.; Hiltunen, Y.; Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1990**, *29*, 2770.