Fundamental Vibrations of Six- and Seven-membered Selenium Sulphide Ring Molecules

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The fundamental vibrations of eleven possible six-membered selenium sulphide ring molecules Se_nS_{6-n}, as well as of all isomers of the two seven-membered rings 1,2-Se_2S_5 and 1,2-Se_5S_2, have been calculated using an extended Urey–Bradley force field in order to support ongoing and future preparative work by providing a convenient method for characterizing the new products which can be prepared by a variety of chemical reactions. The calculated wavenumbers for SeS_5 and 1,2-Se_2S_5 have been used to assign the Raman spectra for both compounds. In general, the results indicate that the stretching vibrations of various selenium sulphides are sufficiently different to allow identification of the species by a detailed analysis of their Raman spectra.

Raman spectroscopy has been shown to be a powerful tool for the study of homocyclic sulphur molecules S_n (n = 6—20), as the spectra of the different species are very characteristic, reflecting not only the molecule size and symmetry but also the bond-distance pattern.[1] It is therefore possible to detect and identify single molecular entities even when investigating mixtures of several homologues. Because of the strong correlation between the wavenumbers of the stretching vibrations and the internuclear distances[2,3] the bond lengths can be predicted from Raman data. The two known homocyclic selenium molecules, Se_6 and Se_8, have also been characterized by Raman spectroscopy.[4,5]

The structural characterization of the sulphur–selenium binary system has turned out to be very problematic, because generally it is not possible to study pure stoicheiometric compounds, as different Se_mS_n species‡ of a given ring size tend to crystallize together forming solid solutions of complex molecular composition.[6] As the sizes of sulphur and selenium atoms are similar, it is also probable that the ring molecules can assume a random orientation in the crystal lattice. Consequently, all selenium sulphide phases which have thus far been investigated by *X*-ray crystallography have disordered crystal structures[6] and no accurate bond parameters (bond lengths and angles) have been obtained for them. At present it seems that *X*-ray diffraction is an unsuitable means to identify and characterize cyclic selenium sulphides and that the most reliable structural information on this complex binary system can be obtained by vibrational analysis.

There have been several investigations on the Raman spectra of cyclic eight-membered selenium sulphides Se_nS_{8-n}.[7-12] The identification of 1,2,3-Se_3S_5[11] and SeS_7[12] as the main components of two mixed sulphur–selenium phases has enabled the force constants to be calculated by using an extended Urey–Bradley force field in the former case, and a valence force field in the latter case. In this paper the fundamental vibrations of cyclic six- and seven-membered Se_mS_n molecules are investigated for the first time, following the recently reported preparation of 1,2-Se_2S_5 and SeS_5 from bis(cyclopentadienyl)titanium pentasulphide and dichlorodiselane.[13] An analogous reaction of $[Ti(C_5H_5)_2Se_5]$ with S_2Cl_2 has been used to produce 1,2-Se_5S_2.[14] In fact, the two titanocene compounds have opened a convenient route to a wide variety of cyclic selenium sulphides which are either stoicheiometrically pure or relatively simple mixtures. Also, recent high-performance liquid chromatographic studies have indicated that the cyclic six- and seven-membered selenium sulphides play a significant part in the sulphur–selenium melt.[15] The present investigation supports the ongoing and future synthetic work in providing means to assign the Raman spectra of new selenium sulphide ring molecules.

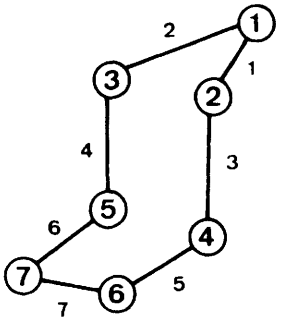

Figure 1. The numbering of atoms and bonds in the seven-membered ring molecule

Calculations

Molecular Geometry.—The isostructural S_6[16] and Se_6[17] molecules are found in the chair conformation as is SeS_5 as judged by the similar morphology of the three crystals in question.[13] Therefore the bond lengths and angles adapted from S_6 and Se_6 were employed in the calculation of the internal co-ordinates of all cyclic Se_nS_{6-n} molecules. The single value for the torsional angles was adjusted individually for each molecule as described earlier for Se_nS_{8-n} molecules.[10] The internal co-ordinates were thus: r_{SS} = 206, r_{SeS} = 221, r_{SeSe} = 236 pm, and α_S = 103 and α_{Se} = 101°. The torsional angles in different molecules ranged from 71.8 to 78.4° which agree closely with those observed for S_6 and Se_6.[16,17]

The overall conformation of each seven-membered selenium sulphide molecule was assumed to be near to that of S_7[18] with one torsional angle approximately 0°. For both 1,2-Se_2S_5 and 1,2-Se_5S_2 there are four possible isomers depending on the positions of the heteroatoms in the molecule. These isomers are named as follows: A (heteroatom positions 1 and 2); B

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‡ In the Se_mS_n compounds, for convenience, the numbered atoms in formulae are those for which m or n is the lowest, whether S or Se.

Table 1. Internal co-ordinates of 1,2-Se_2S_5 and 1,2-Se_5S_2

	Bond length/pm				
Bond[a]	SS[b]	SeS[c]	SeSe[c]	Atom number	Bond angle[a,b]/°
1 and 2	205	220	234	1	Variable
3 and 4	210	225	239	2 and 3	102
5 and 6	200	215	229	4 and 5	105
7	218	233	247	6 and 7	107

[a] See Figure 1. [b] Ref. 18. [c] The single bond lengths of the SS and SeSe bonds have been estimated from S_8[d] and Se_8,[e] respectively. The single bond length of the SeS bond is assumed to be the arithmetic mean of the SS and SeSe single bond lengths. The lengths of the SeSe and SeS bonds in various positions of the seven-membered ring molecule have been estimated by employing the results of a recent *ab initio* study.[19] [d] P. Coppens, Y. W. Yang, R. H. Blessing, W. F. Cooper, and F. K. Larsen, *J. Am. Chem. Soc.*, 1977, **99**, 760; L. K. Templeton, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1976, **15**, 1999; Y. Watanabe, *Acta Crystallogr., Sect. B*, 1974, **30**, 1396. [e] P. Cherin and P. Unger, *ibid.*, 1972, **28**, 313; R. E. Marsh, L. Pauling, and J. D. McCullough, *ibid.*, 1953, **6**, 71; O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, 1980, 624.

Table 2. The Urey–Bradley force constants (N cm^{-1}) for Se_nS_{6-n}, 1,2-Se_2S_5, and 1,2-Se_5S_2

(*a*) Se_nS_{6-n}

Co-ordinate[a]	Force constant[b]		Co-ordinate[a]	Force constant[b]		Co-ordinate[a]	Force constant[b]	
r(SeSe)	K(SeSe)	1.17	α_{Se}	H(Se)	0.03	q_{SeSe}	F(SeSe)	0.23
r(SeS)	K(SeS)	1.48	α_S	H(S)	0.10	q_{SeS}	F(SeS)	0.26
r(SS)	K(SS)	1.78	r/r at Se	P(Se)	0.16	q_{SS}	F(SS)	0.29
τ	Y	0.04	r/r at S	P(S)	0.18			

(*b*) 1,2-Se_2S_5 and 1,2-Se_5S_2

Stretching force constants[c]				Torsion, bending, and interaction force constants[d]					
Co-ordinate[a]	K(SS)	K(SeS)	K(SeSe)	Co-ordinate[a]	Force constant		Co-ordinate[a]	Force constant	
$r_{1,2}$	1.87	1.59	1.31	τ_{1-6}	Y_1	0.05	r/r at S	P(S)	0.29
$r_{3,4}$	1.40	1.19	0.98	τ_7	Y_2	0.09	q_{SeSe}	F(SeSe)	0.21
$r_{5,6}$	2.41	2.05	1.69	α_{Se}	H(Se)	0.02	q_{SeS}	F(SeS)	0.24
r_7	1.09	0.93	0.77	α_S	H(S)	0.08	q_{SS}	D(SS)	0.26
				r/r at Se	P(Se)	0.23	q'	C	0.07

[a] r = Bond length, α = bond angle, τ = torsional angle, q = distance between atoms i and $i + 2$, and q' = distance between atoms i and $i + 3$. For the numbering of the bonds in the seven-membered molecule see Figure 1. [b] K(XX), H(X), P(X), and F(XX) (X = S or Se) are the refined force constants of Se_6 and S_6; other force constants are estimated as mean values of the corresponding force constants of Se_6 and S_6. [c] K(SS) taken from S_7.[25] K(SeS) and K(SeSe) have been scaled from K(SS) as follows: K(SeS) = 0.85K(SS); K(SeSe) = 0.75K(SS).[10] [d] The torsion force constants are from S_7;[25] other force constants are from our previous calculations on Se_nS_{8-n}.[10]

(positions 2 and 4); C (positions 4 and 6); and D (positions 6 and 7). For the numbering of the atoms and bonds in the cyclic seven-membered molecule see Figure 1.

The SS bond lengths were taken from S_7.[18] A recent theoretical study[19] shows that the lengths of SS, SeS, and SeSe bonds vary similarly as a function of the torsional angle. These conclusions were applied in the estimation of the SeS and SeSe bond lengths in different parts of the seven-membered ring molecule. All bond angles were taken from S_7[18] regardless of the type of atom in each site. The bond lengths and angles used in the calculations for the seven-membered molecules are given in Table 1.

Because of the lack of symmetry in isomers A—C the unique torsional angle τ_7 (subscript refers to bond number of central bond defining torsional angle; see Figure 1) is not necessarily equal to 0°. The effect of this torsional angle in these isomers was studied by calculating the fundamental vibrations for three different values of τ_7 (−10, 0, and +10°). Because of the C_s symmetry of isomer D, τ_7 was restricted to the value of 0°. The other torsional angles (τ_1—τ_6) were again adjusted individually for each molecule. The values of these angles in different isomers ranged from 85.8 to 95.2° in agreement with the corresponding angles in γ-S_7 and δ-S_7.[18]

Force Field.—The calculations were carried out with the extended Urey–Bradley force field which has successfully been applied to several homocyclic sulphur and selenium molecules,[1,4,5] heterocyclic S_7NH[20] and $S_4(NH)_4$,[21] S_8O,[22] and S_4N_4.[23] This force field, as applied to cyclic selenium sulphides, has been described earlier.[10] The Se_nS_{6-n} molecules require 8—11 force constants. Their values have been adapted from those of S_6 and Se_6* and are given in Table 2.

Because of the inequivalence of the bonds in the seven-membered ring molcule, four different stretching force constants are needed for every bond type depending on its location in the molecule.[25] The unique torsional angle also demanded a force constant of its own. Therefore, 13—16 force constants are needed to describe adequately the force field in different isomers of 1,2-Se_2S_5 and 1,2-Se_5S_2. Their values are given in Table 2.

The calculations were performed by a CYBER 170-835 computer using the programs by Schachtschneider[26] and Shimanouchi.[27]

Results and Discussion

Se_nS_{6-n}.—The fundamental vibrations calculated for the eleven Se_nS_{6-n} molecules are shown in Table 3. In agreement with Se_nS_{8-n} rings,[10] the SS stretching vibrations lie at 463—437, the SeS modes at 382—324, and the SeSe stretching modes at 253—209 cm^{-1}. The bending and the torsional modes are found at higher wavenumbers for six- than eight-membered species[10] and overlap the SeSe stretching region more severely.

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* The values of the five force constants K(stretching), H(bending), Y(torsion), P(bond–bond interaction), and F(repulsion between atoms i and $i + 2$) for both molecules were obtained by least-squares fitting to the observed wavenumbers.[4,24] The largest deviations between the observed and calculated wavenumbers amounted to 6 and 9 cm^{-1} for S_6 and Se_6, respectively.

Table 3. Fundamental vibrations (cm^{-1}) of cyclic Se$_n$S$_{6-n}$ molecules

SeS$_5$ (C_s)	1,2-Se$_2$S$_4$ (C_2)	1,3-Se$_2$S$_4$ (C_s)	1,4-Se$_2$S$_4$ (C_{2h})	1,2,3-Se$_3$S$_3$ (C_s)	1,2,4-Se$_3$S$_3$ (C_1)	1,3,5-Se$_3$S$_3$ (C_{3v})	1,2-Se$_4$S$_2$ (C_2)	1,3-Se$_4$S$_2$ (C_s)	1,4-Se$_4$S$_2$ (C_{2h})	Se$_5$S (C_s)
463 a'', ν(SS)										
461 a', ν(SS)										
	455 b, ν(SS)			454 a'', ν(SS)						
	454 a, ν(SS)	456 a', ν(SS)	452 a_g, ν(SS)							
448 a', ν(SS)	447 a, ν(SS)	447 a'', ν(SS)	448 a_u, ν(SS)	449 a', ν(SS)	449 a, ν(SS)		450 a, ν(SS)			
437 a'', ν(SS)										
376 a', ν(SeS)		380 a', ν(SeS)	381 b_u, ν(SeS)		375 a, ν(SeS)	381 a_1, ν(SeS)		375 a', ν(SeS)		
		369 a'', ν(SeS)	368 a_g, ν(SeS)			370 e, ν(SeS)			362 a_g, ν(SeS)	
	356 a, ν(SeS)			359 a', ν(SeS)	358 a, ν(SeS)		359 b, ν(SeS)	353 a'', ν(SeS)	357 b_u, ν(SeS)	358 a', ν(SeS)
	352 b, ν(SeS)			349 a'', ν(SeS)	348 a, ν(SeS)		347 a, ν(SeS)	352 a', ν(SeS)	345 a_u, ν(SeS)	345 a'', ν(SeS)
332 a'', ν(SeS)		338 a', ν(SeS)	340 b_g, ν(SeS)		330 a, ν(SeS)	335 e, ν(SeS)			341 b_g, ν(SeS)	
		324 a'', ν(SeS)	324 a_u, ν(SeS)			318 a_2, ν(SeS)		327 a'', ν(SeS)		
284 a', δ										
	270 b, δ									
		259 a',δ		255 a', δ			253 a, ν(SeSe)			253 a', ν(SeSe)
250 a', δ, τ	242 a, δ		240 b_u, δ	242 a', ν(SeSe)				245 a', ν(SeSe)		237 a'', ν(SeSe)
	232 a, ν(SeSe)				231 a, ν(SeSe)		232 b, ν(SeSe)		233 a_g, ν(SeSe)	
		226 a', δ	224 a_g, δ	224 a', δ	228 a, δ	226 a_1, δ			228 a_u, ν(SeSe)	227 a', ν(SeSe)
				220 a'', ν(SeSe)			219 b, δ	218 a'', ν(SeSe)		
					210 a, δ		210 a, ν(SeSe)	207 a', δ		209 a'', ν(SeSe)
200 a'', δ			190 b_g, δ				200 a, δ		190 b_u, δ	
171 a'', τ	178 a, δ					176 a_1, δ		171 a', δ	182 a_g, δ	184 a', δ
161 a', δ	160 b, τ, δ	167 a', δ	167 a_u, δ, τ		160 a, δ					156 a', δ
149 a', τ, δ		151 a'', δ		149 a'', δ		145 e, δ				
		141 a', δ			140 a, δ, τ			142 a'', δ	140 a_g, δ	
	137 b, δ	138 a'', τ	132 a_g, δ	136 a'', τ, δ					135 b_u, τ, δ	
	124 a, δ, τ		127 b_u, τ	127 a', δ	122 a, δ	126 e, δ, τ	123 b, δ	129 a'', δ		
							119 a, δ			116 a', δ
				110 a', δ, τ	113 a, δ		111 b, τ, δ	114 a', δ	109 b_g, δ	
							106 a, δ			106 a'', δ
								100 a', τ, δ		105 a', τ
									98 a_u, δ, τ	95 a'', δ, τ

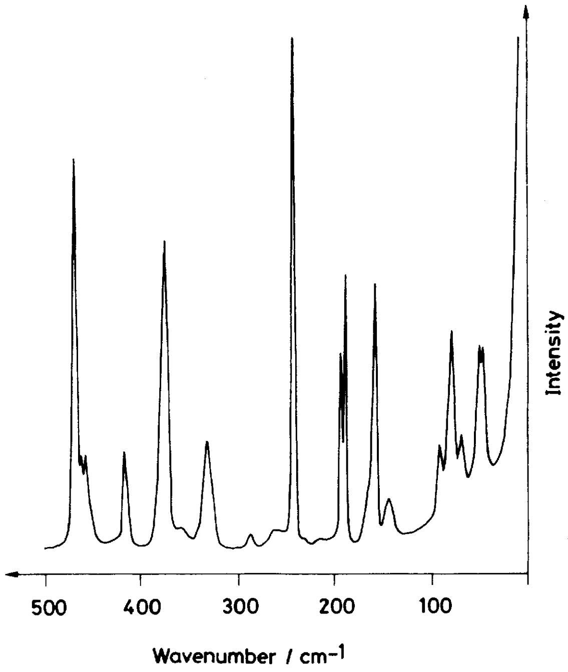

Figure 2. The Raman spectrum of SeS_5 recorded at −110 °C

Table 4. Assignment of the Raman spectrum (cm^{-1}) of SeS_5

Obs.	Calc.*	Difference	Assignment
470vs	473	−3	a', ν(SS)
464w	467	−3	a'', ν(SS)
459w	447	12	a', ν(SS)
419m	425	−6	a'', ν(SS)
378s	379	−1	a', ν(SeS)
361vw			Se_nS_{8-n} impurity
335m	335	0	a'', ν(SeS)
290vw	283	7	a', δ
267vw			Se_nS_{8-n} impurity
246vvs	253	−7	a', δ
197s	203	−6	a'', δ
191s	183	8	a'', τ, δ
161s	162	−1	a', δ
148vw	148	0	a', τ, δ
95w			Lattice vibrations
82m			
72w			
55/51m			

* Refined Urey–Bradley force constants (N cm^{-1}): K(SeS) = 1.561, K(SS) = 1.797, H(Se) = 0.038, H(S) = 0.162, Y = 0.054, P(Se) = 0.223, P(S) = 0.278, F(SeS) = 0.217, and F(SS) = 0.141.

The presence or absence of the SeSe bonds can, however, be deduced from the magnitude of the splitting in the SeS stretching vibrations as shown earlier in the case of Se_nS_{8-n} molecules.[10]

The overall similarity of the Raman spectra of most Se_nS_{6-n} species renders the characterization of mixtures difficult, *cf.* the case of mixed Se_nS_{8-n} phases.[10] Purely stoicheiometric compounds and the main components of simple mixtures can, however, be identified as exemplified by 1,2,3-Se_3S_5[11] and SeS_7.[12]

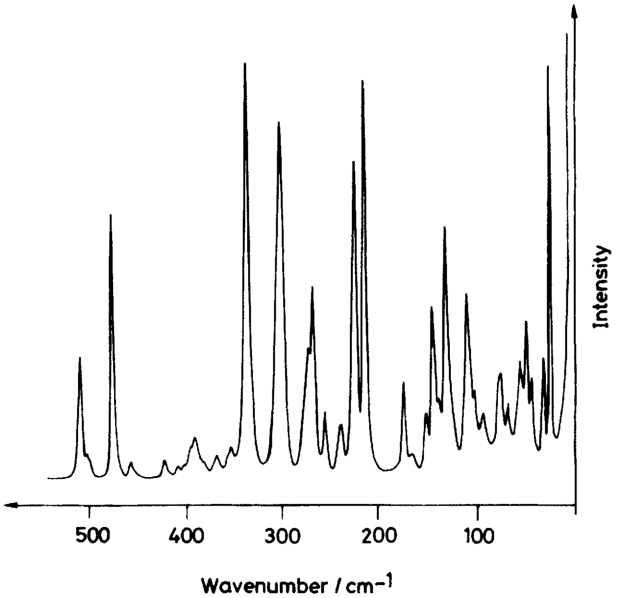

Figure 3. The Raman spectrum of 1,2-Se_2S_5 recorded at −110 °C[13]

The Raman spectrum of SeS_5 is shown in Figure 2. There are four Raman lines in the SS stretching region. The very strong line at 470 cm^{-1} is assigned to a symmetric SS stretch, the calculated value for which is 461 cm^{-1}. The other three lines are assigned to the nearest calculated vibrations. In the SeS stretching region the weak line at 361 cm^{-1} is probably caused by a small amount of Se_nS_{8-n} known to be present in the sample, as these molecules produce an intense Raman line in this region.[11] The wavenumbers of the two remaining lines imply the presence of only two SeS bonds in the Se_nS_{6-n} molecule. Their wavenumbers coincide with the values calculated for the symmetric and asymmetric SeS stretching vibrations of SeS_5. The SeSe stretching vibrations, bending, and torsional modes are less straightforward to assign. The weak line at 267 cm^{-1} is probably due to the intense Raman line of the SeSe stretching in the Se_nS_{8-n} impurity. The strong Raman line at 246 cm^{-1} was assigned to a fully symmetric ring-deformation mode the calculated value for which is 250 cm^{-1}. For S_6 the corresponding vibration lies at 262 cm^{-1}.[24] All other Raman lines were paired off with the nearest calculated wavenumbers. Lines below 148 cm^{-1} were assigned to lattice vibrations.

The least-squares refinement of the nine Urey–Bradley force constants resulted in good agreement between the observed and calculated wavenumbers (largest deviation 12 cm^{-1}) and in reasonable values of both the Urey–Bradley and the valence force constants. The assignment of the Raman spectrum of SeS_5 is shown in Table 4.

1,2-Se_2S_5 *and* 1,2-Se_5S_2.—The fundamental vibrations of 1,2-Se_2S_5 and 1,2-Se_5S_2 isomers are shown in Tables 5 and 6. The stretching modes are sensitive to the positions of the particular bonds in the molecule (compare S_7[25]). The unique torsional angle has a notable effect not only on the torsional modes but also on many stretching and bending modes. The similarity of the bending and torsion regions restricts the initial assignment to the stretching vibrations only.

The Raman spectrum of 1,2-Se_2S_5 is shown in Figure 3. The strong lines at 339 and 304 cm^{-1} must be produced by two rather long SeS bonds implying isomer C (see Table 5) as suggested earlier.[13] The SeS stretching modes of all other isomers occur at higher wavenumbers, ruling out especially isomers B and D (the two SeS stretches occur at 395 and 348 cm^{-1} for isomer B and at 412 and 383 cm^{-1} for isomer D). It is difficult to rule out isomer A even though the SeS stretching

Table 5. The fundamental vibrations (cm^{-1}) of 1,2-Se_2S_5 isomers

Isomer A			Isomer B			Isomer C			Isomer D[a]	S_7[a,b]
τ_7 = −10	0	10°	τ_7 = −10	0	10°	τ_7 = −10	0	10°	τ_7 = 0°	τ_7 = 0°
526 ν_6	526 ν_6	526 ν_6	523 ν_6	523 ν_6	523 ν_6	519 ν_6	520 ν_6	519 ν_6		529 a'', ν_c
515 ν_5	515 ν_5	515 ν_6								516 a', ν_c
						506 $\nu_{1,2}$	505 $\nu_{1,2}$	501 $\nu_{2,1}$	503 a'', ν_a	
			474 ν_2	477 ν_2	477 ν_2					477 a', ν_a
										464 a'', ν_a
						440 $\nu_{2,1}$	427 $\nu_{1,4}$		438 a', ν_b	
417 ν_4	418 ν_4	418 ν_4	415 ν_5	414 ν_5	413 ν_5			419 $\nu_{1,4}$	417 a', ν_a	
									412 a'', ν_c	403 a', ν_b
			395 ν_4	396 ν_4	396 ν_4	395 ν_4	395 ν_4	393 $\nu_{4,2}$		393 a'', ν_b
									383 a', $\nu_{b,c}$	
									379 a'', ν_b	
363 ν_7	363 ν_7	363 ν_7								360 a', ν_d
			354 ν_7	354 ν_7	354 ν_7					
348 ν_2	346 ν_2	345 ν_2	348 ν_1	341 ν_1	348 ν_1		346 ν_3			
333 ν_3	331 ν_3	329 ν_3				331 $\nu_{3,1}$		334 $\nu_{3,1}$		
								327 τ		
						299 ν_7	300 ν_7	297 ν_7	300 a', δ	
							294 ν_5, τ			
			279 δ	279 δ		282 δ, ν_5	277 δ	283 δ, ν_5		280 a'', δ
273 δ	271 δ	270 δ			273 δ				271 a', δ	273 a', δ
					266 τ					
				259 δ, τ		256 $\nu_{5,3}$	256 ν_5	255 ν_5		
			253 δ, τ			255 δ				
245 ν_1,δ	245 ν_1,δ	245 ν_1,δ								244 a'', τ, δ
		239 ν_1			236 δ, τ					238 a', δ, τ
228 ν_1	234 ν_1		235 δ	234 δ	232 δ		230 δ, τ	234 δ	226 a'', δ	
				225 δ, τ		220 δ				
216 δ	216 δ	216 δ	211 δ, τ							
197 δ	201 δ	205 δ	202 ν_3	205 ν_3	208 ν_3	204 δ, τ	205 δ, τ	205 δ, τ		
									192 a', ν_d	193 a', δ
									190 a'', δ, τ	190 a'', δ
163 δ	162 δ	160 δ	160 δ	160 δ	162 δ				166 a', δ	
						152 δ	153 δ	153 δ		153 a', δ, τ
			145 δ	145 δ	146 δ				146 a', δ	
140 δ	139 δ	137 δ							137 a'', δ	142 a'', τ
134 δ, τ	133 δ, τ	133 δ, τ	127 δ, τ	129 δ	131 δ	135 δ	133 δ	133 δ		
						123 δ, τ	124 τ, δ	123 δ, τ		
	110 δ, τ	115 τ				119 τ	117 δ, τ	115 δ, τ	109 a'', τ	
105 τ, δ			101 δ	100 δ	99 δ, τ					

[a] The subscripts a—d refer to symmetry (C_s) related bonds: a, bonds 1 and 2; b, bonds 3 and 4; c, bonds 5 and 6; d, bond 7. [b] Ref. 25.

Table 6. The fundamental vibrations (cm^{-1}) of 1,2-Se_5S_2 isomers

Isomer A			Isomer B			Isomer C			Isomer D*
τ_7 = −10	0	10°	τ_7 = −10	0	10°	τ_7 = −10	0	10°	τ_7 = 0°
						513 ν_5	515 ν_5	515 ν_5	
472 ν_1	463 ν_1	458 ν_1							
			428 ν_3	418 $\nu_{5,3}$	420 ν_3				424 a'', ν_c
			400 ν_5	392 $\nu_{3,5}$	389 ν_5				403 a', ν_c
346 ν_2	350 $\nu_{2,3}$	359 $\nu_{2,3}$	342 ν_1	356 ν_1	353 ν_1				350 a', ν_d
331 ν_3	328 $\nu_{3,2}$	313 $\nu_{3,2}$				330 ν_3	330 ν_3	328 ν_3	
						297ν_7	301 ν_7	300 ν_7	
281 ν_6	281 ν_6	283 ν_6	280 ν_6	280 ν_6	280 ν_6				
271 ν_5	273 ν_5	279 ν_5				270 ν_6	272 ν_6	271 ν_6	
		261 τ, ν_5							260 a'', ν_a
	247 τ		254 ν_2	254 ν_2	254 ν_2	249 ν_2	252 ν_2	252 ν_2	247 a', ν_a
236 δ	231 δ, τ	241 δ, ν_3			236 δ	232 ν_1	239 ν_1	242 ν_1	
			216 δ	225 δ	221 δ, τ	212 τ, δ	222 δ, τ	224 δ, τ	225 a'', τ, δ
211 ν_4	210 ν_4	210 ν_4	207 ν_4	206 ν_4	205 ν_4	199 ν_4	202 ν_4	201 ν_4	209 a', ν_b
204 δ				201 τ					206 a'', δ
186 ν_7	186 ν_7	186 ν_7	188 ν_7	188 ν_7	188 ν_7	190 δ	197 τ, δ	198 δ, τ	198 a'', ν_b
			187 δ, τ						
152 δ, τ	152 δ, τ	153 δ	154 δ	154 δ	154 δ		152 δ	149 δ	146 a', δ
138 δ	137 δ	136 δ	146 τ	147 δ, τ	146 τ	144 δ	138 δ	147 δ	143 a', δ
						125 δ			

Table 6 (*continued*)

Isomer A			Isomer B			Isomer C			Isomer D*
$\tau_7 = -10$	0	10°	$\tau_7 = -10$	0	10°	$\tau_7 = -10$	0	10°	$\tau_7 = 0°$
116 δ	115 δ	115 δ	117 δ	116 δ	115 δ, τ		117 δ	115 δ	115 *a*′, τ
112 δ	111 δ	110 δ	114 δ	113 δ	112 δ		112 δ	111 δ	109 *a*″, δ
99 δ	98 δ	96 δ	98 δ, τ	99 δ	99 δ, τ	98 δ	95 τ	97 δ, τ	99*a*′, τ, δ
						89 δ, τ	87 τ	89 τ, δ	83*a*″, δ, τ
84 δ, τ	85 δ, τ	86 δ, τ	86 δ, τ	86 δ, τ	86 τ	86 τ, δ			
						78 δ			

* Subscripts a—d refer to symmetry (C_s) related bonds: a, bonds 1 and 2; b, 3 and 4; c, 5 and 6; d, 7.

Table 7. Assignment of the Raman spectrum (cm^{-1}) of 1,2-Se_2S_5 (isomer C, $\tau_7 = -10°$)

Obs.	Calc.*	Difference	Assignment
511m	511	0	ν_6(SS)
505 (sh)			479 + 27
479s	479	0	$\nu_{1,2}$(SS)
459vw			228 + 228
425vw	425	0	ν_4(SS)
393w	393	0	$\nu_{2,4}$(SS)
372vw			
357vw			219 + 136
339vs	339	0	ν_3(SeS)
304vs	305	−1	ν_7(SeS)
276 (sh)	283	−7	ν_5(SeSe), δ
271m	270	1	ν_5(SeSe)
259w	253	6	δ, ν_5(SeSe)
242w			219 + 27
228s	225	3	δ
219vs	218	1	δ
179w	169	10	δ
155vw			
149m	155	−6	δ
136m	134	2	δ
113m	123	−10	δ, τ
98vw			Lattice vibrations
79w			
72vw			
59w			
52m			
47w			
34w			
27vs			

* Refined Urey–Bradley force constants (N cm^{-1}): $K_{1,2}$(SS) = 1.611, K_3(SeS) = 1.410, K_4(SS) = 1.439, K_5(SeSe) = 1.520, K_6(SS) = 2.301, K_7(SeS) = 0.902 (the subscripts refer to the bond numbers); H(Se) = 0.052, H(S) = 0.084, Y_{1-6} = 0.079, Y_7 = 0.140, P(Se) = 0.128, P(S) = 0.224, F(SeS) = 0.371, F(SS) = 0.190, and C = 0.084.

modes seem to be at too high wavenumbers and the stretching vibration of the unique SS bond (r_{SS}) which produces a fairly strong Raman line at 362 cm^{-1} in S_7 [25] is absent in the spectrum in Figure 3. Therefore the calculated wavenumbers of both isomers A and C were adjusted to the observed Raman lines by refining the Urey–Bradley force constants. The refinement converged to reasonable (all positive) values of all force constants only for isomer C with τ_7 at −10 °C. The largest deviation between the observed and calculated wavenumbers is 10 cm^{-1}.

The assignment of the Raman spectrum according to isomer C is shown in Table 7. The two weak features at 372 and 155 cm^{-1} cannot be explained by these calculations and are probably caused by a small amount of Se_nS_{8-n} in the sample. The final Urey–Bradley and valence force constants agree well or bear a reasonable relationship with the corresponding force constants of S_7.[25]

Conclusions

The preparative work involving [Ti(C_5H_5)$_2$$S_5$] or [Ti($C_5H_5$)$_2$$Se_5$] has opened a simple route to a variety of cyclic six- and seven-membered selenium sulphides. In this work the suitability of Raman spectroscopy in the identification of these species has been demonstrated.

The fundamental vibrations of all Se_nS_{6-n} (n = 1—5) and of all isomers of both 1,2-Se_2S_5 and 1,2-Se_5S_2 have been calculated using the extended Urey–Bradley force field. The calculated wavenumbers have been compared to the observed Raman spectra of SeS_5 and 1,2-Se_2S_5 and resulted in the complete assignment of these spectra. The refined force constants of both species agree well with those of the related sulphur and selenium molecules demonstrating the reliability of the vibrational analysis (see Table 8).

Our calculations show that it is possible to identify pure

Table 8. Selected valence force constants (N cm^{-1}) for some homo- and hetero-cyclic sulphur molecules

Force constant[a]	SeS_5	1,2-Se_2S_5	S_6[b]	S_7[c]	S_8[d]	Se_8[e]	S_8 + SeS_7[f]	1,2,3-Se_3S_5[g]
f_r(SeSe)		2.06[h]				1.70		1.78
f_r(SeS)	1.70	1.53—1.85					1.850	1.96
f_r(SS)	1.96—2.00	1.75—2.68	2.24	1.51—2.73	2.41		2.061	2.21—2.27
f_α at Se	0.10	0.27				0.17	0.207	0.15—0.17
f_α at S	0.22—0.26	0.17—0.42	0.23	0.26—0.31	0.25		0.223	0.22—0.24
f_τ	0.05—0.06	0.04—0.13	0.05	0.06—0.08	0.03	0.03	0.027—0.036	0.03—0.04
f_{rr}	0.32—0.42	0.43—0.54	0.53	0.46—0.50	0.60	0.39	0.302—0.432	0.52—0.57
$f_{r\alpha}$	0.06—0.10	0.10—0.26	0.22	0.14—0.20	0.18	0.14	0.07	0.13—0.19

[a] f_i = Diagonal force constant; f_{ij} = interaction between the nearest neighbours. [b] Ref. 24. [c] Ref. 25. [d] R. Steudel and H-J. Mäusle, *Z. Naturforsch., Teil A*, 1978, **33**, 951. [e] Ref. 5. [f] Ref. 12. [g] Ref. 11. [h] Bond number 5, see Figure 1.

compounds and the main components of the relatively simple mixtures by inspecting the stretching vibrations. Particularly with the seven-membered ring molecules, the stretching modes provide a sensitive test not only for the molecular species but also for the actual solid-state isomer.

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