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ON THE STRUCTURE OF ARYLSELENIUM TRIBROMIDES

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Summary

The IR and Raman spectra of arylselenium tribromides $X—C_6H_4SeBr_3$ where $X = H, Br, Cl, CH_3$ are reported. It is suggested that the solids are possibly tetramers in the solid state formed by donor-acceptor interaction between units $RSeBr_2^+$ and Br^-. Each selenium atom is in a highly symmetrical or pseudo-symmetrical environment.

Introduction

Arylselenium trihalides may be prepared in a variety of ways, and the methods used have been summarised by several authors [1—3]. The most convenient route to the trihalides is by halogenation of the arylselenocyanate or diaryldiselenide. Little is known about the structure of the arylselenium trihalides but it is of interest to note that CH_3SeCl_3 is thought to be dimeric in methylene chloride [4]. The Lewis base properties of organoselenium trihalides have been pointed out [3] and thus it is easy to envisage the formation of polymeric structures. The IR and Raman spectra of phenyltellurium trihalides have been reported [5] and it is suggested that the compounds are associated to some degree. Dimers involving five co-ordinate atoms are the most probable structures for the chlorides and iodides but the bromides may be even more associated. All structures may be imagined to involve donor-acceptor interaction between $RTeX_2^+$ and X^-. The spectroscopic data for the corresponding arylselenium trihalides has not been reported, and thus it was decided that vibrational analysis of a few members of this class of compound would be worthy of investigation.

A few organoselenium compounds have been examined by X-ray analysis [6—10] and the stereochemistry of the donor atom reported. Some dialkyl and diaryl diselenides [11—13], alkyl and aryl selenocyanates [14,15] diaryl and

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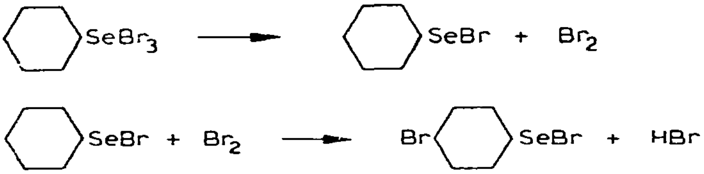
dialkyl selenium dihalides and related compounds [16—18], selenobis(2-mercaptoisobutyric acid) [19] and dichloro- and dibromo-(tetramethylthiourea selenium(II) [10] have been the subjects of IR and Raman analysis. The IR and Raman spectra of the compounds $SeBr_4$, $SeCl_4$ [20] and Se_2Cl_2, Se_2Br_2 [21] and anions $[SeBr_6]^{2-}$ [22,23] have also been reported. Thus, the published spectroscopic and structural data on selenium compounds is rather limited. This may be due in part to the instability of many of these compounds to X-rays, Laser beams and IR radiation.

Some selenium compounds are also unstable to heat. For example, phenylselenium tribromide gives off bromine on heating near the melting point and at 110—115° C bromination of the para position occurs



The most likely stereochemistries for selenium(II) and selenium(IV) may be predicted from the number of lone pairs and number of bond pairs. Molecules of symmetry C_2 or C_{2v} may be postulated for selenium(II) (two lone pairs, two bond pairs) or selenium(IV) (one lone pair and four bond pairs). Hendra and Park [21] have made assignments of the bands observed for Se_2Cl_2 and Se_2Br_2 which are consistent with C_2 symmetry. Hayward and Hendra [20] have suggested from their spectroscopic data that $SeCl_4$ and $SeBr_4$ have a C_{2v} covalent structure. Assignments based on C_{2v} symmetry have also been made for dibromo-(tetramethylthiourea) selenium(II) [10]. The anion $[SeBr_6]^{2-}$ is octahedral although there is a slight difference in the assignments made by two groups of workers [22,23].

The Raman spectra of compounds containing Se—Br bonds are particularly intense. This is not surprising, the most abundant isotopes of selenium are 78 (23.52%) and 80 (49.82%) and of bromine 79 (50.53%) and 81 (49.47%), and thus many of the fundamental vibrations are associated with atoms of nearly equal mass. Arylselenium tribromides resemble solid bromine in being red in appearance and presumably the origin of this colour is the same as that for elemental bromine [24].

Results and discussion

We find that arylselenium tribromides are decomposed by the beam of an IR spectrophotometer but that satisfactory far IR spectra could be obtained using an interferometer. The compounds were ultimately decomposed by long exposure to the Laser beam of the Raman spectrometer but good spectra were obtained initially. Since arylselenium tribromides do decompose on storing, the IR spectra were recorded immediately and the Raman spectra were carried out within 24 h. Analysis of the freshly prepared compounds for selenium content showed that the compounds were of satisfactory purity (Table 1).

TABLE 1

ANALYTICAL DATA FOR THE ARYLSELENIUM TRIBROMIDES

	C	H	Se	M.p. (°C)	DMF [a]
$C_6H_5SeBr_3$	18.10 (18.20) [b]	1.15 (1.27)	20.09 (19.86)	103 (lit. 105)	49
p-Br—$C_6H_4SeBr_3$	15.30 (15.30)	0.70 (0.70)	16.84 (16.67)	132 (lit. 132)	50
p-$CH_3C_6H_4SeBr_3$	20.50 (20.71)	1.60 (1.74)	18.91 (19.27)	115 (lit. 115.6)	50
p-Cl—$C_6H_4SeBr_3$	17.00 (16.89)	0.70 (0.95)	18.73 (18.36)	122 (lit. 123—124)	40

[a] ohm^{-1} cm^2 mol^{-1} 10^{-3} *M* solution at 20°C. [b] Required values in parenthesis.

Examination of the far IR and Raman spectra (Table 2) shows that for C_6H_5-$SeBr_3$, p-Br—$C_6H_4SeBr_3$, p-Cl—$C_6H_4SeBr_3$ and p-$CH_3C_6H_4SeBr_3$ there are fewer coincidences of bands (250—120 cm^{-1}) than found for the corresponding phenyltellurium trihalides [5] suggesting a more symmetrical environment for the selenium atoms.

The strong Raman line at 293 cm^{-1} for di-n-butyl diselenide [13] (cp. 317 cm^{-1} for Br—Br in elemental bromine) and the presence of IR bands at 266, 247 and 236 cm^{-1} for $SeBr_4$ as recorded by Hayward and Hendra [20] suggest that the bands observed between 200—310 cm^{-1} for the arylselenium tribromides are associated with selenium—bromine stretching modes. In their paper on the IR and Raman spectra of Se_2Br_2 (C_2 symmetry) Hendra and Park [21] assign the band at 260 cm^{-1} to ν(Se—Br), ν_4(B) and that at 286 cm^{-1} to ν(Se—Se), ν_1(A). Deformation modes are assigned to bands between 110 and 150 cm^{-1}. For the "T" shaped molecule $SeBr_2$tmtu (where tmtu is tetramethylthiourea) [10] the strong bands at 184 and 150 cm^{-1} are assigned to asymmetric Br—Se—Br stretching and symmetric stretching modes respectively whilst again the lower frequency bands at 100—112 cm^{-1} are assigned to Br—Se—Br deformation modes.

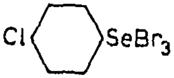
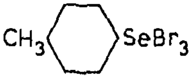
Hayward and Hendra [25] suggest that the IR bands at 164 and 196 cm^{-1} observed for Me_2SeBr_2 are associated with Se—Br stretching modes but the Raman spectra of $(C_6H_5)_2SeBr_2$ shows only two bands, one strong band at 157 cm^{-1} and a weaker one at 249 cm^{-1} [26]. The former is most likely to arise from the symmetric Br—Se—Br stretching vibration (A_1 species for this molecule of symmetry C_{2v}) and the latter is possibly associated with the phenyl u mode [16]. It is interesting to note that both diphenylselenium dibromide and di-p-tolylselenium dibromide have similar structures with longer than expected selenium—bromine bonds [7,27].

Thus, selenium—bromine stretching and deformation vibrations give rise to absorptions between 100—316 cm^{-1} depending on the environment and coordination number of the selenium atom, its formal oxidation state and the selenium—bromine bond length which may vary from 2.32 to 2.62 Å.

The bands in the region 100—220 cm^{-1} for the arylselenium tribromides occur at similar or the same frequencies as those found for $(SeBr_6)^{2-}$ [22,23] but it is of interest to note that the bands which are Raman active are either IR

TABLE 2

THE FAR IR AND RAMAN SPECTRA OF ARYLSELENIUM TRIBROMIDES BETWEEN 50—330 cm^{-1}

								Tentative assignments
IR	Raman $\Delta\nu$	IR	Raman $\Delta\nu$	IR	Raman $\Delta\nu$	IR	Raman $\Delta\nu$	
55s								
105m		103s(sh)		100s		94m		δ(Se—Br)
110s(sh)	120m(sh)	120vs	116s(sh)	121w(sh)		120s		
	(142w)	137s		134s(sh)	132s	140m	136s(sh)	
				152vs				
					158w	161m(sh)	159vs	Phenyl x mode and ν(Se—Br)
	170m		170s	167vs				
179s		177s						
202vs	198vs	203vs		203vs	196s[a]	196vs		ν(Se—Br)
						207vs	208m	
	214vs		211s	210vs		217vs		
220vs		220vs						
							231m	Phenyl u (Se) mode
	242vs		233s		250w		248w	
254vs		250vs		258s			262w	
					267s			
278s	280s	274m(sh)	282vw	280vw		284s		ν(Se—Br)
298s		295s	300vw	302s[b]				
305s					310m[b]	309s		
						316s	316vw	Phenyl t(Se) mode
330s		327s	322vw	330s		330s(sh)		

[a] Phenyl x mode (Cl). [b] Phenyl u mode (Cl).

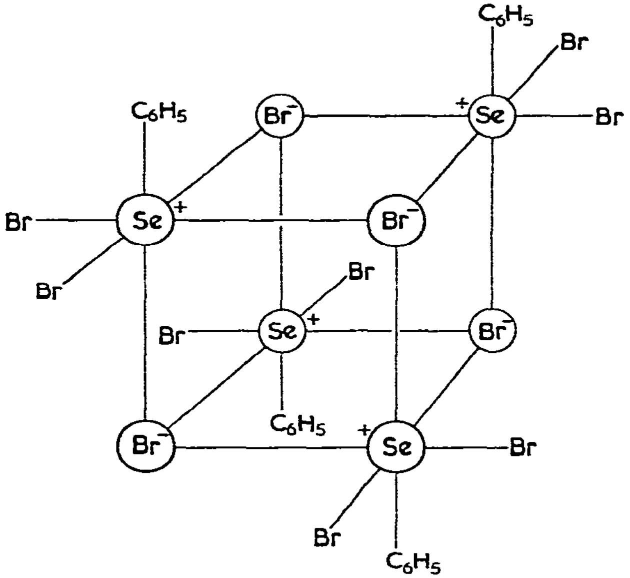


Fig. 1.

or/and Raman active in the arylselenium tribromides and those IR active in $(SeBr_6)^{2-}$ are IR and Raman active in the tribromides. There is also evidence of splitting of bands and this would seem to suggest that the selenium atoms are in a distorted octahedral environment, i.e. one which approximates to D_{3d} or C_{3v} symmetry; the latter being more likely in view of the IR active bands at 170—180 cm^{-1} [ν_1, A_{1g} in $(SeBr_6)^{2-}$] and 140 cm^{-1} [157 cm^{-1}, ν_2, E_g in $(SeBr_6)^{2-}$].

The other bands found for $C_6H_5SeBr_3$ between 230 and 316 cm^{-1} are in the region where vibrational bands are noted for $SeBr_4$ [20], Se_2Br_2 [21], $(C_6H_5)_2SeBr_2$ [26] (and Br_2 itself).

The absorptions in this region probably arise from "stronger" selenium—bromine and the selenium—phenyl vibrations. The conductivity measurements in DMF suggest that the arylselenium tribromides are weakly ionic. If this donor-acceptor interaction between $RSeBr_2^+$ and Br^- units persists in the solid state a distorted octahedral environment for selenium of three long (selenium—bromine) bonds and three short (two selenium—bromine and one selenium—carbon) bonds could be envisaged in the tetramer unit depicted in Fig. 1.

The tetramer unit need not be based on a cube. A distorted cube arrangement also gives rise to Br^- ions which lie on a three fold axis. Tetramer units of a similar type have been proposed for thallium(I) methoxide [28] and basic beryllium acetate [29].

In the tetramer unit proposed for $C_6H_5SeBr_3$ each selenium atom (masses 78 or 80) is surrounded by three bromine atoms (masses 79 or 81) and more closely by two bromine atoms (masses 79 or 80) and one phenyl group (mass 77) i.e. approximate C_{3v} local symmetry. The unit can thus be regarded as of the type MA_3B_3.

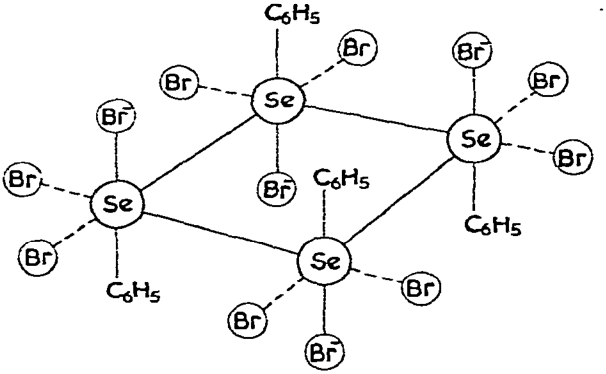


Fig. 2.

The fundamental vibrations for this molecule of point group C_{3v} are as follows:

$\Gamma = 4A_1(\text{R.I.}) + A_2(\text{R}) + 5E(\text{R.I.})$

Twelve to fifteen bands are in fact observed and these are listed together with tentative assignments in Table 2.

The proposed tetramer unit is, of course, not the only structure which could be proposed which would give rise to selenium atoms in an approximate C_{3v} environment. A three dimensional array of $C_6H_5SeBr_2^+$ units and Br^- can be constructed to give the desired environment for the selenium atoms.

Alternatively, a tetramer unit based on selenium—selenium bonds (see Fig. 2) can be envisaged which would also give a local environment of C_{3v} for each selenium atom. Since selenium and bromine have similar masses and would therefore be expected to give rise to bands of similar frequency there is no way of distinguishing between the two structures proposed (Figs. 1 and 2).

Experimental

The arylselenium tribromides were prepared by bromination (using bromine in chloroform) of either the appropriate diaryldiselenide or arylselenocyanate [30,31]. The arylselenocyanates were prepared by addition of potassium selenocyanate to a diazotised arylamine [30,31,32,33].

All compounds were stored in a desiccator.

The arylselenium tribromides were assayed for purity by (*a*) melting point; (*b*) carbon and hydrogen analyses using the usual combustion method; (*c*) selenium content. 20—50 mg of the freshly prepared dry sample was accurately weighed out and dissolved in dry methanol. The iodine liberated an addition of 2 g KI (iodate free) and 2.0 cm^3 of 4 *M* H_2SO_4 was titrated with 0.1 *M* $Na_2S_2O_3$ solution using starch as indicator [34,35].

$$2C_6H_5SeBr_3 + 6I^- \rightleftharpoons C_6H_5SeSeC_6H_5 + 6Br^- + 3I_2$$

hence 1.0 cm^3 of 0.1 *M* $Na_2S_2O_3$ reacts with 2.632 mg Se. The thiosulphate was standardised by Analar KIO_3.

IR spectra

The spectra of the compounds were recorded as Nujol mulls between polythene sheets using a Fourier spectrophotometer F.S. 720 (R.I.I.C.) over the range 400—40 cm^{-1}.

Raman spectra

These were recorded on a Cary 81 spectrometer with an exciting laser line 6328 Å.

Conductivity measurements

These were made on 10^{-3} M solutions of the compounds in dry *N,N'*-dimethylformamide at 20°C using a Mullard Conductivity bridge type E7566/3.

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