intense Raman peak is observed at 249 cm^{-1}. The higher frequency peak is readily assigned to ν_2 based on the relative intensity of this absorption and the observation of a strong Raman band. The lower frequency is not observed in the Raman spectrum and is assigned to the asymmetric mode ν_4. The observed frequencies may be compared with those for dimethylselenium dichloride [280 (m) cm^{-1}, sym Cl–Se–Cl; 244 (s) cm^{-1}, asym Cl–Se–Cl (benzene)[29–31]] which is known to contain a linear Cl–Se–Cl group.[32]

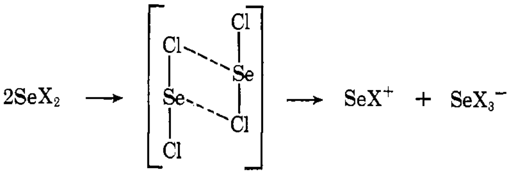
A switch in the highest frequency SeX_2 (X = Cl, Br) mode is seen in both $(CH_3)_2SeX_2$ and SeX_2tmtu molecules. A similar effect has also been observed in dimethyltellurium dihalides.[28]

The substantial shift in selenium(II) halide stretching frequencies in going from the free molecules to the tmtu adducts is similar to the shift which occurs when organotellurium trihalides form tmtu complexes.[1] In both instances bent MX_2 groups of relatively high bond order (~1) are converted to linear groups of low[33,34] bond order.

The Se–S absorptions for the selenium dihalide–tetramethylthiourea adducts have been tentatively assigned in Table II. It is possible that the absorption at 270 cm^{-1} for $SeCl_2$tmtu could be the Se–S stretch for this compound. Assignment is difficult due to the weakness of the Se–S peak, the occurrence of a number of weak ligand absorptions, and the possibility that the Se–S absorption is coincident with the symmetric Se–Cl stretch.

The low solubility and/or reactivity of the selenium dihalide–tetramethylthiourea adducts in common organic solvents precluded obtaining complete solution ir spectral data. Selenium–halogen absorptions (usually strong) could be observed despite the limited solubility of the compounds and were little changed from those seen in the solid state. Evidently the limited association which occurs in the solid state is not sufficient to affect measurably the position of the selenium–halogen frequencies. However, these absorptions were much broader in the solid state, reflecting distortions and concomitant lower symmetry imposed by the molecular lattice.

The stabilization of $SeCl_2$ and $SeBr_2$ by tetramethylthiourea suggests that the instability of these molecules may arise due to polymerization in condensed phases. This could provide a facile pathway for disproportionation through an ionic process such as the one suggested below. Coordination of tmtu to selenium in an SeX_2 molecule evidently lowers the acceptor power of Se sufficiently so as to inhibit the polymerization–disproportionation process. Even after coordination by tmtu, $SeBr_2$ still displays some residual acceptor ability, evidenced by the formation of weakly linked dimers in the solid state.



$$SeX^+ + SeX_2 \longrightarrow X{-}SeSeX_2^+$$

$$XSeSeX_2^+ + SeX_3^- \longrightarrow XSeSeX + SeX_4$$

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Chalcogen Chemistry. VII. Preparation of Compounds Containing the Phenyldibromoselenate(II) Ion[1]

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Phenylselenenyl bromide displays moderate acceptor ability and reacts with alkylammonium and other large cation bromides to produce salts of the general formula $[N^{n+}][C_6H_5SeBr_2]_n$. These red-orange crystalline salts are not appreciably moisture sensitive. In contrast to the reaction of tetramethylthiourea (tmtu) with methylselenium tribromide, the reaction of tmtu with phenylselenium tribromide gives $[tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN$. Molecular weight, proton nmr, and conductivity studies support the proposed formulations for the phenyldibromoselenate(II) salts and indicate the new anion is undissociated in solution. Far-infrared spectral data are consistent with a T-shaped geometry for the phenyldibromoselenate(II) ion, with two bromines occupying the trans positions of the T. In conjunction with the above studies the phase-dependent structures of phenylselenenyl bromide and phenylselenium tribromide were investigated by a variety of techniques. Phenylselenenyl bromide is monomeric in benzene solution, but a moderate degree of association occurs in the solid state. Phenylselenium tribromide is ~80% dissociated in solution to C_6H_5SeBr and Br_2. A semiionic polymeric structure containing five-coordinate square-pyramidal selenium is proposed for solid $C_6H_5SeBr_3$.

The reaction of tetramethylthiourea with both aryl- and alkyltellurium trihalides in aprotic media leads quite straightforwardly to organotrihalo(tetramethylthiourea)tellurium(IV) complexes, presumably containing pentacoordinate tellurium.[2] However, the reaction of tmtu with CH_3SeBr_3 and CH_3SeCl_3 proceeds quite differently to yield, respectively, the novel com-

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[1] Part VI: K. J. Wynne, P. S. Pearson, M. G. Newton, and J. Golen, *Inorg. Chem.*, **11**, 1192 (1972).

[2] K. J. Wynne and P. S. Pearson, *ibid.*, **10**, 2735 (1971).

pounds dibromo(tetramethylthiourea)selenium(II) and dichloro(tetramethylthiourea)selenium(II).[1,3] These compounds may be viewed as base-"stabilized" $SeCl_2$ and $SeBr_2$ molecules, as these species have previously been known at high temperature in the gas phase,[4,5] while $SeBr_2$ has also been known in solution.[6,7] It seemed possible that we might obtain the originally sought $RSeX_3$tmtu complexes by utilizing an R group not easily displaced *via* nucleophilic attack. We therefore investigated the reaction of phenylselenium tribromide with tmtu but found that the reaction proceded in a manner different than that expected, and different from the above described reactions. The results of our investigations are reported below.

Experimental Section

General Information.—Although the compounds prepared in this study were fairly stable upon exposure to moist air, many of the starting materials were susceptible to atmospheric moisture. Therefore all preparations and handling operations were carried out in dry nitrogen filled polyethylene glove bags. Infrared, Raman, and proton nuclear magnetic resonance spectra and molecular weights were obtained in the same manner as previously reported.[1]

Chemicals.—1,1,3,3-Tetramethylthiourea and tetraalkylammonium bromides (Eastman) were used without further purification. Bis(triphenylphosphine)iminium bromide was a gift from Dr. J. K. Ruff. Reagent grade solvents were obtained and used directly after storage over Linde 5A Molecular Sieves, which had previously been heated at 300° for 24 hr *in vacuo*.

Conductivity Measurements.—Conductivity measurements were made employing a standard type conductance cell and a Model 31 conductivity bridge manufactured by Yellow Springs Instrument Co., Inc. Conductivity measurements for each compound were made on solutions in the concentration range 10^{-3}–10^{-4} *M* based on the assumed equivalent weight of the given electrolyte. For each set of data a plot was made of the calculated Λ_{eq} values *vs.* $\sqrt{c}$, where c is concentration. For electrolytes a straight line was obtained that gave, when extrapolated to $c = 0$, Λ_0, the conductance at infinite dilution. Another plot was then made of $\Lambda_0 - \Lambda_{eq}$ *vs.* $\sqrt{c}$. The slope of this straight line is characteristic of the electrolyte type in a given solvent.[8]

Phenylselenenyl Bromide and Phenylselenium Tribromide.—The direct reaction of bromine with diphenyl diselenide[9] in methylene chloride gives high yields of phenylselenium tribromide, mp 100° (lit. mp[10] 105–106°). Phenylselenium tribromide displays an appreciable vapor pressure at 25° so that solvent was removed at 0°. Phenylselenenyl bromide was then prepared by heating phenylselenium tribromide in a vacuum sublimator ($\sim 10^{-2}$ mm) at 40°. Phenylselenenyl bromide, mp 57–60° (lit.[11] 60°), sublimes slowly as dark red crystals.

Preparation of α,α′-Dithiobis(tetramethylformamidinium) Bis(phenyldibromoselenate(II))-Acetonitrile Solvate.—Phenylselenium tribromide (3.96 g, 10.0 mmol) was dissolved in 30 ml of dry acetonitrile. A separate solution of tetramethylthiourea, tmtu (1.32 g, 10.0 mmol), in 10 ml of CH_3CN was added slowly to the above dark red solution of $C_6H_5SeBr_3$ while stirring magnetically. As the last few drops of tmtu was added, the color of the reaction mixture became noticably lighter red. Allowing the final solution to stir 0.1 hr and cooling to −20° produced 3.9 g of red crystals. Evaporation to half the original volume and cooling to −20° gave another 0.4 g, mp 88–90°, yield 91.5% based on $C_6H_5SeBr_3$. *Anal.* Calcd for $Br_4C_{24}H_{37}N_5S_2Se_2$: Br, 34.11; C, 30.74; H, 3.98. Found: Br, 34.33; C, 30.86; H, 3.99.

The same product could also be obtained by reaction of $(tmtu)_2Br_2$[12,13] (2.10 g, 5.0 mmol) with C_6H_5SeBr (2.36 g, 10.0 mmol) in acetonitrile. Cooling the final reaction solution to −20° gave 3.9 g of red crystals, yield 83%. This material was formulated as $(tmtu)_2(C_6H_5SeBr_2)_2 \cdot CH_3CN$ and was recrystallized as dark red crystals from either CH_3CN or pure methylene chloride. The solid was observed to be stable toward atmospheric moisture for ~0.5 hr.

Preparation of α,α′-Dithiobis(tetramethylformamidinium) Bis(phenyldibromoselenate(II)).—It was found that gentle heating of $(tmtu)_2(C_6H_5SeBr_2)_2 \cdot CH_3CN$ at 65° for 3.0 hr under high vacuum was sufficient to remove all acetonitrile. The remaining solid appeared as pale orange flakes, mp 100–102°. *Anal.* Calcd for $Br_4C_{22}H_{34}N_4S_2Se_2$: Br, 35.67; C, 29.46; H, 3.83. Found: Br, 34.74; C, 28.49; H, 3.86.

The volatile material from the above process was collected in a −196° trap and subsequent spectroscopic analysis showed it to be pure acetonitrile. A weight loss study was conducted by heating $(tmtu)_2(C_6H_5SeBr_2)_2 \cdot CH_3CN$ (1.2 g, 1.27 mmol) at 65–70° for 2.0 hr to yield $(tmtu)_2(C_6H_5SeBr_2)_2$ (1.15 g, 1.28 mmol) and acetonitrile (0.5 g, 1.3 mmol) which was collected in a −196° trap. It was also noted during this experiment that 95% of the acetonitrile was driven off within 0.25 hr of heating time.

Preparation of Tetraethylammonium, Tetrapropylammonium, and Bis(triphenylphosphine)iminium Phenyldibromoselenate(II).—These three salts were prepared in a similar manner. The preparation of tetraethylammonium phenyldibromoselenate(II) is representative of this group and is given below. Analytical data and information on the other salts are briefly summarized.

Tetraethylammonium Phenyldibromoselenate(II).—Phenylselenenyl bromide (2.36 g, 10.0 mmol) in 20 ml of chloroform was added slowly to a solution of tetraethylammonium bromide (1.32 g, 10.0 mmol) in 30 ml of dichloromethane. The reaction solution gradually became more red as the C_6H_5SeBr solution was added. Stirring the final mixture an additional 0.1 hr and cooling to −20° produced 3.2 g of pale orange plates. Cooling the filtrate to −20° gave another 0.3 g of product, yield 89.0% based on phenylselenenyl bromide, mp 103–105°. This material could be recrystallized from methylene chloride, acetonitrile, or a 1:1 CH_2Cl_2–$CHCl_3$ solvent mixture. *Anal.* Calcd for $Br_2C_{14}H_{25}NSe$: Br, 35.84; C, 37.67; H, 5.65; N, 3.14. Found: Br, 35.97; C, 37.64; H, 5.51; N, 3.06. This solid was stable toward atmospheric moisture for ~1.0 hr.

Tetrapropylammonium Phenyldibromoselenate(II).—This compound was prepared in chloroform and crystallized *only* from a 1:1:4 benzene–toluene–chloroform solvent mixture, mp 78–81°. *Anal.* Calcd for $Br_2C_{18}H_{33}NSe$: C, 43.02; H, 6.63; N, 2.79; Br, 31.83. Found: C, 43.12; H, 6.63; N, 2.69; Br, 31.79.

Bis(triphenylphosphine)iminium Phenyldibromoselenate(II).—This compound was prepared and crystallized in chloroform, mp 180–182°, yield 91%. *Anal.* Calcd for $Br_2C_{42}H_{35}NP_2Se$: C, 59.01; H, 4.13; Br, 18.71. Found: C, 58.97; H, 3.88; Br, 18.52.

Tetrabutylammonium bromide reacted with C_6H_5SeBr in chloroform–carbon tetrachloride to give an oil which crystallized upon standing at −20° for a few weeks. The product melted at ~25° and was not investigated further. Presumably, this compound is $[(C_4H_9)_4N][C_6H_5SeBr_2]$.

Results and Discussion

Phenylselenenyl Bromide and Phenylselenium Tribromide.—Before presenting our results on the phenyldibromoselenate(II) salts it is appropriate to discuss the nature of the starting materials, as little is known about these compounds. Phenylselenium tribromide is a pinkish red crystalline compound which is rather unstable. The vapor of bromine is clearly seen over solid $C_6H_5SeBr_3$ at 25°, while cryoscopic molecular weight measurements indicate that the compound is ~80% dissociated in benzene (*ca.* 0.01–0.02 *m*) at 5° (Table I). A conductivity measurement at about

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TABLE I

MOLECULAR WEIGHT AND CONDUCTIVITY DATA FOR PHENYLSELENENYL BROMIDE, PHENYLSELENIUM TRIBROMIDE, AND DIBROMOPHENYLSELENATE(II) SALTS

Compound	Mol wt		Slope[c] of $\Lambda_0 - \Lambda_{eq}$ *vs.* $\sqrt{c}$
	Calcd	Found	
$[tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN$	937.0/4 = 234.3	259[a,b]	575
$[tmtu]_2[C_6H_5SeBr_2]_2$	896.0/3 = 298.6	279[b,d]	540
$[(C_2H_5)_4N][C_6H_5SeBr_2]$	446.0/2 = 223.0	216[b,d]	300
$\{[(C_6H_5)_3P]_2N\}[C_6H_5SeBr_2]$	854.0/2 = 427.0	415[a,b]	360
C_6H_5SeBr	235.9	271[e] (0.0220 *m*) 253[e] (0.0110 *m*) 256[e] (0.0080 *m*)	
$C_6H_5SeBr_3$	395.7/2 = 197.9	236[e] (0.023 *m*) 246[e] (0.0176 *m*) 248[e] (0.0110 *m*) 260[e] (0.0136 *m*)	14.2[f]

[a] Average of three runs. [b] In nitrobenzene. [c] In nitromethane. [d] Average of two runs. [e] In benzene. [f] Λ_{eq} at 1.62×10^{-3} *M*.

10^{-3} *M* clearly indicates the dissociation must be mainly a nonionic process, as much greater specific conductivities are observed for electrolytes at this concentration.[14] Finally the proton nmr spectrum is similar to that observed for phenylselenenyl bromide, though the ortho and meta and para multiplets are shifted slightly downfield (Table II) as one would expect.

TABLE II

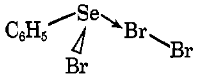
PROTON NMR DATA FOR DIPHENYL DISELENIDE, PHENYLSELENENYL BROMIDE, PHENYLSELENIUM TRIBROMIDE, AND DIBROMOPHENYLSELENATE(II) SALTS (PHENYL REGION ONLY)[a]

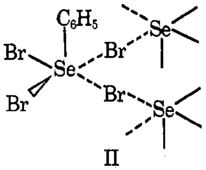
	Shift, $-\delta$	
	Ortho	Meta, para
$(C_6H_5)_2Se_2$	7.62	7.22
C_6H_5SeBr	7.84	7.40
$[(C_2H_5)_4N][C_6H_5SeBr_2]$	7.97	7.30
$[(C_3H_7)_4N][C_6H_5SeBr_2]$	7.97	7.29
$C_6H_5SeBr_3$	7.91	7.45

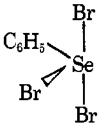
[a] In CH_2Cl_2 *vs.* internal TMS.

The above results suggest that phenylselenium tribromide is substantially dissociated in solution according to eq 1. The behavior of $C_6H_5SeBr_3$ thus appears to lie between that of $SeBr_4$ which is completely decomposed in solution[6,7] and that of diphenylselenium dibromide which is ~50% dissociated at 10^{-3} *F* in CCl_4.[15] Two formulations seem reasonable possibilities for phenylselenium tribromide, in the solid state, the donor–acceptor complex I and the semiionic polymer II. Structure I is analogous to that found for the bromine–thiophane adduct,[16] while II, which contains square-pyramidal selenium(IV), is similar to that found for β-chloroethyltellurium trichloride.[17] Because maximum coordination (limited by strong trans bond lengthening of organo group(s)) generally occurs in solid selenium(IV) and tellurium(IV) halides and organohalides,[2] the molecular structure III seems unlikely.

$$C_6H_5SeBr_3 \rightleftarrows C_6H_5SeBr + Br_2 \qquad (1)$$


I


II


III

Only one high-frequency Se–Br absorption should occur for I (C_1 site symmetry for Se) and III (C_s), while two are expected for II (C_s site symmetry for Se). Our far-infrared spectrum[18-20] of solid $C_6H_5SeBr_3$ (Table III) appears to be consistent with structure II, as two relatively high-frequency Se–Br frequencies are observed and are assigned to terminal $SeBr_2$ modes. This view is similar to our interpretation of the infrared spectra of methylselenium trichloride[21,22] and organotellurium tribromides.[2] Also, the terminal $SeBr_2$ frequencies in $C_6H_5SeBr_3$ are close to the symmetric and antisymmetric As–Br absorptions observed for methyldibromoarsine[23] (263 and 278 cm^{-1}, respectively). We therefore favor the semiionic structure II for $C_6H_5SeBr_3$, though our evidence is not direct and intermediate structures are possible.

Phenylselenenyl bromide is a dark red crystalline material which is best purified by sublimation at 45° (10^{-2} mm). Our molecular weight data (Table I) indicate that this compound is molecular in benzene solution. The proton nmr spectrum (Table II) shows a general downfield shift relative to diphenyl diselenide, as expected.

The infrared spectrum[17] of phenylselenenyl bromide is reported and assigned in Table III. The Se–Br stretch for C_6H_5SeBr in benzene solution is close to that observed for ν_4 in Se_2Br_2 (292 cm^{-1}),[24] but a marked decrease of *ca.* 52 cm^{-1} occurs in the Se–Br stretch for C_6H_5SeBr in going from solution to the solid state. This suggests considerable intermolecular association may occur in the solid state through bromine–selenium bridging.

Phenyldibromoselenate(II) Salts.—Phenylselenenyl bromide reacts with tetraethylammonium, tetrapropylammonium, and bis(triphenylphosphine)iminium (PPN)[25] bromide to give compounds of the general formula $[N^{n+}][C_6H_5SeBr_2]_n$, where N is a large cation. These compounds are red-orange crystalline materials which are only slightly moisture sensitive. They are soluble in a variety of polar organic solvents such as chloroform and methylene chloride and also polar donor solvents such as acetonitrile and nitromethane.

Tetramethylthiourea (tmtu) reacts with phenylselenium tribromide in acetonitrile to give red-orange crystalline $[tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN$ in high yield according to eq 2. The product may be recrystallized

$$2tmtu + 2C_6H_5SeBr_3 \longrightarrow [tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN \qquad (2)$$

unchanged out of methylene chloride. Acetonitrile may be removed quantitatively at 65° to give yellow

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TABLE III

INFRARED SPECTRAL DATA (33–600 CM^{-1}) AND ASSIGNMENTS[a]

C_6H_5SeBr			$C_6H_5SeBr_3$	$(C_6H_5)_2Se_2$		
Nujol mull	Benzene	Chloroform[b]	Nujol mull	Nujol mull	Benzene	Assignments
515 w	515 w					
462 m	462 m	470 s	461 w	464 s	468 s	Phenyl "y"[c]
					411 m	
					370 m	
306 m } br	308 m } br	308 s } br	307 s }		306 w	Phenyl "t"[c]
246 s }	297 s }	299 s }	292 s } br			Se–Br str
			256 s }	268 m		
	220 m					
				181 ms, br	210 w, br	Se–Se str
197 s	190 s	193 m	205 w			Se–Br bend
87 s			80 s			
54 m			55 m			

$[(C_2H_5)_4N][C_6H_5SeBr_2]$		$[(C_3H_7)_4N][C_6H_5SeBr_2]$		$[(C_2H_5)_4N]Br$	$[(C_2H_5)_4N]Br_3$		
Nujol mull	Chloroform[b]	Nujol mull	Raman spectrum	Nujol mull	Nujol mull	Chloroform[b]	Assignments
531 w	510 m						Phenyl "y"[c]
475 ms	470 s	470 w	474 vw				
			371 vw				
		350 w	346 vw				
311 w	308 m	309 wm	311 vw				Phenyl "t"[c]
271 m			278 w				
248 m	222	221 m	218 w	224 w	230 w		Alkylammonium cation
	213 w						
	188 ms		164 sh, vw			197 s	Br–Se–Br or Br_3 asym str
141 s, br		150 s, br			180 s		
	134 wm		157 vs			155 m	Br–Se–Br or Br_3 sym str
			119 sh, w				
82 m		82 s	98 sh, w				Br–Se–Br bend
58 m		33–50 s	77 m	72 s, br			Lattice modes

$[tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN$		$[tmtu]_2[C_6H_5SeBr_2]_2$		$[tmtu]_2Br_2$	Assignments
Nujol mull	Chloroform[b]	Nujol mull	Chloroform[b]		
474 m				475 m	Phenyl "y"[c] + $(tmtu)_2^{2+}$
		335 w		330 w	
306 w					Phenyl "t"[c] $(C_6H_5SeBr_2^-)$
282 w		275 w		272 w	Phenyl "t"[c] $(tmtu)_2^{2+}$
248 w		248 m			
220 m	218 s	220 m	218 m	190 m	
150 s } br	150 wm	145 s, br	155 wm, br		Br–Se–Br asym str
108 s }		(90 w, sh)?		95 w, br	Br–Se–Br sym str
61 w					
38 w					

$[PPN][C_6H_5SeBr_2]$ Nujol mull	$[PPN]Br$ Nujol mull	Assignments
560 s }	566 s }	
535 s } br	538 s } br	
498 s }	500 s }	
463 m	459 m	
447 w	448 m	
	440 s	
400 s		
332 w	337 m	
282 w	282 w	
264 s		
252 sh, m	252 m	
226 m	225 m	
206 m		
174 m		Br–Se–Br asym str
120 s, br		Br–Se–Br sym str
80 s	75 m, br	
57 s		

[a] Key: w, weak; m, medium; s, strong; br, broad; v, very; sh, shoulder. [b] Chloroform windows are 110–250, 290–360, and 430–460 cm^{-1} in the region investigated. [c] Phenyl modes; see ref 19.

$[tmtu]_2[C_6H_5SeBr_2]_2$. This nonsolvate forms an oil on attempted recrystallization (CH_2Cl_2, $CHCl_3$, CH_3NO_2) unless acetonitrile is present, in which case crystalline $[tmtu]_2[C_6H_5SeBr_2]_2 \cdot CH_3CN$ is re-formed.

The reaction of tmtu with phenylselenium tribromide stands in contrast to that of tmtu with methylselenium tribromide. In the latter case the organo group is nucleophilically displaced with reduction of Se to give dibromo(tetramethylthiourea)selenium(II). The reduction of $C_6H_5SeBr_3$ by tmtu bears a formal similarity to that of phenyltellurium trichloride by thiourea. In the latter case tellurium(II) complexes result.[26]

The reaction described by eq 2 evidently consists of

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[26] O. Foss and S. Hauge, *Acta Chem. Scand.*, **13**, 2155 (1959).

two steps. First bromine from the dissociation of $C_6H_5SeBr_3$ oxidizes tmtu to α,α'-dithiobis(tetramethylformamidinium) dibromide (eq 3). This bromide salt

$$2\text{tmtu} + \text{Br}_2 \longrightarrow [\text{tmtu}]_2\text{Br}_2 \qquad (3)$$

generated *in situ* may then react with C_6H_5SeBr according to eq 4. Supporting this view, independently

$$[\text{tmtu}]_2\text{Br}_2 + 2\text{C}_6\text{H}_5\text{SeBr} \xrightarrow{\text{CH}_3\text{CN}} [\text{tmtu}]_2[\text{C}_6\text{H}_5\text{SeBr}_2]_2\cdot\text{CH}_3\text{CN} \qquad (4)$$

prepared[12,13] $[\text{tmtu}]_2Br_2$ reacted with C_6H_5SeBr to give $[\text{tmtu}]_2[C_6H_5SeBr_2]_2\cdot CH_3CN$ in high yield according to eq 4. α,α'-Dithiobis(tetramethylformamidinium) bis(phenyldibromoselenate(II)) is quite stable to moist air but decomposes in an X-ray beam.

Evidence for the existence of the phenyldibromoselenate(II) anion in all of the above compounds comes from proton nmr, conductivity, molecular weight, and far-infrared spectral data.

Solution Studies.—Concentration-independent molecular weights were obtained in nitrobenzene (Table I) for the tetraalkylammonium, PPN^+, and $[\text{tmtu}]_2^{2+}$ salts close to that expected assuming ionization according to eq 5 (and liberation of CH_3CN for the solvate). No

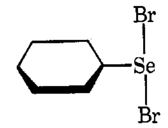
$$[\text{N}^{n+}][\text{C}_6\text{H}_5\text{SeBr}_2]_n \longrightarrow \text{N}^{n+} + n\text{C}_6\text{H}_5\text{SeBr}_2^- \qquad (5)$$

further dissociation of $C_6H_5SeBr_2^-$ to C_6H_5SeBr and Br^- apparently occurs, as this would have resulted in substantially lower apparent molecular weights. Conductivity data yielded slopes listed in Table I resulting from plots of $\Lambda_0 - \Lambda_e$ *vs.* $\sqrt{c}$[8] entirely in agreement with the appropriate electrolyte type for the respective phenyldibromoselenate(II) salts.

Integration of the proton nmr spectra was important in providing a check on the analytical data and fully supported the proposed formulas. Unchanged cation peaks were observed in all cases and served to indicate that no bromination or other reaction had occurred on the cation. Broad multiplets were observed for the ortho and for the meta and para protons in $C_6H_5SeBr_2^-$ (Table II). The multiplet due to the meta and para protons undergoes an expected upfield shift of about 0.1 ppm relative to C_6H_5SeBr. However, the ortho protons shift downfield by about 0.13 ppm relative to C_6H_5SeBr. Evidently a neighbor anisotropy deshielding effect[27,28] due to the proximity of large bromine atoms masks inductive effects.

Far-Infrared Spectral Data.—Far-infrared spectra on the phenyldibromoselenate(II) salts (Table III) were of considerable utility in helping to establish the structure of the new anion. The most salient features of these data are the extremely low Se–Br stretching frequencies. No peaks assignable to Se–Br vibrations occur above 200 cm^{-1} for the phenyldibromoselenate(II) salts in the solid state or in chloroform solution. Instead, the highest Se–Br peak ranged from 141–174 cm^{-1} in the solid state and from 150 to 188 cm^{-1} in solution. These are among the lowest Se–Br stretching frequencies yet observed. The Se–Br stretching frequencies appear generally to increase with increasing cation size. The assignment of symmetric and antisymmetric stretching modes for $C_6H_5SeBr_2^-$ has been made based on the relative intensity of these peaks and by analogy with the assignments for dimethylselenium dibromide (196 (s) cm^{-1}, antisym Br–Se–Br;[29] 167 (m) cm^{-1}, sym Br–Se–Br[30]). A Raman spectrum of tetrapropylammonium phenyldibromoselenate(II) (Table III) also supports the proposed assignment with an intense band occurring at 157 cm^{-1} due to the symmetric Br–Se–Br stretch.

The closeness of the Se–Br frequencies observed for $C_6H_5SeBr_2^-$ to those of $(CH_3)_2SeBr_2$ and $SeBr_2$tmtu[1] and to the corresponding modes in the tribromide ion[31,32] strongly suggests the existence of a linear Br–Se–Br group in salts containing phenyldibromoselenate(II). A T-shaped structure is therefore suggested for the new anion



The low selenium–bromine stretching frequencies suggest long Se–Br bonds, the presence of which may lend a certain ease of distortability to the anion. This would account for the rather wide range of Se–Br frequencies observed.

The new compounds we report are useful in providing a demonstration of the acceptor ability of arylselenenyl bromides. The $C_6H_5SeBr_2^-$ ion also possibly provides a model for intermediates involved in the electrophilic attack of selenenyl halides on olefins.[33] One of the most essential roles of selenium chemistry is in providing compounds of greater stability than that of their sulfur analogs which may serve as models for unstable intermediates in sulfur chemistry. The phenyldibromoselenate(II) ion may therefore be of use in providing a model for attack on dicoordinate sulfur.[34] The preparation of compounds containing the phenyldibromoselenate(II) ion is interesting in providing a new class of T-shaped molecules which are stable enough to allow spectroscopic study with relative ease. The results of such studies should be important in providing information concerning bonding and also the stereochemical activity of the 4s electrons.

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[29] G. C. Hayward and P. J. Hendra, *J. Chem. Soc. A*, 1760 (1969).

[30] K. J. Wynne, unpublished results.

[31] Frequencies observed for $[(C_6H_5)_4N]Br_3$ in the solid state and in chloroform solution are listed in Table III. Compare with 180 (s) and 169 cm^{-1} found previously.[32]

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