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Chalcogen Chemistry. VI. Preparation and Properties of Dichloro- and Dibromo(tetramethylthiourea)selenium(II). Preliminary Results on the Crystal and Molecular Structure of $SeBr_2tmtu$[1]

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Methylselenium trichloride and selenium tetrachloride react with tetramethylthiourea (tmtu) to give dichloro(tetramethylthiourea)selenium(II), $SeCl_2tmtu$. This compound is a moisture-sensitive yellow-orange crystalline material which is soluble in polar organic solvents. Molecular weight, proton nmr, and infrared and Raman spectral studies are consistent with the existence of T-shaped molecules in solution and in the solid state. Methyl- and ethylselenium tribromide and selenium tetrabromide react with tetramethylthiourea to give dibromo(tetramethylthiourea)selenium(II), $SeBr_2tmtu$. This red crystalline compound is perfectly stable to moist air. Preliminary X-ray crystallographic data indicate the compound consists of T-shaped $SeBr_2tmtu$ molecules with bromines in the trans positions of the T. Pertinent distances and angles are as follows: $Se–Br_1$, 2.569 (3); $Se–Br_2$, 2.620 (3); S–Se, 2.212 (4) Å; $Br_1–Se–Br_2$, 174.70 (10); $Br_1–Se–S$, 93.71; $Br_2–Se–S$, 91.31 (13)°. Loosely held dimers are formed due to a Se–Br contact trans to sulfur at 3.34 Å. The far-infrared and Raman spectra of $SeBr_2tmtu$ are discussed in light of the structural data. Our results indicate that $SeCl_2$ and $SeBr_2$ are base "stabilized" by the formation of tetramethylthiourea adducts.

Selenium(II) chloride and bromide have previously been known at high temperatures in the gas phase,[2,3] while $SeBr_2$ has also been identified in solution.[4,5] While investigating the acceptor behavior of organoselenium trihalides, we have discovered a synthetic route which results in the base stabilization of $SeCl_2$[6] and $SeBr_2$[7] as crystalline tetramethylthiourea (tmtu) adducts. We report below the synthesis and properties of these adducts as well as preliminary X-ray crystallographic results concerning the structure of dibromo(tetramethylthiourea)selenium(II).

Experimental Section

General Information.—The atmospheric moisture sensitivity of most of the compounds involved in this study necessitated handling these materials *in vacuo* or in dry nitrogen-filled glove bags. Infrared and proton nuclear magnetic resonance spectra and molecular weight data were obtained as reported previously.[1] Proton chemical shifts are all measured *vs.* internal tetramethylsilane.

The Raman spectra were measured on a Spex Ramalog double monochromator (Model 1401) using a Carson (Model 201) krypton laser. The 6471-Å (70-mW) excitation line was used for $SeBr_2tmtu$ while the 5682-Å line (30-mW) was used for $SeCl_2tmtu$. Spectra were obtained rapidly to avoid spurious peaks due to decomposition products. An ITT Model FW-130 PM tube with S-20 response using dc amplification was used. Scanning speeds and slit widths gave a resolution of about 5 cm^{-1}. Calibration was accomplished using carbon tetrachloride. Samples were studied in sealed glass capillaries.

Chemicals.—Reagent grade chlorine, bromine, and 1,1,3,3-tetramethylthiourea (Eastman) were used without further purification. Methylene chloride was dried by storing over Linde 5A Molecular Sieves and used directly. Methylselenium trichloride was prepared according to the literature method.[8] Methyl- and ethylselenium tribromide[9] (mp 74–76°) were prepared in an analogous manner. Selenium tetrachloride and tetrabromide were also prepared by standard methods in the literature.[10]

Preparation of Dichloro(tetramethylthiourea)selenium(II).—A solution of tmtu (1.5 g, 11.3 mmol) in 50 ml of CH_2Cl_2 was added slowly to a solution of methylselenium trichloride (1.84 g, 9.15 mmol) also in 50 ml of CH_2Cl_2 with rapid magnetic stirring. The reaction mixture became cloudy when approximately 20% of the tmtu had been added, but the final solution was a clear, bright yellow. The solution was evaporated to one-fifth the original volume and cooled to −20°. Filtration yielded 1.3 g of yellow solid, yield 50%. Recrystallization from chloroform or methylene chloride gave yellow-orange moisture-sensitive crystals, mp 137–139°. *Anal.* Calcd for $C_5Cl_2H_{12}N_2SSe$: C, 21.17; H, 4.29; Cl, 25.14; Se, 27.99. Found: C, 21.00; H, 4.21; Cl, 26.44; Se, 27.05. This compound is very moisture sensitive and solutions tend to decompose, especially with donor solvents and/or in the presence of excess tmtu.

The same product was also obtained by adding tmtu (4.0 g, 30.0 mmol) in 25.0 ml of dichloromethane to a stirred suspension of $SeCl_4$ (10.0 mmol) in 50.0 ml of CH_2Cl_2. However, the precipitate obtained from evaporation and cooling was always contaminated with a certain amount of the disulfide salt $(tmtu)_2Cl_2$.[11,12] This material, which is very soluble in all common organic solvents, could usually be separated from the $SeCl_2tmtu$ complex by recrystallizing twice from methylene chloride (3.0 g/100 ml).

Preparation of "Se_5S_3."—When solutions of $SeCl_2tmtu$ were allowed to stand for several hours, a red crystalline precipitate formed. The rate of formation was observed to be faster in more polar solvents and in the presence of excess tmtu. It was noted that exposing a solution to the atmosphere induced very rapid formation of the red material within a period of 15–30 minutes. This material was collected and pumped to dryness under high vacuum. The solid was insoluble in most organic solvents and water. A very slight degree of solubility was noted in CS_2. The crude and recrystallized (CS_2) material melted with decomposition at 105–110°. An elemental analysis showed essentially no carbon, hydrogen, chlorine, or nitrogen, but a sulfur analysis gave 18.63%. A proton nmr spectrum in CS_2 showed no discernible peaks, while the solid-state ir spectrum (35–4000 cm^{-1}) did not reveal any detectable absorptions. Based on the limited analytical data, we assumed this decomposition product of $SeCl_2tmtu$ to be "Se_5S_3" (calcd S = 19.55%). The product of this peculiar reaction has not been investigated further and it cannot be ascertained with presently available data whether it is a pure compound. When a suspension of this material was chlorinated in benzene, a solid precipitated. This material was moisture sensitive and sublimed at 175–200° in a sealed tube suggesting the product was $SeCl_4$.

Preparation of Dibromo(tetramethylthiourea)selenium(II).—Methylselenium tribromide (4.52 g, 13.5 mmol) was suspended

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[11] O. Foss and W. Johanessen, *Acta Chem. Scand.*, **15**, 1940 (1961).

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in 200 ml of CH_2Cl_2 with rapid magnetic stirring. A 50-ml CH_2Cl_2 solution of tmtu (1.83 g, 13.8 mmol) was then slowly added to the CH_3SeBr_3 suspension. The initial deep red CH_3SeBr_3 solution showed no appreciable color change until about one-third of the tmtu solution had been added at which time the solution became cloudy yellow. When half of the tmtu solution had been added, the reaction mixture started to turn red. The final solution was a clear reddish orange. After filtering a trace of insoluble material from the reaction flask, the pale reddish orange filtrate was cooled to −20°. Filtration gave 2.84 g of reddish orange crystals, mp 185–187°. Evaporation and cooling produced an additional 1.0 g of product, net yield 78%. *Anal.* Calcd for $Br_2C_5H_{12}N_2SSe$: Br, 43.08; C, 16.17; N, 7.55; H, 3.26; Se, 21.28. Found: Br, 42.82; C, 16.34; N, 7.71; H, 3.20; Se, 21.36. Although not appreciably soluble in any common solvent including water, this compound could be recrystallized from CH_2Cl_2 (0.7 g/100 ml) or a 1:1 CH_3NO_2–CH_2Cl_2 solvent mixture.

The same product was obtained using ethylselenium tribromide as the starting material. The compound was observed to be stable for months toward air oxidation and moisture, both in the solid state and in solution.

We were also able to prepare $SeBr_2$tmtu from the reaction of selenium tetrabromide with tmtu. Solid selenium tetrabromide (2.0 g, 5.0 mmol) was added in ∼0.1-g portions to a solution of tmtu (2.0 g, 15.0 mmol) in 200 ml of CH_2Cl_2 with rapid magnetic stirring. The final light red reaction mixture was stirred an additional 0.5 hr, filtered, and cooled to −20°. Slightly soluble $SeBr_2$tmtu precipitated nicely, leaving the very soluble salt $(tmtu)_2Br_2$;[12,13] yield 1.40 g, 75%.

$SeBr_2$tmtu was found to exhibit a density of 2.22 ± 0.05 g/ml by flotation in a CH_2Br_2–C_6H_5 solvent mixture. Dibromo(tetramethylthiourea)selenium(II) crystallizes in the triclinic system with the following unit cell dimensions: *a*, 7.840; *b*, 8.663; *c*, 9.503 Å; *α*, 108.14; *β*, 109.27; *γ*, 93.69°.

Results and Discussion

Methylselenium trichloride and methyl- and ethylselenium tribromide react with tetramethylthiourea in polar aprotic media to yield crystalline dihalo(tetramethylthiourea)selenium(II) complexes according to eq 1. Support for this equation came from proton

$$RSeX_3 + \text{tmtu} \longrightarrow RX + SeX_2\text{tmtu} \qquad (1)$$

nuclear magnetic resonance data which showed the presence of alkyl halide in the reaction solutions. Other peaks are seen due to intermediates and decomposition products and are discussed in more detail below.

Dichloro(tetramethylthiourea)selenium(II) is an orange-yellow, crystalline, moisture-sensitive substance. It is soluble in polar organic solvents such as methylene chloride, chloroform, and nitrobenzene but insoluble in nonpolar organic solvents. Dibromo(tetramethylthiourea)selenium(II) is a red-orange crystalline material which in distinct contrast to $SeCl_2$tmtu is stable toward atmospheric moisture. $SeBr_2$tmtu is markedly less soluble in polar organic solvents than its chlorine analog but may be recrystallized from methylene chloride, nitromethane, or a mixture of these two solvents.

An alternate synthetic route to the dihalo(tetramethylthiourea) complexes was found in the reaction of the respective selenium tetrahalide with tmtu according to eq 2. Proton nmr spectra of reaction solu-

$$SeX_4 + 3\text{tmtu} \longrightarrow (\text{tmtu})_2X_2 + SeX_2\text{tmtu} \qquad (2)$$

tions supported the proposed equation as separate peaks were seen for $(\text{tmtu})_2^{2+}$ and SeX_2tmtu in the required 2:1 ratio. This reaction is formally similar to that between acidified (HX) methanolic tellurium dioxide solutions and tmtu which gives TeX_2tmtu complexes.[11,14,15]

The reaction of $SeBr_4$ with tmtu is the preferred route for the preparation of $SeBr_2$tmtu due to the high yield and the ready accessibility of $SeBr_4$. Although $SeCl_4$ is more readily accessible than CH_3SeCl_3, the latter gives a cleaner reaction with tmtu and does not necessitate the separation of $SeCl_2$tmtu from large quantities of $(\text{tmtu})_2Cl_2$.

Molecular Weight Data.—An average molecular weight of 255 was determined from three cryoscopic determinations in nitrobenzene for $SeCl_2$tmtu; this is close to the calculated formula weight 282.1. These data suggest that the compound is essentially monomeric in solution. It was noted that drastically lower molecular weights were obtained for solutions that were more than *ca.* 1 hr old, indicating that moderately rapid decomposition was taking place. Although we established from our nmr studies that no measurable decomposition of $SeCl_2$tmtu occurred in nitrobenzene during the period of time normally required for a molecular weight determination, it is conceivable that a small amount of decomposition might have gone undetected and could account for the slightly low molecular weights observed. The evidence of extensive decomposition was the deposition of red crystals of approximate empirical formula Se_5S_3. This behavior was also observed in chloroform and methylene chloride but at a much slower rate than in nitrobenzene.

We were not able to obtain satisfactory molecular weight data for $SeBr_2$tmtu due to the low solubility of this compound in the cryoscopic solvents benzene, sulfolane, and nitrobenzene.

Proton Nuclear Magnetic Resonance Data.—The methyl groups in 1,1,3,3-tetramethylthiourea are equivalent on the nmr time scale with chemical shifts of δ −3.02 in nitrobenzene and δ −3.04 in chloroform. For $SeCl_2$tmtu downfield shifts to δ −3.29 in $CHCl_3$, δ −3.46 in $C_6H_5NO_2$, and δ −3.35 in CH_2Cl_2 were observed, while $SeBr_2$tmtu displayed shifts of δ −3.40 in CH_2Cl_2 and δ −3.57 in nitrobenzene. The shift to low field for the tmtu resonance in the complexes is as expected due to simple inductive effects. The magnitude of the shift (*ca.* 0.3–0.4 ppm) downfield for $SeCl_2$tmtu is consistent with our molecular weight results on this compound and gives further evidence that the complex is an undissociated monomer in solution. It is interesting that the ^{1}H shift for $SeBr_2$tmtu is further downfield than that for $SeCl_2$tmtu in both methylene chloride and nitrobenzene. This strongly suggests that $SeBr_2$tmtu is also undissociated in solution.

Addition of tmtu to freshly prepared solutions of $SeCl_2$tmtu and $SeBr_2$tmtu resulted in the observation of a sharp peak of intermediate chemical shift. Evidently rapid exchange of coordinated and bulk tmtu occurs on the nmr time scale. Solutions of $SeBr_2$tmtu were stable indefinitely in the presence of tmtu in moderate excess, while the presence of excess tmtu caused rapid decomposition of $SeCl_2$tmtu. This was indicated by the appearance of a peak at δ −3.47 (CH_2Cl_2) due to $(\text{tmtu})_2Cl_2$ and also by the precipitation of Se_5S_3.

After the reaction of CH_3SeBr_3 with tmtu, only CH_3Br and $SeBr_2$tmtu peaks were observed in the expected integral ratio (eq 1). However, as mentioned

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(15) O. Foss, S. Husbye, and K. Maroy, *ibid.*, **17**, 1806 (1963).

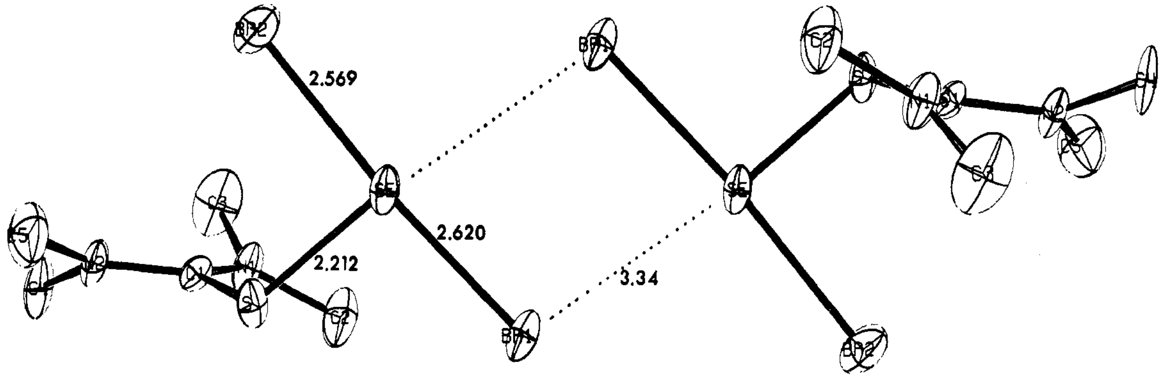

Figure 1.—The molecular structure of $SeBr_2$tmtu.

above, $SeCl_2$tmtu decomposes rapidly in the presence of tmtu. This parasitic reaction is fast enough to compete successfully with the redox reaction and leads to the presence of peaks due not only to CH_3Cl and $SeCl_2$tmtu but also to $(tmtu)_2Cl_2$. From the integration of the ^1H nmr spectrum, it appeared in one reaction that about 66% of the tmtu initially present was used up in the decomposition reaction.

The isolation of selenium(II)-containing complexes from the reaction of methylselenium trichloride and tribromide and ethylselenium tribromide with tmtu stands in contrast to the stability of organotrihalo(tetramethylthiourea)tellurium(IV) complexes.[1,16] However, some evidence was obtained for the transient intermediacy of a Se^{IV}–tmtu complex. Yellow precipitates formed then redissolved in the reaction of CH_3SeCl_3 and CH_3SeBr_3 with tmtu. It is possible that these precipitates were CH_3SeX_3tmtu complexes which rapidly underwent decomposition.

Proton nmr spectra on freshly prepared CH_3SeCl_3–tmtu solutions (CD_2Cl_2) containing excess CH_3SeCl_3 gave additional evidence concerning the intermediacy of a Se^{IV}–tmtu complex. In addition to CH_3Cl, $SeCl_2$tmtu, and $(tmtu)_2Cl_2$ peaks, absorptions of varying intensity were seen at *ca.* δ −4.0 and −3.6. The latter absorption could be due to tmtu bound to CH_3SeCl_3, as tmtu in CH_3TeCl_3tmtu exhibits a proton resonance of δ −3.50.[1] The somewhat broad peak at $\delta \sim -4.0$ varied in position and was assigned to CH_3–Se. The position (compare with CH_3SeCl_3, δ −4.36[8]) and breadth of this peak may be due to a CH_3SeCl_3–tmtu complex undergoing rapid exchange with excess CH_3SeCl_3 present in these solutions. Similar results were observed for a CH_3SeBr_3–tmtu solution, although the reaction was much faster and intermediate absorptions were quite weak. These nmr spectra suggested that the final products were generated by nucleophilic attack of Cl^- or Br^- on the alkyl group of $RSeX_3$ rather than attack on carbon by tmtu. This was evident by the fact no peaks attributable to an isothiouronium salt, RS–C–$[N(CH_3)_2]_2{}^+X^-$,[17] were apparent in any of our proton nmr spectra. In summary, our nmr data and other observations are consistent with the scheme outlined below (eq 3–5) for the generation of the dihalo(tetramethylthiourea)selenium(II) complexes.

$$RSeX_3 + \text{tmtu} \xrightarrow{\text{fast}} RSeX_3\text{tmtu} \tag{3}$$

$$RSeX_3\text{tmtu} \rightleftharpoons RSeX_2\text{tmtu}^+ + X^- \tag{4}$$

$$RSeX_2\text{tmtu}^+ + X^- \longrightarrow RX + SeX_2\text{tmtu} \tag{5}$$

We note in passing that the $(tmtu)_2X_2$ (X = Cl, Br) salts showed a chemical shift markedly dependent on X. For $(tmtu)_2Cl_2$ in methylene chloride, a single absorption occurred at δ −3.42 and for $(tmtu)_2Br_2$ this resonance was observed at δ −3.12. A chemical shift difference was also apparent in nitrobenzene: $(tmtu)_2Cl_2$, δ −3.57; $(tmtu)_2Br_2$, δ −3.26. Solvent dependence of the chemical shift was not unexpected, but the marked anion dependence was surprising. We have no ready explanation for this observation except to speculate that it may be due to differing degrees of ion pairing between the two salts.

Preliminary Results on the Crystal and Molecular Structure of $SeBr_2$tmtu.—Before discussing the far-infrared and Raman data on the dihalo(tetramethylthiourea)selenium(II) adducts it is appropriate to discuss the preliminary results of an X-ray crystallographic structural determination on $SeBr_2$tmtu.[18] The compound crystallizes in space group $P\bar{1}$ with two molecules per unit cell. The structure of $SeBr_2$tmtu is shown in Figure 1, while pertinent bond distances may be found in Table I.

TABLE I

BOND DISTANCES AND BOND ANGLES FOR $SeBr_2$tmtu

Atoms	Distance, Å	Atoms	Angle, deg
Br_1–Se	2.569 (3)	Br_1–Se–Br_2	174.70 (10)
Br_2–Se	2.620 (3)	Br_1–Se–S	93.71 (14)
S–Se	2.212 (4)	Br_2–Se–S	91.31 (13)
C_1–S	1.751 (15)	Se–S–C_1	102.3 (5)
C_1–N_2	1.340 (20)	N_1–C_1–N_2	119.7 (13)
C_1–N_1	1.340 (20)		

The crystal consists of T-shaped $SeBr_2$tmtu molecules with two bromine atoms occupying the trans positions of the T. The molecules are loosely joined into dimers by intermolecular selenium–bromine contacts (3.34 Å) trans to sulfur which are considerably shorter than the sum of the van der Waals radii (3.95 Å). No other Se atom distances are sufficiently close to warrant mention at this stage. The short Se–Br distances (2.569, 2.620 Å) are not exactly equal but are close to being so. The bromine which is involved in weak bridging exhibits the longer of the two trans Se–Br distances. If one considers only the closest (<3 Å) bonded atoms, Se can be considered to be three-coordinate. Supporting this view are the infrared spectral data discussed below which are readily inter-

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[16] K. J. Wynne and P. S. Pearson, *J. Chem. Soc. D*, 556 (1970).

[17] H. Lecher and C. Heuck, *Justus Liebigs Ann. Chem.*, **438**, 169 (1924).

[18] A full detailed account of the structural determination which was carried out with the aid of a Nonius diffractometer will appear separately in due course.

TABLE II[a]

INFRARED AND RAMAN SPECTRAL DATA (50–600 CM^{-1})

Dibromotetramethylthiourea)selenium(II)				
Ir				
Nujol mull	CH_2Cl_2[b]	Raman (solid)	C_{2v}	Type
477 w				
455 w		456 vw		
				tmtu peaks
410 wm		402 w		
		392 vw		
370 w		371 w		
323 w				
240 wm, sh			$\nu_1(A_1)$	Se–S str
184 s	178 m		$\nu_4(B_1)$	Asym Br–Se–Br str
150 s, sh	155 s	159 m	$\nu_2(A_1)$	Sym Br–Se–Br str
100 m, br		112 s	$\nu_3(A_1)$	Br–Se–Br def
		77 m		

Dichloro(tetramethylthiourea)selenium(II)					
Ir					
Nujol mull	Chloroform[c]	Methylene chloride[b]	Raman (solid)	C_{2v}	Type
415 w			484 vvw		
			450 vw		
			406 m		tmtu peaks
			387 w		
			369 wm		
325 w					
270 m, sh		270 w	266 w		
252 m, s	248 w	248 w	249 s	$\nu_2(A_1)$	Sym Cl–Se–Cl str
	233 w, sh			$\nu_1(A_1)$	Se–S str
210 s	205 s	205 s		$\nu_4(B_1)$	Asym Cl–Se–Cl str
170 w, sh	165 w	170 w	156 w, sh		
138 m			138 m	$\nu_3(A_1)$	C–Se–Cl def
128 m, sh					

[a] Key: w, weak; m, medium; s, strong; br, broad; v, very; sh, shoulder. [b] CH_2Cl_2 windows are 150–275, 300–440, and 480–600 cm^{-1} in the region investigated. [c] Chloroform windows are 110–250, 290–360, and 430–460 cm^{-1} in the region investigated.

pretable based on three-coordinate Se. If the Se–Br contact trans to sulfur is included, then the coordination about Se is distorted square planar. The structure is similar to that found for $TeBr_2$tmtu[19] though the association into dimers appears to be stronger in $TeBr_2$tmtu.

Only bond distances for tetravalent selenium systems containing a linear Br–Se–Br grouping have been previously reported.[20] As would be expected, the average Se–Br distance in $SeBr_2$tmtu (2.59 Å) is somewhat longer than the corresponding value for selenium(IV) systems (*ca.* 2.54 Å[20]). The bromines in the Br–Se–Br group are bent away from sulfur, the included angle being the smallest yet observed (174.7°) for a nominally "linear" Br–Se–Br group.

It is interesting that, despite the Se–Br interaction trans to sulfur, the S–Se bond distance is precisely that expected for a normal covalent S–Se bond (2.21 Å).

Unfortunately, only the Se–Br bond distance (2.32 Å) is known for the free $SeBr_2$ molecule.[21] It seems likely however, especially in view of the bond distance, that the $SeBr_2$ molecule is bent with a Br–Se–Br angle close to 100°. Assuming this reasonable value, it is clear that, like many acceptors such as BCl_3, $SnCl_4$, etc., the $SeBr_2$ molecule undergoes a substantial reorganization upon adduct formation with the Br–Se–Br angle opening by more than 70°. The change in Se–Br bonding parallels that which occurs in going from selenium diselenocyanate to the "triselenocyanate" or cyanobis(selencyanato)selenate(II) ion.[22]

Infrared and Raman Spectral Data.—The ir spectral data for $SeCl_2$tmtu and $SeBr_2$tmtu are presented in Table II. The only infrared absorption of substantial interest for $SeCl_2$tmtu and $SeBr_2$tmtu in the rock salt region is that due to the N–C–N antisymmetric stretch. This occurs at 1535 cm^{-1} for tmtu in Nujol but is shifted to high frequency (1585 cm^{-1}, $SeCl_2$tmtu; 1590 cm^{-1}, $SeBr_2$tmtu) in the adducts. This shift is a useful test for tmtu coordination.[1,16]

The substantial reorganization which occurs in going from the free selenium dihalides to the adducts is clearly reflected in the low-frequency infrared and Raman spectral data (Table II). No ir or Raman spectral data are available for the $SeBr_2$ molecule, but it is likely[5] that the highest stretching frequency is near 290 cm^{-1}, as the highest Se–Br stretching frequencies for the closely related Se_2Br_2[23,24] (ν_4 292 cm^{-1}) and C_6H_5SeBr[25] (297 cm^{-1} in benzene) molecules are close to this value. In contrast the highest Se–Br stretching frequencies for $SeBr_2$tmtu are found at 184 and 150 cm^{-1} in the infrared spectrum and at 159 cm^{-1} in the Raman spectrum. The 184-cm^{-1} absorption for $SeBr_2$tmtu is assigned to $\nu_4(B_1)$ based on the absence of this absorption in the Raman spectrum. The strong Raman peak at 159 cm^{-1} and the ir absorption at 150 cm^{-1} are then assigned to $\nu_2(A_1)$.[26,27] These assignments are similar to the corresponding modes in dimethylselenium dibromide (196 (s) cm^{-1}, asym Br–Se–Br;[28] 167 (m) cm^{-1}, sym Br–Se–Br[29]). The Se–Br frequencies for $SeBr_2$tmtu are somewhat lower than those for dimethylselenium dibromide as the latter compound probably has shorter Se–Br distances like its aryl analogs.[20]

For $SeCl_2$[2] the symmetric (ν_1) and asymmetric (ν_3) stretching frequencies occur at 415 and 377 cm^{-1}. A drastic decrease in Se–Cl stretching frequencies occurs upon coordination of tmtu to $SeCl_2$. In $SeCl_2$tmtu Se–Cl bands (ir) are seen at 248 and 205 cm^{-1}, while an

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[22] O. Foss and S. Hauge, *Acta Chem. Scand.*, **17**, 1807 (1963); O. Foss, *Pure Appl. Chem.*, **24**, 31 (1970); S. Hauge, *Acta Chem. Scand.*, **25**, 3081, 3103 (1971).

[23] H. Stammreich and R. Forneris, *Spectrochim. Acta*, **8**, 46 (1956).

[24] Note with reference to the argument presented above concerning the highest stretching frequency in $SeBr_2$ that ν_1 for $SeCl_2$ (415 cm^{-1})[2] is close to ν_4 for Se_2Cl_2[23] (418 cm^{-1}).

[25] K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **11**, 1196 (1972).

[26] Based on the known crystal and molecular structure, assignments have been made assuming C_{2v} site symmetry around selenium as in BrF_3.[27]

[27] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, **54**, 344 (1971).

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

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

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]

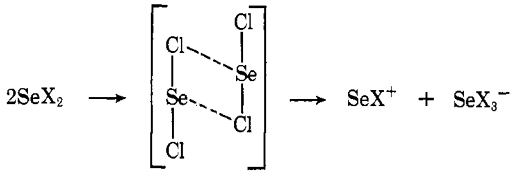
A switch in the highest frequency SeX_2 (X = Cl, Br) mode is seen in both $(CH_3)_2SeX_2$ and SeX_2tmtu molecules. A similar effect has also been observed in dimethyltellurium dihalides.[28]

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.



$$SeX^+ + SeX_2 \longrightarrow X\text{–}SeSeX_2^+$$
$$XSeSeX_2^+ + SeX_3^- \longrightarrow XSeSeX + SeX_4$$

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(30) Note values previously reported[31] are incorrect.

(31) K. J. Wynne and J. W. George, *J. Amer. Chem. Soc.*, **87**, 4750 (1965).

(32) A. W. Cordes, "Symposium on Stereochemistry of Inorganic Compounds," Banff, Alberta, Canada, 1968.

(33) Simple approximate molecular orbital theory[34] predicts a bond order of ~0.5.

(34) R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962).

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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).