Lewis-Base Behavior of Selenium(IV) Halides. II. Methylselenium Trichloride and Trimethylselenium Chloride[1]

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Abstract: Crystalline methylselenium trichloride was prepared by the chlorination of methylene chloride solutions of dimethyl diselenide. Interestingly, molecular weight data suggest methylselenium trichloride exists mainly as a dimeric species in methylene chloride. Infrared and proton magnetic resonance spectra are consistent with this view. Unlike the di- and monochlorides methylselenium trichloride did not form an isolable adduct with boron trichloride. Trimethylselenium chloride was prepared from methyl chloride and dimethyl selenide. The infrared spectrum supports the ionic formulation $(CH_3)_3Se^+Cl^-$ for the solid. Trimethylselenium chloride forms a 1:1 adduct with boron trichloride. The infrared spectrum may be readily interpreted in terms of a trimethylselenium(IV) tetrachloroborate formulation. Proton magnetic resonance data for compounds prepared above and related compounds are presented and discussed.

We have previously reported the preparation of dimethylselenium dihalides and their boron trihalide adducts.[1] The latter were shown to be monohalogenodimethylselenium(IV) tetrahaloborates. To extend our investigation of the Lewis-base properties of methylselenium halides, we have prepared methylselenium trichloride and trimethylselenium chloride and have examined their behavior with boron trichloride. Although CH_3SeCl_3 and $(CH_3)_3SeCl$ have been cited by other workers in discussions of nomenclature[3] and as examples of selenium compound class types,[3,4] we have been unable to find any specific report of their preparation, isolation, or properties. The results of our work are reported below.

Experimental Section

General. All experiments described below were carried out in a nitrogen-filled glove bag or standard vacuum line. When handling volatile toxic materials, the glove bag was vented to a fume hood.

Infrared spectra were obtained using a Perkin-Elmer Model 21 equipped with NaCl or CsBr optics, Model 237B, Infracord Model 137, and Beckman IR-11 spectrophotometers.[5] Samples were prepared as Nujol mulls, except for the trimethylselenium chloride-boron trichloride adduct, which was prepared by solvent evaporation. Polyethylene (0.5 mm) or KBr (0.5 mm) liquid cells were used for CH_3SeCl_3 solution spectra (concentration 47 mg/ml). Nuclear magnetic resonance spectra were obtained using a Varian A-60 nmr spectrometer.

Molecular Weights. Molecular weight measurements on CH_3SeCl_3 were attempted using a Mechrolab Model 301 A vapor pressure osmometer. The rapid reaction of halocarbon solutions of CH_3SeCl_3 with the stainless steel parts of the osmometer rendered this method useless. After considerable experimentation, reproducible molecular weight data were finally collected by vapor pressure lowering in methylene chloride. The limited solubility, sensitivity to moisture, and instability of methylselenium trichloride solutions in methylene chloride made the use of a specially designed apparatus necessary. The sample chamber consisted of a 25-ml flat-bottom flask equipped with a break-seal, an 18/9 ball joint constricted 1 in. below the ball, and a small Teflon stir bar. Methylselenium trichloride was weighed in this vessel, which was then attached to the vacuum line, evacuated, and sealed at the constriction. The sample container was then sealed to one side of a differential manometer similar to that used by Parry.[6] After rupturing the break-seal a weighed and nonweighed amount of CH_2Cl_2 was distilled into the reference and sample chambers, respectively. The system was warmed to ambient temperature (28° or above) and the sample dissolved with the aid of a magnetic stirrer. Sample and reference containers were immersed in a vigorously stirred 2-l. dewar of water maintained at 26.00 ± 0.02°. No differential pressure was detected when the system was checked with pure solvent *vs.* pure solvent. A wide-bore (13-mm i.d.) manometer was used. Mercury heights (±0.05 mm) were measured with a Gaertner M-911 cathetometer. All-glass and Teflon vacuum stopcocks fitted with Viton A "O" rings were used throughout this system.

Chemicals. Boron trichloride (Matheson CP) was distilled *in vacuo* and the center fraction used. Chlorine and methyl chloride (both Matheson CP) were used without further purification. The infrared spectrum and vapor tension of volatile materials established their purity. Dimethyl selenide and dimethyl diselenide were prepared by the method of Bird and Challanger.[7] By weighing 10 ml of the pure liquid, the density of $(CH_3)_2Se_2$ was determined to be 2.1 g/ml. Methylene chloride was refluxed over anhydrous phosphorus pentoxide for 1-2 hr and then fractionally distilled.

Methylselenium Trichloride. Dimethyl diselenide (26.4 g, 0.14 mole) was dissolved in 900 ml of cooled (5°) CH_2Cl_2. Chlorine was rapidly passed through the solution. During the 40-min reaction time the cold solvent gradually warmed to 35° due to the exothermic reaction. The initially light red solution turned dark red, lighter red, then abruptly light yellow when the reaction was complete. A small amount of insoluble material was filtered (2 g), and the filtrate was cooled to −20° for 24 hr. Filtration yielded 38.7 g of pale yellow, crystalline CH_3SeCl_3. Concentrating and cooling the filtrate gave 4.9 g of additional product, over-all yield 83%. *Anal.* Calcd for CH_3SeCl_3: C, 6.00; H, 1.50; Se, 39.4; Cl, 53.09. Found: C, 6.20; H, 1.45; Se, 39.1; Cl, 53.2.

Methylselenium trichloride as prepared above from dilute solution was moderately soluble (*ca.* 6 g/100 ml at 25°) in CH_2Cl_2 forming light yellow solutions. Cooling these solutions to −20° produced 4.9 g of recrystallized CH_3SeCl_3/100 ml of CH_2Cl_2.

Chlorination of more concentrated solutions of dimethyl diselenide (*e.g.*, 21 g/100 ml of CH_2Cl_2) caused the precipitation of a relatively CH_2Cl_2-insoluble form of CH_3SeCl_3. When this solid was added to CH_2Cl_2 very little was seen to dissolve, a slurry forming after the addition of only a small amount. A large excess of solute was added, the mixture filtered, and the filtrate cooled to

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[1] Part I: K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, **87**, 4750 (1965).

[2] (a) University of Georgia; (b) University of Massachusetts.

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[4] H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).

[5] The authors are grateful to Professor Herbert Strauss, University of California, Berkeley, for the use of the Beckman IR-11.

[6] R. W. Parry, G. Kodama, and D. R. Schultz, *J. Am. Chem. Soc.*, **80**, 24 (1958).

[7] M. B. Bird and F. Challanger, *J. Chem. Soc.*, 570 (1942).

$-20°$. Only 0.4 g of CH_3SeCl_3/100 ml of CH_2Cl_2 crystallized. The selenium analysis, infrared spectrum, and thermal behavior of the insoluble form were indistinguishable from the soluble form. This problem was not investigated further. We report results obtained exclusively from experiments utilizing recrystallized CH_3SeCl_3 prepared from dilute diselenide solution.

Attempted Reaction of Methylselenium Trichloride with Boron Trichloride. (1) Boron trichloride (12 ml, 0.147 mole) in 35 ml of CH_2Cl_2 was added to 200 ml of a CH_2Cl_2 solution of CH_3SeCl_3 (9.2 g, 0.046 mole). After 5 hr at 25° the initially yellow solution became deep red. After cooling the solution to $-25°$, filtering, and evaporating the filtrate, 6.4 g (70%) of CH_3SeCl_3 was recovered.

(2) Methylselenium trichloride (7.8 g, 0.039 mole) was shaken with a threefold excess of BCl_3 in a sealed tube for 12 days at 25°. After removal of BCl_3 *in vacuo*, 7.3 g (95%) of CH_3SeCl_3 was recovered.

Trimethylselenium Chloride. Dimethyl selenide was allowed to react at 25° in a sealed tube with excess methyl chloride. Colorless crystals of $(CH_3)_3SeCl$ formed in small amount after 1 day and in large amount after 1 week. The tube was then opened, excess CH_3Cl was removed in a stream of dry nitrogen, and last traces were removed *in vacuo*; mp 183–184°. *Anal.* Calcd for $(CH_3)_3SeCl$: C, 22.6; H, 5.66; Se, 49.5; Cl, 22.2. Found: C, 22.5; H, 5.50; Se, 48.80; Cl, 22.9.

Trimethylselenium chloride is insoluble in chloroform, very slightly soluble in methylene chloride and nitromethane, and soluble in methanol, from which it is recrystallizable. Upon exposure to the atmosphere the white solid turns to a clear liquid in a few minutes.

Trimethylselenium Chloride–Boron Trichloride Adduct. A slurry of $(CH_3)_3SeCl$ in CH_2Cl_2 was treated with a threefold excess of BCl_3 for 24 hr in a sealed tube with occasional shaking. The contents of the tube was filtered yielding a colorless solid, mp 168–170°. *Anal.* Calcd for $(CH_3)_3SeCl \cdot BCl_3$: Se, 28.4. Found: Se, 27.8, 29.1; av, 28.4.

The adduct was slightly soluble (*ca.* 0.4 g/100 ml) in CH_2Cl_2 and could be recrystallized from this solvent giving flat, easily deformed plates.

Results and Discussion

Methylselenium Trichloride. Aryl- and alkylselenium trihalides have been prepared from concentrated solutions of the appropriate selenic and hydrohalic acid,[8a] and also from the halogenation of a diselenide in a halocarbon solvent.[8b] We have prepared methylselenium trichloride by the latter method. This substance is soluble with slow decomposition in polar solvents such as methylene chloride and nitrobenzene. The nmr spectrum of CH_3SeCl_3 in CH_2Cl_2 was monitored over an 8-day period. The results showed methyl chloride as the main proton-containing decomposition product. After 8 days approximately 30% of the sample had decomposed. Crystalline methylselenium trichloride starts turning orange slowly at 81° and rapidly above 90°. The solubility and thermal stability of CH_3SeCl_3 are of interest in view of the known properties of methylsulfur trichloride.[9] This latter substance was reported to decompose at 31° and was insoluble in solvents with which it did not react.

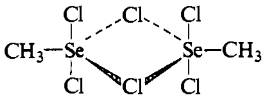
The rate of decomposition of CH_3SeCl_3 in CH_2Cl_2 was slow enough to permit molecular weight measurements by vapor pressure lowering. Initial equilibrium was established within 1 hr after dissolution of the solute. Thereafter the differential pressure decreased at the rate of 0.1–0.2 mm/hr, presumably due to the formation of CH_3Cl. Each set of readings was extrapolated to obtain the differential pressure at zero time. An average molecular weight of 468 (av dev 25) was obtained from nine determinations, compared to the formula weight of 200.3. The observed molecular weight was concentration independent in the range that could be studied (0.11–0.19 *m*). Owing to the unexpectedly high molecular weight of the trichloride, its solubility and instability were limiting factors in obtaining a more accurate value. The molecular weight data indicate methylselenium trichloride is extensively associated in CH_2Cl_2 solution. The dimeric formulation $(CH_3SeCl_3)_2$ seems to best explain the data. The high results obtained may be due to unaccounted decomposition or to the presence of small amounts of higher aggregates.

The single sharp resonance at -4.36 ppm (Table I) supports the existence of one major species in solution. However, this resonance observation would also be expected for a mixture of polynuclear species in rapid equilibrium, or if accidental equivalency of methyl protons in different species occurred.

Five infrared absorptions were observed for CH_3SeCl_3 in CH_2Cl_2. These are listed together with assignments in Table II. These are based on previous assignments of Se–Cl,[1,10] Se–C,[1,11] and CH_3–Se[12] vibrations. The existence of single absorptions in the Se–C methyl rocking region also suggests the presence of one principal species in solution. The methyl rocking frequency seems particularly sensitive to a change of environment, as two absorptions are observed in this region for the solid presumably due to differences in site symmetry.

Based on our molecular weight, ir, and nmr data, the existence of CH_3SeCl_3 as the dimer $(CH_3SeCl_3)_2$ seems likely. Association has been shown to occur in other chalcogen halides. The molecular weight of methyltellurium tribromide in benzene solution was found to be concentration dependent.[13] The *n* value increased from 1.45 to 1.98 when concentration was increased from 0.0087 to 0.07 *M*. Tellurium tetrachloride has been reported to exist as a trimer in benzene solution.[14]

Methylselenium trichloride exhibits three absorptions in the Se–Cl stretching region. These may be interpreted in terms of the dimer of D_{2h} symmetry shown below.



The suggested assignment is the following: 350 cm^{-1}, axial Se–Cl stretch; 258 cm^{-1}, bridging Se–Cl; and 180 cm^{-1}, Cl–Se–Cl bending mode. The proposed structure assumes a "stereochemically inactive" pair of electrons on selenium, which has been shown to be the case in a number of X-ray studies on five-coordinate selenium(IV) compounds.[15]

The ir absorptions and assignments for solid CH_3SeCl_3 are listed in Table II. The large difference between Se–Cl frequencies observed in methylselenium trichloride and those for $SeCl_3^+$ in $SeCl_3^+AlCl_4^-$ and $SeCl_3^+SO_3Cl^-$[10,16] and the $(CH_3)_2SeCl^+$ ion militates against the ionic formulation $CH_3SeCl_2^+Cl^-$. Also, only a very

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[13] M. Chen and J. W. George, *J. Am. Chem. Soc.*, **90**, 4580 (1968).

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[15] For example, $SeOCl_2 \cdot 2py$: I. Linqvist and G. Nahringbauer, *Acta Cryst.*, **12**, 638 (1959).

[16] H. Gerding, *Rec. Trav. Chim.*, **75**, 589 (1956).

Table I. Dimethyl Selenide, Dimethylselenium Dihalides, the Boron Trihalide Adducts of These Compounds, Dimethyl Diselenide, Methylselenium Trichloride, and Trimethylselenium Chloride

Compound	Chemical shift, ppm[a]	Compound	Chemical shift, ppm[a]
$(CH_3)_2Se$	1.93[b]	$(CH_3)_2SeBr_2 \cdot BBr_3$	3.63
$(CH_3)_2Se_2$	2.53[b]	$(CH_3)_2SeBCl_3$	2.29
$(CH_3)_2SeCl_2$	3.64	$(CH_3)_2SeBBr_3$	2.35
$(CH_3)_2SeCl_2 \cdot BCl_3$	3.69	CH_3SeCl_3	4.36
$(CH_3)_2SeBr_2$	3.61	$(CH_3)_3SeCl$	2.96[c]

[a] Chemical shift ± 0.01 ppm; *vs.* internal TMS in CH_2Cl_2. [b] Carbon tetrachloride solvent. [c] Methanol solvent.

Table II. Infrared Spectra and Frequency Assignments for CH_3SeCl_3, $(CH_3)_3SeCl$, and $(CH_3)_3SeBCl_4$

	CH_3SeCl_3[a]	CH_3SeCl_3[b]	$(CH_3)_3SeCl$[a]	$(CH_3)_3SeBCl_4$[a,c]
				1433 m
	1390 s[e]			1416 m
				1312 w–m
Sym CH_3 deform	1262 m		1264 w–m	1271 s
			1250 w	
Methyl rock	934 m–s	936	990 s	979 m–s
	925 s		905 m	908 w
				894 m
	744 w			
				745 s sh } brd
B–Cl ν_3, $(\nu_1+\nu_4)$[d]				693 vs } brd
				661 vs } brd
Se–C	564 m	567	602 m	605 m
			580 m	580 m
				521 m
Se–Cl	340 s, brd	345 s		
	205 s, brd	258 m		
		180 m		
C–Se–C deform			272	
	55 v w			

[a] Nujol mulls. [b] CH_2Cl_2 solution CH_2Cl_2 absorbs 100% from 140 to 33 cm^{-1}; hence this region could not be examined. [c] Region below 500 cm^{-1} not examined. [d] ν_3 = antisym B–Cl, ν_1 = sym B–Cl, ν_4 = B–Cl deformation. [e] Intensity key: v w = very weak; m = medium; s = strong; sh = shoulder; brd = broad.

weak restrahlen band was observed at 55 cm^{-1}. For an ionic substance one would have expected a much stronger absorption.

Absorptions are nearly the same for solid and solution spectra in the Se–C and high-frequency Se–Cl regions. As mentioned above the methyl rock at 936 cm^{-1} in solution splits into two peaks in the solid. Interestingly, although two peaks were observed in the low-frequency Se–Cl region (258 and 180 cm^{-1}), only one broad absorption at 205 cm^{-1} is observed in the solid. These observations suggest that the axial chlorines remain relatively unperturbed in going from solution to the solid. As association is observed in solution, equal or more association would be expected in the solid. Thus the bending and bridging modes observed in solution may be degenerate in the solid and give rise to a single broad band due to equatorial chlorine bridging, perhaps forming infinite chains.

Methylselenium trichloride, in contrast to $(CH_3)_2SeCl_2$ and $(CH_3)_3SeCl$, does not form an isolable adduct with BCl_3. Increasing substitution of chlorine for methyl groups may have increased the positive charge on selenium through an inductive effect. This would make loss of a chloride ion more unfavorable for the trichloride and qualitatively explain our observation. From our observations we cannot exclude the possibility of a weak complex of CH_3SeCl_3 with BCl_3. Lack of reaction may also be related to the associated nature of the trichloride. The dimer may be viewed as an already existing donor–acceptor species, from which a chloride ion may not be readily removed by another acceptor.

Trimethylselenium Chloride. We have prepared $(CH_3)_3SeCl$ by the usual method[17] of mixing an alkyl halide with the appropriate selenide. Triphenylselenium chloride[18] and trimethylselenium iodide[19] have been shown by X-ray investigations to have structures of the type $R_3Se^+X^-$, the latter having a mean C–Se–C angle of 98.5°. A similar structure would be expected for $(CH_3)_3SeCl$, and the interpretation of the infrared spectrum is consistent with the formulation $(CH_3)_3Se^+Cl^-$, the cation possessing approximate C_{3v} symmetry. As indicated in Table II, no absorption occurs in the region (300–400 cm^{-1}) commonly associated with Se covalently bonded to Cl. By analogy with assignments for $(CH_3)_3S^+$ and $As(CH_3)_3$,[20] the bands at 580 and 602 cm^{-1} are assigned to symmetric and antisymmetric Se–C stretching modes, respectively. The CH_3 rocking and symmetric CH_3 deformation frequencies are similarly assigned and are listed in Table II. Finally, the low-frequency absorption at 272 cm^{-1} may be a C–Se–C deformation mode similar to that found for $(CH_3)_3S^+$ and $As(CH_3)_3$ at 320 and 238 cm^{-1}, respectively.

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Trimethylselenium Chloride–Boron Trichloride Adduct. The compound $(CH_3)_3SeCl \cdot BCl_3$ exhibited considerable thermal stability, melting 85° higher than the parent chloride. Infrared absorptions are listed in Table II, and assignments for the $(CH_3)_3Se^+$ cation are the same as in the case of $(CH_3)_3SeCl$. However, the peak at 521 cm^{-1} not present in the parent chloride remains unassigned. The strong absorptions between 745 and 661 cm^{-1} are characteristic of the tetrachloroborate ion[21] and are assigned as before.[1] Thus our infrared data are readily interpreted in terms of the ionic formulation trimethylselenium(IV) tetrachloroborate, $[(CH_3)_3Se]^+[BCl_4]^-$.

Proton magnetic resonance data for dimethyl selenide, dimethylselenium dihalides, the boron trihalide adducts of these compounds, dimethyl diselenide, methylselenium trichloride, and trimethylselenium chloride are given in Table I. The chemical shifts are those observed for compounds discussed in this paper and in an earlier report.[1]

Increasing substitution of Cl for methyl groups shifts the resonance position in the series $(CH_3)_nSeX_{4-n}$ ($n = 1, 2, 3$) to lower field. The uniform differences in chemical shifts along the series are unexpected and are probably fortuitous. The monochloride is expected to exist as solvated ions in methanol. The di- and trichlorides are monomeric and dimeric, respectively, in CH_2Cl_2. Because no two members have the same state of aggregation in a single solvent, there is no basis for attempts to relate differences in chemical shifts to the state of aggregation of a third member. However, the shift to lower field with increasing Cl substitution suggests that the expected deshielding of the methyl protons with substitution of a more electron-withdrawing substituent on Se is of overriding influence on the chemical shifts. The effects of aggregation and ionic dissociation may be of much smaller magnitude.

Oxidation of selenide to Se(IV) or attachment of a Lewis acid to selenide caused a downfield shift in resonance. This shift is correlated with the withdrawal of electron density from the selenium atom upon ether oxidation or coordination, but is much more pronounced in the former case.

Only a slight difference in the methyl resonance position is observed for the parent dichloride and BCl_3 adduct (0.05 ppm) and the dibromide and BBr_3 adduct (0.02 ppm). In contrast, the differences between the resonance of $(CH_3)_2Se$ and $(CH_3)_2SeBCl_3$, and $(CH_3)_2Se$ and $(CH_3)_2SeBBr_3$, are 0.36 and 0.42 ppm, respectively. These observations are consistent with the previous conclusion[1] that the dihalide adducts are largely dissociated in solution. But for the $(CH_3)_2Se \cdot BCl_3$ adduct the relatively large shift downfield is consistent with ir and molecular weight data which show this species to be essentially undissociated in solution. The downfield shift for $(CH_3)_2Se \cdot BBr_3$ into the same region observed for $(CH_3)_2Se \cdot BCl_3$ points to it being nondissociated also. The greater shift (0.06 ppm) for $(CH_3)_2Se \cdot BBr_3$ relative to $(CH_3)_2Se \cdot BCl_3$ is in agreement with nmr data on trimethylamine adducts of BCl_3 and BBr_3.[22] The greater shift downfield for the resonance of the $(CH_3)_3N \cdot BBr_3$ adduct was rationalized as due to the greater Lewis acidity of BBr_3.

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