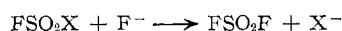
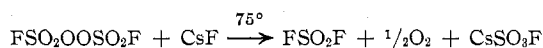


If fluorine fluorosulfonate were formed (as found by Dudley), then under these experimental conditions it would react with the alkali metal fluoride as described above. The lack of oxygen difluoride formation when potassium fluorosulfonate was used is perhaps a result of the increased temperature. The fluorination of sodium fluorosulfonate was performed in a flow system.⁵ Thus removal of the fluorine fluorosulfonate could occur before complete reaction with the sodium fluoride was possible.

Cesium fluoride was found to attack several other fluorosulfuryl derivatives to produce sulfuryl fluoride (see Table I). The generalized reaction is

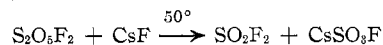


The fate of the new anion, X^- , depended on its nature. For example, when peroxydisulfuryl difluoride was heated to 75° in the presence of cesium fluoride, oxygen as well as sulfuryl fluoride was obtained.



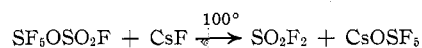
The attack by fluoride ion is believed to occur on the sulfur rather than on oxygen since no fluorine fluorosulfonate or oxygen difluoride was found. The postu-

lated intermediate peroxyfluorosulfonate salt, $\text{Cs-OOSO}_2\text{F}$, could not be isolated as it apparently decomposed to oxygen and cesium fluorosulfonate under the experimental conditions. The ratio of oxygen to sulfuryl fluoride found was in good agreement with the above reaction scheme. On the other hand, when pyrosulfuryl fluoride was treated with cesium fluoride at 50° the only volatile product produced was sulfuryl fluoride.



In fact a 50% conversion of pyrosulfuryl fluoride to sulfuryl fluoride was found to occur at 150° in a "clean prefluorinated" monel bomb, whereas no decomposition was noted in glass. The metal fluorides in the bomb were sufficiently active to cause decomposition, presumably in the same manner.

The attack of fluoride ion on the sulfur atom in the sulfuryl group was again demonstrated when $\text{SF}_5\text{OSO}_2\text{F}$ was heated with cesium fluoride at 100° .



Little or no sulfur hexafluoride was obtained. Thus the attack occurred primarily on the sulfur atom in the sulfuryl group and not on the sulfur atom in the pentafluorosulfur group. After the reaction was complete, fluorine was expanded into the reactor containing the salt residue. Pentafluorosulfur hypofluorite was produced, suggesting the presence of the salt CsOSF_5 .

CONTRIBUTION NO. 1652 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES, CALIFORNIA

The Synthesis and Properties of Some Halogen and Interhalogen Addition Compounds of 1,4-Selenothiane

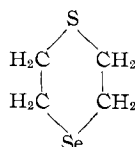
By J. D. McCULLOUGH

Received March 23, 1964

The following halogen and interhalogen addition compounds of 1,4-selenothiane have been prepared: $\text{C}_4\text{H}_8\text{SSeCl}_2$, $\text{C}_4\text{H}_8\text{S- SeBr}_2$, $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{I}_2$, $\text{C}_4\text{H}_8\text{SSe} \cdot \text{ICl}$, $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{ICl}$, $\text{C}_4\text{H}_8\text{SSe} \cdot \text{IBr}$, and $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{IBr}$. The compositions have been established through combustion analysis for carbon and hydrogen, iodometric determination of equivalent weights, and comparison of the densities computed from single-crystal X-ray diffraction data with those determined by flotation. Probable molecular structures are suggested on the basis of the present and previous X-ray diffraction studies and a knowledge of the dissociation constants of related compounds in solution.

Introduction

A study of halogen and interhalogen addition compounds of 1,4-selenothiane



provides an opportunity to observe competition of two types. One area of competition is that between selenium and sulfur for the halogen or interhalogen

when the latter are limiting reagents. The other is the competition between tendencies to form more conventional covalent compounds *vs.* tendencies to form molecular or charge-transfer complexes. The present study reports the preparation and characterization of seven halogen or interhalogen addition compounds of 1,4-selenothiane and suggests probable molecular structures for some of them. Complete structural studies of several of the compounds by three-dimensional X-ray diffraction methods are in progress. The results of these studies should provide answers to a number of interesting questions arising from the above competition.

TABLE I
 PHYSICAL AND CRYSTALLOGRAPHIC DATA FOR ADDITION COMPOUNDS OF 1,4-SELENOTHIANE

| | C ₄ H ₈ SSeCl ₂ | C ₄ H ₈ SSeBr ₂ | C ₄ H ₈ SSe·2I ₂ | C ₄ H ₈ SSe·ICl | C ₄ H ₈ SSe·2ICl | C ₄ H ₈ SSe·IBr | C ₄ H ₈ SSe·2IBr |
|--|--|--|---|---------------------------------------|--|---------------------------------------|--|
| Color | White | Yellow | Garnet-red | Yellow | Garnet-red | Yellow-orange | Red-orange |
| Dec. temp., °C. | 138 | 129 | 131 | 124 | 128 | | 139 |
| Carbon, % | | | | | | | |
| Calcd. | 20.18 | 14.70 | 7.12 | 14.58 | 9.76 | | 8.27 |
| Found | 19.90 | 14.72 | 7.23 | 14.43 | 9.73 | | 8.35 |
| Hydrogen, % | | | | | | | |
| Calcd. | 3.39 | 2.46 | 1.19 | 2.45 | 1.64 | | 1.39 |
| Found | 3.36 | 2.59 | 1.27 | 2.49 | 1.79 | | 1.58 |
| Equiv. wt. | | | | | | | |
| Calcd. | 119.0 | 163.5 | 168.7 | 164.8 | 123.0 | 187.0 | 145.2 |
| Found | 119.5 | 163 | 169 | 167 | | | 146 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | P2 ₁ /c | P2 ₁ /c | P2 ₁ /c | Pbca | P2 ₁ /c | Pbca | P2 ₁ /c |
| a, Å. | 11.35 | 11.55 | 6.80 | 20.38 | 6.75 | 20.58 | 6.05 |
| b, Å. | 6.28 | 6.50 | 6.38 | 9.70 | 9.02 | 9.81 | 11.60 |
| c, Å. | 12.10 | 12.10 | 16.69 | 9.00 | 9.42 | 9.18 | 8.48 |
| β | 112° 20' | 112° 50' | 114° 6' | | 102° 35' | | 100° 35' |
| Molecules per unit cell | 4 | 4 | 2 | 8 | 2 | 8 | 2 |
| Density (X-ray), g. cm. ⁻³ | 1.98 | 2.60 | 3.39 | 2.46 | 2.92 | 2.68 | 3.30 |
| Density (obsd.), g. cm. ⁻³ | 1.95 | 2.55 | 3.33 | 2.44 | 2.91 | 2.65 | 3.30 |

Experimental

Materials.—The 1,4-selenothiane was a sublimed portion of the preparation described earlier.¹ Reagent grade iodine (J. T. Baker) and bromine (Merck) were used without purification. Chlorine was taken from a commercial cylinder (Matheson) and dried by passage through concentrated sulfuric acid. Solutions of the halogens were prepared in dried reagent grade carbon tetrachloride (J. T. Baker) and the respective concentrations determined iodometrically with the following results: Cl₂, 0.530 *M*; Br₂, 1.48 *M*; and I₂, 0.0571 *M*. Solutions of ICl (0.104 and 0.201 *M*) and IBr (0.0970 *M*) were prepared by adding weighed samples of iodine to measured volumes of the appropriate halogen solution and diluting to volume with carbon tetrachloride. A 0.330 *M* solution of ICl in ethylene chloride was also prepared. As there is some loss of halogen in handling, the concentrations of the solutions were redetermined from time to time, as needed. Recrystallization solvents were reagent grade or White Label products.

X-Ray Diffraction.—Small single crystals of the various compounds were selected and sealed in thin-walled glass capillaries to prevent vaporization and/or decomposition of the specimens. Precession photographs were prepared by use of Mo Kα radiation (λ 0.7107 Å.) and rotation and Weissenberg photographs were prepared by use of either Mo Kα or Cu Kα (λ 1.5418 Å.) radiation. A sufficient number of zero- and upper-level photographs were prepared in each case to permit the space group assignment to be made with considerable reliability.

Densities.—Densities of single crystals were determined by the flotation method by use of a series of calibrated liquids. The densities thus observed are compared with those calculated from the X-ray data in Table I.

Equivalent Weights.—Halogen addition compounds of selenides have been shown to react quantitatively with aqueous potassium iodide to form triiodide which may be titrated with standard thiosulfate solution.² Interhalogen addition compounds react similarly. For the present determinations, the weighed sample (25–100 mg.) was placed in a dry 50-ml., glass stoppered, conical flask with 2–3 ml. of ethylene chloride. The sample was dissolved and a solution prepared from 1 g. of KI, 10 ml. of water, and 1 ml. of 3 *N* H₂SO₄ was added. The ethylene chloride served as a preliminary indicator but 1 ml. of starch indicator was added near the end point.

Preparation of Addition Compounds.—A weighed sample of sublimed 1,4-selenothiane was placed in a dry, 25-ml. or 50-ml. glass-stoppered conical flask and dissolved in 5–15 ml. of carbon tetrachloride or ethylene chloride as specified later. The halogen or interhalogen solution was added from a buret with a Teflon stopcock. In all but the two cases noted later the yields of addition compounds are probably quantitative except for losses in handling.

C₄H₈SSeCl₂.—To 0.300 g. (0.00180 mole) of selenothiane in 15 ml. of ethylene chloride, 3.40 ml. of 0.530 *M* Cl₂ in carbon tetrachloride was added a few drops at a time. A white precipitate appeared locally but dissolved when the mixture was shaken. The resulting solution was concentrated by evaporation of solvent to yield 0.35 g. (82%) of a white, crystalline solid. This was recrystallized from ethylene chloride.

C₄H₈SSeBr₂.—To 0.344 g. (0.00206 mole) of selenothiane in 10 ml. of carbon tetrachloride, 1.48 *M* bromine solution was added dropwise. A fine, yellow precipitate formed immediately and settled out to give a clear, almost colorless solution. This behavior continued until 1.40 ml. of bromine solution (0.00207 mole of Br₂) had been added. A permanent color of bromine resulted when an additional drop of bromine was added. The yield of crude product was 0.68 g. (95%). Recrystallization from chloroform gave transparent yellow laths or plates.

C₄H₈SSe·2I₂.—To 0.114 g. (0.000683 mole) of selenothiane in 10 ml. of carbon tetrachloride, 24.0 ml. of 0.057 *M* iodine (0.00137 mole of I₂) was added. The yield was 0.43 g. or 93%. The product was recrystallized from ethylene chloride to give small garnet-red needles.

C₄H₈SSe·ICl.—To 0.1190 g. (0.000712 mole) of selenothiane in 10 ml. of ethylene chloride was added 2.18 ml. of 0.328 *M* ICl solution in ethylene chloride (0.000715 mole of ICl). When the solvent was allowed to evaporate, yellow-orange crystals of the desired complex formed. The yield was 0.21 g. or 89%. The product was recrystallized from ethylene chloride to give small, transparent plates and laths.

C₄H₈SSe·2ICl.—To 0.0950 g. (0.000567 mole) of selenothiane in 10 ml. of ethylene chloride was added 5.70 ml. of 0.201 *M* ICl solution in carbon tetrachloride (0.00115 mole of ICl). There was no immediate formation of crystals but on standing overnight a mixture of small, yellow-orange laths and larger dark red polyhedra was formed. Some of the latter showed gradation in color from orange to dark red while others were a uniform dark red. As the crystals stand in contact with the solution, the dark crystals slowly grow at the expense of the lighter ones. One

(1) J. D. McCullough and P. Radlick, *Inorg. Chem.*, **3**, 924 (1964).

(2) J. D. McCullough, *J. Am. Chem. Soc.*, **64**, 2672 (1942).

preparation was thus converted almost completely to the dark crystals by standing 3 months at laboratory temperature. The smallest of the uniform dark crystals were chosen for the X-ray diffraction study and density determination.

$C_4H_8SSe \cdot 2IBr$.—Iodine monobromide solution (0.097 *M*) in carbon tetrachloride was added slowly to 0.177 g. (0.00106 mole) of selenothiane in 10 ml. of ethylene chloride. The solution remained clear on mixing until 9 ml. of *IBr* solution had been added. At this point red-orange needles began to form and continued to do so until 22.0 ml. (0.00213 mole of *IBr*) had been added. The yield was 0.55 g. or 89%. Recrystallization from ethylene chloride gave fine, red-orange needles.

$C_4H_8SSe \cdot IBr$.—To 0.0805 g. (0.000482 mole) of selenothiane in 10 ml. of ethylene chloride was added 4.95 ml. of 0.097 *M* *IBr* solution in carbon tetrachloride (0.000480 mole of *IBr*). Red-orange needles of the 1:2 complex formed immediately but were redissolved by heating and adding 10 ml. more of ethylene chloride. On cooling, crystals of the 1:2 complex again formed. The mother liquor was decanted and permitted to evaporate slowly at room temperature to produce shiny yellow-orange plates of the 1:1 complex along with a small additional yield of the 1:2 complex. The mother liquor was again decanted and specimens of the plates were selected for the X-ray study and density measurement. Evaporation of the final mother liquor gave more of the 1:1 complex along with crystals of 1,4-selenothiane.

Results and Discussion

Composition and Properties of the Compounds.—The composition of the compounds was established by means of the analytical and X-ray diffraction data which are given in Table I along with some physical properties. Analytical data on $C_4H_8SSe \cdot IBr$ were not possible because the supply of pure material was limited to selected single crystals; however, its composition was established through isomorphism with $C_4H_8SSe \cdot ICl$ and the agreement of the X-ray and flotation densities.

Reaction of Iodine with C_4H_8SSe .—Only one crystalline addition compound of iodine with 1,4-selenothiane could be obtained, namely $C_4H_8SSe \cdot 2I_2$. The addition of a relatively small volume of iodine solution to a carbon tetrachloride solution of C_4H_8SSe produced fine needles of the 1:2 complex, in spite of the fact that selenothiane was in great excess. This behavior is interesting since only the 1:1 complex has been detected spectrophotometrically in solution, even when iodine is in 40-fold excess.³

Reaction of Iodine Monochloride with C_4H_8SSe .—The reaction of *ICl* with 1,4-selenothiane is complicated, not only by the formation of two crystalline complexes, but also by the disproportionation of $C_4H_8SSe \cdot 2ICl$ to give $C_4H_8SSeCl_2$ and I_2 . This disproportionation appeared to be more extensive in carbon tetrachloride than in ethylene chloride and made it impossible to purify $C_4H_8SSe \cdot 2ICl$ by recrystallization. In contrast, $C_4H_8SSe \cdot ICl$ may be purified by recrystallization from ethylene chloride.

Reaction of Iodine Monobromide with C_4H_8SSe .—The reaction of selenothiane and *IBr* appears to be less complicated than that with *ICl*. In this case disproportionation was not observed and the 1:2 complex was obtained quite pure. On the other hand, the 1:1 complex could be obtained pure only by selecting

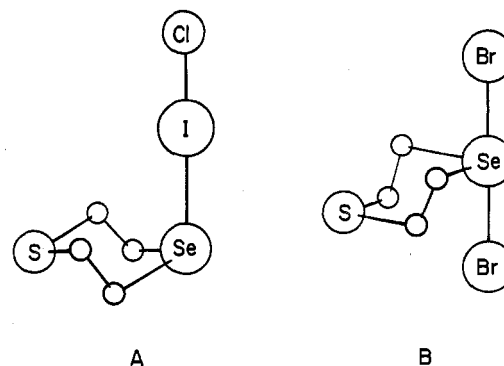


Fig. 1.—Suggested molecular structures: A, $C_4H_8SSe \cdot ICl$; B, $C_4H_8SSe \cdot Br_2$.

individual crystals from a mixed product obtained from a solution in which selenothiane was in excess.

Structures of the Addition Compounds.—Although the structure of only one of the addition compounds of 1,4-selenothiane is known at present with any certainty, it is possible, on the basis of the present and previous studies, to make some reasonable speculations regarding the probable molecular structures of several of them. The information drawn upon here is not only from X-ray diffraction studies but also from a knowledge of dissociation constants of some related compounds and complexes in solution.³

A study of the crystal structure of $C_4H_8SSe \cdot 2I_2$ ⁴ showed this complex to be isomorphous with $C_4H_8S_2 \cdot 2I_2$.⁵ Molecules of the latter complex are centrosymmetric with linear S-I-I groups oriented in equatorial positions on the six-membered ring. In contrast, crystals of $C_4H_8Se_2 \cdot 2I_2$ ⁶ contain centrosymmetric molecules with linear Se-I-I groups oriented axially. Apparently the equatorial bonding tendency of sulfur wins out in crystalline $C_4H_8SSe \cdot 2I_2$ in spite of the fact that selenium forms stronger bonds to iodine in solution.^{3,7}

The requirement that molecules of $C_4H_8SSe \cdot 2I_2$ be centrosymmetric can be satisfied only by a statistical disorder in which the S and Se ends of the molecule are crystallographically indistinguishable. This type of disorder has also been found in 1,4-selenothiane¹ and is present in crystals of its 1:2 complexes with *ICl* and *IBr*. All four substances crystallize in the monoclinic space group $C_{2h}^2-P2_1/c$ with two molecules per unit cell, a situation which requires the molecule to be centrosymmetric. In the light of these similarities, it is surprising that there are no isomorphous pairs among the three 1:2 complexes. With regard to the molecular structures, it is highly probable that the 1:2 interhalogen complexes involve linear Se-I-Cl, S-I-Cl, Se-I-Br, and S-I-Br groups, but on the basis of present information, one can only speculate regarding axial vs. equatorial orientation to the ring system. The structure of the formally similar complex $C_4H_8O_2 \cdot 2ICl$ has been reported

(4) H. Hope and J. D. McCullough, *Acta Cryst.*, **15**, 806 (1962).

(5) G. Y. Chao and J. D. McCullough, *ibid.*, **13**, 727 (1960).

(6) G. Y. Chao and J. D. McCullough, *ibid.*, **14**, 940 (1961).

(7) N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).

(3) J. D. McCullough and I. C. Zimmermann, *J. Phys. Chem.*, **65**, 888 (1961).

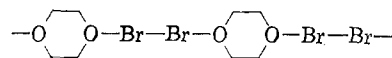
by Hassel and Hvoslef.⁸ The space group of the dioxane complex is C_{2h}^3-C2/m with two formula units of $C_4H_8O_2 \cdot 2ICl$ per unit cell. Thus isomorphism with either selenothiane complex is ruled out.

The crystallographic data for the isomorphous 1:1 ICl and IBr complexes of selenothiane do not require the molecules to have any special symmetry. However, it seems probable that the molecules will be found to approximate structure A in Fig. 1, which has a mirror plane through the four heavy atoms. A complete structural study of these complexes is in progress and it will be of interest to see if the ICl (or IBr) is bonded in *axial* or in *equatorial* positions, and also if the sulfur atom becomes involved in the bonding, say with a chlorine atom of another molecule.

A similar situation with regard to molecular symmetry applies to the isomorphous pair of addition compounds of selenothiane with chlorine and bromine. Again it is expected that the molecule will approximate

(8) O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **10**, 138 (1956).

mirror symmetry by a plane through the four heavy atoms, but here linear Cl-Se-Cl and Br-Se-Br bonding should occur with the orientation perpendicular to the plane of the C-Se-C bonds,⁹ as shown in structure B of Fig. 1. The structure predicted here is in sharp contrast to that found by Hassel and Hvoslef for the 1:1 complex of dioxane with bromine.¹⁰ The latter was found to contain linear polymers of the type



Structural studies of the chlorine and bromine addition compounds of 1,4-selenothiane are in progress.

Acknowledgment.—The author is pleased to acknowledge the financial assistance of the National Science Foundation under Grant NFS-G24997, and also the assistance of Miss Heather King, who performed the carbon and hydrogen analyses.

(9) R. E. Marsh and J. D. McCullough, *Acta Cryst.*, **3**, 41 (1950).

(10) O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 873 (1954).

CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Thermodynamics of Binary Alloys. I. The Lithium-Bismuth System¹

BY MELVIN S. FOSTER, SCOTT E. WOOD, AND CARL E. CROUTHAMEL

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Electromotive force measurements have been made on cells of the type $Li|LiCl-LiF|Li$ in Bi (X_{Li} = atom fraction Li) for compositions of the alloy from pure Bi to Bi saturated with $Li_3Bi(s)$ and for temperatures between 775 and 1100°K. The electrolyte consisted of 70 mole % LiCl and 30 mole % LiF. A secondary reference electrode which consisted of Bi saturated with $Li_3Bi(s)$ was used in most of the cells in place of the Li anode. Its potential was independently measured against the Li electrode. From the measurements, a least-squares derived equation relating the excess chemical potential (cal./mole) of Li in the alloy as a function of temperature and composition for the region studied was found to be

$$\Delta\mu_{Li}^E = [9397 + 18.16T - 0.0109T^2] + [7103 - 19.44T + 0.0068T^2]X_{Li}$$

The standard free energy of formation of $Li_3Bi(s)$ has been derived as a function of temperature.

Introduction

Electromotive force measurements of concentration cells without transference which may be of interest in a regenerative cell system have yielded information concerning the thermodynamic properties of the binary lithium-bismuth system.

Lithium has been used as one of the components of the binary system for several reasons. Lithium has a low equivalent weight and forms relatively stable intermetallic compounds with many of the more noble elements. The stability of these compounds gives rise to substantially larger cell voltages in concentration cells without transference than those predicted from ideal solution theory. Lithium has the least solubility in its fused halides of any of the alkali metals,² permitting operation of cells containing Li

metal and fused Li halides at elevated temperatures without appreciable solubility of Li in the salt. This solubility would result at best in an irreversible transfer of Li between electrodes and at worst might result in an internal electrical short circuit of the cell through increased electronic conductance of the electrolyte.³

Based upon information given by Hansen and Anderko,⁴ some of the metals which combine with Li to form intermetallic compounds whose melting points are higher than either element include Sn, Ga, In, Pb, Bi, Tl, Zn, Cd, and Hg. Of these combinations, the Li-Bi system has been investigated first.

Experimental

Materials.—Only reagent grade LiCl and LiF were used in this study. The electrolyte used was the eutectic composition

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *J. Phys. Chem.*, **66**, 572 (1962).

(3) H. R. Bronstein and M. A. Bredig, *ibid.*, **65**, 1220 (1961).

(4) M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, N. Y., 1958.