

to as liposomes or Bangosomes.²⁸ These spherical bilayer structures have many of the properties of biological membranes. Due to the complexity of the structures present in these systems, it is not surprising that kinetic anomalies were observed. The source of the effects on the rate and extent of addition of cyanide to pyridinium ions elicited by these surfactants is unclear

(28) A. D. Bangham, *Progr. Biophys. Mol. Biol.*, **18**, 29 (1968).

though those factors which are important in the case of the simple zwitterionic surfactant may be important here as well.

Finally, we may note that in a basic way the reactions studied in this investigation mimic enzymatic reactions involving the nicotinamide nucleotide coenzymes. The importance of electrostatic factors in promoting the simple organic reactions suggests that such factors may be important for the enzymatic ones as well.

Group VI-Halogen Adducts. Trisubstituted vs. Tetrasubstituted Structures in Solution^{1a}

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Abstract: The structures of the complexes between group VI heterocycles (thiane or selenane) and halogens (bromine or iodine) have been determined in solution. Analysis of coupling-constant ratios for both the 2,3 and 3,4 segments of the ring characterize the selenane-bromine complex as a trigonal bipyramid (tetrasubstituted) and the selenane-iodine and both thiane complexes as simple charge-transfer molecular adducts (trisubstituted). The ionic character of the complexes was assessed by conductance measurements. The thiane-bromine complex is highly ionic, the selenane-bromine complex exhibits a very low conductance, and the iodine complexes are intermediate in behavior. Ionic character was placed on a relative scale by comparison with the halosulfonium and haloselenonium tetrafluoroborates, which are entirely ionic.

Dialkyl sulfides, selenides, and tellurides react instantaneously with molecular halogens to form Lewis acid-base complexes of the σ - σ type (eq 1). The



ease of formation and isolation, the brilliant colors of some of the adducts, and their structural complexity have made these compounds a constant object of study for over a century. Husemann reported and characterized possibly the first such adduct (iodine and 1,4-dithiane) in 1863.² The major thrust of the structural work to date has consisted of X-ray crystallographic determinations,³ particularly by the groups of Hassel and McCullough. Some attention has been devoted recently to the measurement of equilibrium constants for complex formation in solution.⁴ We report herein the first quantitative efforts to define the structures of these adducts in solution.

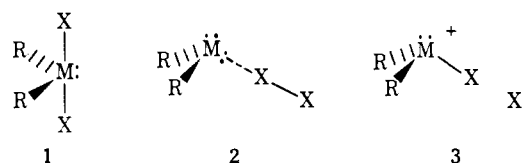
(1) (a) This work was supported by the National Science Foundation (Grant No. GP-22942), the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center, and the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4,5); (b) National Institutes of Health Fellow, 1967-1971; (c) National Science Foundation Trainee, 1968-1969.

(2) A. Husemann, *Justus Liebigs Ann. Chem.*, **126**, 269 (1863).

(3) (a) O. Hassel and C. Römning, *Quart. Rev., Chem. Soc.*, **16**, 1 (1962); (b) C. K. Prout and J. D. Wright, *Angew. Chem., Int. Ed. Engl.*, **7**, 659 (1968); (c) H. A. Bent, *Chem. Rev.*, **68**, 590 (1968); (d) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

(4) J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.*, **65**, 888 (1961); E. T. Strom, W. L. Orr, B. S. Snowden, Jr., and D. E. Woessner, *ibid.*, **71**, 4017 (1967); M. Tamres and S. Searles, Jr., *ibid.*, **66**, 1099 (1962).

From the mass of structural data reported on these group VI-group VII complexes, two general classes of bonding situations have emerged: those (1) in which the group-VI atom (M) lies between the two halogen atoms (X—M—X), and those (2) in which M



is at the terminus ($M \cdots X-X$). In the former class ("tetrasubstituted"), the atom M forms the center of a trigonal bipyramid with covalent bonds to both halogen atoms. In the latter class of simple charge-transfer molecular complexes ("trisubstituted"), the bonding between M and the halogen molecule has been likened to that in the hydrogen bond.³ The $M \cdots X-X$ angle is very close to 180°, and the strength of the complex may be related to the deviations of the X—X bond from its natural length. These two classes grade naturally into each other.^{3,5}

In addition to classification as either molecular complexes (MC) or trigonal bipyramids (TB), these molecules may be characterized according to the ionic or covalent nature of the bonds. Organic chemists, in fact, have favored depicting many of these molecules as halosulfonium or haloselenonium halides (3).⁶ The

(5) H. Hope and J. D. McCullough, *Acta Crystallogr.*, **17**, 712 (1964).

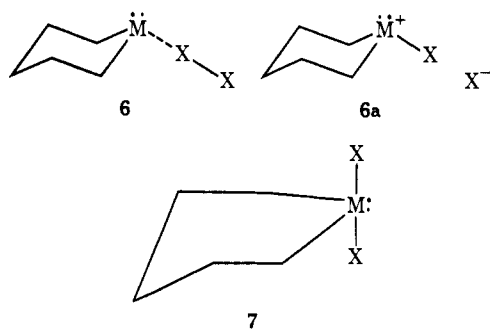
(6) For example, see D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

crystal structure of thiophane dibromide has been interpreted in terms of a molecular complex with considerable ionic character, because of the short S—Br and long Br—Br bond lengths.⁷

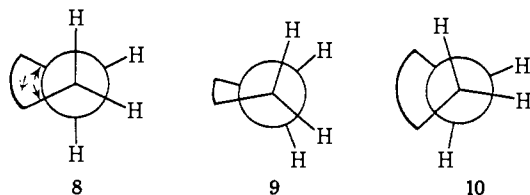
In analyzing the structures of these molecules in solution, we have chosen to approach the questions of molecular geometry and ionic character independently. By measuring a sequence of nmr coupling constants, we can unambiguously differentiate the trigonal-bipyramidal structure from the linear molecular complex (see below). From conductance and chemical-shift measurements, we can assess the degree of ionic character. The combination of techniques produces a complete description of the structures of this class of molecules in solution. We selected the pentamethylene heterocycles thiane (4) and selenane (5) to serve as the group VI donors, because analysis



of the ring coupling constants serves as a means to differentiate the MC and TB structures. Complexation of a halogen molecule with thiane or selenane, as in 2, should bring about a minimum distortion of the ring as a whole (6). If charge transfer is extreme, the representation 6a may be preferable but ring distortions are still small. Formation of a trigonal bipyramid, with its large C—M—C bond angle, on the other hand, brings about enormous distortions (7).



We utilize the *R*-value method to assess the nature of the distortions present in the rings.⁸ In a distortion-free CH₂—CH₂ fragment (8) of a ring, the ratio (*R*) of the average vicinal trans coupling constant to the average vicinal cis coupling constant is in the range 1.9–2.2. A flattening of this fragment (eclipsing of the substituents, 9) lowers *R*; a puckering (10) raises



R. The *R* value is related directly to the internal dihedral angle ψ for the fragment by eq 2.

(7) G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pedone, and R. Albert, *J. Amer. Chem. Soc.*, **92**, 4002 (1970).

(8) J. B. Lambert, *ibid.*, **89**, 1836 (1967); J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971); H. R. Buys, *Recl. Trav. Chem. Pays-Bas*, **88**, 1003 (1969).

$$\cos \psi = \left(\frac{3}{2 + 4R} \right)^{1/2} \quad (2)$$

To analyze the entire structure of pentamethylene compounds such as 4 and 5, the two deuterated versions of the molecules 11 and 12 are required. From



11 comes the dihedral arrangements of the 2,3 and 5,6 portions of the ring. From 12 comes the shape of the 3,4,5 portion. Accordingly, we have prepared the deuterated derivatives of thiane and selenane and converted them to the bromine and iodine adducts. All the vicinal coupling constants for the ring were then measured, and from these the shapes of the ring and the classification as MC or TB was obtained.

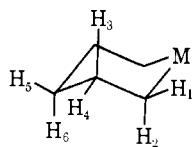
To decide to what extent the complexes are ionic, we have measured their conductances in ethylene chloride solution. The fully covalent trigonal bipyramid (2, 7) should exhibit little or no conductance. The molecular complex should exhibit a conductance that is proportional to the extent that 4 (6a) contributes instead of 3 (6). The shielding of the α protons also serves as a measure of ionic character. We have therefore recorded the chemical shifts of the α and β protons for thiane, selenane, and their adducts.

The chemical-shift, *R*-value, and conductance results form a comprehensive picture in which selenane dibromide is found to be a nonionic trigonal bipyramid, whereas selenane diiodide, thiane dibromide, and thiane diiodide are molecular complexes with varying degrees of ionic character.

Results

The syntheses of the specifically deuterated precursors to 11 and 12 have been outlined elsewhere.^{8,9} Experimental details are given for the 2,2,5,5 derivative because only a preliminary report was previously recorded.⁹ Spectral analyses were carried out for nine pentamethylene systems: S, SBr₂, SI₂, +SCH₃, Se, SeBr₂, SeI₂, Te, and TeBr₂. The solvent in each case but one (SBr₂) was ethylene chloride, and the temperature was 37°. Because of its instability, the sulfur dibromide had to be analyzed at –15° in methylene chloride. Ethylene chloride was chosen as solvent because it shows no tendency to complex with the halogen. Spectra were recorded with simultaneous deuterium irradiation. The spectral analyses of thiane and both its bromine and iodine derivatives proved to be essentially identical with respect to coupling constants, though quite different for chemical shifts. The spectra for selenane and its derivatives showed strong differences in both categories. Figures 1 and 2 show the observed/calculated spectra for the 4,4- and 2,2,5,5-deuterated derivatives, respectively, of selenane. All the thiane spectra closely resemble this set. Figures 3 and 4 present the observed/calculated spectra for the 4,4- and 2,2,5,5-deuterated derivatives, respectively, of selenane dibromide. The spectra of selenane diiodide were intermediate in form and are

(9) J. B. Lambert and R. G. Keske, *Tetrahedron Lett.*, 4755 (1967).

Table I. Coupling Constants and *R*-Value Analyses

	S	+SCH ₃ I ⁻	Se	M SeI ₂	SeBr ₂	Te	TeBr ₂
$J_{13} = J_{24}^c$	2.96 ^a	3.24	3.09 ^b	3.32	4.70	3.12	5.2
$J_{14} = J_{23}$	8.15 ^b	8.63	8.24 ^b	8.33	7.75	8.62	7.8
$\Delta J_{gem}(\alpha, \beta)^c$	0.0	2.3	1.5	3.1	3.0	2.5	3.5
$J_{35} = J_{46}$	3.28	3.59	3.14	3.04	2.90		2.56
$J_{36} = J_{45}$	8.47	8.30	8.63	8.44	8.88		9.21
$\Delta J_{gem}(\beta, \gamma)^c$	0.0	0.7	0.2	0.5	0.6		0.0
$R_{\alpha\beta} = J_{14}/J_{13}$	2.65	2.66	2.66	2.51	1.65	2.76	1.5
$\psi_{\alpha\beta}$, deg	61	61	61	60	53.5	61	52
$R_{\beta\gamma} = J_{36}/J_{35}$	2.58	2.31	2.75	2.78	3.07		3.60
$\psi_{\beta\gamma}$, deg	60	59	61	61.5	63		64

^a All coupling constants are reported in Hz. ^b These coupling constants differ slightly from those reported in ref 8, but the *R* values are essentially unchanged. The earlier A-60 measurements were probably not so well calibrated as the present ones. ^c The spectrum is sensitive only to the difference between geminal coupling constants.

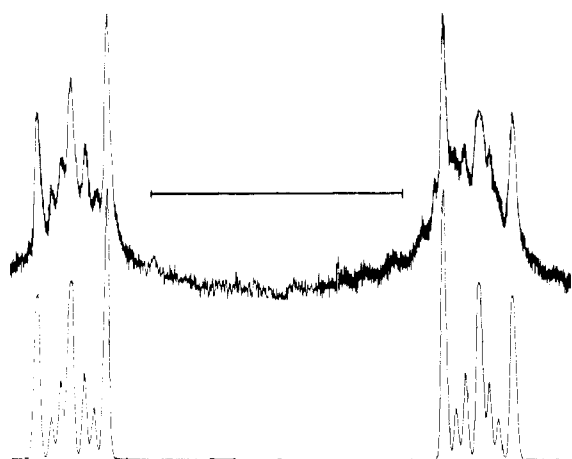


Figure 1. The observed and calculated 90-MHz proton spectra of selenane-4,4-*d*₂ in ethylene chloride at 37° with deuterium decoupling. The calibration bar represents 40 Hz.

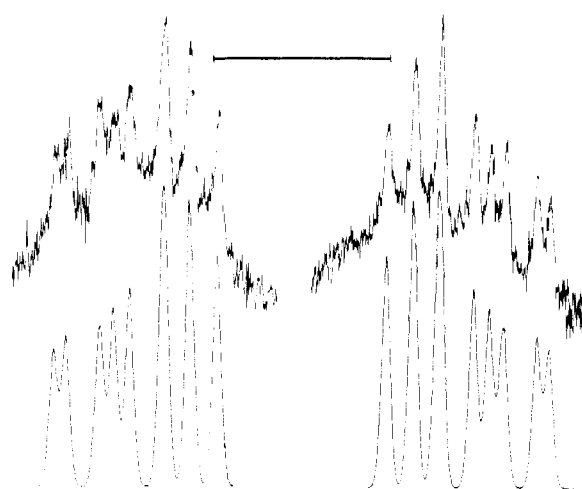


Figure 2. The observed and calculated 90-MHz proton spectra of selenane-2,2,5,5-*d*₄ in ethylene chloride at 37° with deuterium decoupling. The α -proton singlet is omitted. The calibration bar represents 15 Hz.

omitted.¹⁰ The considerable differences between the spectra for selenane and its dibromide reflect large distortions of the ring on complexation. The analyses for the tellurium compounds have been reported earlier.^{8,9}

The results of the analyses, including the calculation of ψ from eq 2, are given in Table I. A tabulation of the chemical-shift measurements may be found in Table II.

Table II. Chemical Shifts^a

	α protons	β protons	γ protons
S	2.54	1.76	1.53
SI ₂	2.97	1.96	
SBr ₂	3.10	1.95	
Se	2.62	1.89	1.53
SeI ₂	2.99	2.00	1.64
SeBr ₂	3.97	2.28	1.79

^a In units of δ (ppm downfield from TMS).

(10) Reproductions of these spectra may be found in the Ph.D. dissertation of D. H. Johnson, Northwestern University, 1971.

The conductance of each of the adducts (SBr₂, SI₂, SeBr₂, SeI₂) was measured by two methods: (1) directly from a solution containing a weighed amount of the crystalline solid, and (2) from a solution containing equimolar amounts of added donor (thiane, selenane) and acceptor (Br₂, I₂). The agreement between the two methods of preparation was satisfactory. The results are listed in Table III in units of μ mhos/mol. Conversion to specific conductance was not considered necessary, since all measurements were made with the same cell, the constant of which was found to be stable. A convenient model for a purely ionic species is furnished by the fluoroborate salts of the adducts. Treatment of a solution of the adduct with silver fluoroborate results in precipitation of an equivalent amount of silver halide and formation of the salt in solution (eq 3). Conductances of these solutions were measured under conditions of inert atmosphere, and the results are included in Table III.

"Titration" of thiane or selenane solutions with

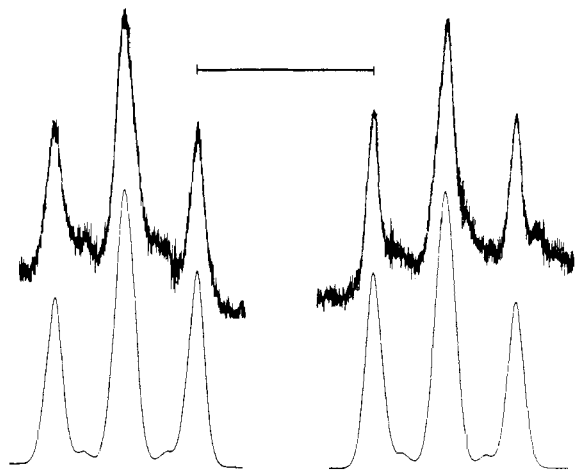


Figure 3. The observed and calculated 90-MHz proton spectra of selenane-4,4- d_2 dibromide in ethylene chloride at 37° with deuterium decoupling. The calibration bar represents 15 Hz.

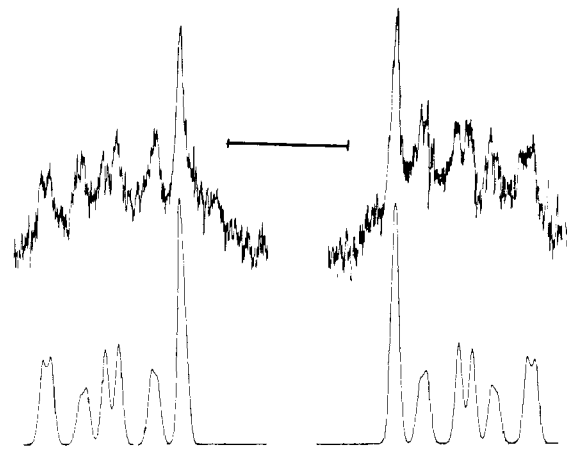
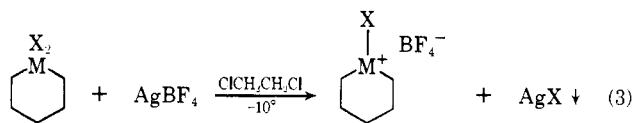


Figure 4. The observed and calculated 90-MHz proton spectra of selenane-2,2,5,5- d_4 dibromide in ethylene chloride at 37° with deuterium decoupling. The α -proton singlet is omitted. The calibration bar represents 10 Hz.

Table III. Molar Conductances of Adducts in Ethylene Chloride^a

	Br ₂	I ₂
Thiane, method A ^b	1.4×10^3	2×10^2
Thiane, method B ^c	2×10^3	3×10^2
Thiane (BF ₄ ⁻ salt)	1×10^4	5×10^4
Selenane, method A ^b	1×10^1	7×10^2
Selenane, method B ^c	1×10^1	3×10^2
Selenane (BF ₄ ⁻ salt)	5×10^3	6×10^4

^a In $\mu\text{mhos/mol}$ at 0°; for thiane dibromide at -10°. ^b Adduct formed by the addition of equivalent amounts of donor and acceptor to the solvent. ^c Crystalline adduct added to the solvent.



bromine or iodine results in a different type of behavior for almost each pair of reagents. Figures 5, 6, and 7 present some of these titration curves. The conductance is expressed in units of μmhos , corrected for dilution due to the increase in solvent volume upon addition of the halogen solution. Addition of bromine to thiane (Figure 5) results in a linear increase in conductance up to the point of equivalent amounts of donor and acceptor. The solution of bromine with selenane is almost nonconducting up to this point (Figure 6). As an excess of bromine is added to either donor, the conductance shoots up rapidly. Even after a several-fold excess of bromine is added, the conductance is still increasing, although the curves flatten out. Bromine alone in ethylene chloride exhibits no appreciable conductance. The conductances are stable in the time coordinate. If the solution is held at any point along the titration curve for a period of several hours, no change in conductance is observed.

Addition of iodine to a solution of either donor yields a somewhat different behavior, illustrated in Figure 7 for the case of selenane (thiane gives an essentially identical result). There is a linear increase in conductance up to the equivalence point. With an excess of iodine, again the conductance continues to increase, although at a lower rate than with bromine. The conductances of the thiane and selenane solutions

with iodine are intermediate between those for thiane dibromide and selenane dibromide. Iodine alone in ethylene chloride has no significant conductance.

Two points are noteworthy in these conductance experiments. First, the conductance of selenane dibromide is much lower than those for the other three adducts. Second, solutions of all four adducts increase in conductance when excess halogen is added. The solution structures of these materials must take both these facts into account, as well as the chemical-shift and coupling-constant data.

Discussion

The results reported in the previous section were obtained with the objective of classifying each adduct as either a molecular complex (6), in which the atoms are bonded in the order M-X-X, or a trigonal bipyramid (7), with the atoms bonded in the order X-M-X. In addition, each geometric modification may exhibit a varying degree of ionic character, or be in equilibrium with an ionic form such as 6a. From the above data, clear-cut conclusions can be drawn about these structural aspects for each of the four adducts in solution.

Thiane Dibromide. The ring shapes for thiane, thiane dibromide, and the *S*-methylsulfonium salt are all very similar (Table I). The $R_{\alpha\beta}$ and $R_{\beta\gamma}$ are in the range 2.3–2.6, corresponding to $\psi = 59$ –61°. This small puckering with respect to cyclohexane ($\psi \sim 56^\circ$) comes from the decreased C-S-C bond angle.⁸ The ring conformation is therefore relatively unchanged on complexation with bromine, and the trigonal-bipyramidal geometry may be excluded. Because differences in ionic character do not appear to affect the ring shape (compare thiane with its *S*-methyl derivative), the *R*-value approach gives no information on this question. The α -proton resonance of thiane is shifted 0.56 ppm downfield on complexation with bromine, indicating some shift of electron density from sulfur to bromine. Addition of bromine to the five-membered thiophane gives rise to a somewhat larger shift of 0.78 ppm.⁷ The ionic character of the complex must be greater in the five-membered ring.

Thiane dibromide exhibits the highest conductance of the complexes examined (Table III). It conducts

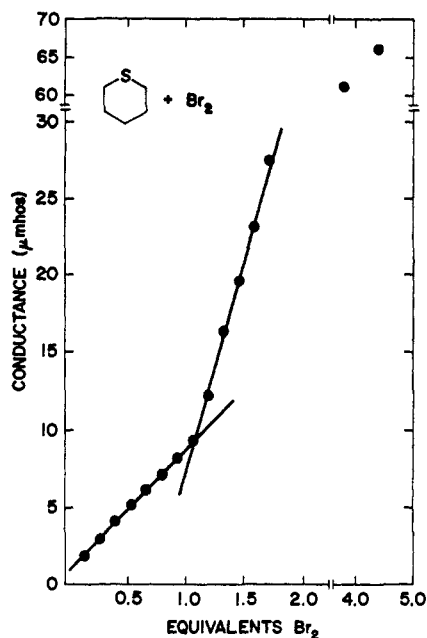


Figure 5. The conductance of a solution of thiane in ethylene chloride at -10° as a function of added equivalents of bromine in ethylene chloride.

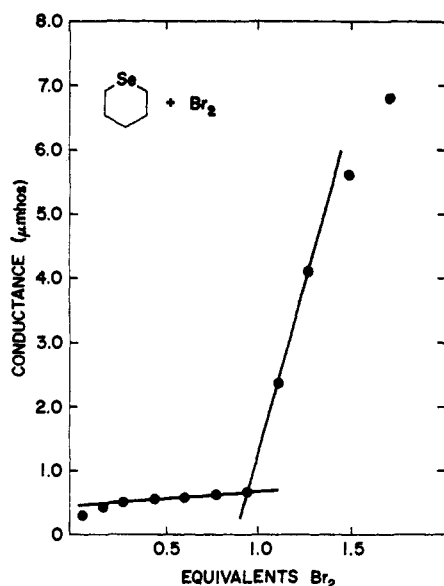


Figure 6. The conductance of a solution of selenane in ethylene chloride at 0° as a function of added equivalents of bromine in ethylene chloride.

one-fifth as well as the fully ionic fluoroborate derivative. Exact calculation of the fraction ionic character cannot be made since the anions (Br^- and BF_4^-) are different and their relative mobilities are not known in ethylene chloride. The sharp increase in conductance observed when excess bromine is added to thiane can be accounted for in terms of a shift in equilibrium between the molecular complex and a bromosulfonium tribromide (eq 4). Alternatively, the additional bromine may simply enhance the ionic character of a single existing species. When several equivalents of excess bromine are added, the conductance approaches that of the fluoroborate derivative. Under such con-

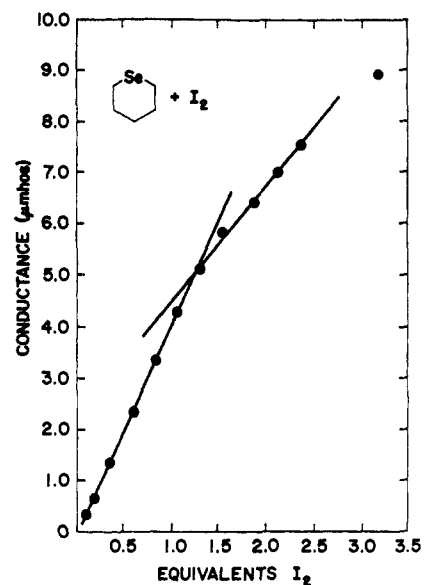
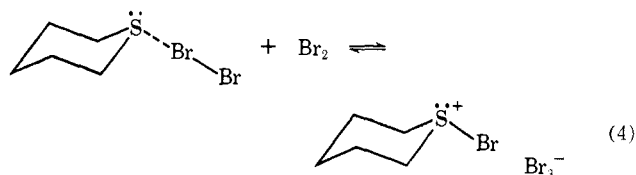


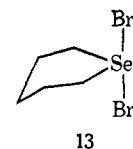
Figure 7. The conductance of a solution of selenane in ethylene chloride at 0° as a function of added equivalents of iodine in ethylene chloride.



ditions, the adduct closely resembles a wholly ionic halosulfonium salt.

The only available crystal structure for a sulfide-bromine adduct is that of thiophane dibromide.⁷ An S-Br-Br geometry was found in which the S-Br distance is only 0.09 Å longer than the covalent bond length and the Br-Br distance is 0.43 Å longer than in molecular bromine. The structure in the solid was therefore characterized as a molecular complex tending toward a halosulfonium salt.⁷ In solution we conclude that thiane dibromide is a molecular complex with a modest degree of ionic character; with excess bromine present the structure tends toward a more ionic representation.

Selenane Dibromide. The $R_{\alpha\beta}$ value of 1.65 indicates that the ring is considerably flattened in the vicinity of the heteroatom. This is the behavior expected for the trigonal bipyramid, in which the selenium atom is tetrasubstituted. The larger C-Se-C angle forces the ring to flatten.⁸ In response to this distortion, the opposite end of the ring puckers slightly, $R_{\beta\gamma} = 3.07$. The overall shape of the ring, as indicated by the R -value analysis, is illustrated in structure 13. A sim-



ilar, but even more extreme shape was found for tellurane dibromide in solution,⁹ $R_{\alpha\beta} = 1.5$, $R_{\beta\gamma} = 3.6$. 1,4-Thiaselenane dibromide¹¹ and diphenylselenide

(11) L. Battelle, C. Knobler, and J. D. McCullough, *Inorg. Chem.*, **6**, 958 (1967).

dibromide¹² have been found to have the trigonal-bipyramid structure in the solid. We have obtained preliminary crystal data on selenane dibromide itself and found that it too is present in the solid as a trigonal bipyramid.¹³

Selenane dibromide is effectively nonconducting (Figure 6), in contrast to thiane dibromide. One can therefore conclude that the trigonal bipyramid is nonionic. Since addition of excess bromine stimulates an increase in conductance, there may be an ionic form available to the molecule. The conductance increases at a much lower rate, however, than in the thiane-bromine system (Figure 5). After several equivalents of bromine is added to selenane, the conductance is still only a small fraction of that in the fluoroborate derivative. The chemical shift of the α resonance in selenane dibromide is 1.35 ppm downfield from that in selenane itself. This is the largest such shift observed in this study (Table II). Because the complex is not ionic, this shift must arise from the formal charge build-up associated with conversion from disubstituted to tetrasubstituted selenium with additional covalent polar bonds.

Thiane Diiodide. Like the bromine complex of thiane, the iodine complex retains the same coupling constants as in the parent. The structure in solution is therefore designated to be a molecular complex. An X-ray study of the iodine adduct of 1,4-dithiane indicates that the structure in the solid is also a molecular complex.¹⁴ Introduction of iodine shifts the α -proton resonance of thiane diiodide downfield by 0.43 ppm, compared to 0.56 ppm for bromine (Table II). The lower ionic character of the complex is also evident from the conductance, which is less than 0.5% of that for the iodosulfonium fluoroborate derivative. In the titration experiment, the conductance continues to increase after the equivalence point is passed, but in contrast to the bromine adducts, the rate decreases slightly (Figure 7). We conclude that thiane diiodide exists in solution as a simple molecular complex in which the iodine-iodine bond is largely unperturbed. Addition of excess iodine may increase the ionic character of the complex or favor a greater proportion of an ionic form (eq 4).

Thiane diiodide in the solid phase exhibits interesting thermochromic behavior. At room temperature the crystals are deep violet, at -78° bright orange, and at -190° light yellow. The more ionic bromine complex of thiane is gold at room temperature. As the temperature is lowered, the iodine chromophore apparently is weakened by increased charge transfer. A series of crystal-structure determinations at various temperatures would be of interest to find out if the actual structure of the molecule, in terms of the I-I bond length, varies with temperature.

Selenane Diiodide. The iodine complex of selenane is very similar to that of thiane. The R values are little changed by complexation (Table I). The α -proton resonance is shifted 0.37 ppm downfield. The con-

ductance, though significant, is still less than 1% of the iodoselenonium fluoroborate. An increase in conductance is induced by an excess of iodine. The structural picture is therefore similar to that of thiane diiodide: a molecular complex with low ionic character.

Conclusions

From the R -value analysis we have found that in solution selenane dibromide exists as a trigonal bipyramid, whereas selenane diiodide, thiane dibromide, and thiane diiodide are molecular complexes. The information derived from chemical-shift measurements and conductance studies supports strong covalent bonding for the selenane dibromide, considerable ionic character for thiane dibromide, and slight ionic character for the two diiodides. All four complexes are in equilibrium with a more ionic form that is favored by addition of excess halogen. From these conclusions we can tabulate the types of adducts observed in solution, and from these infer the structures of the remaining complexes in this series (Table IV). In

Table IV. Structural Classification for Group VI-Halogen Adducts in Solution

	S	Se	Te
I ₂	MC	MC	(TB) ^a
Br ₂	MC	TB	TB
Cl ₂	(TB) ^a	(TB) ^a	(TB) ^a

^a Inferred.

no case do the structures in solution vary significantly from those in the solid.³

The structures of these complexes have been discussed by Baenziger, *et al.*,^{3d} by analogy with the trihalogens. The central atom is always the largest. Thus the large tellurium atom tends toward the center (X-Te-X) and the small chlorine atom tends toward the outside (Cl-M-Cl), so that these atoms favor the trigonal bipyramid in their complexes. Similarly, the small sulfur atom favors the outside (S-X-X) and the large iodine atom the inside (M-I-I), so these atoms generally form molecular complexes. Conclusions are not so straightforward when the group VI and halogen atoms are from the same row in the periodic table. These problems have been met by a restatement of the explanation in terms of electronegativities; the atom with the lowest electronegativity assumes the central position. The placement of highly electronegative elements in the apical positions of the trigonal bipyramid is in accord with the well-known behavior of phosphoranes. The Pauling-Allred electronegativities for the six atoms under discussion are S (2.58), Se (2.55), Te (2.01), Cl (3.16), Br (2.96), and I (2.66).¹⁵ Thus tellurium with the lowest and chlorine with the highest electronegativities would always be the center and outer atoms, respectively, in trigonal bipyramids. For "same-row" complexes, trigonal bipyramids are predicted in each case (S-Cl, Se-Br, and Te-I). Molecular complexes are expected for S-I and Se-I. The only complex that fails to follow this pattern is the

(15) A. L. Allred and W. L. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(12) J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.*, **63**, 803 (1941).

(13) Unpublished work with N. K. Kim. The selenium and bromine atoms were easily discerned in the Patterson synthesis, but the analysis was not refined to include the rest of the ring.

(14) G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **13**, 727 (1960).

one between sulfur and bromine. Sulfur, with its lower electronegativity, should favor a trigonal bipyramid.^{3d} Considerations according to size, however, suggest that the larger bromine atom would prefer to be in the center, as in the molecular complex. Both in the solid⁷ and in solution, bromine-sulfur adducts clearly favor the simple molecular complex, rather than the trigonal bipyramid. Until a more refined theory is available, the structures of group VI-halogen complexes from different rows in the periodic table are best explained by simple considerations of size, and for same-row complexes, by electronegativity.

Experimental Section

Nmr spectra were recorded at 60 MHz on Varian Associates T-60 and A-60 spectrometers and at 90 MHz on a Bruker HFX-10 spectrometer. The A-60 was equipped with a Varian V-6040 variable-temperature assembly. The Bruker HFX-10 was equipped with a variable-temperature unit, a heteronuclear broad-band noise decoupler driven by a Schomandl frequency synthesizer, and a Fabriktek Model 1074 time-averaging computer. Conductances were measured by means of an Industrial Instruments Inc. conductance bridge, Model RC 16B2. Control Data Corporation Models 3400 and 6400 digital computers equipped with a CalComp plotting accessory were used for analysis and plotting of the nmr spectra. Melting points (uncorrected) were determined in a Thiele tube apparatus.

1,5-Dibromopentane-3,3-*di* was prepared by a reported method.¹⁶

Cyclopentanone-2,2,5,5-*d*₄ was prepared by the treatment of cyclopentanone with D₂O and K₂CO₃ in five stages.

1,5-Pentandiol-2,2,5,5-*d*₄ was obtained by the Baeyer-Villiger oxidation of cyclopentanone-2,2,5,5-*d*₄ according to the procedure of Sager and Duckworth,¹⁷ followed by LiAlH₄ reduction of the resulting lactone.

1,5-Dibromopentane-2,2,5,5-*d*₄ was prepared by reaction of the labeled diol with PBr₃ according to a literature procedure.¹⁸

Thiane (4, thiacyclohexane) was prepared from 1,5-dibromopentane according to a reported procedure.^{8,18}

Selenane (5, Selenacyclohexane). A mixture of 30 g (0.25 mol) of sodium formaldehydesulfoxylate, 8.3 g (0.11 g-atom) of selenium powder, 23.3 g (0.58 mol) of NaOH pellets, and 133 ml of water was refluxed 15 min with magnetic stirring in a 500-ml, three-necked flask, followed by dropwise addition of 14.6 ml (0.107 mol) of 1,5-dibromopentane over a period of 20 min while maintaining a gentle reflux. The flask was then converted for steam distillation with a coolant-coil-type condenser and an ice-bath cooled receiver. Steam distillation was continued until the condensate no longer contained two phases. The distillate was saturated with NaCl to facilitate separation of the two layers. The denser selenide was isolated, dried over molecular sieves, and further purified by bulb-to-bulb distillation, to produce in 55% yield a clear, colorless liquid, which was stored over molecular sieves.

Thiane Dibromide. A solution of 0.2 ml of thiane in 5 ml of pentane was cooled in an ice-salt bath. Magnetic stirring was begun,

and a cold solution of bromine in pentane was added dropwise until the color from one more drop of bromine did not immediately dissipate upon its addition to the mixture. The bright yellow crystals were collected on filter paper by rapid suction and washed with cold pentane. The crystals, which decompose in a few minutes at room temperature, were rapidly transferred to an nmr tube and stored at -78° .

Selenane Dibromide. The same procedure was followed as for thiane dibromide, except that the addition of the bromine solution was carried out at 0° . The thermal stability of the deep yellow selenane adduct, mp 119.5–120.5° dec, permits more leisurely handling in comparison to the thiane dibromide. *Anal.* Calcd for C₅H₁₀SeBr₂: C, 19.04; H, 3.17. Found: C, 19.28; H, 3.32.

Thiane Diiodide. The procedure followed was the same as for selenane dibromide except an iodine solution in pentane was added to the thiane at 0° to give dark violet crystals that decompose on heating, mp 73.5–74.5°. *Anal.* Calcd for C₅H₁₀SI₂: C, 16.85; H, 2.81. Found: C, 16.82; H, 2.77.

Selenane Diiodide. The same procedure was followed as for thiane diiodide to give red-brown crystals, mp 110.5–112.0° dec. *Anal.* Calcd for C₅H₁₀SeI₂: C, 14.88; H, 2.48. Found: C, 14.75; H, 2.53.

S-Bromopentamethylenesulfonium Fluoroborate. To an oven-dried, 150 × 16-mm Pyrex tube was added 0.257 g (1.25 mmol) of AgBF₄. The tube was sealed with a rubber septum. These operations were carried out in a dry-nitrogen purged glove bag. To a solution of 0.140 ml (1.4 mmol) of thiane (previously dried over molecular sieves) in 10 ml of ethylene chloride cooled to -10° was added 2.80 ml of a previously prepared 0.500 M bromine solution in ethylene chloride. All volume measurements and liquid transfers were made by syringe. The resulting thiane dibromide solution was transferred to the previously prepared vial of silver fluoroborate. The tube was immediately cooled to -10° and shaken vigorously to ensure complete mixing. The tube was centrifuged to compact the AgBr, and the sample was stored at -7° in the refrigerator for 48 hr. The supernatant containing the sulfonium fluoroborate in solution was removed *via* syringe from the reaction tube and transferred to the previously weighed and dried conductance cell. The reaction tube was washed with three 5-ml portions of ethylene chloride followed each time by centrifugation, with the supernatant added to the conductance cell. Additional solvent was added to the conductance cell to reach the level used in conductance measurements.

S-Iodopentamethylenesulfonium Fluoroborate. The procedure outlined for the corresponding S-bromo fluoroborate was followed.

Se-Bromopentamethyleneselenonium Fluoroborate. The procedure outlined for the fluoroborate derivative of thiane dibromide was followed.

Se-Iodopentamethyleneselenonium Fluoroborate. The procedure outlined for the fluoroborate derivative of thiane dibromide was followed.

Conductance titrations were carried out by placing an ethylene chloride solution of thiane or selenane in the conductance cell at 0° (-10° for thiane dibromide). Volumetrically calibrated amounts of halogen in the same solvent were added in a stepwise fashion, and the conductance was measured after each addition. The conductance of the solutions did not vary with time. The cell constant was found to be 0.247 cm⁻¹ from measurements on a 0.01 M aqueous solution of KCl at 25°. It was not considered necessary to convert the raw conductance data to conductivity (specific conductance), since the same cell was used throughout this study and the cell constant remained unchanged.

(16) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, **89**, 5921 (1967).

(17) W. F. Sager and A. Duckworth, *ibid.*, **77**, 188 (1955).

(18) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).