Reaction of SF_6 with a Solution of Sodium in a Diphenyl–Ethylene Glycol Dimethyl Ether Mixture. A.—Excess SF_6 was distilled into a flask containing sodium solution. Slow reaction occurred at −78° during 75 min. between the SF_6 and the frozen solution. The flask was placed in a −64° bath and was allowed to warm slowly during 15 hr. to −10°. During this time, the color of the sodium solution was completely discharged.

B.—The weight of a sample of SF_6 (40–80 mg.) was accurately determined by measuring its pressure when present in a known volume at a given temperature. It was distilled into a 100-ml. flask containing approximately 20 ml. of the sodium solution. After warming the flask to room temperature, it was swirled gently for 2 or 3 min. and then cooled in liquid nitrogen and then rewarmed to room temperature. Approximately 5–10 ml. of water was added dropwise to destroy the unreacted sodium, and the contents of the flask were transferred to a 250-ml. separatory funnel. The flask was then washed three times with approximately 15 ml. of isopropyl ether and three times with approximately 15 ml. of water, and the washings were added to the separatory funnel. After vigorous shaking, the lower aqueous layer was allowed to pass through a filter into a 250-ml. volumetric flask. The ether was extracted three times with 25 ml. of water which was transferred to the volumetric flask. After diluting the solution to 250 ml., F^- was determined volumetrically by the thorium nitrate method[9] and S^{-2} was determined volumetrically by an iodometric method.[10] It was found in preliminary experiments that the fluoride and sulfide ions did not mutually interfere with their estimations by the analytical methods employed.

The values obtained for sulfur upon analyzing eight different samples of SF_6 by the above method were all within ±0.16% of the calculated value of 21.95%. In six different samples, the fluorine analyses all fell within ±0.66% of the calculated value of 78.05%.

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(9) C. Eger and A. Yarden, *Anal. Chem.*, **28**, 512 (1956).

(10) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 2182; H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 400–409; C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Vol. IB, Elsevier Publishing Co., Princeton, N. J., 1961, p. 249.

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The Crystal Structure of 1,4-Diselenane Tetrachloride

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1,4-Diselenane tetrachloride ($Cl_2SeC_4H_8SeCl_2$), Fig. 1, is closely related to two organoselenium compounds for which crystal structures have been determined; these are the corresponding tetraiodide[1] and the parent compound, 1,4-diselenane.[2] In diphenylselenium dibromide and dichloride, selenium lies at the center of a distorted trigonal bipyramid with the X–Se–X bond angle approximately 180°. It was shown recently by Chao and McCullough[1,3] that iodine forms molecular complexes with 1,4-diselenane and 1,4-dithiane rather than true iodides.[4] The crystal and molecular structures of the compounds formed between diselenane and chlorine or bromine were not known and prompted this investigation of 1,4-diselenane tetrachloride.

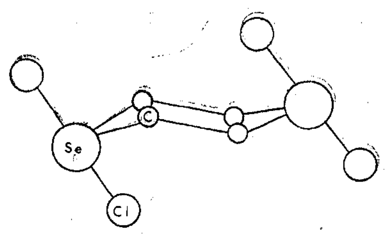

Fig. 1.—1,4-Diselenane tetrachloride.

Experimental

Single crystals of 1,4-diselenane tetrachloride (henceforth referred to as $DSCl_4$) were difficult to prepare; its solubility in common solvents is very limited and solutions had to be prepared at relatively low temperatures since $DSCl_4$ was found to decompose rapidly at temperatures close to 100°. Very thin platelets were obtained by passing chlorine gas over a solution of diselenane in *o*-dichlorobenzene. X-Ray patterns of single crystals obtained in this manner gave limited intensity data; the diffraction spots were weak and diffuse and it was clear that better crystals were needed. Some improvement occurred when less common solvents were used. $DSCl_4$ was found to be soluble in several inorganic liquid halides and attempts were made to recrystallize from $AsCl_3$, $POCl_3$, and $SeOCl_2$. The latter was found to be the most satisfactory and a single crystal was chosen from a mixture obtained by evaporating a solution of $DSCl_4$ in $SeOCl_2$ under reduced pressure. The diffraction patterns obtained from these crystals, though better than those previously recorded, were still poor, primarily because the material decomposed on exposure to X-rays. Nevertheless, enough reflections were recorded so that it was possible to proceed with the determination of the molecular configuration and approximate bond lengths.

Weissenberg and precession photographs were obtained using filtered Cu and Mo radiations. The unit cell is orthorhombic with $a = 12.12 \pm 0.02$, $b = 12.43 \pm 0.02$, and $c = 6.43 \pm 0.01$ Å. These cell dimensions were computed from a diffractometer record of powdered $DSCl_4$. Intensity data for the three principal zones were recorded and reflections of the following types were systematically absent: ($hk0$) and h odd; ($0kl$) with k odd; and ($h0l$) with l odd. Upper-layer Weissenberg photographs showed the cell to be primitive; the space group is therefore Pbca. Reflections of the type ($0kl$), though suitable for space group determination, were too diffuse to be useful in the structure determination. The intensities of 96 reflections, 65 ($hk0$) and the remainder ($h0l$), were measured and used in the subsequent analysis.

Measurements of the density by flotation in methylene iodide–carbon tetrachloride solutions indicated $\rho = 2.41$ g./cm.$^{-3}$; if we assume there are four molecules per unit cell, the calculated density is 2.44 g./cm.$^{-3}$. The linear absorption coefficient of $DSCl_4$ is 187 cm.$^{-1}$ for Cu Kα and 114 cm.$^{-1}$ for Mo Kα. It was clear that recorded intensity data were strongly affected by absorption, and corrections for this effect, based on the assumption that the crystal approximated a sphere with a radius of 0.35 mm., were applied to the measured intensities.[5] The crystal used was a well-formed parallelepiped with edges in the ratio of approximately 1:2:5. The usual Lorentz polarization corrections were applied to the measured intensities.

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(1) G. Y. Chao and J. D. McCullough, *Acta Cryst.*, **14**, 940 (1961).

(2) R. E. Marsh and J. D. McCullough, *J. Am. Chem. Soc.*, **73**, 1106 (1951).

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

(4) O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 273 (1954).

(5) W. L. Bond, *Acta Cryst.*, **12**, 375 (1959).

Determination of the Structure and Discussion

A Patterson (*hk*0) projection was evaluated using the "photosummateur,"[6] and selenium atom positions were readily determined. Structure factors were calculated based on selenium contributions only, and approximate chlorine positions were obtained from the first (*hk*0) electron density map. These were refined by the usual iterative procedures using the photosummateur. Approximate carbon atom positions could be inferred from the positions of carbon peaks on this map. To establish these more precisely and to rule out the possibility that these "peaks" might be due to Fourier series termination effects, a difference electron density map $\rho_{\text{obsd}} - \rho_{\text{calcd}}$ (Se), was computed; the carbon atoms were clearly displayed on that map. The discrepancy factor, $R = \Sigma \left| |F_{\text{obsd}}| - |F_{\text{calcd}}| \right| / \Sigma |F_{\text{obsd}}|$, using F_{calcd} based on Se and Cl contributions, was 0.17 for this zone.

A similar procedure was followed using (*h*0*l*) data. Selenium atoms were well resolved in the electron density map; chlorine atoms were also visible but carbon atoms could not be located. The discrepancy factor for this zone was 0.21. Again, only Se and Cl contributions were included in F_{calcd}.

The $DSCl_4$ molecule has the expected chair form, and the atomic arrangement about the selenium atom is best described in terms of a trigonal bipyramid with the Cl–Se–Cl angle close to 180°. Only four of the five apices of the trigonal bipyramid are occupied; two by chlorine atoms and two by carbon atoms. Only eight of the ten outer electrons in selenium are involved in these bonds; one equatorial position is presumably "occupied" by the pair of unshared electrons. This arrangement has been reported before for other organoselenium compounds[7] and it differs from the arrangement found for the compounds formed between iodine and 1,4-diselenane or 1,4-dithiane.[1,3] In those two cases, the iodine molecule forms a complex with selenium or sulfur with an effective Se–I–I or S–I–I bond angle of 180°. No unusual contact distances were observed in $DSCl_4$. Atomic position parameters are listed in Table I and interatomic distances in Table II.

Standard deviations in atomic coordinates were calculated for the heavy atom using Cruickshank's method[8]; for selenium $\sigma_x = \sigma_y = \sigma_z = 0.005$ Å.; for each chlorine the corresponding standard deviations are 0.013 Å. These calculated errors lead to uncertainties of 0.023 Å. for the Se–Cl bonds and 0.014 Å. for the intramolecular Se–Se nonbonded distance across the ring system.

Table I

Atom Parameters in 1,4-Diselenane Tetrachloride[a]

	x	*y*	*z*
Se	0.024	0.146	0.060
Cl_1	0.153	0.140	0.310
Cl_2	−0.107	0.140	−0.185
C_1	0.104	0.055	−0.117
C_2	0.061	0.034	−0.114

[a] Estimated standard deviations of coordinates are listed in the text.

Table II

Interatomic Distances in 1,4-Diselenane Tetrachloride (Å.)

Se–Se	Intramolecular	3.75 ± 0.01
Se–Cl_1		2.24 ± 0.02
Se–Cl_2		2.24 ± 0.02
Se–C_1		1.86 (estd.)
Se–C_2		1.88 (estd.)
Se_I–Se_{II}	Intermolecular	4.12 ± 0.01
Cl_I–Cl_{II}		3.78 ± 0.03
Cl_I–Cl_{III}		4.23 ± 0.03

The Se–Cl distance of 2.24 ± 0.02 Å. in $DSCl_4$ may be compared with the Se–Cl bond of 2.30 Å. found in diphenylselenium dichloride.[9] The Se–Se intramolecular distance is 3.75 ± 0.01 Å. compared to the 3.66 reported by Marsh and McCullough for diselenane.[2] The Se–Se distance in $DSCl_4$ differs by only one standard deviation from the corresponding distance in the iodide complex (3.75 *vs.* 3.76 Å.). The increased Se–Se length in the complexes compared to diselenane has been attributed to flattening of the chair form of the ring[1] in the former. The average Se–C–C angle is 115° compared to the average of 108° found in diselenane. In $DSCl_4$, this angle cannot be determined with useful precision in view of the uncertainty in the carbon atom positions. However, by analogy with the iodine complex of diselenane, the increased Se–Se intramolecular distance is probably due to this type of chair flattening.

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[6] G. von Eller, Thesis, University of Paris, 1955.

[7] G. D. Cristofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, **11**, 782 (1958).

[8] D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949).

[9] J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **64**, 508 (1942).

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Formation of Disilanyl and Trisilanyl Ions

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It has been reported that potassium hydride reacts with disilane to produce silane and potassium silyl.[1] To determine whether potassium silyl reacts with disilane, the potassium hydride–disilane reaction was repeated using excess disilane. We found that all of the disilane was converted into silane in approximately a 1:1 ratio.

To investigate this system further, potassium hydride was treated with excess disilane. The solvent was removed from the filtered solution and the resulting solid

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[1] M. A. Ring and D. M. Ritter, *J. Am. Chem. Soc.*, **83**, 802 (1961).