Determination of the Structure and Discussion

A Patterson ($hk0$) 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 ($hk0$) 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, $R = \Sigma||F_{\text{obsd}}| - |F_{\text{calcd}}||/\Sigma|F_{\text{obsd}}|$, using F_{calcd} based on Se and Cl contributions, was 0.17 for this zone.

A similar procedure was followed using ($h0l$) 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).

was shown to have a K^+ to SiH_3^- ratio of 1.00:1.04. Other samples of potassium silyl prepared in this manner reacted with disilane, yielding silane as the only volatile product. The resulting solid yielded silane, disilane, and trisilane in varying amounts when treated with hydrogen chloride. However, most of the silicon remained in the solid after the reaction with hydrogen chloride.

The products but not their quantities can be accounted for by the reactions

$$Si_2H_6 \xrightarrow{KSiH_3} SiH_4 + (1/x)(SiH_2)_x \tag{1}$$

$$KSiH_3 + Si_2H_6 \longrightarrow SiH_4 + KSi_2H_5 \tag{2}$$

$$KSi_2H_5 + Si_2H_6 \longrightarrow SiH_4 + KSi_3H_7 \tag{3}$$

$$KSi_2H_5 + HCl \longrightarrow Si_2H_6 + KCl \tag{4}$$

$$KSi_3H_7 + HCl \longrightarrow Si_3H_8 + KCl \tag{5}$$

Reaction 1 resembles the recently reported base-catalyzed condensations of silyl compounds.[2,3]

Experimental

General Experimental Methods.—The manipulative methods were those in general use for work under high vacuum. Disilane was prepared by the reduction of hexachlorodisilane with lithium aluminum hydride.[4] The volatile products were identified from vapor pressure measurements and by obtaining their infrared spectra and comparing these data with those reported in the literature.

Reaction between Potassium Hydride and Disilane.—Potassium hydride (0.78 mmole) and disilane (1.46 mmoles) were allowed to react in monoglyme for 24 hr. Silane (1.46 mmoles) was the only volatile product. Treatment of the solid products with excess hydrogen chloride yielded silane (0.45 mmole) and disilane (0.06 mmole).

Preparation of Potassium Silyl.—Disilane (0.48 mmole) was allowed to react with excess potassium hydride in monoglyme. After 24 hr., silane (0.46 mmole) was obtained and all of the disilane had been consumed. The solvent was distilled from the filtered solution and treatment of the resulting solid with excess hydrogen chloride yielded silane (0.200 mmole) and a trace of monoglyme. Analysis showed that 0.192 mg.-atom of potassium was present.

Before the solid was treated with hydrogen chloride, it was colored, but after the reaction it was white.

Reaction between Potassium Silyl and Disilane.—Potassium silyl (0.36 mmole, a quantity assumed from the amount of chloride ion found in the solid after the reaction with hydrogen chloride) was allowed to react with disilane (0.52 mmole) in monoglyme (4 ml.); after 24 hr., silane (0.49 mmole) was obtained and all of the disilane was consumed. Hydrogen chloride (0.59 mmole) was condensed onto the resulting solid after the solvent had been removed. The volatile materials were identified as silane (0.13 mmole), disilane (0.033 mmole), and trisilane (0.043 mmole).

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[3] A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 1934 (1963).

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Correspondence

"Symbiotic" Ligands, Hard and Soft Central Atoms

Sir:

Pearson[1] recently published a fascinating paper entitled "Hard and Soft Acids and Bases." However, it is not certain that the central atoms in definite oxidation numbers can be arranged according to a single parameter, going from extreme Chatt–Ahrland (a) "hard acid" to (b) "soft acid." Thus, the (b) class seems to involve three rather disparate categories[2]: unusually low oxidation numbers; certain high oxidation numbers; and the s^2-family Sn(II), Sb(III), Tl(I), Pb(II), and Bi(III) showing (b) characteristics toward heavy halides and chalcogenides but definite (a) aversion against σ-bonded cyanides and amines. Many chemists would not admit that an element with highly varying oxidation number z, say manganese, would show (b) character as well for high z (+4 or +7) as for low z (−1 or +1), the maximum (a) tendencies occurring at an intermediate value of z, here +2. The M(a)–NCS and M(b)–SCN bonds formed by the ambidentate ligand thiocyanate are frequently used as a test case,[3] and it would not be surprising if Fe(II) was found to bind N and Fe(III) S, showing a maximum (a) tendency for $z = +2$. By the same token, the molybdenum(III) complex[4] $Mo(NCS)_6^{3-}$ is (a) and the dark red Mo(V) thiocyanates possibly belong to class (b). The question really is whether the covalent bonding becomes so much stronger for increasing z-values that the actual, fractional charge of the central atom rather decreases, promoting (b) behavior again. There is some evidence from the nephelauxetic effect[5] that this phenomenon occurs.

Closely connected with Pearson's ideas is the question why soft (b) ligands flock together in the same complexes, a true inorganic symbiosis. Bjerrum[6] emphasized that mixed complexes MX_aY_b of moderately different pairs of ligands, say water and ammonia, or fluoride and water, usually tend to be even more frequent than suggested by the statistical contribution to

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[2] C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963.

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